BOOK OF ABSTRACTS

1ST HIGHLIGHTING SCIENCE MEETING

AND

PANIC

PHOBIA ANNUAL NANOPHOTONICS INTERNATIONAL CONFERENCE

POLYTHEA
HOW LIGHT CAN SAVE LIVES

PANIC
nano conference

26-28 MAY 2021

WROCLAW UNIVERSITY OF SCIENCE AND TECHNOLOGY

WROCLAW, POLAND

POLYTHEA HOW LIGHT CAN SAVE LIVES
Politechnika Wrocławska
PhoBiA Photonics & Bionanotechnology Association
PANIC nano conference

1 st HighLIGHTing Science Meeting & PANIC 2021

PhoBiA Annual Nanophotonics International Conference

26 - 28 May 2021

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

Printed by
Oficyna Wydawnicza Politechniki Wrocławskiej
Wybrzeże Wyspiańskiego 27, 50-370 Wrocław Tel./fax: (0-71) 328 29 40
www.oficyna.pwr.edu.pl

ISBN 978-83-7493-169-4

Cover design

Marta Piksa

Editors

Dominika Benkowska-Biernacka

Manuela Grelich-Mucha

Agata Hajda

Anna Pniakowska

Technical support

Maciej Lipok

Table of content

PANIC 2021

PhoBiA Annual Nanophotonics International Conference

26 May 2021, Wrocław, Poland

Committees and organizers

Scientific committee

Prof. Pierre-François Brevet, Université Claude Bernard Lyon 1
Prof. Marcin Drąg, Wroclaw University of Science and Technology
Prof. Martí Gich, Consejo Superior de Investigaciones Científicas
Prof. Anna Pawlik, Polish Academy of Sciences
Prof. Marek Samoć, Wrocław University of Science and Technology
Prof. Katarzyna Matczyszyn, Wrocław University of Science and Technology
Prof. Joanna Olesiak-Bańska, Wroclaw University of Science and Technology
Prof. Joanna Cabaj, Wrocław University of Science and Technology
Prof. Artur Podhorodecki, Wrocław University of Science and Technology
Dr Mateusz Bański, Wrocław University of Science and Technology
Dr Andrzej Żak, Wroclaw University of Science and Technoloogy

Organizing committee

Prof. Katarzyna Matczyszyn - association tutor
Prof. Joanna Olesiak-Bańska – association tutor
Dr Mateusz Bański - association tutor

Krzysztof Nadolski
Maciej Lipok
Dominika Benkowska-Biernacka
Manuela Grelich-Mucha
Marta Piksa
Anna Pniakowska
Magda Antoniak
Sebastian Mucha
Patryk Fałat
Agata Hajda
Nina Tarnowicz-Staniak
Patryk Obstarczyk
Katarzyna Nawrot
Alina Chmielowska
Kayode Olaleye
Maksymilian Dereniowski

Organizers

PhoBiA
Photonics & Bionanotechnology Association

POLYTHEA
HOW LIGHT CAN SAVE LIVES

Wrocław University
of Science and Technology

Faculty of Chemistry
Wroclaw University of Science and Technology

Faculty of Fundamental Problems of Technology
Wroclaw University of Science and Technology

Patronage

Prof. Arkadiusz Wójs, D.Sc., PhD, Eng.

Rector of Wroclaw University of Science and Technology

Prof. Piotr Młynarz, D.Sc., PhD
Dean of the Faculty of Chemistry

Prof. Paweł Machnikowski, D.Sc., PhD, Eng.
Dean of the Faculty of Fundamental Problems of Technology

Kulisy W3

Conference programme

26 MAY (Wednesday)		
Hours	**Activity**	
8:10-8:30	Opening ceremony	
Session I		
8:30-8:45	**Plenary session I**	**K. Nawrot** *"How to introduce fluorescent nanoparticle into a biological system?"*
8:45-9:00		**M. Antoniak** *"Co-encapsulated CdSe QDs and* Fe_3O_4 *NPs for Two-photon and Hyperthermia Applications"*
9:00-9:15		**P. Sędzicki** *"XPS/AES analysis of Cu:Zn ratio in CuO/ZnO and* Cu_3N*/ZnO nanocomposites"*
9:15-9:30		**A. Ścigała** *"Nanodimensional copper nitride – synthesis of nanowire arrays"*
9:30-9:45		**R. Lysowski** *"CLOU properties of Fe-Mn-Zr oxide system examined in TGA"*
9:45-10:00	Short break	
Session II		
10:00-10:15	**Plenary session II**	**P. Obstarczyk** *"Supramolecular chemistry of gold nanoclusters formation: new luminescent bio-markers"*
10:15-10:30		**P. Fałat**, *„Stokes and anti-Stokes emission enhancement in* Y_2SiO_5*:Pr ceramics co-doped with* Li^+ *ions"*
10:30-10:45		**S. Mucha** *"One- and two-photon excited fluorescence of acetone-derived polymer dots with strong protein-driven enhancement"*
10:45-11:00		**E. Olegovna Tikhodeeva** *"Formation of conjugates of silicon dioxide nanoparticles with Al-sulfophthalocyanine molecules for photodynamic therapy"*
11:00-11:40	**Chihaya Adachi** *"Stable Pure-blue Hyperfluorescence Organic Light-emitting Diodes with High-efficiency and Narrow Emission"*	
11:40-12:00	Short break	
Session III		
12:00-12:40	**Ken-Tye Yong** *"Nanomaterials for Biophotonic – Challenges and Opportunity"*	
12:40-12:55	**Plenary session III**	**M. Piksa** *"Photoinactivation of clinical strains of staphylococcus bacteria with the use of organic light emitting diode"*
12:55-13:10		**M. Grelich-Mucha** *„The importance of H-bonding network for amyloid fibrils autofluorescence"*

13:10-13:30		**M. Lipok** *„Fantastic amyloids and how to understand them?"*
13:30-13:45		**K. Nadolski** *„Sensitivity to surrounding medium changes of the Second Harmonic Generation in Gold Nanoparticles"*
13:45-13:55	Short break	
13:55-14:55	**Poster Session I**	
14:55-15:00	Technical break	
Session IV		
15:00-15:15	**Plenary session IV**	**D. Benkowska-Biernacka** *"Biologically derived lyotropic mesophases doped with triangular carbon nanostructures"*
15:15-15:30		**A. Pniakowska** *"Two-photon absorption and photoluminescence of atomically precise gold-doped silver nanoclusters"*
15:30-15:45		**A. Butrymowicz** *"New palladium(II) complexes with perfluorinated amidinates as precursors in vapor deposition methods"*
15:45-16:00		**K. Madajska** *„New perfluorinated copper amidinate and imidoylamidinate as precursors for Chemical Vapour Deposition (CVD)"*
16:00-16:15		**N. Tarnowicz-Staniak** *"Catalytic Effect of Gold Nanoparticles on the Z-E Isomerization of Azobenzene"*
16:15-16:30		**D. Hlushchenko** *"2D material active layer fabrication for Light Emitting Devices (LEDs)"*
16:30-16:40	Short break	
16:40-17:40	**Poster Session II**	
17:40-18:00	**Voting**	
18:00-18:40	**Ivan I. Smalyukh** *"Light-powered motors and reconfigurable low-symmetry fluids in nematic dispersions of discs"*	
18:40-19:00	**Closing ceremony**	

Poster session I

Poster session I		
Poster	**Topic**	**Presenting Author**
P1	A simple test to detect γ-butyrolactones in *Streptomyces coelicolor*	Adrianna Jastrzemska
P2	Searching for the target of histidine kinase by *in-vivo* luciferase reporter system in *Streptomyces coelicolor* A3(2)	Mateusz Wenecki
P3	Application of luciferase reporter system to study a specialized metabolic pathway of *Streptomyces coelicolor* A3(2)	Marta Derkacz
P4	The effect of antimicrobial photodynamic therapy on *Pseudomonas aeruginosa* using red light and 5-aminolevulinic acid	Ewelina Wanarska
P5	The effect of low-temperature plasma on phytopathogenic fungi	Daria Kocek
P6	AdpA protein interactions with gene promoters within the chloramphenicol biosynthetic gene cluster	Olimpia Żuchowicz
P7	Influence of Zn^{2+} on formation of amyloids of amylin analogs	Agata Hajda
P8	Electrochemical detection of drugs using nanofiber-based sensors	Kinga Halicka
P9	Self-assembled bilosomes as a co-delivery system of multifunctional therapeutic agents	Ewelina Waglewska
P10	Myelin structures formed by thermotropic liquid crystals in aqueous surfactant solutions	Wanyan Ma
P11	In-situ TEM observations of photosensitizer-bacteria interactions	Olga Kaczmarczyk

Poster session II

Poster session II		
Poster	**Topic**	**Presenting Author**
P12	Crystal phases determining properties of Fe-Mn-Zr oxide based oxygen carriers	Magdalena Gawlas
P13	Chemical Looping with Oxygen Uncoupling window examination with application of thermogravimetric instrument for powdered OCs	Anita Pawluk
P14	Electron irradiation influence on the temperature dependence of fluctuation conductivity and pseudogap in $YBa_2Cu_3O_{7-\delta}$ single crystals	Eugene Petrenko
P15	Analysis of sensitivity and reliability of the single $NaYF_4$: Er^{3+}, Yb^{3+} upconverting nanocrystals reporting temperature	Katarzyna Hołodnik
P16	Development of a fabrication method of the polymer layers containing semiconductors nanocrystals	Mateusz Pieprz
P17	Shape modifications of anisotropic gold nanoparticles	Alina Chmielowska
P18	Detection of defects and impurities in ZnO thin films by photoluminescence studies	Przemysław Sędzicki
P19	Synthesis of Luminescent Carbon Nanodots and Carbon Nanorods for their Application in the Fabrication of Polymer Thin Films	Kayode James Olaleye, Bayan Sinokrot
P20	Optical and morphological properties of PVP, PMMA and PBMA thin films	Małgorzata Sypniewska
P21	Acetone-derived fluorescent polymer dots: remarkable optical properties and interactions with serum albumins	Agnieszka Krystyniak
P22	New approach to the synthesis of highly bioactive nanoglass	Weronika Bodylska

Invited speakers

Stable Pure-blue Hyperfluorescence Organic Light-emitting Diodes with High-efficiency and Narrow Emission

Chihaya Adachi
Center for Organic Photonics and Electronics Research (OPERA), Kyushu University
744 Motooka, Nishi, Fukuoka 819-0395, Japan

Organic light-emitting diodes (OLEDs) are a promising light-source technology for future generations of display. Despite great progress in the field, there is an ongoing challenge to realize blue OLEDs with sufficient color purity, lifetime and efficiency for applications. Here we report pure-blue (CIE x, y color coordinates of [0.13, 0.16]) OLEDs with high-efficiency (external quantum efficiency of 32 % at 1000 cd m^{-2}), narrow-emission (full-width half maximum of 19 nm), and good stability (LT_{95} of 18 hours at an initial luminance of 1000 cd m^{-2}). The design is based on a two-unit stacked tandem hyperfluorescence OLED with an improved singlet-excited energy transfer process from a sky-blue TADF assistant dopant (HDT-1) to a pure-blue emitter (v-DABNA). We will discuss the detailed working mechanism including fast upconversion and efficient FRET processes. With stricter control of device fabrication and procedures it is expected that device lifetimes will further improve to rival commercial fluorescent blue OLEDs.

Reference:

[1] Chin-Yiu Chan; Masaki Tanaka; Yi-Ting Lee; Yiu-Wing Wong; Hajime Nakanotani; Takuji Hatakeyama; Chihaya Adachi, Stable pure-blue hyperfluorescence organic light-emitting diodes with high-efficiency and narrow emission, Nature Photonics, **15**, 203, (2021).

Nanomaterials for Biophotonics – Challenges and Opportunity

Ken-Tye Yong

Faculty of Engineering, School of Biomedical Engineering,
The University of Sydney

During the last 20 years, different nanomaterials have been applied in healthcare applications such as cancer imaging, lymph node mapping and brain diseases therapy. These nanomaterials can be engineered to serve as a platform for challenges in highly sensitive optical diagnostic tools, biosensors, and guided imaging and therapy.

Nanomaterials surface can be decorated with functional biomolecules to selectively target specific sites in vitro and in vivo. Importantly, they possess unique tunable spectral and optoelectronic properties, which have significant advantages for various biological applications such as tumor growth monitoring, single biomolecule detection, targeted drug delivery therapy, and control release of gene silencing materials. The flexibility and versatility of nanomaterials may provide the keys to answer important biological questions and ultimately improve diagnostics and therapy of human diseases.

A synergistic combination of nanomaterials with biophotonics provides unprecedented opportunities to address many current challenges in disease diagnosis and therapy. For example, quantum dots, gold nanoparticles, gold nanorods, gold nanoshells, upconversion nanocrystals, iron oxide nanoparticles, carbon nanotubes, carbon dots, silica nanoparticles, aggregation-induced emission (AIE)-based nanoparticles, etc. are among the commonly investigated nanomaterials in biophotonics. The flexibility in optical and electronic tuning allows these nanomaterials to emit or scatter from visible to near-infrared (NIR) region, an essential characteristic for tailoring specific needs in biophotonic applications.

In this talk, we will highlight the use of nanomaterials with different sizes, compositions, and shapes for biophotonic and nanomedicine applications (e.g. guided bioimaging, multimodal imaging, sensing, in vivo surgery, gene delivery, etc). Also, we will discuss important factors on designing bioconjugated nanomaterials for biophotonic applications as well as the future trend of using nanomaterials in the biophotonic and nanomedicine field. Certainly, the in vitro and in vivo nanotoxicity of nanomaterials will be one of the main challenges to be overcome if we would like/want to pursue in vivo biophotonic or nanomedicine technologies with nanomaterials.

The toxicity assessment of nanomaterials in cell culture and animal models will be presented. This talk is intended to promote the awareness of past and present developments of nanomaterials in biomedical fields, the potential toxicity of nanomaterials, and the approaches to engineer new types of safe nanomaterials, whereby encouraging researchers to think about exciting and promising biophotonic and nanomedicine applications with nanomaterials in the near future.

Light-powered motors and reconfigurable low-symmetry fluids in nematic dispersions of discs

Ivan I. Smalyukh
Department of Physics, University of Colorado, Boulder, CO 80309, USA
Soft Materials Research Center and Materials Science and Engineering Program, Department of Electrical, Computer, and Energy Engineering, University of Colorado, Boulder, CO 80309, USA
Renewable and Sustainable Energy Institute, National Renewable Energy Laboratory and University of Colorado, Boulder, CO 80309, USA
E-mail address: ivan.smalyukh@colorado.edu

Biological motors are marvels of nature that inspire creation of their synthetic counterparts with high efficiency, spontaneous self-assembly and diverse functions. We describe colloidal motors with a repetitive light-driven rotation of thin discs immersed in a liquid crystal and powered by a continuous exposure to unstructured ~1 nW light [1]. Dispersing many charged colloidal discs in a nematic host provides a platform for observing many low-symmetry equilibrium liquid crystalline phases and out-of-equilibrium dynamic states. Depending on temperature, concentration and surface charge of the discs, we find nematic, smectic and columnar organizations with symmetries ranging from uniaxial to orthorhombic and to monoclinic [2]. Most importantly, we demonstrate the possibility of thermal, optical and magnetic control of low-symmetry self-assembly and the monoclinic colloidal nematic order. We characterize this pseudo-polar monoclinic orientational order, along with the phase diagrams, orientational distribution functions and order parameters, as well as their dynamic evolution under out-of-equilibrium conditions. Our findings may lead to opto-mechanical devices and colloidal machines compatible with liquid crystal display technology, as well as low-symmetry active and driven soft matter.

References:

[1] Y. Yuan, Q. Liu, B. Senyuk and I.I. Smalyukh. Elastic colloidal monopoles and out of equilibrium interactions in liquid crystals. *Nature* **570**, 214–218 (2019).
[2] H. Mundoor, J.-S. Wu, H. Wensink and I.I. Smalyukh. Monoclinic liquid crystals from discs and rods. *Nature* **590**, 268-274 (2021).

Plenary sessions

How to introduce fluorescent nanoparticles into a biological system?

Katarzyna C. Nawrot, Marcin Nyk
Advanced Materials Engineering and Modeling Group, Wroclaw University of Science and Technology
E-mail address: katarzyna.nawrot@pwr.edu.pl

Due to quantum confinement effect and – connected to this phenomenon – advantageous absorption and fluorescence, including nonlinear optical properties, nanomaterials are considered as excellent candidates for bioimaging. However, their frequent hydrophobicity and negative or unknow impact on leaving cells are barriers for bioapplications. Here, we present chosen strategies leading to more cell-friendly nanomaterials as well as several approaches to introduce the material to the exact desired place in the diagnosed body.

Despite encapsulation, optical properties of fluorescent nanomaterials do not need to be weeker than in case of raw nanomaterials. [1] Moreover, even if the final material is designed to have multiple functions, the preparation may be a simple one-step approach. [2]

Research funded by National Science Centre, Poland under Grant no. UMO-2018/29/B/ST4/02172

References:

[1] Nawrot KC, Zareba JK, Toporkiewicz M, Chodaczek G, Wawrzynczyk D, Kulbacka J, Bazylinska U, Nyk M. Polymeric Nanocarriers with Luminescent Colloidal Nanoplatelets as Hydrophilic and Non-Toxic Two-Photon Bioimaging Agents. International Journal of Nanomedicine. In Press 2021
[2] Fahmi M.Z. et al., Simple and fast design of folic acid-based carbon dots as theranostic agent and its drug release aspect. Materials Chemistry and Physics, 2021, 267, 124597

Co-encapsulated CdSe QDs and Fe_3O_4 NPs for Two-photon and Hyperthermia Applications

Magda A. AntoniakMarcin Nyk

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

E-mail address: magda.antoniak@pwr.edu.pl

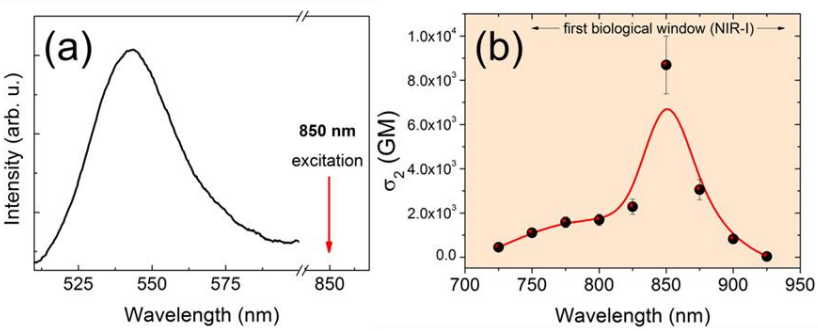


Fig. Representative spectrum of two-photon excited emission under 850 nm fs laser excitation (a), wavelength dependence of the two-photon absorption cross-section σ_2 (black dots) for co-encapsulated CdSe QDs and Fe_3O_4 NPs (b); taken per single nanocapsule. Line connecting the experimental points is meant to guide the eyes.

Ferrite nanoparticles (NPs), especially magnetite (Fe_3O_4), exhibit superior magnetic properties and show a great potential in bio-related applications including their exploitation in so-called heat-triggered or thermo-stimulated processes.[1] Simultaneously, colloidal quantum dots (QDs) are interesting candidates for bioimaging because of large one- and two-photon absorption cross-sections.[2]

In order to merge magnetic and optical properties in a single material, we obtained hybrid nanostructures consisting of Fe_3O_4 NPs and CdSe QDs co-encapsulated in polymeric nanocapsules (NCs). To characterize the morphology of NCs, transmission electron microscopy (TEM), energy dispersive X-ray analysis (EDX) and X-ray scattering technique were used. We studied linear and nonlinear optical properties (the two-photon absorption cross-section σ_2) and investigated individual NCs using scanning confocal fluorescence microscope. Moreover, temperature effects on NCs were measured using alternating magnetic field (AMF) and/or near-infrared laser (808 nm) stimulation. In conclusion, we have shown that CdSe/Fe_3O_4 co-loaded NCs can be potentially used as multifunctional nano-platform for bioimaging and thermo-stimulated applications.

Acknowledgements: MA & MN acknowledge support from the National Science Centre, Poland under Grant no. UMO- 2018/30/E/ST5/00718.

References:

[1] Mura, S., Nicolas, J. & Couvreur, P., Stimuli-responsive nanocarriers for drug delivery. Nature Material 12, 991–1003, 2013.

[2] Antoniak M.A., Grzyb J., Nyk M., Preserved two-photon optical properties of hydrophilic proteins-conjugated quantum dots. Journal of Luminescence 209, 57-60, 2019.

XPS/AES analysis of Cu:Zn ratio in CuO/ZnO and Cu_3N/ZnO nanocomposites

[1]P. Sędzicki[2]R. Szczęsny, [3]M.Trzcinski, [1]B. Derkowska-Zielińska,
[1]Institute of Physics, Faculty of Physics, Astronomy and Informatics,
Nicolaus Copernicus University in Torun, Grudziadzka 5, 87-100 Torun, Poland
[2]Faculty of Chemistry, Nicolaus Copernicus University, Gagarina 7, 87-100 Torun, Poland
[3]Institute of Mathematics and Physics,
UTP University of Science and Technology, S. Kaliskieg 7, 85-796 Bydgoszcz, Poland

E-mail address: sedzicki@doktorant.umk.pl

Stoichiometric, binary copper (I) nitride (Cu_3N) is non-toxic material with many potential applications, including new memory chips, high-capacitance batteries or isolative-layer in magnetic tunnel junctions [1]. Zinc oxide (ZnO) is conductive oxide used in optoelectronic devices. It should be mentioned that ZnO was used as an additive to Cu_3N due to thermal stability and ease of parallel synthesis in a single batch. Initially, Cu/Zn nitrates reacted with $NaHCO_3$ in the aquatic solution of PVP. The reaction products were deposited on silicon, sequentially annealed in the: air and (later) ammonia. We showed the synthesis of two nanocomposites: (CuO/ZnO) and (Cu_3N/ZnO). X-ray photoelectron spectroscopy (XPS) and Auger electrons spectroscopy (AES) were used for composition verification. The Cu:Zn ratio in nanocrystalline films was calculated without emission or absorption coefficients from any XPS/AES databases. In the case of elements heavier (Cu, Zn) than complementary ones (O, N, C), XPS/AES peaks, shown in Fig. 1. can be treated simply as pathways of relaxation for X-ray-excited samples. Integration of areas under Cu/Zn peaks, performed after removal of background and deconvolution of AES peaks, showed that Cu:Zn ratio can be calculated from combined XPS/AES spectra.

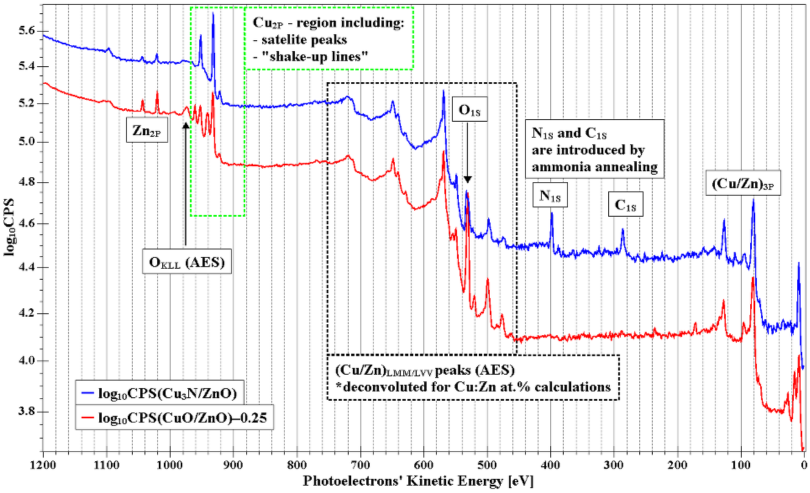


Fig. 1. XPS/AES spectra of (CuO/ZnO) and (Cu_3N/ZnO) nanocomposites.

---

[1] Ścigała A., Szłyk E., Dobrzańska L., Gregory D. H., & Szczęsny R., (2021), From binary to multinary copper based nitrides–Unlocking the potential of new applications. Coordination Chemistry Reviews 436, 213791.

Nanodimensional copper nitride – synthesis of nanowire arrays

Aleksandra Ścigała, Edward Szłyk, Robert Szczęsny

Faculty of Chemistry, Nicolaus Copernicus University in Toruń, Gagarina 7, 87-100 Toruń, Poland
a.scigala@doktorant.umk.pl

Metal nitrides are one of the most stable group of compounds and have long been known for their unique, versatile physicochemical properties. Among them, copper nitride (Cu_3N) has attracted considerable interest in recent years due to its application potential in fields, such as optical data storage, catalysis and energy conversion. It is a metastable semiconductor with a specific cubic anti-ReO_3 crystal structure. Although it has been studied extensively for a long time, there are still significant gaps in the knowledge of its properties and methods of synthesis. Cu_3N has been mostly fabricated by physical deposition techniques until the beginning of 21st century, when significant increase in the number of Cu_3N chemical synthesis methods has been observed [1-2].

It is well known, that the properties of the compound may vary depending on its morphology and dimensions. In our study, the challenge to develop a simple procedure to synthesize copper nitride nanowire arrays was taken up, combining the advantages of both chemical and physical methods. The synthesis in principle includes two steps: (i) a solution growth of $CuO/Cu(OH)_2$ structures on Cu surface with thermal decomposition to pure CuO, and (ii) ammonolysis reaction of CuO precursor to Cu_3N. The as-obtained specimens were studied using scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), UV-Vis spectroscopy and ellipsometry [3]. It was found that the shape, size and composition of the structures were affected by deposition technique of initial Cu surface as well as the solution growth conditions. In contrast, the annealing and ammonolysis processes had no impact on the final morphology and size of the nanowires.

The results indicate that the ammonolysis reaction is a good choice for the controllable synthesis of well-defined Cu_3N nanostructures starting from various copper-based precursors. The large surface area of the nanowires could be considered as being particularly important for potential applications in the field of catalysis. Moreover, the obtained films can constitute a basis for more complex hybrid or composite materials, e.g. by the addition of polymer or subsequent deposition of another material [3].

References:

[1] Greenwood Norman N., Earnshaw Alan, Chemistry of the Elements, Butterworth-Heinemann, 1997.
[2] Ścigała Aleksandra, Szłyk Edward, Dobrzańska Liliana, Gregory Duncan H., Szczęsny Robert, From binary to multinary copper based nitrides – Unlocking the potential of new applications, Coordination Chemistry Reviews, 436, 213791, 2021.
[3] Scigala Aleksandra, Szłyk Edward, Rerek Tomasz, Wiśniewski Marek, Skowronski Lukasz, Trzcinski Marek, Szczesny Robert, Copper Nitride Nanowire Arrays – Comparison of Synthetic Approaches, 14, 603, 2021.

CLOU properties of Fe-Mn-Zr oxide system examined in TGA

Rafal LYSOWSKI Magdalena GAWLAS, Ewelina KSEPKO

Author affiliations: Wroclaw University of Science and Technology, Poland
E-mail address: rafal.lysowski@pwr.edu.pl

Chemical Looping Combustion is a combustion technology where oxygen is provided to a fuel by some substance called oxygen carrier (OC). OC is releasing oxygen when it is reacting directly with substrate (fuel).

Process of oxidation of OC and combustion of fuel occurs in two separate reactors, which is preventing direct contact of air and combusting material. That approach is making purifying fumes easier by preventing formation of nitrogen oxides and eliminating the necessity of separating carbon dioxides from combustion products.

Chemical Looping Combustion with Oxygen Uncoupling (CLOU) is a novel approach to CLC technology that uses properties of some materials to bind oxygen in some range of temperatures then releasing it in another, usually higher. CLOU technology is similar to CLC and has all advantages of combustion in pure oxygen without necessity of using energy consuming oxygen separators, also, in comparison to CLC, is having better performance with combustion of solid fuels. All CLOU materials also have some CLC capabilities.

Typical materials that are used as CLC/CLOU are metal oxides or their derivatives like perovskites or spinels, both synthetic and natural in origin.

Oxygen carrier that is used in the process, besides of high oxygen transport capacity, should be characterized also by low price, ability to maintain its stability during numerous cycles of reduction/oxidation and its safety to the environment.

Promising materials that fulfill these conditions are mixed OCs composed with Fe-Mn-Zr oxides. While iron oxides are showing some CLC properties by themselves, an addition of manganese oxides make it possible to obtain low cost materials with CLOU properties. While, zirconium oxide is used in this work as a stabilizing agent for improving its mechanical strength. CLOU properties obtained were tested using Thermogravimetric analysis (TGA). TGA is one of the best ways to examine CLOU/CLC properties in the laboratory scale, due to the possibility of competitive conditions that can occur in regeneration reactors in various temperatures and number of cycles.

During the research, four OC mixed oxygen materials from the Fe-Mn-Zr family were tested. Applied Fe/Mn mass ratios (wt%) were: 50:30 (F50M30), 55:25 (F55M25), 60:20 (F60M20) and finally 65:15 (F65M15) all with addition of 20wt% of ZrO_2 as a stabilizing agent. Those OCs were compared to the control material composed of Fe oxide with ZrO_2 addition.

All materials were tested in a range of temperatures 800-1200°C to choose the most optimal chemical OCs composition and to define the optimal working condition for each sample.

Acknowledgement: The work was financed in part from the National Science Centre, Poland Project No. 2020/37/B/ST5/01259.

Supramolecular chemistry of gold nanoclusters formation: new luminescent bio-markers

Patryk Obstarczyk[1], Anna Pniakowska[1], Marcin Grzelczak[1], Joanna Olesiak-Bańska[1]
[1]Advanced Materials Engineering and Modelling Group, Wrocław University of Science and Technology, Wrocław, Poland
E-mail address: Patryk.obstarczyk@pwr.edu.pl

Gold nanoclusters with dimensions comparable to the Fermi wavelength of electrons in gold are novel group of nanomaterials with molecular-like and size-dependent optical properties arising from discrete electronic level transitions. Remarkable control over their chemical formation is attracting an ever-growing attention, especially in terms of bio-imaging[1]. In our work we present the supramolecular approach for the gold nanoclusters formation. We synthesized amphiphilic and luminescent (with emission band maxima located in the NIR range of the wavelength spectra) nanomaterials for misfolded protein aggregates – amyloids[2] - staining. Crown ether used as capping-agent in our studies possess host-guest functionality being prone to interact with small cations[4,5]. Upon ligand complexation we observed efficient modulation of gold nanoclusters hydrophobicity (fig. 1), which is of great importance for various biological systems. Our fluorescent and cation sensitive material was applied for amyloid fibrils staining for both: electron- and light-based microscopy techniques.

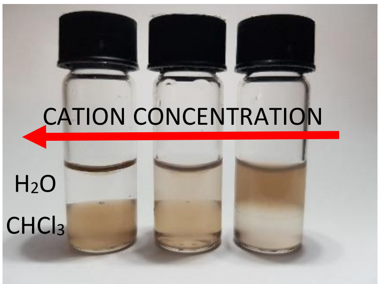


Fig. 1. Gold nanoclusters phase transfer (from aqueous to organic) efficiency dependence on cation concentration.

References:

[1] Olesiak-Bańska, J.; Waszkielewicz, M.; Obstarczyk, P.; Samoć, M. Two-Photon Absorption and Photoluminescence of Colloidal Gold Nanoparticles and Nanoclusters, Chem. Soc. Rev., 2019,48, 4087-4117

[2] Iadanza, M.G., Jackson, M.P., Hewitt, E.W. et al. A new era for understanding amyloid structures and disease. Nat Rev Mol Cell Biol, 2018, 19, 755–773

[3] Grzelczak, M. P.; Hill, A. P.; Belic, D.; Bradley, D. F.; Kunstmann-Olsen, C.; Brust, M. Design of Artificial Membrane Transporters from Gold Nanoparticles with Controllable Hydrophobicity. Faraday Discuss. 2016, 191, 495–510

[4] Wasada, H.; Tsutsui, Y.; Yamabe, S. Ab Initio Study of Proton Affinities of Three Crown Ethers. Journal of Physical Chemistry 1996, 100, 7367–7371

Stokes and anti-Stokes emission enhancement in Y_2SiO_5:Pr ceramics co-doped with Li^+ ions

Patryk Fałat[1], Min Ying Tsang[1], Szymon Zelewski[2], Dominika Wawrzyńczyk[1], Marcin Nyk[1]
[1]Advanced Materials Engineering and Modelling Group, Faculty of Chemistry,
Wrocław University of Science and Technology, 50-370 Wrocław, Poland
[2]Department of Semiconductor Materials Engineering, Faculty of Fundamental Problems of Technology,
Wrocław University of Science and Technology, 50-370 Wrocław, Poland

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

Rich energy level structure, the unique feature of lanthanide ions, provides the opportunity to manipulate the ratio of excitation to emission photons with a high degree of precision. For that very matter, such optical processes as up-conversion or quantum cutting are possible to realize in rare-earth-bearing materials *via* $4f^N \rightarrow 4f^N$ electronic transitions, thus they are widely exploited for optical and photonic applications. [1]

It is often observed in lanthanide-doped materials that emission intensity is not consistent with the simple prediction, i.e. the emission intensity is not always linear function of doping ions concentration. Concentration quenching and parasitic energy migration processes are the most frequent causes of decreased emission intensity values. Therefore numerous attempts to eradicate such hindrances are undertaken, e.g. additional element incorporated into host matrix. [2]

In this work the results of optical experiments performed on synthesized Y_2SiO_5 ceramics co-doped with Pr^{3+} and Li^+ ions are presented. The materials were obtained from corresponding nitrate salts and TEOS in ethanol, followed by drying in a muffle furnace and calcination at 1000°C for 3h. The Stokes emission intensity for Y_2SiO_5:Pr, Li after 213 nm pulsed laser excitation shows fifteenfold increase, compared to Y_2SiO_5:Pr. The anti-Stokes process of up-conversion also occurs after 447 nm diode laser irradiation. The emission peak in UV-C region is 1.5 times stronger than for Pr^{3+} only doped ceramics.

The results gathered in this study are of great importance for enhancing UV-C up-conversion in materials bearing both Pr^{3+} and Li^+ ions, not only at macroscale, but also at nanoscale.

Acknowledgments

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

References:

[1] Chen G. Ågren H., Ohulchanskyy T.Y, Prasad P.N. *Light upconverting core-shell nanostructures: nanophotonic control for emerging applications.* Chemical Society Reviews 44, 1680-1714 (2015).
[2] Cates E. L., Cho M., Kim J.-H. *Converting Visible Light into UVC: Microbial Inactivation by Pr^{3+}-Activated Upconversion Materials.* Environmental Science&Technology 45, 3680–3686 (2011).

One- and two-photon excited fluorescence of acetone-derived polymer dots with strong protein-driven enhancement

Sebastian G. Mucha[1], Agnieszka Krystyniak[2], Lucyna Firlej[1], Katarzyna Matczyszyn[2]
[1] Laboratoire Charles Coulomb, UMR5221, Université de Montpellier (CNRS), Montpellier, France,
[2] Advanced Materials Engineering and Modelling Group, Faculty of Chemistry, Wroclaw University of Science and Technology, Wyb. Wyspiańskiego 27, 50-370 Wroclaw, Poland
sebastian.mucha@umontpellier.fr

In recent years, luminescent carbon-based dots (CDs) have been extensively studied in many fields, as promising alternative candidates for semiconductor nanoparticles. Prepared by low-cost fabrication routes and highly biocompatible, they can be used as luminescent probes in biochemical and pharmaceutical assays with globular proteins, such as human and bovine serum albumins (HSA and BSA). So far, fluorescence studies on interactions between such albumins and luminescent species (e.g. semiconducting nanostructures or organic dyes) relied on fluorescence quenching: (i) either the ultraviolet-excited emission of albumins decreased in the presence of quenching agents, or (ii) albumins reduced the intensities of some fluorescence properties (e.g. two-photon excited photoluminescence, TPE-PL) of the new species.[1] Moreover, many of the fluorescent probes suffer from low chemical and photostability, and unknown toxicity.

Here we present a new, facile, and low-cost method of fabrication of acetone-derived polymer carbon dots (PDs) (alkali-assisted aldol reaction mechanism), and analyze structural and optical properties of pure PDs and PDs-albumins composites.[2,3] As-prepared amorphous-like PDs reveal a narrow distribution of sizes, great chemical stability, and are rich in polar moieties. Upon one-photon (OPE, from ultraviolet to blue color region) and two-photon (TPE) excitation they show long lasting blue and green photoluminescence (PL). Two-photon absorption spectra (TPA) fully cover the red and near-infrared regions ($\lambda_{max.}$ = 760 nm). Unexpectedly, the OPE and TPE-PL strongly increase in the proteinous environments: the emission becomes more intense and stable, and TPA cross-sections are enhanced. Conformational changes in protein structure and the binding parameters indicate strong PDs-albumins interactions due to efficient complexation in simulated physiological conditions and their chemical resistance.

Therefore, PDs-albumins complexes seem to be promising candidates to use in biochemical assays, or in other domains requiring the use of OPE and TPE luminescent materials (f. ex., in the analysis of biopolymer matrixes).

References:

[1] Deiana Marco, Mettra Bastien, Mazur, Leszek M., Andraud Chantal, Samoć Marek, Monnereau Cyrille, Matczyszyn Katarzyna, *Two-Photon Macromolecular Probe Based on a Quadrupolar Anthracenyl Scaffold for Sensitive Recognition of Serum Proteins under Simulated Physiological Conditions*, ACS Omega 2017, 2, 5715– 5725;
[2] Mucha Sebastian G., Firlej Lucyna, Bantignies Jean-Louis, Żak Andrzej, Samoć Marek, Matczyszyn Katarzyna, *Acetone-derived luminescent polymer dots: a facile and low-cost synthesis leads to remarkable photophysical properties*, RSC Advances 2020, 10, 38437-38445;
[3] Mucha Sebastian G., Krystyniak Agnieszka, Firlej Lucyna, Samoć Marek, Matczyszyn Katarzyna, *Protein-driven enhancement of one- and two-photon excited emission in acetone-derived polymer dots*, [In preparation]

Formation of conjugates of silicon dioxide nanoparticles with Al-sulfophthalocyanine molecules for photodynamic therapy

Tikhodeeva Ekaterina Olegovna, Orlova Anna Olegovna
ITMO University, St. Petersburg 197101, Russia
tikhodeeva@itmo.ru

A mixture of Al-sulfophthalocyanine (Al-Pc) molecules with various sulfonation degrees is the main component of Photosens, a drug used for photodynamic therapy. This treatment method involves the use of a special drug (photosensitizer) and an external light source. By themselves, these components are not active, but their combined use, i.e., local excitation of the drug by light leads to a number of chemical reactions that result in cell death. Unfortunately, there is a risk that the photosensitizer will be activated by sunlight or room lighting, which will cause damage to healthy tissues. This side effect can be reduced by increasing the selectivity of photosensitizer accumulation in cancer. It can be achieved by conjugating the molecule to nanoparticles (NP). The creation of such conjugates provides an opportunity to concentrate the molecules on the NPs surface and increase the efficiency of their delivery to the cells (for example, by attaching specific antibodies to the NPs). Based on these concepts, the idea of creating conjugates of Al-Pc with positively charged NPs was proposed.

In this work, conjugates with two types of NPs were formed: nanoparticles of porous silicon dioxide (Si) and nanoparticles of silicon dioxide doped with AgInS2 quantum dots (Si-AIS). The use of the latter provided an opportunity to study the conjugate properties in more detail by analyzing the fluorescence resonance energy transfer (FRET) from the NPs to the molecules. The conjugates were formed due to the electrostatic interaction of negatively charged sulfo groups of the Al-Pc and positively charged amino groups on the NP surface. According to the results of centrifugation, the efficiency of the conjugate formation in water reached 95%. The analysis of the spectral characteristics of aqueous solutions revealed the aggregation of Al-Pcs in the conjugates. However, it is expected that the activity of the photosensitizer inside the cells will not be suppressed, since several studies [1] state the monomerization of Al-Pcs within the cells.

A frequent phase of the drug studies is research on cell lines, so the conjugate behaviour in the cell culture media was considered. When the conjugates were transferred to the culture media, a significant change in their properties was discovered: signs of Al-Pc monomerization were observed. Analysis of the magnetic circular dichroism spectra showed that the transfer of conjugates to the culture medium promotes the monomerization of Al-Pc but does not lead to the complete decomposition of their aggregates. The decrease in the FRET efficiency from AIS-Si to Al-Pc also indicated a partial conjugate decomposition in the culture medium. A strong influence of the relative concentration of the components on the properties of the conjugates, especially on the Al-Pc aggregation degree, was revealed.

References:

[1] Martynenko I.V. Investigation of luminescent properties of complexes of semiconductor quantum dots with tetrapyrrole compounds. Dissertation. Saint Petersburg National Research University of Information Technologies, Mechanics and Optics. P. 168. 2015.

Photoinactivation of clinical strains of *staphylococcus* bacteria with the use of organic light emitting diode

M. Piksa[1], C. Lian[2], S. Persheyev[2], I. D. W. Samuel [2], K. Pawlik[1],
K. Matczyszyn[3]
1. Ludwik Hirszfeld Institute of Immunology and Experimental Therapy,
Polish Academy of Sciences, Poland
2. Organic Semiconductor Centre, School of Physics and Astronomy,
University of St Andrews, UK
3. Advanced Materials Engineering and Modelling Group, Faculty of Chemistry,
Wroclaw University of Science and Technology, Poland

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

Antimicrobial photodynamic therapy (APDT) poses an alternative for antibiotics in case of bacterial infections with high clinical potential. It based on photoinactivation of undesired cells consisted of three elements: photosensitizer, light source and oxygen available in the environment of pathogens. In the results, reactive oxygen species (ROS) are produced and considered as a main antimicrobial agent[1].

For over five years World Health Organization has been alerting about the worldwide danger of the spreading antibiotic resistance[2]. Unfortunately, this problem is still growing and greatly threatens public health. Antibiotic resistance spread fast among health-care-associated pathogens and endanger *ipso facto* already weakened part of society – patients of hospitals. Significant groups of pathogens are *Staphylococcus* ssp. where the most common is *Staphylococcus aureus* and its multiple antibiotic resistance strains including MRSA and VRSA[3,4]. For the above reasons, we investigate photoinactivation of *Staphylococcus* spp. isolated from clinical specimens as an alternative to infection treatment.

The assessment of the photoinactivation efficiency in the fight with *Staphylococcus* ssp. was investigated with the use of ten clinical strains of *staphylococci* isolated from diabetic patients. The experiments were performed with the use of methylene blue as a photosensitizer (proven effectiveness; medically approved). An organic light-emitting diode (OLED) was used as a light source providing a homogeneous area of illumination.

All isolated *Staphylococcus* strains were effectively killed via photoinactivation with a reduction equal at least to 99%, showing that antimicrobial photodynamic therapy poses an attractive alternative to fight *staphylococci*. Nevertheless, the reduction level differed depending on the bacterial strain which may be correlated with the cell wall and cell membrane composition.

References:

[1] Wilson Brian, Patterson Michael, The physics, biophysics and technology of photodynamic therapy, *Physics in Medicine and Biology* 2008 53 (9), 61-109.
[2] WHO | WHO's first global report on antibiotic resistance reveals serious, worldwide threat to public health. WHO (2014).
[3] Calfee DP. Prevention and control of health care-associated infections. In: Goldman L, Schafer AI, eds. Goldman-Cecil Medicine. 26th ed. Philadelphia, PA: Elsevier; 2020:chap 266.
[4] Centers for Disease Control and Infection website. Healthcare settings: preventing the spread of MRSA. www.cdc.gov/mrsa/healthcare/index.html. Updated February 28, 2019. Accessed October 22, 2019.

The importance of H-bonding network for amyloid fibrils autofluorescence

Manuela Grelich-Mucha[a], Ana M. Garcia[b]Vladimir Torbeev[b], Katarzyna Ożga[c], Łukasz Berlicki[c], Joanna Olesiak-Bańska[a]

[a]Advanced Materials Engineering and Modelling Group, Wroclaw University of Science and Technology, Wybrzeze Wyspianskiego 27, 50-370 Wroclaw, Poland.
[b]Institut de Science et d'Ingénierie Supramoléculaires (ISIS), International Center for Frontier Research in Chemistry (icFRC), University of Strasbourg, CNRS UMR 7006, Strasbourg, France.
[c] Department of Bioorganic Chemistry, Faculty of Chemistry, Wroclaw University of Science and Technology, Wybrzeze Wyspianskiego 27, 50-370 Wroclaw, Poland
E-mail address: manuela.grelich@pwr.edu.pl

Amyloid fibrils are filamentous supramolecular nanostructures that are associated with some dysfunctions including Alzheimer’s disease. Their common feature is the presence of β-sheet structure running along the fibril axis.[1] A crucial role is played by H-bonding network, which not only stabilizes their structure, but also provides the driving forces for aggregation.[2, 3] The fibrillar structures possess intrinsic fluorescence properties.[4, 5, 6] Recently, it has been reported that differences in H-bonding pattern impact on the position of autofluorescence spectra.[6]

We have synthesized Aβ(35-42) and depsiAβ(35-42) in which an ester-bond moiety was incorporated between 35th and 36th. amino acid residues. We have also synthesized *L*- and *D*-transthyretin (TTR) (105-115)-fragment peptide sequences. AFM imaging was performed in order to control the ongoing morphology changes. The samples were analyzed using ATR-FTIR and fluorescence spectroscopy approaches.

Obtained results evidence the role of H-bonds on the optical properties and morphology of investigated samples. The disruption of H-bonding network caused by the presence of an ester bond in depsiAβ(35-42) slows down fibrillogenesis. Furthermore, it has an impact on emission band position. A different arrangement of β-sheets in enantiomers and racemate of TTR(105-115) also determines the position of fluorescence emission band. The outcomes evidence the critical role of H-bonding network on autofluorescence properties of amyloid fibrils.

References:

[1] T.P. Knowles, A.W. Fitzpatrick, S. Meehan, H.R. Mott, M. Vendruscolo, C.M. Dobson, M.E. Welland, Role of Intermolecular Forces in Defining Material Properties of Protein Nanofibrils, Science 318(5858) (2007) 1900-1903.

[2] Sarah L. Shammas, Tuomas P.J. Knowles, Andrew J. Baldwin, Cait E. MacPhee, Mark E. Welland, Christopher M. Dobson, Glyn L. Devlin, Perturbation of the Stability of Amyloid Fibrils through Alteration of Electrostatic Interactions, Biophysical Journal 100(11) (2011) 2783-2791.

[3] K. Tsemekhman, L. Goldschmidt, D. Eisenberg, D. Baker, Cooperative hydrogen bonding in amyloid formation, Protein Science 16(4) (2007) 761-764.

[4] D. Pinotsi, L. Grisanti, P. Mahou, R. Gebauer, C.F. Kaminski, A. Hassanali, G.S. Kaminski Schierle, Proton Transfer and Structure-Specific Fluorescence in Hydrogen Bond-Rich Protein Structures, Journal of the American Chemical Society 138(9) (2016) 3046-3057.

[5] L. Grisanti, M. Sapunar, A. Hassanali, N. Došlić, Toward Understanding Optical Properties of Amyloids: A Reaction Path and Nonadiabatic Dynamics Study, Journal of the American Chemical Society 142(42) (2020) 18042-18049.

[6] M. Grelich-Mucha, A. M. Garcia, V. Torbeev, K. Ozga, L. Berlicki, J. Olesiak-Banska, Autofluorescence of amyloids determined by enantiomeric composition of peptides, The Journal of Physical Chemistry B, 2021 (accepted).

Fantastic amyloids and how to understand them?

Maciej Lipok, Manuela Grelich-Mucha, Joanna Olesiak-Bańska

Advanced Materials Engineering and Modelling Group, Faculty of Chemistry, Wrocław University of Science and Technology
maciej.lipok@pwr.edu.pl

Early detection of Alzheimer and Parkinson diseases is a pressing matter in rapidly aging community of XXI century. Key issue is detecting and fully understanding amyloid fibrils - protein aggregates connected with neurodegenerative diseases which exhibit characteristic autofluorescence from energy levels unavailable to protein monomers.[1] However, some amyloids also exhibit two-photon excited autofluorescence which we reported for amyloid spherulites earlier this year, and which could be used for their label-free detection.[2]

During our research we have observed that amyloid fibrils autofluorescence is redshifted comparing to one-photon spectra. To find out the origin of autofluorescence redshift we built a system being able to measure two-photon excited lifetimes using standard TCSPC and pulse picker combined with Ti:Sapphire Chameleon femtosecond laser. Using the system we have measured dyes, such as fluorescein, and different types of lysozyme amyloids to determine which factors influence their two-photon excited autofluorescence.

Our measurements have shown that two-photon excited autofluorescence lifetimes of amyloids are highly dependent on the wavelengths used for excitation. (Fig. 1a) Moreover, they are different from one-photon excited autofluorescence lifetimes leading to conclusion that two-photon excited autofluorescence originates from different energy levels than one-photon fluorescence. (Fig. 1b)

a **b**

Figure 1 Crystalline lysozyme amyloids two-photon excited lifetimes for different excitation wavelengths (a) Comparison between one-photon and two-photon excited lifetime decays of crystalline lysozyme fibers (b).

References:

[1] Sirangelo, I., Borriello, M., Irace, G. & Iannuzzi, C. Intrinsic blue-green fluorescence in amyloyd fibrils. AIMS Biophysics 5, 155-165, (2018).

[2] Obstarczyk P., Lipok M.,Grelich-Mucha M., Samoć M., Olesiak-Bańska J., „Two-photon excited polarization-dependent autofluorescence of amyloids as a label-free method of fibril organization imaging", Journal of Physical Chemistry Letters, 2021, vol. 12, nr 5, s. 1432-1437,

Sensitivity to surrounding medium changes of the Second Harmonic Generation in Gold Nanoparticles

Krzysztof Nadolski[1,2], Estelle Salmon[1], Christian Jonin[1], Katarzyna Matczyszyn[2],
Pierre-Francois Brevet[1,*]
[1]Institut Lumière Matière, Université Claude Bernard Lyon 1, CNRS UMR 5306, Villeurbanne, France.
[2]Advanced Materials Engineering and Modelling Group, Wroclaw University of Science and Technology, Wroclaw, Poland.
**E-mail address: pfbrevet@univ-lyon1.fr*

Plasmonic nanoparticles, especially gold ones, have gained raising interest thanks to the Localized Surface Plasmon Resonance (LSPR) phenomenon [1]. They are widely applied to chemical and biological sensing notably [2]. The most common optical phenomenon employed is colorimetry, where an LSPR peak shift is used for instance toxic metal detection [3]. However, applying nonlinear optical phenomena may augment the sensing sensitivity. In the present work, we have investigated Second Harmonic Generation in gold nanoparticles with respect to the surrounding medium change. Different amounts of glycerol were added to an aqueous solution to change the refractive index of the solution. In order to explain the nature of the processes, simulations were performed. SHG emerges as a true candidate to improve the sensing performance in comparison to the colorimetric method.

References

[1] Louis C., Pluchery O., *Gold Nanoparticles for Physics, Chemistry, and Biology*. Imperial College Press: 2012.
[2] Saha K., Agasti S. S., Kim C., Li X., Rotello V.. Gold nanoparticles in chemical and biological sensing. *Chemical Reviews* **2012,** 112.
[3] Priyadarshini E., Pradhan N.. Gold nanoparticles as efficient sensors in colorimetric detection of toxic metal ions: A review. *Sensors and Actuators B: Chemical* **2017,** 238, 888-902.

Biologically derived lyotropic mesophases doped with triangular carbon nanostructures

D. Benkowska-Biernacka[1], S.G. Mucha[2], Katarzyna Matczyszyn[1]

[1]Advanced Materials Engineering and Modelling Group,
Wroclaw University of Science and Technology, Faculty of Chemistry, Poland
[2] Laboratoire Charles Coulomb, University of Montpellier, CNRS, Montpellier 34095, France
dominika.benkowska@pwr.edu.pl

Many biologically relevant entities show a unique ability to create liquid crystalline arrangement. The examples of mesophases are observed in complex biological systems, for instance in the cell membrane and myelin sheath [1]. The combination of luminescent nanostructures with the biological component, such as phospholipids [2], gains considerable attention due to its potential application in bioimaging. The important advantage of the hybrid material made of a single type of biomacromolecules is obtaining a simplified model of the biological system.

Presented studies focus on the formation and analysis of lyotropic myelin figures (MFs) consisted of phospholipids and doped with triangular carbon nanodots (CNDs). Polarized light microscopy and confocal microscopy techniques were used to investigate the morphology of multi-layered structures. Moreover, we determined the possibility to use of two-photon fluorescence microscopy to examine MFs.

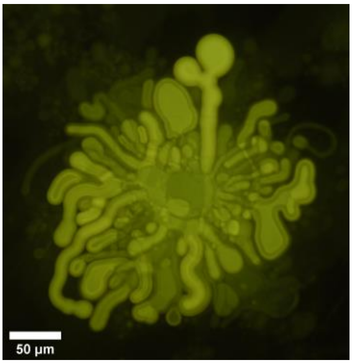


Fig. 1. The fluorescent image of myelin figures doped with CNDs.

References:

[1] D. Benkowska-Biernacka, I. I. Smalyukh, K. Matczyszyn, Morphology of Lyotropic Myelin Figures Stained with a Fluorescent Dye, J. Phys. Chem. B, 124, 52, 11974–11979 (2020)

[2] N. Kanwa, M Kavana, A. Chakraborty, Discriminatory Interaction Behavior of Lipid Vesicles toward Diversely Emissive Carbon Dots Synthesized from Ortho, Meta, and Para Isomeric Carbon Precursors, Langmuir, 36, 35, 10628–10637 (2020)

Two-photon absorption and photoluminescence of atomically precise gold-doped silver nanoclusters

Anna Pniakowska[1], Patryk Obstarczyk[1], Kumaranchira Ramankutty Krishnadas[2],
Thomas Bürgi[2], Joanna Olesiak-Bańska[1]

[1]Advanced Materials Engineering and Modelling Group, Wroclaw University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wroclaw, Poland
[2]Université de Genève, Département de Chimie Physique, 30 Quai Ernest-Ansermet, 1211 Geneva 4, Switzerland

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

Atomically-precise nanoclusters (NCs) are promising group of luminescent nanomaterials possessing firmly established absorption bands arising from discrete electronic energy levels structure. Despite well-defined geometrics, composition and molecular-like behavior of magic-sized nanoclusters, the relation between structure and spectroscopic transitions still remains unclear. Moreover, the nonlinear third-order optical processes observed in silver, gold and silver-gold nanoclusters are still poorly understood. Nevertheless, broadly studied nanoclusters gain much attention since reported two-photon absorption cross-section of NCs reveals giant values varying from 10^2 to 10^4 GM. Great potential beyond these results refers mainly to single wavelength excitation providing outstanding but very limited third-order nonlinear optical information. [1, 2]

In our work we present the influence of gold dopant on two-photon absorption and two-photon photoluminescence of silver nanoclusters. We examined $[Ag_{25}(DMBT)_{18}][(PPh_4)]$, $[Ag_{24}Au_1(DMBT)_{18}][(PPh_4)]$, $[Ag_{25-x}Au_x(DMBT)_{18}][(PPh_4)]$, nanoclusters in comparison to $[Au_{25}(PET)_{18}][TOAB]$ nanoclusters. Herein, we present high two-photon absorption cross sections for the broad two-photon excitation 1050-1550nm wavelength range. Comparing gold-doped nanoalloys to Ag_{25} nanoclusters we report strong enhancement of nonlinear response upon replacing single gold atoms in the cluster core.

Strong nonlinear response of fluorescent nanoclusters at the near infrared biological window opens up wide range of applications in multiphoton bio-imaging and bio-sensing. In addition, better understanding the influence of the ligand and metallic core composition on NCs linear and nonlinear optical properties is crucial for these applications where high power laser illumination is needed. [3]

References:

[1] Ramakrishna G, Varnavski O, Kim J, Lee D, Goodson T. Quantum-Sized Gold Clusters as Efficient Two-Photon Absorbers. Journal of the American Chemical Society. 2008;130(15):5032-3.
[2] Olesiak-Banska J, Waszkielewicz M, Obstarczyk P, Samoc M. Two-photon absorption and photoluminescence of colloidal gold nanoparticles and nanoclusters. Chemical Society Reviews. 2019;48(15):4087-117.
[3] Waszkielewicz M, Olesiak–Banska J, Grzelczak M, Sánchez–Iglesias A, Pniakowska A, Samoc M. Enhanced one-photon and two-photon excited luminescence of polymer-stabilized AuAg nanoclusters aggregates. Journal of Luminescence. 2020;221:116994.

New palladium(II) complexes with perfluorinated amidinates as precursors in vapor deposition methods

Aleksandra Butrymowicz [1], Iwona B. Szymańska [1]
Faculty of Chemistry, Nicolaus Copernicus University in Toruń [1]
E-mail addresses: aleksandra.butrymowicz@doktorant.umk.pl
pola@umk.pl

The vapor deposition methods: CVD – Chemical Vapor Deposition and FEBID/FIBID – Focused Electron/Ion Beam Induced Deposition enables to obtain 2D or 3D deposits, which are attractive due to the possibility of using them in nanoelectronics, biological diagnostics and detection of substances using surface-enhanced Raman spectroscopy (SERS) [1]. A significant advantage of the latter is the possibility of obtaining nanostructures of a specific shape and size because of the ability to control the electron/ion beam. Coordination compounds of metals are used in the above methods of obtaining nanomaterials as precursors being a metal source [2], [3].

The synthesis of new palladium(II) complexes with perfluorinated amidinates was developed. Based on the IR and EI MS spectra analysis, the ligand bridging coordination was confirmed and also, the tri-nuclear structure of compounds was proposed $[Pd_3((NH)_2CR_f)_6]$, where $R_f = CF_3$, C_2F_5. Based on the results obtained with the use of VT IR – Variable Temperature Infrared Spectroscopy, TGA, EI MS the parameters of the CVD process were chosen, and palladium deposits were obtained for both precursors.
The EI MS, ESD – Electron Stimulated Desorption, and SEM/EDX studies were carried out to determine the interaction of the compounds with low and high energy electrons. The EI MS spectra analysis results indicate interaction with electrons of the order of 70eV in the gas phase. The following fragments containing palladium: $[Pd_2((NH)_2CR_f)_2]^{+\bullet}$, $[Pd_3((NH)_2CR_f))_6]^{+\bullet}$, $[Pd_3]^+$ were detected. On the other hand, in the solid phase, results of the ESD experiment showed practically no interaction of the complex $[Pd_3((NH)_2CC_2F_5)_6]$ with low-energy electrons (100eV). However, based on the results of SEM/EDX, the interaction with high-energy electrons (energy 30keV) was observed.

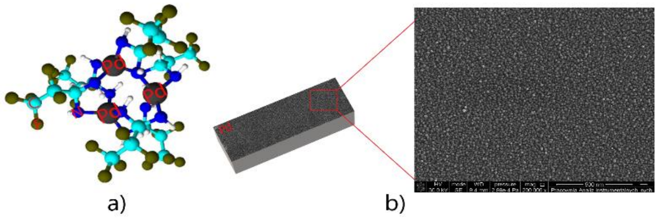


Figure 2 a) Structure of $[Pd_3((NH)_2CC_2F_5)_6]$, b) CVD deposit: T_V=240°C, T_D= 340°C, $p=10^{-1}$ mbar.

References:

[1] Li. P, Liu N., Yu H., Wang F., Liu L., Lee G., Wang Y. and Li W. J., 'Silver nanostructures synthesis via optically induced electrochemical deposition', *Sci. Rep.*, vol. 6, no. June, 1–8, 2016.
[2] Barth S., Huth M. and Jungwirth F., 'Precursors for direct-write nanofabrication with electrons', *J. Mater. Chem. C*, vol. 8, no. 45, 15884–15919, 2020.
[3] Chizari S., Shaw L. A., Behera D., Roy N. K., Zheng X., Panas R. M., Hopkins J. B., Chen S., Cullian M. A., 'Current challenges and potential directions towards precision microscale additive manufacturing – Part III:Energy induced deposition and hybrid electrochemical processes', *Precision Engineering*, vol. 68. Elsevier Inc., 174–186, 2021.

New perfluorinated copper amidinate and imidoylamidinate as precursors for Chemical Vapour Deposition (CVD)

K. Madajska[1], I. B. Szymańska[1]
Author affiliations: [1]Faculty of Chemistry, Nicolaus Copernicus University in Toruń, Gagarina 7, 87-100 Toruń, Poland
E-mail address: 502533@doktorant.umk.pl, pola@umk.pl

It is commonly known that Cu and Ag complexes with non-fluorinated amidinates are a good source of volatile metal carriers and proposed as precursors in vapour deposition methods such as ALD (Atomic Layer Deposition) and CVD [1–3]. Perfluorinated ligands exhibit increased volatility compared to non-fluorinated analogues, favourably affecting the reactions' efficiency in vapour deposition methods [4]. In the available literature, only silver(I) and mercury(II) compounds with perfluorinated amidinates are known: $[Ag_2((NH)_2CCF_3)_2]$, $[Ag_2((NH)_2CC_2F_5)_2]$, $[Hg((NH)_2CC_2F_5)_2]$, which however, have not been tested for use in vapor deposition methods [5].

Here we report on our volatility studies of user-friendly copper amidinate and imidoylamidinate complexes: $[Cu_2(\mu{-}(NH)_2CC_2F_5)_2]$ and $[Cu\{NHC(C_2F_5)NC(CH_3)NH\}_2]$ (Figure 3).

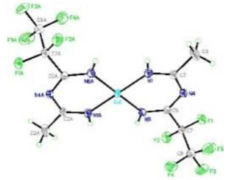


Figure 3 Single crystal X-ray structure of $[Cu(NHC(C_2F_5)NC(CH_3)NH)_2]$.

The sublimation experiment exhibited that they go into the gas phase at only 100°C without decomposition. Moreover, thermal analysis, EI MS spectrometry, and variable temperature infrared spectroscopy were carried out to determine the volatility of compounds and the decomposition mechanism. CVD deposition was also performed using these new Cu compounds as precursors.

References:

[1] Whitehorne T.J.J, Coyle J.P., Mahmood A., Monillas W.H., Yap G.P.A., Barry S.T., Group 11 Amidinates and Guanidinates: Potential Precursors for Vapour Deposition, Eur. J. Inorg. Chem. (2011) 3240–3247. https://doi.org/10.1002/ejic.201100262.
[2] Lim B.S., Rahtu A., Park J.S., Gordon R.G., Synthesis and Characterization of Volatile, Thermally Stable, Reactive Transition Metal Amidinates, Inorg. Chem. 42 (2003) 7951–7958. https://doi.org/10.1021/ic0345424.
[3] Li Z., Barry S.T., Roy R.G.G., Synthesis and Characterization of Copper(I) Amidinates as Precursors for Atomic Layer Deposition (ALD) of Copper Metal, Inorg. Chem. 44 (2005) 1728–1735. https://doi.org/10.1021/ic048492u.
[4] Mishra S., Daniele S., Metal-Organic Derivatives with Fluorinated Ligands as Precursors for Inorganic Nanomaterials, Chem. Rev. 115 (2015) 8379–8448. https://doi.org/10.1021/cr400637c.
[5] Reilly W.L., Brown H.C., Reactions of Perfluoronitriles. I. Synthesis of Derivatives of Perfluoroamidines, N-Substituted Perfluoroamidines and Perfluorothioamides, J. Am. Chem. Soc. 78 (1956) 6032–6034. https://doi.org/10.1021/ja01604a021.

Catalytic Effect of Gold Nanoparticles on the Z-E Isomerization of Azobenzene

Nina Tarnowicz-Staniak[1], Marek Grzelczak[2], Katarzyna Matczyszyn[1]
[1]Advanced 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

Photocatalytic effect of gold nanoparticles has been studied since 1981, when the theoretical background for the process was described for the first time. [1] We presented our insight into the topic of plasmon-assisted photocatalysis during PANIC 2019 Conference. We reported the use of AuPd bimetallic nanoparticles immobilized on the cellulose fibers in the bio-inspired process of cofactor (NAD^+) regeneration. [2]

However, as it has been shown for the Z-E isomerization of azobenzene [3-5], gold nanoparticles can also catalyse reactions in the dark. Studies report the increase in the rate constant values of the thermal recovery of photochromic molecules due to the presence of gold nanoparticles. [3] The proposed mechanism postulates the electron transfer from the photochromic molecule to the nanoparticle and formation of radical cation intermediate able to undergo Z-E isomerization. This reaction is subsequently followed by the electron transfer from the surface of the nanocatalyst back to the photochromic molecule. [3, 5] Moreover, it has been proven that the catalytic effect is more pronounced for *para*-substituted azobenzenes. [3]

However, to the best of our knowledge, literature reports only the use of spherical gold nanoparticles as catalysts for thermal Z-E isomerization of azobenzene. Hence in our research, we have focused on the investigation of the influence of anisotropic rod-like gold nanostructures on the same reaction monitored for a model azobenzene molecule.

References:

[1] A. Nitzan, L.E. Brus, *J. Chem. Phys.* 1981, 75, 2205– 2214.
[2] N. Tarnowicz-Staniak, S. Vázquez-Díaz, V. Pavlov, K. Matczyszyn, M. Grzelczak, ACS Appl. Mater. Interfaces 2020, 12, 17, 19377–19383.
[3] G.L. Hallett-Tapley *et al.*, *Chem. Commun.*, 2013,49, 10073-10075.
[4] S. Simoncelli, P.F. Aramendía, *Catal. Sci. Technol.*, 2015,5, 2110-2116.
[5] E. Titov *et al.*, *J. Phys. Chem. C*, 2015, 119, 30, 17369–17377.

2D material active layer fabrication for Light Emitting Devices (LEDs)

[a), b)] Daria Hlushchenko, [c),d)] Robert Kudrawiec

[a)] Lukasiewicz Research Network – PORT Polish Center for Technology Development,

[b)] Wroclaw University of Science and Technology

[c)] Lukasiewicz Research Network – PORT Polish Center for Technology Development,

[d)] Wroclaw University of Science and Technology

daria.hlushchenko@pwr.edu.pl

2D materials show significant advantages for optoelectronic devices due to unique optical and electronic properties. First, their optical responses cover most of the electromagnetic (EM) wavelengths, ranging from ultraviolet to terahertz, and even the microwave region [1]. As a result, atomically thin layered 2D materials can integrated with many other materials and structures. Vertical stacking of atomically thin layered materials opens new possibilities for the fabrication of heterostructures with favorable optoelectronic properties. The combination of graphene, hexagonal boron nitride and semiconducting transition metal dichalcogenides (TMDs) allows fabrication of electroluminescence (LEDs) devices, which are compatible with a wide range of substrates.

In most cases, LED consist from protective layer on top, transparent electrodes (graphene), active layer, optical cavity and hybrid platform (fig.1). As protective layer was chosen sol-gel coating. Active layer represented as heterostructure h-BN/TMDs/h-BN. Graphene used as transparent electrodes due to high thermal conductivity and stability.

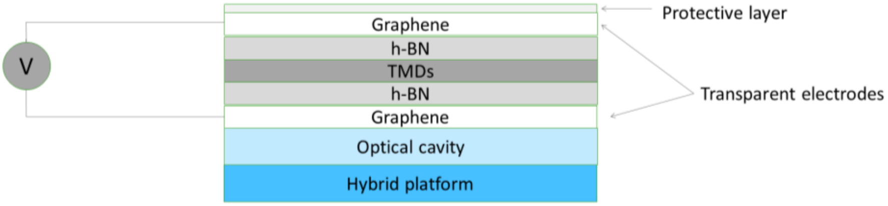


Fig. 1. Principal scheme of LED on the basis on 2D materials (Graphene, h-BN, TMDs)

Moreover, combining optical elements of large band-gap, high-index 3D semiconductors (such as GaN, AlGaN or Si3N4) with 2D TMDCs would present an effective approach in design LEDs [1]. Such semiconductors are promising materials for optoelectronics because of their direct band gap and high electron mobility.

References:

[1] Yuanming Z., Sijiong M., Dongwei S., Neng L., Fei M., Jinxia X., Xianan C. Improved Charge Injection and Transport of Light-Emitting Diodes Based on Two-Dimensional Materials. *Appl. Sci.* 2019, *9*(19), 4140; https://doi.org/10.3390/app9194140.

Poster session I

A simple test to detect γ-butyrolactones in *Streptomyces coelicolor*

Adrianna Jastrzemska, Bartosz Bednarz, Magdalena Kotowska, Krzysztof Pawlik
Hirszfeld Institute of Immunology and Experimental Therapy, Polish Academy of Sciences
adrianna.jastrzemska@hirszfeld.pl

Streptomyces are Gram-positive, aerobic soil bacteria, which are characterized by complex fungal-like morphological differentiation. They produce more than 70% of commercially available antibiotics. Many species of *Streptomyces* are capable of producing more than 20 secondary metabolites and the production process itself is extremely sensitive to growth conditions and is associated with the accumulation of signaling molecules such as γ-butyrolactones [1,2].

Eight γ-butyrolactones produced by *Streptomyces coelicolor A3(2)* have been determined so far and described as SCB 1-8. The most common is butanolide 1 (SCB1) [3,4]. SCBs have been shown to activate the polyketide synthase *cpk* gene cluster, which contains the key SCB biosynthetic gene - *scbA* [5,6]. This cluster's products are detected as a yellow pigment excreted to the medium (yCPK) also known as coelimycin P1 and P2 [7].

Here we present a simple test to detect γ-butyrolactones in the culture medium, based on the relationship between γ-butyrolactone occurrence and the production of coelimycin.

References:

[1] Challis GL, Hopwood DA. Synergy and contingency as driving forces for the evolution of multiple secondary metabolite production by Streptomyces species. *Proc. Natl. Acad. Sci.*, **100**, 14555–61 (2003).

[2] Hong B, Phornphisutthimas S, Tilley E, Baumberg S, McDowall KJ. Streptomycin production by Streptomyces griseus can be modulated by a mechanism not associated with change in the adpA component of the A-factor cascade. *Biotechnol. Lett.*, (2007).

[3] Sidda JD, Poon V, Song L, Wang W, Yang K, Corre C. Overproduction and identification of butyrolactones SCB1–8 in the antibiotic production superhost Streptomyces M1152. *Org. Biomol. Chem.*, **14**, 6390–3 (2016).

[4] Takano E. γ-Butyrolactones: Streptomyces signalling molecules regulating antibiotic production and differentiation. *Curr. Opin. Microbiol.*, **9**, 287–94 (2006).

[5] Takano E, Kinoshita H, Mersinias V, Bucca G, Hotchkiss G, Nihira T, Smith CP, Bibb M, Wohlleben W, Chater K. A bacterial hormone (the SCB1) directly controls the expression of a pathway-specific regulatory gene in the cryptic type I polyketide biosynthetic gene cluster of Streptomyces coelicolor. *Mol. Microbiol.*, **56**, 465–79 (2005).

[6] Liu G, Chater KF, Chandra G, Niu G, Tan H. Molecular Regulation of Antibiotic Biosynthesis in Streptomyces. *Microbiol. Mol. Biol. Rev.*, **77**, 112–43 (2013).

[7] Pawlik K, Kotowska M, Kolesiński P. Streptomyces coelicolor A3(2) Produces a New Yellow Pigment Associated with the Polyketide Synthase Cpk. *J. Mol. Microbiol. Biotechnol.*, **19**, 147–51 (2010).

Searching for the target of histidine kinase by *in-vivo* luciferase reporter system in *Streptomyces coelicolor* A3(2)

Mateusz Wenecki, Bartosz Bednarz, Magdalena Kotowska, Krzysztof Pawlik
Hirszfeld Institute of Immunology and Experimental Therapy, Polish Academy of Sciences, Wrocław
mateusz.wenecki@hirszfeld.pl

The soil-dwelling, gram-positive bacteria from the genus *Streptomyces* are prolific producers of secondary metabolites, many of which are beneficial to humans. One of such metabolites of the model organism *Streptomyces coelicolor* A3(2) is the yellow polyketide coelimycin, the role of which is still unclear in biological terms. Genes necessary for its biosynthesis are clustered together in a silent biosynthetic gene cluster (BGC) *cpk*. Its expression occurs only when certain environmental conditions are met and is dependent on quorum sensing – a bacterial communication mechanism utilizing gamma-butyrolactones as signaling molecules [1,2,3]. Studying the regulation of BGC transcription may aid in unlocking the silenced biosynthetic potential of *Actinobacteria spp.* [4].

The luciferase-based reporter assay is an established utility to measure gene transcription in *Streptomyces coelicolor* A3(2) *in vivo* [5]. The chosen promoters are cloned upstream of *lux* genes and their transcriptional activity can be measured automatically in a UV/VIS plate reader/incubator. We measured *cpk* promoter activities in *S. coelicolor* A3(2) mutant lacking the *cpk* cluster-encoded histidine kinase *orfB* gene, to reveal its role in regulating the *cpk* cluster. We were able to detect shifts in promoter activity profiles between the mutant and the wild type strain M145, which suggests that OrfB histidine kinase may influence *cpk* gene transcription by modulating the action of *cpk* cluster activatory protein CpkO. Harnessing luciferase activity reporter assays allows for detailed gene transcription profiling over the whole *Streptomyces* life-cycle in an easy-to-read, small-scale experiments in 96-well plates.

References:

[1] Pawlik Krzysztof, Kotowska Magdalena, Kolesiński Piotr, *Streptomyces coelicolor* A3(2) produces a new yellow pigment associated with the polyketide synthase Cpk, Journal of Molecular Microbiology and Biotechnology, 19(3): 147–151, 2010
[2] Takano Erico, γ-Butyrolactones: *Streptomyces* signalling molecules regulating antibiotic production and differentiation, Current Opinion in Microbiology, 9(3): 287–294, 2006
[3] Bednarz Bartosz, Kotowska Magdalena, Pawlik Krzysztof Jakub, Multi-level regulation of coelimycin synthesis in *Streptomyces coelicolor* A3(2), Applied Microbiology and Biotechnology, 103:6423–6434, 2019
[4] Lee Nami, Hwang Soonkyu, Lee Yongjae, Cho Suhyung, Palsson Bernhard and Cho Byung-Kwan, Synthetic Biology Tools for Novel Secondary Metabolite Discovery in Streptomyces, Journal of Microbiology and Biotechnology, 29(5): 667–686, 2019
[5] Craney Arryn, Hohenauer Tobias, Xu Ye, Navani Naveen Kumar, Li Yingfu and Nodwell Justin, A synthetic *luxCDABE* gene cluster optimized for expression in high-GC bacteria, Nucleic Acids Research, 35(6), e46, 2007

Application of luciferase reporter system to study a specialized metabolic pathway of *Streptomyces coelicolor* A3(2)

Marta Derkacz, Bartosz Bednarz, Magdalena Kotowska, Krzysztof Pawlik
Hirszfeld Institute of Immunology and Experimental Therapy, Polish Academy of Sciences, Wrocław
marta.derkacz@hirszfeld.pl

Side effect of luciferase enzymatic reaction is spontaneous emission of 490 nm light. Light intensity is proportional to promoter activity of a DNA fragment cloned in luciferase reporter plasmid [1].

Streptomyces are gram-positive bacteria living in the soil. They have an important ecological role in biogenic elements turnover [2] and produce a multitude of antibiotics and many other bioactive molecules useful to human health [3].

Final product of the *S. coelicolor* A3(2) polyketide synthase encoded in the *cpk* gene cluster is a yellow pigment (yCPK) - coelimycin P1 and P2 [4, 5]. Its colorless intermediate(s) (abCPK) demonstrate weak antibiotic activity against *Bacillus subtilis*, *Micrococcus luteus* and *Escherichia coli*. Deletion of *scF* gene caused inhibition of the yCPK synthesis, while abCPK was retained [4]. The physiological and regulatory functions of the CPK compounds are still unclear [5].

In this work luciferase reporter system was used to check the activity of the *cpk* cluster promoters. The selected promoters regions were cloned upstream of the lux operon and the promoter activity was measured by luminescence detection in wild type strain and *scF* deletion strain (*ΔscF*). Result analysis showed bigger activity of the majority of promoters in *ΔscF* strain, than in the wild type. This suggests that a compound generated in this biosynthetic pathway between abCPK and yCPK has a negative effect on the *cpk* cluster expression.

References:

[1] Craney A, Hohenauer T, Xu Y, Navani NK, Li Y, Nodwell J. A synthetic luxCDABE gene cluster optimized for expression in high-GC bacteria. Nucleic Acids Res. 2007;35(6):e46. doi: 10.1093/nar/gkm086. Epub 2007 Mar 1. PMID: 17337439; PMCID: PMC1874620.

[2] R.F. Seipke, M. Kaltenpoth, M.I. Hutchings, Streptomyces as symbionts: an emerging and widespread theme?, FEMS Microbiol Rev. 36 (2011) 862–876.

[3] D.A. Hopwood, Streptomyces in Nature and Medicine. The Antibiotic Makers, Oxford University Press, New York, NY, 2007

[4] Gottelt M, Kol S, Gomez-Escribano JP, Bibb M, Takano E. Deletion of a regulatory gene within the cpk gene cluster reveals novel antibacterial activity in Streptomyces coelicolor A3(2). Microbiology (Reading). 2010 Aug;156(Pt 8):2343-2353. doi: 10.1099/mic.0.038281-0. Epub 2010 May 6. PMID: 20447997.

[5] Bednarz, B., Kotowska, M. & Pawlik, K.J. Multi-level regulation of coelimycin synthesis in Streptomyces coelicolor A3(2). Appl Microbiol Biotechnol 103, 6423–6434 (2019).

The effect of antimicrobial photodynamic therapy on *Pseudomonas aeruginosa* using red light and 5-aminolevulinic acid

EwelinaWanarska[1], Irena Maliszewska[1]
[1]*Department of Organic and Medicinal Chemistry, Wrocław University of Science and Technology*
ewelina.wanarska@pwr.edu.pl, irena.helena.maliszewska@pwr.edu.pl

Nowadays drug resistance of microorganisms is a widely-spread, global issue. The solution of this problem may be antimicrobial photodynamic therapy (aPDT) which can be the alternative or supplement to conventional antibiotic treatment. This therapy targets lipids, proteins and nucleic acids, causing major damage in microbial cells [1]. This form of treatment, using three component- visible light, photosensitizer (non-toxic dye) and oxygen- can successfully "fight" with bacterial infections. A photosensitizer activated by light with appropriate wavelength is transitioning from a low-energy ground state to a singlet excited state. Thereafter, the photosensitizer may decay back to its ground state with fluorescence emission, or it may go into a higher energy triplet state. The triplet state photosensitizer can react with biomolecules in two different ways.

Electron can be transferred to the biomolecules with generation of reactive oxygen species (ROS) (Type I of mechanism) or energy can be directly transferred to the oxygen with formation of singlet oxygen (Type II of mechanism). During these interactions, highly reactive oxygen species are produced which are detrimental to the integrity of the cell membrane, causing irreversible damage to the cell [2].

It is described that microorganisms own endogenous metabolites, which excited by light behave like photosensitizers. The mostly known is protoporphyrin IX (Pp IX), naturally synthesized by cells from 5-aminolevulinic acid, a component of the heme formation pathway. Excitation of Pp IX with light can cause effective cell photo-destruction. Another approach to the problem is cell photosensitization with exogenous component 5-ALA. This compound, participating in the heme biosynthesis pathway, is a natural precursor of Pp IX [3]. This pro-drug cannot generate reactive oxygen species, but when added exogenously, it is converted into protoporphyrin IX [4].

In this study the effect of red laser light (635 nm) alone and with 5-aminolevulinic acid (2.5 mM) in time on *Pseudomonas aeruginosa* was tested. Light exposure only caused 77.1% reduction in *P. aeruginosa* cells. The photodynamic therapy process using 5-ALA caused up to 99.88% mortality of tested bacteria.

References:

[1] Rosa, L.P.; da Silva, F.C. Antimicrobial Photodynamic Therapy: A New Therapeutic Option to Combat Infections. Journal of Medical Microbiology & Diagnosis, 3, 1-7, 2014.
[2] Cieplik, F.; Dongmei, D.; Crielaard, W.; Buchalla, W.;Hellwig, E.; Al-Ahmad, A.; Maisch, T. Antimicrobial Photodynamic Therapy - What We Know and What We Don't. Critical Reviews in Microbiology, 44, 571-589, 2018.
[3] Castano, A.P.,;Demidova, T.N.; Hamblin, M.R. Mechanisms in Photodynamic therapy: Part One-Photosensitizers, Photochemistry and Cellular Localization. Photodiagnosis and Photodynamic Therapy, 1, 279-293, 2004.
[4]Harris, F.; Pierpoint, L. Photodynamic Therapy Based on 5-Aminolevulinic Acid and Its Use as an Antimicrobial Agent. Medicinal Research Reviews, 32, 1292-37, 2012

The effect of low-temperature plasma on phytopathogenic fungi

Daria Kocek[1], Irena Maliszewska[1], Tomasz Czapka[2]
[1] Department of Organic and Medicinal Chemistry, Wrocław University of Science and Technology, Wrocław, Poland
[2] Department of Electrical Engineering Fundamentals, Wrocław University of Science and Technology, Wrocław, Poland
daria.kocek@pwr.edu.pl, irena.helena.maliszewska@pwr.edu.pl, tomasz.czapka@pwr.edu.pl

Plasma is commonly referred to as the fourth state of matter in which an increase in the energy level of a material converts its state from solid to liquid to gas and ultimately to an ionized gas state [1]. Due to the complex physical and chemical processes taking place in low-temperature plasma, it acquires unique properties. Depending on parameters such as gas composition, flow rate, humidity, temperature and excitation properties, many different biologically active agents are produced. These agents are radicals and chemical products, e.g. NxOy, atomic oxygen (O), ozone (O_3), hydroxyl (OH), reactive oxygen (ROS) and nitrogen species (RNS), high energy UV radiation, radiation in the visible and infrared spectral range, charged particles, alternating electric fields, heat as well as physical and chemicaletch processes. Especially the combination of different factors makes plasma attractive because it is almost impossible for pathogens to develop resistance to these different types of plasma stressors [2].

In recent years, low-temperature plasma sterilization has become more common in various fields such as materials science, medicine, as well as in preservation of foods. It is widely believed that low-temperature plasma can overcome many of the limitations of traditional sterilization techniques and is considered one of the most promising sterilization methods. Plasma sterilization is characterized by a number of advantages, including safety and efficacy, cost effectiveness, shorter sterilization time, low processing temperature, and use in both living and nonliving materials [3], [4].

The effect of low-temperature plasma on phytopathogenic fungi was investigated. It was shown that low-temperature plasma is highly effective in inactivating microbial pathogens on solid and porous surfaces in a short time.

These study suggest that the use of low-temperature plasma is a highly effective disinfection method and can be successfully used to inactivate pathogenic microorganisms from various surfaces.

References:

[1] Bourke P, Ziuzina D, Han L, Cullen PJ, Gilmore BF. Microbiological interactions with cold plasma. Journal of Applied Microbiology 123, 308--324, 2017
[2] Ehlbeck J, Schnabel U, Polak M, Winter J, von Woedtke Th, Brandenburg R, von dem Hagen T, Weltmann K-D. Low Temperature Atmospheric Pressure Plasma Sources for Microbial Decontamination. J. Phys. D: Appl. Phys. 44 013002, 2011
[3] Chang Y, Chen G. Oral bacterial inactivation using a novel low-temperature atmospheric-pressure plasma device. ScienceDirect 11(1):65–71, 2016
[4] Sakudo A, Yagyu Y, Onodera T. Disinfection and Sterilization Using Plasma Technology: Fundamentals and Future Perspectives for Biological Applications. Int. J. Mol. Sci. 20, 5216, 2019

AdpA protein interactions with gene promoters within the chloramphenicol biosynthetic gene cluster

Olimpia Żuchowicz, Marcin Wolański

University of Wrocław, Faculty of Biological Sciences, Genetics and Experimental Biology, 1st year, 2nd degree

zuchowiczolimpia@gmail.com

Streptomyces are gram-positive bacteria that produce various secondary metabolites, natural substances often exhibiting medical importance, for instance, antibiotics; immunosuppressants; antihelminthics. The genes responsible for the biosynthesis of those substances usually form large gene clusters. These clusters are often precisely controlled by a plethora of different factors including external signal molecules as well as numerous protein transcription factors [1].

Streptomyces venezuelae is model organism known also for the production of chloramphenicol. Regulation of gene expression of chloramphenicol biosynthetic gene cluster (Cml-BGC) is still not well understood. For a long time, it was assumed that the Cml-BGC did not have its own specific transcriptional regulators, which could control the core biosynthetic genes and chloramphenicol production [2].

The AdpA transcriptional regulator is relatively well studied due to its important role in controlling biosynthesis of antibiotics, e.g. undecyloprodigiosin and actinorhodin, and morphological differentiation in *Streptomyces* [3]. Preliminary results suggest, that in *S. venezuelae* AdpA is able to bind several gene promoters within Cml-BGC. In this study, presumed AdpA-controlled gene promoters were fluorescently labeled and tested for interaction with recombinant AdpA protein using electrophoretic mobility shift assay (EMSA). Presumably in most *Streptomyces* AdpA regulates its own gene expression. In order to study if this is the case in *S. venezuelae* interaction of AdpASv with its native promoter region was investigated. In addition, to examine whether AdpA proteins can cross-interact with *adpA* promoters of orthologues *Streptomyces*, AdpAs of *S. venezuelae* and *S. coelicolor* were tested against their native and heterologous promoter regions.

In this study, we confirm that AdpASv can specifically interact with several gene promoters (*sven_p0915*, *sven_p0916* and *sven_p0925*) within Cml-BGC. In addition, it turned out that AdpASc can cross-interact with the same gene promoters of Cml-BGC suggesting that both AdpASv and AdpASc recognize the same DNA sequences.
What is more, both AdpA protein orthologs were found to interact similarly with *adpA* gene promoters derived from native and heterologous *Streptomyces* species. The influence of AdpASv on the regulation of gene expression within Cml-BGC is currently further investigated.

References:

[1] Chater 2010 Liu, G., Chater, K. F., Chandra, G., Niu, G., & Tan, H. (2013). Molecular Regulation of Antibiotic Biosynthesis in Streptomyces. Microbiology and Molecular Biology Reviews, 77(1), 112–143.

[2] Sekurova, O. N., Zhang, J., Kristiansen, K. A., & Zotchev, S. B. (2016). Activation of chloramphenicol biosynthesis in Streptomyces venezuelae ATCC 10712 by ethanol shock: Insights from the promoter fusion studies. Microbial Cell Factories, 15(1), 1–10.

[3] Wang, W., Ji, J., Li, X., Wang, J., Li, S., Pan, G., Fan, K., & Yang, K. (2014). Angucyclines as signals modulate the behaviors of Streptomyces coelicolor. Proceedings of the National Academy of Sciences of the United States of America, 111(15), 5688–5693.

P7

Influence of Zn^{2+} on formation of amyloids of amylin analogs

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, Wrocław, Poland
[b]Faculty of Chemistry, University of Wroclaw, Wroclaw, Poland

According to data provided by WHO around 422 million people worldwide have diabetes and most of them suffer for type 2 (T2D).[1] Mainly adults get T2D, it occurs when the body becomes resistant to insulin or doesn't make enough insulin. It has been proven that many factors influence the development of diabetes, but not all processes have been thoroughly studied, mainly due to the inconclusive results and complexity of the processes occurring in the body. In the progress of T2D and in the degenerative process of β-cells aggregation of amylin takes part.[2,3] Another known symptom of T2D is zinc deficiency. What is worth mentioning - amylin and zinc are both stored in β-cell granules and together released into the bloodstream.[3] The interactions of zinc ions with amylin may have an impact on the development of the T2D. To better understand the effect of the ion, studies on amylin analogues that differ by several amino acid residues should be considered.[4]

The goal of the study was to investigate influence of the Zn^{2+} on amylin analogues like pramlintide, acetylated pramlintide, rat amylin and fragment 1-19 of human amylin. During the study, the morphology of the resulting structures was checked at different time points. The research technique used was AFM. Based on the research, the differences in the morphology (e.g length, diameter) of fibers and oligomers were detected. Only pramlintide aggregated while other polypeptides not. For pramlintide zinc ions showed catalytic properties, but interestingly for acetylated pramlintide, no fiber formation was observed with or without ions. Since pramlintide is administered intravenously in form of acetate salt as a drug, we expected its solubility.[5] The fact that the non-acetylated form aggregated under the influence of ions but acetylated no, shows how many factors affect the formation of amyloid. For rat amylin and a fragment of human amylin amorphous aggregates were observed with no distinct tendency.The research allows to approximate the influence of zinc ions as one of the factors during amyloid formation process.

Acknowledgements

This work was supported by the NONA project carried out within the First Team program of the Foundation for Polish Science (First TEAM/2017-3/27) co-financed by the European Union under the European Regional Development Fund.

References:

[1] World Health Organization. Global report on diabetes. Geneva: World Health Organization; 2016.
[2] Kahn, S. E., D'Alessio, D. A., Schwartz, M. W., Fujimoto, W. Y., Ensinck, J. W., Taborsky, G. J., Jr., and Porte, D., Jr. (1990) Evidence of cosecretion of islet amyloid polypeptide and insulin by beta-cells. Diabetes 39, 634−638.
[3].Wineman-Fisher, V. & Miller, Y. Insight into a New Binding Site of Zinc Ions in Fibrillar Amylin. (2017).
[4] 1. Łoboda, D. & Rowińska-Żyrek, M. Zn(II) - pramlintide: Stability, binding sites and unexpected aggregation. J. Inorg. Biochem. 174, 150–155 (2017).
[5] 1. Edelman, S., Maier, H. & Wilhelm, K. Pramlintide in the Treatment of Diabetes Mellitus. BioDrugs 22, 375–386 (2008).

Electrochemical detection of drugs using nanofiber-based sensors

Kinga Halicka, Joanna Cabaj
Department of Organic and Medicinal Chemistry, Wroclaw University of Science and Technology,
Wybrzeze Wyspianskeigo 27, 50-370 Wroclaw, Poland
E-mail address: kinga.halicka@pwr.edu.pl

1. Introduction

A sensor is a device that transforms chemical information into an interpretable signal. In an electrochemical system, a reaction between the analyte and modified electrode results in an electrical signal. If the recognition reaction involves biomolecules, the system is considered a biosensor. Introduction of nanomaterials, such as nanofibers, into the construction of (bio)sensors improves the performance of detection platforms thanks to their specific properties, the most important being nanoscale size, porosity, and large surface area to volume ratio [1-3].

2. Results

Various drugs could be detected with nanofiber-based electrochemical sensors. Salandari-Jolge et al. fabricated a voltammetric sensor for the detection of an anticancer drug, methotrexate, based on $CuCr_2O_4$/CuO, with the detection limit (LOD) of 25 nM [4]. Bahrami et al. developed a platform for morphine detection using magnetic nanofibers and achieved the LOD of 1.9 nM [5]. Using carbon nanofibers, tramadol (an opioid pain medication) was detected with the detection limit of 0.016 nM by Jahromi et al. [6]. Modified carbon nanofibers were also applied to detect an antibiotic – metronidazole, using differential pulse voltammetry. Obtained sensor exhibited the LOD of 0.13 nM [7].

3. Conclusions

Monitoring of drugs presence and concentration is essential for proper patient care. The use of nanomaterial-based sensing platforms allows the detection of even trace amounts of various medically relevant molecules, enabling good healthcare, as well as control of the quality of products that may potentially contain such substances.

References:

[1] Hulanicki A, Głąb S, Ingman F, Chemical sensors: definitions and classification, Pure and Applied Chemistry 63(9), 1247-1250 (1991)

[2] Hammond JL, Formisano N, Estrela P, Carrara S, Tkac J, Electrochemical biosensors and nanobiosensors, Essays in Biochemistry 60, 69–80 (2016)

[3] Rezaei B, Ghani M, Shoushtari AM, Rabiee M, Electrochemical biosensors based on nanofibres for cardiac biomarker detection: A comprehensive review, Biosensors and Bioelectronics 78, 513-523 (2016)

[4] Salandari-Jolge N, Ensafi AA, Rezaei B, A novel three-dimensional network of $CuCr_2O_4$/CuO nanofibers for voltammetric determination of anticancer drug methotrexate, Analytical and Bioanalytical Chemistry 412, 2443–2453 (2020)

[5] Bahrami G, Ehzari H, Mirzabeigy S, Mohammadi B, Arkan E, Fabrication of a sensitive electrochemical sensor based on electrospun magnetic nanofibers for morphine analysis in biological samples, Materials Science and Engineering C 106, 110183 (2020)

[6] Jahromi Z, Mirzaei E, Savardashtaki A, Afzali M, Afzali Z, A rapid and selective electrochemical sensor based on electrospun carbon nanofibers for tramadol detection, Microchemical Journal 157, 104942 (2020)

[7] Vilian A.T.E., K.S. Ranjith, S.J. Lee, R. Umapathi, S.K. Hwang, C.W. Oh, Y.S. Huh, Y.K. Han, Hierarchical dense Ni−Co layered double hydroxide supported carbon nanofibers for the electrochemical determination of metronidazole in biological samples, Electrochim. Acta. 354 (2020) 136723

Self-assembled bilosomes as a co-delivery system of multifunctional therapeutic agents

Ewelina Waglewska, Agata Pucek-Kaczmarek, Urszula Bazylińska
Department of Physical and Quantum Chemistry, Faculty of Chemistry, Wroclaw University of Science and Technology, Wybrzeze Wyspianskiego 27, 50-370 Wroclaw, Poland
E-mail address: ewelina.waglewska@pwr.edu.pl

Bilosomes are defined as the novel generation of "soft" lipid vesicular nanocarriers. These spontaneously formed structures are considered highly biocompatible, biodegradable, and non-toxic. Embedding bile salts into the phospholipid bilayer may increase the colloidal stability of the system and improve the bioavailability of poorly soluble therapeutics. For this reason, bilosomes are extensively explored as promising alternatives for conventional liposomes, which may be applied as interesting bioinspired nanoplatform for therapeutic and diagnostic applications [1].

The main goal of our research was to design a new colloidal drug delivery nanoplatform and characterize its physicochemical properties. The influence of the preparation method was analyzed on the mean particle size (dynamic light scattering), surface charge (electrophoretic light scattering), shape, and morphology (transmission electron microscopy). The turbidimetric method, which is based on the multiple light scattering technique, was used to evaluate the kinetic stability of the optimized nanosystem. Finally, to check the encapsulation efficiency (UV-Vis spectroscopy) in the optimized vesicles, two anticancer compounds (i.e., hydrophilic methylene blue and hydrophobic curcumin) were used as model active agents [2].

As a result, our phosphatidylcholine/cholesterol-based vesicular system modified by bile salt-sodium cholate hydrate and additionally functionalized with a biocompatible triblock copolymer – Pluronic P123 exhibits the nanometric size ($D_H < 150$ nm), negative surface charge ($\zeta \sim -35$ mV), and very high kinetic stability. Most importantly, the high encapsulation efficiency of the hybrid model compounds with different hydrophobicity demonstrated that a promising nanoplatform for drug delivery, diagnostics, and anticancer therapy was obtained [2].

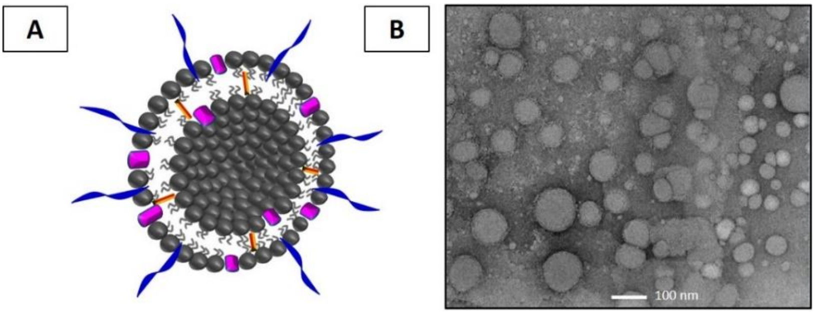


Figure 1. Schematic structure (A) and TEM image (B) of the surface-modified bilosomes.

References:
[1] Rizwanullah, Z.S.; Rizwanullah, M.; Mir, S.R.; Amin, S. Bilosomes nanocarriers for improved oral bioavailability of acyclovir: A complete characterization through in vitro, ex-vivo and in vivo assessment. J. Drug Deliv. Sci. Technol., 57, 101634 (2020).
[2] Waglewska, E.; Pucek-Kaczmarek, A.; Bazylińska, U. Novel surface-modified bilosomes as functional and biocompatible nanocarriers of hybrid compounds. Nanomaterials, 10, 2472 (2020).

Myelin structures formed by thermotropic liquid crystals in aqueous surfactant solutions

Wanyan MA, Dominika Benkowska-Biernacka, Katarzyna Matczyszyn
Wroclaw University of Science and Technology, Faculty of Chemistry
Advanced Materials Engineering and Modelling Group
E-mail address: mawanyan@outlook.com

The thermotropic myelin structure is a self-assembled lamellar structure formed by smectic-A liquid crystalline phase in an aqueous surfactant solution. Rodlike molecules assemble to form a bilayer chain, where there is a defect line forming in the core simultaneously. The myelin structure is birefringent, which can be visualized and characterized by the polarized light microscope.

In this study, we analyze myelin structures formed by 4'-n-octyl-4-cyanobiphenyl (8CB) in aqueous CTAB solutions with different concentrations at a certain temperature. Moreover, we investigated myelin structures with a compensator and stained them with different dyes to observe them under fluorescence microscope.

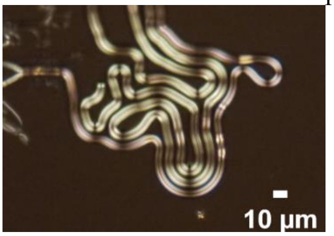


Figure1. The polarized light microscope image of myelin structures formed by 8CB in 10wt.% CTAB aqueous solution at 25°C.

References

[1] Karthik Peddireddy, Pramoda Kumar, Shashi Thutupalli, Stephan Herminghaus, and Christian Bahr. *Myelin Structures Formed by Thermotropic Smectic Liquid Crystals*. Langmuir 2013 29 (50), 15682-15688.

[2] Igor Muševič, Karthik Peddireddy, Marusa Mur, Khoa V. Le, Simon Čopar, Christian Bahr, and Venkata S. R. Jampani. *Self-shaping of liquid crystals into superstructures for photonic applications*. Proc. SPIE 11707, Emerging Liquid Crystal Technologies XVI, 117070F (5 March 2021).

In-situ TEM observations of photosensitizer-bacteria interactions

Olga Kaczmarczyk[1], Andrzej Żak[2], Marta Piksa[3], Katarzyna Matczyszyn[1]
[1] Faculty of Cehmistry, Wrocław University of Science and Technology Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland
[2] Faculty of Mechanical Engineering, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland
[3] Ludwik Hirszfeld Institute of Immunology and Experimental Therapy, Rudolfa Weigla 12, 53-114 Wroclaw, Poland
234071@student.pwr.edu.pl

An excellent example of how light-matter interaction can result in an advantageous outcome is photodynamic therapy (PDT). This type of therapy has been studied especially for non-invasive treatments of dermatological and oncological disorders as well as for drug-resistant microbial infections (antimicrobial photodynamic therapy, aPDT) [1]. With the growing interest in light-induced processes, there is a natural demand for performing such experiments in Transmission Electron Microscope *in-situ*. Observations of many dynamic processes require their natural environment, which is a liquid solution of the photosensitizer. It is possible to prepare such specimens for Transmission Electron Microscopy (TEM) by creating so-called liquid cells [2]. The profound understanding of processes occurring during aPDT observed on a microscopic level could help to explain the unknown course of the first stages of therapy and optimize the operation of new photosensitizers.

With a specially designed light illumination system in TEM [3] combined with liquid cell fabrication, it became possible to perform *in-situ* observations of interactions of bacteria encapsulated with a photosensitizer. In this research, the effect of methylene blue on *Staphylococcus aureus* upon 660 nm light illumination was studied. First changes in bacteria were observed after just 1 minute of intensive irradiation. Control of electron dose is very important for any observations in liquid. Therefore, an additional experiment of the damaging effect of different electron doses on bacteria was performed to distinguish it from the interaction with a photosensitizer. The results showed noticeable changes in bacteria outer membranes after applying light, which was the incontestable effect of interaction with an excited methylene blue.

References:

[1] Lian C., Piksa M., Yoshida K., Persheyev S., Pawlik K.J., Matczyszyn K, Samuel I.D.W., Flexible organic light-emitting diodes for antimicrobial photodynamic therapy, Npj Flex. Electron. 3 (2019) 1–6.

[2] Textor M., De Jonge N., Strategies for Preparing Graphene Liquid Cells for Transmission Electron Microscopy, Nano Lett. 18 (2018) 3313–3321.

[3] Żak A, The method of illuminating the sample in the transmission electron microscope and the assembly for illuminating the sample in a transmission electron microscope,. Patent Application P.433650, Polish Patent Office, (2020).

Poster session II

Crystal phases determining properties of Fe-Mn-Zr oxide based oxygen carriers

Magdalena GAWLAS, Rafal LYSOWSKI, Ewelina KSEPKO

Author affiliations: Wroclaw University of Science and Technology, Poland
E-mail address: 234200@student.pwr.edu.pl
ewelina.ksepko@pwr.edu.pl

Some chemical compounds have an ability to give away oxygen when heated to high temperature. These materials are called oxygen carriers and the property is known as 'Chemical-Looping with Oxygen Uncoupling' (CLOU) which might be practically used for power generation application in “green technologies”. A good example of such CLOU materials are various simple oxides e.g. manganese, cobalt and copper. Also, there are known more complex CLOU materials, such as perovskites and spinels having specific crystal structure.

These advanced CLOU materials were synthesized in this work from simple oxides such as MnO_2, Fe_2O_3 and ZrO_2 with use of mechanical mixing and final high temperature calcination. Various Fe:Mn ratios have been used to compare synthesized products in terms of their crystal structure and phase composition. As part of this paper, synthesized materials were analysed using X-ray powder diffraction method - XRD. This allowed the both oxides spinel and perovskite phases of iron and manganese to be formed. In those mixtures zirconium oxide addition was applied since it is an important ingredient. The reason for that is being an inert material improving mechanical properties of CLOU materials. Furthermore, thermogravimetric analysis – TGA, allowed us to confirm that synthesized materials evolved an oxygen from their structure under high temperature and are successfully able to regenerate later. Additionally, it was concluded that among tested samples, high manganese content correlated fine with good CLOU properties.

Acknowledgement: The work was financed in part from the National Science Centre, Poland Project No. 2020/37/B/ST5/01259.

Chemical Looping with Oxygen Uncoupling window examination with application of thermogravimetric instrument for powdered OCs

Anita PAWLUK, Ewelina KSEPKO, Magdalena GAWLAS, Rafal LYSOWSKI

Author affiliations: Wroclaw University of Science and Technology, Poland
E-mail address: ewelina.ksepko@pwr.edu.pl

Chemical Looping Combustion with Oxygen Uncoupling (CLOU) may be attractive and practically applied as a highly promising fuel combustion method. It is valuable since it enables carbon capture and storage purposes without additional expenses. In this method combustion air and fuel are never mixed up. For this reason practically it may improve the environment protection from the power generation sector. The harmful for human beings emissions from gaseous and fossil fuels combustion are in this technology expressively reduced.

A special attention can be paid to both gaseous and fossil fuels utilization for the power sector, however it can be only applied when specific material of given functionality is produced. Such a material is called an oxygen carrier, due its basic function which is transportation of oxygen to a fuel.

In this paper a specific low cost, fine powdered oxygen carrier made of zirconia, iron and finally manganese were tested with a thermogravimetric analyzer (TGA). The aim was to find the right temperature CLOU window in which the obtained materials may operate in a reversible manner. Dynamic thermal analysis was carried both at first the oxidizing (air) and the inert (N_2) conditions up to 1200°C. The obtained data showed that the TGA analysis can be a valuable instrument for reactivity and potential application evaluation as a fast and reliable tool.

Acknowledgement: The work was financed in part from the National Science Centre, Poland Project No. 2020/37/B/ST5/01259.

Electron irradiation influence on the temperature dependence of fluctuation conductivity and pseudogap in $YBa_2Cu_3O_{7-\delta}$ single crystals

Eugene Petrenko[1], Liudmyla Omelchenko[1], Andrei Solovjov[1], Ruslan Vovk[2]
[1]B.Verkin Institute for Low Temperature Physics and Engineering of NAS of Ukraine,
Nauky Ave., 47, Kharkiv 61103, Ukraine
[2]Physics Department, V. Karazin National University, 4 Svoboda Sq., 61077 Kharkiv, Ukraine
petrenko@ilt.kharkov.ua

The effect of electron irradiation with energy of 2.5 MeV on the temperature dependences of the resistivity $\rho(T)$ of an optimally doped $YBa_2Cu_3O_{7-\delta}$ single crystal has been studied. Based on this information, the corresponding temperature dependences of both fluctuation conductivity, $\sigma'(T)$, and the pseudogap, $\Delta^*(T)$, have been calculated within the local pair model. It is shown that with an increase in the irradiation dose φ, the value of $\rho(300\ K)$ increases linearly, while critical temperature T_c decreases linearly. At the same time, the value of $\rho(100\ K)$ increases nonlinearly, demonstrating a feature for $\varphi = 4.3 \cdot 10^{18}$ e/cm^2, which is also observed on the number of other dose dependent parameters. Regardless of the irradiation dose, in the temperature range from T_c up to T_{01}, $\sigma'(T)$ obeys the classical fluctuation theories of Aslamazov - Larkin (3D-AL) and Maki-Thompson (2D-MT), demonstrating 3D-2D crossover with increasing temperature. The crossover temperature T_0 makes it possible to determine the coherence length along the c-axis, $\xi_c(0)$, which increases by ~ 2.6 times under irradiation. Furthermore, the range of superconducting fluctuations above T_c also noticeably increases.

At $\varphi = 0$, a "classical" dependence of $\Delta^*(T)$ is observed with a maximum at BEC-BSC crossover temperature $T_{pair} \sim 120$ K and a clear minimum at $T = T_{01}$. It was found for the first time that at $\varphi = 4.3 \cdot 10^{18}$ e/cm^2 the shape of $\Delta^*(T)$ changes strongly and becomes the same as in optimally doped YBCO single crystals with defects, which is accompanied by a sharp decrease in T_{pair} and the pseudogap opening temperature T^*, while at $T_c(\varphi)$ there are no singularities. With an increase in the irradiation dose up to $\varphi = 8.8 \cdot 10^{18}$ e/cm^2, the shape of $\Delta^*(T)$ is restored and becomes the same as in well-structured YBCO films. Moreover, in this case, T_{pair} and T^* increase noticeably. The comparison of the experimental results with the Peters-Bauer theory shows that at $\varphi = 0$ the density of local pairs near T_c is $<n_\uparrow n_\downarrow> \approx 0.3$, which is a typical value for HTSCs. At low radiation doses, $<n_\uparrow n_\downarrow>$ rapidly increases to $<n_\uparrow n_\downarrow> \approx 0.35$ at $\varphi = 1.4 \cdot 10^{18}$ e/cm^2, and then decreases linearly to $<n_\uparrow n_\downarrow> \approx 0.25$ at $\varphi = 8.8 \cdot 10^{18}$ e/cm^2.

References:

[1] R. V. Vovk, A. L. Solovjov, Electric transport and pseudogap in high-temperature superconducting compounds of system 1-2-3 under conditions of all-round compression. Low Temp. Phys. **44**, 111–153 (2018).

[2] A. L. Solovjov et al. Specific temperature dependence of pseudogap in $YBa_2Cu_3O_{7-\delta}$nanolayers. *Phys.Rev.B.* **94**, 224505 (1-11) (2016).

Analysis of sensitivity and reliability of the single $NaYF_4$: Er^{3+}, Yb^{3+} upconverting nanocrystals reporting temperature

K. Hołodnik[1], U. Kostiv[2], D. Horák[2], A. Podhorodecki[1], B. Krajnik[1*]

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

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

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

Upconverting nanoparticles (UCNPs) doped with Er^{3+}/Yb^{3+} ions have been recently intensively studied and used for the *in vivo* temperature measurements. The green luminescence of Er^{3+} ions occurs at 520 nm (called G_1) and 541 nm (called G_2) [1]. The luminescence intensities ratio of these bands (G_2/G_1) is temperature dependent and allows for the precise temperature characterization [2]. 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 to overcome the negative effects of ensemble averaging, which takes place in bulk materials. Effective measurement optimization is crucial for the practical application of lanthanide-based nanothermometers in biochemistry and cell biology.

Our primary single nanocrystals studies indicated that its individual properties are various within one sample and the dispersion of the photoluminescence is significant, which resulted in lack of reproducibility of the reported temperature. In this report we would like to present, that optimization of the experimental system and improving the method of conducting the analysis led us to better size and shape control pf the pairs of single temperature reporting UCNPs, which significantly influences the reliability of the measurements by reducing standard uncertainty and increasing the slope of the fit curve.

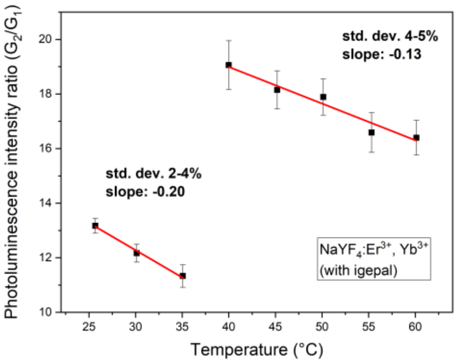


Figure. 1. The average value of the G_2 to G_1 ratio of 30 single UCNPs as a function of the temperature of the surroundings. Measurement was carried out with a careful size and shape control. The standard deviation decreased drastically compared to the previous results.

References:

[1] U. Kostiv, H. Engstová, B. Krajnik, M. Šlouf, V. Proks, A. Podhorodecki, P. Ježek and D. Horák; Monodisperse Core-Shell $NaYF_4$:Yb^{3+}/Er^{3+} @ $NaYF^4$:Nd^{3+}-PEG-GGGRGDSGGGY-NH_2 Nanoparticles Excitable at 808 and 980 nm: Design, Surface Engineering, and Application in Life Sciences, Front. Chem., 12 June 2020

[2] F. Vetrone, R. Naccache, A. Zamarrón, A. J. de la Fuente, F. Sanz-Rodríguez, L. M. Maestro, E. M. Rodriguez, D. Jaque, J. G. Sole, J. A. Capobianco; Temperature sensing using fluorescent nanothermometers, ACS Nano, Vol. 4, Iss. 6 (2010)

[3] B. Krajnik, L. Golacki, U. Kostiv, D. Horak and A. Podhorodecki; Single-Nanocrystal Studies on the Homogenity of the Optical Properties of $NaYF_4$: Yb^{3+}, Er^{3+}, ACS Omega (2020)

Development of a fabrication method of the polymer layers containing semiconductors nanocrystals

Mateusz Pieprz [1], Anna Lesiak [1,2], Mateusz Bański [2]
[1]Wrocław University of Science and Technology, Faculty of Chemistry, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland
[2]Wrocław University of Science and Technology, Faculty of Fundamental Problems of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

E-mail address: 233574@student.pwr.edu.pl

Semiconductor quantum dots (QDs) present unique photophysical and chemical properties, which may be controlled based on the size, shape and elemental composition of QDs. Moreover, they are characterized by a high quantum emission yield, wide absorption spectrum, narrow emission profile, large achievable Stokes shift and high surface-to-volume ratio [1]. Due to this, QDs find many interesting applications such as lasers, light emitting diodes, detectors [2]. One of the method to receive new possibilities of QDs application and obtain new properties is developing materials with QDs suspended inside them [3]. For optical applications, such matrices should be transparent, colorless and resistant to UV radiation [4]. In present work, polymethyl methacrylate was used as a matrix, which meets the properties listed above. The aim of the work was to check whether the addition of QDs during the polymerization process will affect the reaction efficiency as well as optical parameters such as photoluminescence or material absorbance

References:

[1] A. Lesiak, M. Bański, K. Halicka, J. Cabaj, A. Żak, A. Podhorodecki, pH dependent fluorescence of thiol coated CdSe/CdS quantum dots in an aqueous phase, Nanotechnology, **2021**, 32 (7), 1-10
[2] A. Lesiak, K. Drzozga, J. Cabaj, M. Banski, K. Malecha, A. Podhorodecki, Optical Sensors Based on II-VI Quantum Dots, Nanomaterials, **2019**, 9(2), 192
[3] S. Padmaja, S. Jayakumar, Tunable luminescence and transmittance nature of CdS:PMMA nanocomposites for optoelectronic applications Optics and Laser Technology **2019** 112 409-412
[4] Vishal Mathur, Manasvi Dixit, K.S.Rathore, N.S. Saxena, K.B. Sharma Morphological and mechanical characterization of a PMMA/CdS nanocmposite, Front. Chem. Sci. Eng. **2011**, 5(2) 258-263

Shape modifications of anisotropic gold nanoparticles

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

Nanoparticles show unique optical, electrical and catalytic properties. Among them the most important and unique feature is the presence of Localized Surface Plasmon Resonance (LSPR), which is the collective oscillations of free electrons on the surface of metallic nanoparticles. Through well designed synthesis we can control the shape, size, and aspect ratio of NPs, what defines the LSPR position and leads to different properties of nanoparticles. [1,2] Anisotropic nanoparticles (NPs) have distinctly different properties from isotropic nanoparticles. Examples of such NPs can be nanorods (NRs) and nanobipyramids (BPs). In case of anisotropic NPs, we can distinguish longitudinal (l-LSPR) and transverse (t-LSPR) surface plasmon resonances. The ability to control both plasmon resonances, makes them excellent candidates for use in photocatalysis, sensing and drug delivery. [3]

Further fine-tuning of the morphology of anisotropic NPs may lead to great improvements of their properties and applications. In particular, the use of chiral thiol molecules like L-cysteine or L- and D-penicillamine may lead to chirality transfer to NP structure. Other way to introduce chirality to NPs is changing their geometry, to obtain new shape being related to chiroptical activity. [3,4,5]

The phenomenon of NPs chirality is still not well understood and described. Therefore, this issue is extremely interesting and provides a great field for new research directions. Further development in this field is promising and could lead to new applications of chiral anisotropic NPs. [4,5]

My research is focused on the synthesis of anisotropic gold nanoparticles like BPs and NRs using seed mediated growth and their further shape modifications. I study the role of chiral thiols in the post-synthetic modification of shapes based on the UV-Vis spectra and TEM imaging. I have already made some observations of the position and shape of the LSPR depending on the concentration of the components used during the synthesis, which suggest changes in morphology. These changes can be confirmed by visible blueshift of the UV-Vis spectra. I have also observed a circular dichroism (CD) signal in the short-wavelegth range, confirming the chirality of nanoparticles, as it is not assigned to the thiol used. Although CD activity origin remains unclear and further studies are necessary.

References:

[1] Xia Y., Xia X. and Peng H.-Ch., Shape-Controlled Synthesis of Colloidal Metal Nanocrystals: Thermodynamic versus Kinetic Products, J. Am. Chem. Soc., 2015, 137, 7947-7966

[2] Grzelczak M., Pérez-Juste J., Mulvaney P. and Liz-Marzán L. M., Shape control in gold nanoparticle synthesis, *Chem. Soc. Rev.,* 2018, 37, 1783-1791

[3] Wang W., Erofeev I., Nandi P., Yan H., and Mirsaidov U., Evolution of Anisotropic Arrow Nanostructures during Controlled Overgrowth, Adv. Funct. Mater., 2021, 2008639

[4] Zheng G., He J., Kumar V., Wang S., Pastoriza-Santos I., Pérez-Juste J., Liz-Marzán L. M. and Wong K.-Y., Discrete metal nanoparticles with plasmonic chirality, Chem. Soc. Rev., 2021, 50, 3738–3754

[5] Wang Y., He W., Li C. H., Xia C., Yan Y., Li C. M. and Huang C. Z., Chirality transfer of cysteine to the plasmonic resonance region through silver coating of gold nanobipyramids, Chem. Commun., 2021, 57, 3211–3214

Detection of defects and impurities in ZnO thin films by photoluminescence studies

[1]P. Sedzicki, [2]E. Nowak, [2]M. Szybowicz, [1]B. Derkowska-Zielinska,
[1]Institute of Physics, Faculty of Physics, Astronomy and Informatics,
Nicolaus Copernicus University in Torun, Grudziadzka 5, 87-100 Torun, Poland
[2]Faculty of Materials Engineering and Technical Physics,
Poznan University of Technology, Piotrowo 3, 60-965 Poznan, Poland

E-mail address: sedzicki@doktorant.umk.pl

The wide-bandgap, conductive transparent oxides like ZnO are essential for many optoelectronic devices, including solar cells and organic light-emitting diodes. Optimization and tuning of material properties are possible due to the intentional introductions of dopants and changes in the preparation procedure. Furthermore, the annealing conditions need adjustment depending on the batch components used for ZnO synthesis, so elimination of an unwanted, gas-forming elements will be possible during the crystallization of thin films deposited on glass by a spin-coating method.

We investigated the photoluminescence of ZnO thin layers annealed in the temperature range of 230-600 °C in combination with an annealing length from 2 hours up to 10.5 hours at room temperature. The prepared ZnO thin films show emission in UV and in the visible part of the spectra. We found differences in the observed spectra that depend on the annealing process. We suppose that the annealing process contributed to the formation of native defects in the structure. It can be concluded that the annealing conditions could be selected depending on the specific needs.

Also, temperature-dependent photoluminescence (PL) spectra of ZnO thin films were registered in the wide range (T = 12-400 K) of temperature. He-Cd laser (λ_{EX} = 325 nm) was used as an excitation source to study activation energies of various dopants presented in ZnO thin films. We found that PL spectra increased with decreasing temperature. We did not find emissions bands that can be directly linked to organic-waste products, which suggest proper disposal of potential impurities.

Synthesis of Luminescent Carbon Nanodots and Carbon Nanorods for their Application in the Fabrication of Polymer Thin Films

Kayode James Olaleye[1], Bayan Sinokrot[1], Sebastian G. Mucha[2], Katarzyna Matczyszyn[1]
[1] Advanced Materials Engineering and Modelling Group, Wroclaw University of Science and Technology, Wyb. Wyspianskiego 27, 50-370 Wroclaw, Poland
[2] Laboratoire Charles Coulomb, UMR5221, University of Montpellier - CNRS, Montpellier, France
E-mail address: 257384@student.pwr.edu.pl , 253098@student.pwr.edu.pl

Carbon is known for its biocompatibility, and nanomaterials made of it are expected to have the same property. For example, nitrogen-doped carbon nanodots (CNDs) are a form of luminescent carbon-based dots (CDs) with excellent and tunable optical properties, long-term colloidal stability, unusual environmental friendliness, and low-cost fabrication. CDs have potential applications in biomedical and optoelectronics.[1] Despite the fact that spherical CDs have received a lot of attention, there have been reports on elongated carbon nanomaterials known as carbon nanorods (CNRs), especially light-emitting anisotropic CNRs. An appropriate surfactant determines their anisotropic structure, and domains of polycyclic aromatic hydrocarbons embedded into an inorganic framework decide their optical properties.[2]

The solvothermal methods were applied to produce CNRs and CNDs. For CNDs using folic acid molecules (FA) as precursors with steady-state and time-resolved spectroscopic techniques, the strong luminescence of blue-emitting nitrogen-doped CNDs in aqueous suspensions were identified.[3] Hydrophobic CNRs were synthesized by self-assembly in inverse micelles by a surfactant (POSS-$C_3H_6NH_2$) interacting with citric acid in a nonpolar solvent (Fig.1a, b). Subsequently, interactions between as-obtained nanostructures (CNRs and CNDs) and proper polymers (i.e. PVC) are studied via the spin-coating method of thin-film production. Further investigations on the optical properties of as-prepared composites have been done to check for possible applications (Fig.1c).

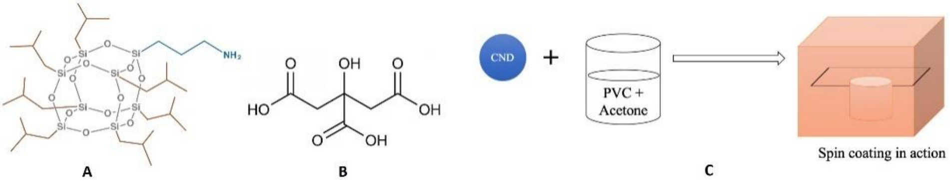


Fig. 1 General overview of polymer thin film production with blue-emitting folic acid-based CNDs and Chemical structures for **a**. Surfactant (POSS-$C_3H_6NH_2$) and **b**. Precursor (Citric acid) of CNRs synthesis.

References:

1. Haifang L., Zhaohui L, Yuanqiang S., Xin G., Yalei H., Hongmin M., Jia G. and Lingbo Q. (2018). Synthesis of Luminescent Carbon Dots with Ultrahigh Quantum Yield and Inherent Folate Receptor Positive Cancer Cell Targetability. Scientific reports, 8.
2. Xiong Y., Zhang X., Richter A., Li Y., Döring A., and Kasák P. (2019). Chemically Synthesized Carbon Nanorods with Dual Polarized Emission. ACS Nano, 13(10), 12024-12031.
3. Shan H., Hangna Q., Jiangning X., Chusheng H., Wei S., Baoqing H., and Qi X. (2016) Systematical Investigation of in vitro Molecular Interaction Between Fluorescent Carbon Dots and Human Serum Albumin. RSC Adv. 6, 44531 – 44542.

Optical and morphological properties of PVP, PMMA and PBMA thin films

M. Sypniewska[a], L. Skowronski[b], B. Derkowska-Zielinska[a]

[a]Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University in Torun, Grudziadzka 5, Torun 87-100, Poland
[b]Institute of Mathematics and Physics, UTP University of Science and Technology, S. Kaliskiego 7, 85-796, Bydgoszcz, Poland

[c]Faculty of Chemistry, Nicolaus Copernicus University in Torun, Gagarina 7, Torun 87-100, Poland

E-mail address: msyp@doktorant.umk.pl

The unique properties of polymeric materials, such as light weight, high flexibility, and the ability to be manufactured at low temperature and low cost, make them suitable for many applications (e.g., in optoelectronics or photonic) [1].

PVP is a bulky polymer with C=O, C-N and CH_2 functional groups that is widely used in the synthesis of nanoparticles (NP) [2]. PVP is an excellent stabilizer that prevents aggregation of NP by repulsive forces that arise from its hydrophobic carbon chains and interact with each other [3]. PBMA can be used as a polymer matrix to synthesize various nanocomposites due to its transparency and ease of processing [4]. PMMA is one of the most widely used polymers in materials engineering due to its high chemical resistance, simple synthesis, low optical loss in the visible spectrum, good tensile strength and good insulation properties, as well as good transparency [1,4].

In this work, we investigated the optical and morphological properties of polyvinylpyrrolidone (PVP), poly(methyl methacrylate) (PMMA) and poly(butyl methacrylate) (PBMA) thin layers using AFM, SEM, IR spectroscopy and *spectroscopic ellipsometry (SE)*. Photoluminescence (PL) properties were also analyzed.

References:

[1] Ismail, L.N.; Zulkefle, H.; Herman,S.H.; Mahmood, M.R. Influence of Doping Concentration on Dielectric, Optical, and Morphological Properties of PMMA Thin Films, Advances in Materials Science and Engineering, vol.2012, 1-5, 2012.

[2] Yan, E.; Huang, Z.; Xin, Y.;Zhao, Q.; Zhang,W. Polyvinylpyrrolidone/tris(8-quinolinolato) aluminium hybrid polymer fibers by electrospinning, Mat. Lett., 60, 2969-2973, 2006.

[3] Koczkura, K.M.; Mourdikoudisb, S.; Polavarapud, L.; Skrabalak, S.E. Polyvinylpyrrolidone (PVP) in nanoparticle synthesis , Royal Society of Chemistry, 44,17883-17905, 2015.

[4] Derkowska-Zielinska, B.; Krupka, O.; Smokal,V.; Grabowski, A.; Naparty, M.; Skowronski, L. Optical properties of disperse dyes doped poly(methyl methacrylate). Mol. Cryst. Liq. Crystals, 639, 87-93, 2016.

Acetone-derived fluorescent polymer dots: remarkable optical properties and interactions with serum albumins

Agnieszka Krystyniak [1], Sebastian G. Mucha [2], Lucyna Firlej [2], Katarzyna Matczyszyn [1]
[1] Advanced Materials Engineering and Modelling Group, Wroclaw University of Science and Technology, Wyb. Wyspianskiego 27, 50-370 Wroclaw, Poland
[2] Laboratoire Charles Coulomb, UMR5221, University of Montpellier - CNRS, Montpellier, France
E – mail: 234210@student.pwr.edu.pl

Carbon dots are an emerging class of carbon-based nanomaterials and attracted a lot of interest from scientists worldwide due to their prominent optical properties. Besides they also possess low toxicity and high biocompatibility which make them suitable candidates for applications in the biomedical field. In comparison to fluorescent organic dyes or semiconductor quantum dots, carbon dots own numerous advantages, such as simple synthesis, bright emission, and resistance to photobleaching or aging. They can be widely used in drug delivery, biosensing, or bioimaging, but also in the optoelectronics industry (e.g. OLED or solar cells) and in photocatalysis. [1][2][3]

Polymer dots (PDs) are a subgroup of carbon dots, derived through polymerization of small molecules (e.g. acetone) and strong crosslinking of as-obtained polymer chains. In PDs plenty of functional groups are preserved in coiled polymer chains, which are partially responsible for their chemical and optical properties. PDs are usually fabricated in the bottom-up route, for example in solvothermal synthesis. [2][4]

Human serum albumin (HSA) and bovine serum albumin (BSA) are globular proteins in blood plasma that plays a key role in the effective distribution of many substances (e.g. drugs) among different body entities. [5]

Here, the optical properties of PDs in different aqueous suspensions were described using steady–state and time-resolved spectroscopic techniques. Subsequently, interactions between hydrophilic fractions of PDs and albumins were studied, following enhancement of the fluorescence from PDs in the presence of albumins and the proteins' fluorescence quenching by the addition of the PDs.

References:

[1] K. Hola, M. Sudolska, S. Kalytchuk, D. Nachtigallova, A. L. Rogach, M. Otyepka, R. Zboril, "Graphitic Nitrogen Triggers Red Fluorescence in Carbon Dots", ACS Nano, 11, 2017.
[2] T. Songyuan, Z. Shoujun F. Tanglue, X. Chunlei S. Yubin, Y. Bai, "The polymeric characteristics and photoluminescence mechanism in polymer carbon dots: A review." Materials Today Chemistry, 6, 2017.
[3] Mucha, S.G., Firlej L., Bantignies J.-L., Żak A., Samoć M., Matczyszyn K., Acetone-derived luminescent polymer dots: a facile and low-cost synthesis leads to remarkable photophysical properties, RSC Adv., 10, 2020.
[4] J. Shao, S. Zhu, H. Liu, Y. Song, S. Tao, B. Yang, "Full – color emission polymer carbon dots with quench – resistant solid – state fluorescence", Advanced Science, 4, 2017.
[5] E. Tazikeh, L. Karami, "Molecular Dynamics Simulation and Free Energy Studies on the Interaction of Salicylic Acid with Human Serum Albumin (HSA)", Physical Chemistry Research, 5, 2017.

New approach to the synthesis of highly bioactive nanoglass

W. Bodylska[1,2], M. Fandzloch[1], A. Lukowiak[1], Y. Gerasymchuk[1]
[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, Norwida 4/6, 50-373 Wrocław, Poland*
E-mail address: werronikab@gmail.com

Bioglass® 45S5 created by Larry Hench in the 1970s is the first example of bioactive ceramics that has a great ability to bond with bones and soft tissues and is successfully applied as an implantable material in orthopaedics and dentistry [1]. The chemical composition, size, and porosity of glasses strongly affect their bioactivity thus, the synthesis process – ability to produce crystallization-free bioactive glass – is crucial. Bioactive glasses are mostly produced by the traditional melting or sol–gel method [2].

Following this topic, the aim of our research was the development of a one-step synthesis of nanometric and, above all, highly bioactive glass in a simple binary system CaO–SiO_2. The solvothermal path allowed to obtain amorphous and favorably mesoporous glass called solvBG76.The bioactivity of newly synthesized glass nanoparticles was assessed *in vitro* in Dulbecco's phosphate-buffered saline via monitoring the formation of hydroxyapatite on glass surface during a different time of incubation. The composition, structure, and morphology of the powder before and after incubation were characterized by using EDS, XRD (Fig. 1a), IR-ATR, XPS and Raman spectroscopies, TEM (Fig. 1b) and SEM techniques. During contact with the medium, the bioactive glass undergoes degradation and this aspect was also investigated using ICP-OES technique. The results showed that solvBG76 represent a promising material since the first changes indicative of hydroxyapatite formation were observed in less than 4 h of incubation in the medium.

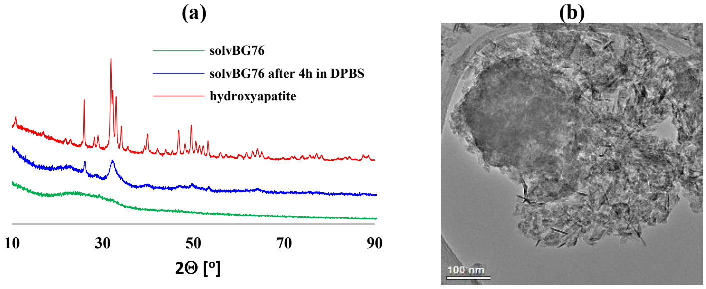


Fig. 1 (a) XRD pattern for solvothermally synthesized nanoglass solvBG76 and hydroxyapatite as a reference. **(b)** HR-TEM of solvBG76 after 3 weeks of incubation in DPBS at 37 ºC.

References:
[1] Hench L.L., Bioactive materials: the potential for tissue regeneration, J. Biomed. Mat. Res., 41, 511–518, 1998.
[2] Łukowiak A., Lao J., Lacroix J., Nedelec J.M., Bioactive glass nanoparticles obtained through sol-gel chemistry, Chem. Commun., 49, 6620–6622, 2013.

Acknowledgement
This work was supported by the National Science Centre [grant number 2016/22/E/ST5/00530]. Authors would like to thank XL Sci-Tech for the supply of 45S5 glass.

1 st HighLIGHTing Science Meeting

27 - 28 May 2021

Organizers and patronages

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement n°764837. The content of this communication reflects only the author's view and the Research Executive Agency is not responsible for any use that may be made of the information it contains

European Commission

Horizon 2020
European Union funding
for Research & Innovation

POLYTHEA
HOW LIGHT CAN SAVE LIVES

University of St Andrews

Université de Neuchâtel
unine

Politechnika Wrocławska

Trinity College Dublin
Coláiste na Tríonóide, Baile Átha Cliath
The University of Dublin

Université
de Limoges

UNIVERSITY
OF AMSTERDAM

· U C ·

UNIVERSIDADE DE COIMBRA

Industrial partners

BIOEMTECH

biolitec research GmbH

Inserm
La science pour la santé
From science to health

PorphyChem
Porphyrin Chemicals & Engineering

Selvita

Organizing committee

Emma Robbins
Zoi Melissari
Dáire Gibbons
João Simoes
Bhavya Khurana
Harry Sample
Nidia Maldonado-Carmona
Claire Donohoe
Piotr Gierlich
Manuel Gallardo Villagran

Conference programme

27 MAY (Thursday)		
Hours	**Activity**	
8:45-9:00	Opening ceremony	
Session I		
9:00-10:00	**Plenary session**	**Prof. Santi Nonell**
10:00-10:20		**Dr Arno Wiehe**
10:20-10:40	Coffee break & poster session	
10:40-11:00	**Plenary session**	**Dr Fabienne Dumoulin**
11:00-12:00		**Dr Pilar Acedo**
12:00-13:30	Lunch break	
Session II		
13:30-14:30	**Plenary session**	**Dr Mikhail Filatov**
14:30-14:50		**TBA**
14:50-15:10	Coffee break & Poster session	
15:10-16:10	**Plenary session**	**Dr Francesca Giuntini**
16:10-16:30		**Prof. Tayyaba Hasan**
16:30-17:30	Flash presentations	

28 MAY (Friday)		
Hours	**Activity**	
8:45-9:00	Opening of the 2nd day	
Session I		
9:00-10:00	**Plenary session**	**Dr Sabrina Oliveira**
10:00-10:20		**Prof. Ifor Samuel**
10:20-10:40	Coffee break & poster session	
10:40-11:40	**Plenary session**	**Prof. Janusz Dąbrowski**
11:40-12:00		**TBA**
12:00-13:30	Lunch break	
Session II		
13:30-14:30	**Plenary session**	**Dr Gilles Gesser**
14:30-14:50		**Prof. Luis Arnaut**
14:50-15:10	Coffee break & Poster session	
15:10-16:10	**Plenary session**	**Prof. Marek Samoć**
16:10-16:30		**Horizon Europe**
16:30-17:30	Flash presentations	
17:30-18:00	Closing remarks	

Abstracts

Lyotropic myelin structures consisted of phosphatidylcholines

Dominika Benkowska-Biernacka, Katarzyna Matczyszyn
Advanced Materials Engineering and Modelling Group,
Wroclaw University of Science and Technology, Faculty of Chemistry, Poland

The well-known example of lyotropic liquid crystals is myelin sheath which plays a crucial role in action potential propagation. The study of this biological membrane still gains considerable attention due to unsolved questions about causes of its degradation processes [1]. Here, we present research into formation and imaging of artificial myelin structures (MS) consisted of phosphatidylcholines stained with fluorescent dye [2]. Combination of polarized light microscopy and fluorescent microscopy was employed to study of multilayered microstructures. Additionally, two-photon excited fluorescence microscopy was applied to observe three-dimensional MS.

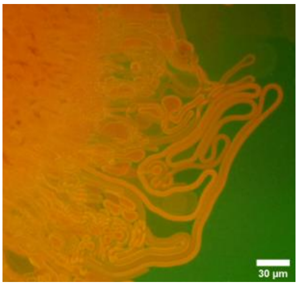


Fig. 1. The fluorescent image of myelin structures stained with Nile Red and fluorescein.

Keywords:
Lyotropic liquid crystals, polarized light microscopy, two-photon excited fluorescence microscopy

References:

[1] B. Zalc, F. Rosier, Myelin: The Brain's Supercharger, Oxford University Press, 2018, 160-188
[2] D. Benkowska-Biernacka, I. I. Smalyukh, K. Matczyszyn, Morphology of Lyotropic Myelin Figures Stained with a Fluorescent Dye, J. Phys. Chem. B, 2020, 124,11974–11979

Theranostic consequences of modulating lipid-based NIR photonanomedicine nanoarchitecture in orthotopic head and neck cancer

Chanda Bhandari[a], Mina Guirguis[a], Kenneth Hoyt[a], Tayabba Hasan[b] and Girgis Obaid[a]
[a]*Department of Bioengineering, University of Texas at Dallas, Richardson, Texas 75080, U.S.*
[b]*Wellman Center for Photonanomedicine, Massachusetts General Hospital and Harvard Medical School, Boston, Massachusetts 02114, U.S.*
Email address: chanda.bhandari@utdallas.edu

Lipid-based NIR activable photonanomedicines (PNMs) are an increasingly attractive platform for photodynamic-based therapies owing to their tunability, high payload multi-agent delivery and tumor selectivity.[1] Such PNMs contain lipidated photosensitizer molecules which possess either a membrane-inserting or membrane-protruding nanoarchitecture. The existence and extent of a functional impact that such membrane nanoarchitectures have on NIR activable PNMs as platforms for photodynamic-based theranostics has not been explored to date. The membrane-inserting nanoarchitecture was provided by a lipid conjugate of Benzoporphyrin derivative (BPD) and the membrane-protruding nanoarchitecture was provided by a lipid conjugate of IRDye700DX. Lipid conjugates of clinically used photosensitizers (Benzoporphyrin derivative (BPD) and IRDye700DX) were prepared and incorporated into nanoliposomal platforms. These nanoarchitectures were confirmed by photophysical analyses and by computational predictions of membrane partitioning.

Results showed that the membrane-protruding nanoarchitecture is more efficient in the production of reactive oxygen and nitrogen species than the membrane-inserting nanoarchitecture upon the excitation with 690 nm LED light. In contrast, the membrane-inserting nanoarchitecture demonstrated 9.9-fold greater phototoxicity of FaDu human head and neck cancer cells at a 500 nM photosensitizer equivalence. We also evaluated the photo-triggered drug release capacity of the two variants in which the membrane inserting nanoarchitecture was 13.2-fold slower than membrane-protruding nanoarchitecture. Given their ultimate value as tumor selective platforms for photodynamic-based therapies, we explored their ability to selectively accumulate in orthotopic FaDu human head and neck tumors. We found that the membrane inserting nanoarchitecture was more than 6-fold efficient at selective tumor delivery. These findings thus provide critical insights into how the membrane nanoarchitectures of NIR activable PNMs can be customized and tailored for specific desired therapeutic and theranostic utilities.

Keywords:

photonanomedicines, photodynamic therapy, head and neck cancer

References:

[1] Bhandari, C., Guirguis, M., Savan, N.A., Shrivastava, N., Oliveira, S., Hasan, T. and Obaid, G., 2021. What NIR photodynamic activation offers molecular targeted nanomedicines: Perspectives into the conundrum of tumor specificity and selectivity. *Nano Today*, 36, p.101052.

The impact of atropisomerim on Redaporfin photodynamic therapy efficacy

Claire Donohoe[a,b], Fábio Scharble[a], Mariette M. Pereira[a], Mathias O. Senge[b], Luís G. Arnaut[a], Lígia C. Gomes-da-Silva[a]
a Department of Chemistry, University of Coimbra, Rua Larga, 3004-535 Coimbra, Portugal
b Medicinal Chemistry, Trinity Translational Medicine Institute, Trinity Centre for Health Sciences, St. James's Hospital, Trinity College Dublin, The University of Dublin, Dublin 8, Ireland
E-mail address: donohoc2@tcd.ie

Atropisomerism presents an intriguing, often neglected, source of structural variety in drug development. Such diversity in tetrapyrrole structures may enhance photosensitizer development for photodynamic therapy (PDT) and related drug developments. The present work demonstrates that the photosensitizer redaporfin (and related pre-cursor porphyrin molecules) atropisomers can be separated, do not interconvert at room temperature and exert different biological effects. Redaporfin, a pre-clinical synthetic sulfonamide fluorinated bacteriochlorin, presents ideal properties for studying PDT including enhanced photostability and strong absorption at 750 nm. Hindered rotation of the C_m-aryl-macrocyclic bonds of the bacteriochlorin and porphyrin structures results in different spatial orientations of the sulfonamide groups in the meta positions. They are defined as: α_4 when all of the sulfonamide substituents of the phenyl groups are on the same side of the macrocycle plane; $\alpha_3\beta$ when three of the sulfonamides are on the same side of the plane and one is on the opposite side; $\alpha_2\beta_2$ when two sulfonamide groups are on each side and adjacent to each other and finally, $\alpha\beta\alpha\beta$ when two sulfonamides are on each side but alternate in the positions with respect to the macrocycle. Although the photo- and physicochemical properties of the four atropisomers are similar, their therapeutic efficacies are dramatically different. *In vitro* studies have demonstrated significant variability of the atropisomer phototoxicity and cellular internalization levels. In particular, the α_4 atropisomer has displayed the highest levels of uptake and phototoxicity. Atropisomers have presented similar mechanisms of cellular uptake, primarily passive diffusion with subcellular localization in the endoplasmic-reticulum-Golgi complex. Heightened α_4 internalization by cells of the tumor microenvironment has been observed *in vivo*. Efficacy studies have indicated that atropisomer activity varies *in vivo* when sufficient time for photosensitizer tumor cell internalization occurs. A better understanding of how atropisomerism impacts therapeutic effects may contribute to the establishment of enhanced drug development strategies.

Keywords:

Redaporfin, Atropisomerism, Photodynamic-Therapy, Anti-Cancer Activity

References:

[1] L.G. Arnaut, M.M. Pereira, J.M. Dabrowski, E.F. Silva, F.A. Schaberle, A.R. Abreu, L.B. Rocha, M.M. Barsan, K. Urbanska, G. Stochel, C.M. Brett, *Chemistry*, 2014, **20**, 5346-5357
[2] L.B. Rocha, L.C. Gomes-da-Silva, J.M. Dabrowski, L.G. Arnaut, *Eur J Cancer,* 2015, **51**, 1822-1830.

Halogenated Quinazolin-4(3*H*)-ones as Potent DNA Photo-cleavers

Melissari Zoi,[1] Mikra Chrysoula,[2] Fylaktakidou Konstantina*[,1,2]
[1]*Molecular Biology and Genetics Department, Democritus University of Thrace, 68100 Alexandroupolis, Greece,*
[2]*Chemistry Department, Laboratory of Organic Chemistry, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece*
E-mail address of the presenting author: kfylakta@chem.auth.gr

Quinazolinone (QNZ) heterocycles are considered "privileged structures" in medicinal chemistry [1]. A recent photophysical study for QNZ scaffold has shown a high photo-stability of the frame [2]. Nevertheless, in the past, the central nervous acting muscle relaxant drug "Afloqualone", a commercially available QNZ drug, has been proved phototoxic to bacteriophage lambda, exhibiting DNA photo-cleavage activity under a photodynamic way [3,4]. Working with simple QNZs we have found that converting Schiff bases into metal coordinated compounds not only QNZs were becoming photo-responding in visible light, but they were also acting under a photo-dynamic control [5,6]. Arguing the role of the metal, we have considered a structure activity relationship study on the simplest Quinazolin-4(3*H*)-one derivatives, where 6-Br and 6-I-QNZs were found photo-toxic under UVB irradiation (**3**, **4**, Fig (A, C)), [7]. Reviewing the literature, it is evident that halogenated QNZs have high possibilities to exhibit antimicrobial and cytotoxic activity [8]. Thus, continuing the study of QNZ as photo-sensitizers, we have synthesized hydroxamic acids **7-10** via their benzoxazinones (Fig. B) using thermal conditions that gave very poor yields of the desired compounds. The yields were, however, considerably elevated and the reaction time has been reduced when microwave irradiation has been applied.

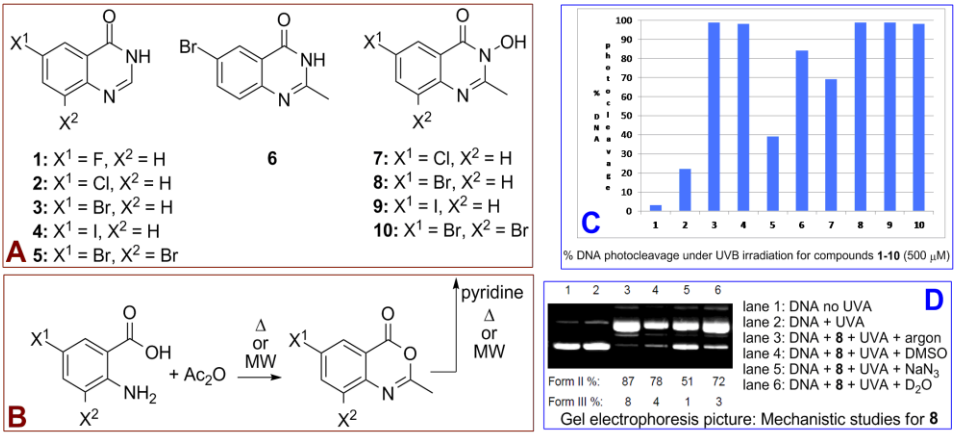


Figure: A: Structures of QNZ 1-6 and B: synthesis of QNZ hydroxamic acids 7-10. C: Comparative diagram for the % DNA photocleavage activity of compounds 1-10 under UVB irradiation at 500 µM. D: Gel electrophoresis picture conserning the mechanistic studies for the % DNA photocleavage of compound 8 under UVA irradiation.

All halogenated hydroxamic acids **7-10** have shown better activity than their related simple quinazolinones **2-5**. Interestingly, compound **8** showed activity also under UVA irradiation. The mechanism of action under anaerobic conditions showed probably C-halogen bond homolysis and under aerobic conditions the formation of singlet oxygen ($^1O_2$). The same has been observed in the case of compound **3**, however, only under UVB [7]. Therefore, based on these results, halogenated QNZ, and especially the hybrid hyroxamic acid quinazolinones, maybe promising lead compounds for cancer photo-therapies or photo-inactivation of bacteria.

Keywords:

Quinazolin-4(3H)-ones, DNA photo-cleavage, C-halogen bond homolysis

References:

[1] S. Gatadi, T.V. Lakshmi and S. Nanduri, *Eur. J. Med. Chem.* 2019, **170**, 157.
[2] S. Maiti, J. Kim, J. H. Park, et. al. and S. Y. Hong, *J. Org. Chem.* 2019, **84**, 6737.
[3] H. Fujita and I. Matsuo, *Chem. Biol. Interact.* 1987, **64**, 139.
[4] H. Tanizawa, Y. Taking, T. Oku, H. Hashizumi, Y. Iwamoto and T. Itoyama, *Chem. Pharm. Bull.* 1992, **40**, 1868.
[5] C. Kakoulidou, P. S. Gritzapis, A. G. Hatzidimitriou, K. C. Fylaktakidou and G. Psomas, *J. Inorg. Biochem.* 2020, **211**, art. no. 111194.
[6] C. Kakoulidou, et. al, K. C. Fylaktakidou and G. Psomas, *J. Inorg. Biochem.* 2021, art. no. 111448, *in press*.
[7] A. Panagopoulos, et. al. and K. C. Fylaktakidou, *Photochem. Photobiol.* 2021, *in press*, https://doi.org/10.1111/php.13376.
[8] E. Jafari, M. R. Khajouei, F. Hassanzadeh, G. H. Hakimelahi and G. A. Khodarahmi, *Res Pharm Sci.* 2016, **11**, 1.

Synthesis and photophysical studies of porphyrin-lignin conjugates

Dáire J. Gibbons[a, b], Nicolas Villandier[b], Stéphanie Leroy-Lhez[b] and René M. Williams[a]
[a] *Molecular Photonics Group, Van 't Hoff Institute for Molecular Sciences (HIMS), University of Amsterdam, PO Box 94157, 090 GD Amsterdam,The Netherlands*
[b] *Laboratoire PEIRENE - EA 7500, Faculté des Sciences et Techniques, 123 avenue Albert THOMAS, 87060, Limoges, France*
Email: Dairegibbons0@gmail.com

Problem, methods, major results and conclusions.

Porphyrins are the most studied and well-known photosensitizers (PSs) used in photodynamic therapy (PDT).[1] Upon light irradiation, porphyrin PSs are capable of generating singlet oxygen and reactive oxygen species, and possess tumour localizing properties.[2] Combining the production of these reactive oxygen species and their biological uptake, these compounds seemed to be ideal PSs.

However over the last two decades, porphyrins by themselves, or so-called "first generation PSs", have shown to possess several disadvantages that include mainly poor near infrared light absorption and cutaneous photosentivity.[3] In the last 15 years, research into the so called "second generation" and "third generation" PSs has led to a plethora of porphyrin derivatives being synthesized with the aim of improving its photodynamic efficacy against cancer.[4] The PEIRENE laboratory in Limoges, France, has a large variety of interdiscplinary experience in the investigation of porphyrins (and their derivatives) for photodynamic therapy. Furthermore, they have experience in the chemical modification of lignin to further investigate it's potential. Lignin, a side-product made in the paper industry, has been used in delivery systems for different pharmaceutical applications and more recently has been reported to produce singlet oxygen once acetylated.[5, 6] Within this work, and with the aim of improving the photodynamic efficacy of porphyrinoid species, novel porphyrin-lignin conjugates were synthesized that display improved photophyiscal properties compared to their porphyrin parent compounds.

Keywords:

Porphyrin, lignin, triplet excited state

References:

[1] S. K. Pushpan, S. Venkatraman, V. G. Anand, J. Sankar, D. Parmeswaran, S. Ganesan and T. K. Chandrashekar, *Current Medicinal Chemistry – Anti-Cancer Agents,* 2002, **2**, 187.
[2] J. M. Dąbrowski, B. Pucelik, A. Regiel-Futyra, M. Brindell, O. Mazuryk, A. Kyzioł, G. Stochel, W. Macyk, and L. G. Arnaut, *Coordination Chemistry Reviews,* 2016, **325**, 67.
[3] A. E. O'Connor, W. M. Gallagher and A. T. Byrne, *Photochemistry and Photobiology,* 2009, **85**, 1053.
[4] A. T. P. C. Gomes, M. G. P. M. S. Neves and J. A. S. Cavaleiro, *Anais da Academia Brasileira de Ciências*, 2018, **90**, 993.
[5] P. Figueiredo, K. Lintinen, J. T. Hirvonen, M. A. Kostiainen and H. A. Santos, *Progress in Materials Science*, 2018, **93**, 233.
[6] G. Marchand, C. A. Calliste, R. M. Williams, C. McLure, S. Leroy-Lhez and N. Villandier, *Chemistry Select*, 2018, **20**, 5512.

Covalently cross-linked tetrafunctionalized *m*-THPC chitosan hydrogels as delivery platforms

Piotr Gierlich,[a,b] Claire Donohoe,[a,b] Kevin Behan,[d] Lígia C. Gomes-da-Silva,[b] Daniel Kelly,[d] Mathias O. Senge[a,c]

[a] Medicinal Chemistry, Trinity Translational Medicine Institute, Trinity Centre for Health Sciences, Trinity College Dublin, The University of Dublin, St. James's Hospital, Dublin 8, Ireland.
[b] Department of Chemistry, University of Coimbra, Rua Larga, 3004-535 Coimbra, Portugal.
[c] School of Chemistry, SFI Tetrapyrrole Laboratory, Trinity Biomedical Sciences Institute, 152-160 Pearse Street, Dublin 2, Ireland
[d] Trinity Centre for Biomedical Engineering, Trinity Biomedical Sciences Institute, Trinity College Dublin, 152-160 Pearse Street, Dublin 2, Ireland.
E-mail address: gierlicp@tcd.ie

Photodynamic therapy (PDT) is an anti-cancer treatment method, which uses the combined effect of a photosensitizing drug, light, and oxygen to cause selective damage to target tissue.[1] The second generation photosensitizer (PS) 5,10,15,20-tetrakis(*m*-hydroxyphenyl)chlorin (*m*-THPC) is a widely characterized, clinically tested, and commercially available drug.[2] In order to develop advanced treatment modalities there is a need for improved drug delivery platforms. Hydrogels, which have been investigated as effective drug delivery systems, can prevent PSs aggregation due to their ability to swell in aqueous media.[3] Chitosan (CS), a natural polysaccharide, is a suitable biodegradable material for hydrogel formulation and has been used in pharmaceutical applications on account of its lack of toxicity and good biocompatibility.[4] Herein, *m*-THPC was used as a starting point to obtain a library of compounds aimed at overcoming PS limitations while maintaining its photophysical and clinical properties. Substitution, esterification and Sonogashira coupling reactions were employed to modify the *m*-THPC skeleton providing aldehyde and carboxylic acid moieties used as a suitable synthetic handle for covalent cross-linking in the formation of CS hydrogels. Injectable, self-healing properties of hydrogels were confirmed by the rheological analysis. Tetrafunctionalized *m*-THPC derivatives, maintaining efficient singlet oxygen generation are under ongoing *in vitro* evaluation against melanoma cancer cells (B16F10). Prepared hydrogel formulations are expected to allow for a local, injectable administration towards melanoma tumors, while preventing from systemic side effects related to the *m*-THPC treatment.

Keywords:

Photodynamic therapy, Hydrogel, Drug Delivery

References:

[1] T. J. Dougherty, C. J. Gomer, B. W. Henderson, G. Jori, D. Kessel, M. Korbelik, J. Moan, Q. Peng, *J. Nat. Cancer Inst.* 1998, *90*, 889–905.
[2] M. O. Senge, J. C. Brandt, *Photochem. Photobiol.* **2011**, *87*, 1240–1296.
[3] B. Khurana, P. Gierlich, A. Meindl, L. C. Gomes-da-Silva, M. O. Senge, *Photochem. Photobiol. Sci.* **2019**, *18*, 2613–2656; b) S. Belali, H. Savoi, J. M. O'Brien, A. A. Cafolla, B. O'Connell, A. R. Karimi, R. W. Boyle, M. O. Senge, *Biomacromolecules* **2018**, *19*, 1592–1601.
[4] M. Dash, F. Chiellini, R. M. Ottenbrite, E. Chiellini, *Prog. Polym. Sci.* **2011**, *36*, 981–1014.

New applications of two-dimensional infrared spectroscopy to investigate biomaterials

G.Giubertoni[1], F.Caporaletti[1], P.R. Laity[2], C. Holland[2], and S.Woutersen[1]
Author affiliations: [1]University of Amsterdam, [2] University of Sheffield
E-mail address of the presenting author: g.giubertoni@uva.nl

Two-dimensional infrared spectroscopy (2DIR) is a recently developed technique that provides reliable and detailed information on molecular structure, interaction, and hydration. Similar to 2D-NMR, where spin-spin couplings provide structural information, 2DIR spectroscopy measures couplings between vibrations to probe molecular structure. Since the spectra are measured using femtosecond infrared pulses, 2DIR can provide snapshots of molecular structures with unprecedented temporal resolution, and makes it possible to measure ultrafast (<ps) fluctuations in the structure/conformation in real time. 2DIR Spectroscopy is currently applied in various scientific fields, ranging from biochemistry and polymer physics to photophysics. Detailed molecular knowledge obtained using 2DIR has allowed us to gain ground-breaking new insights into a wide range of systems with varying molecular complexities and nature, such as water[1], proteins,[2] and organic semiconductors[3]. In spite of the unique features of 2DIR, its use is often hampered by practical limitations. In particular, studies of organic films or solid samples are complicated because of light scattering due to the presence of structures with sizes comparable to the infrared wavelength; and the measurements of protein samples commonly require high-level purification, high (non-physiological) concentrations, and the use of heavy water as a solvent.

Recently, however, 2DIR researchers have started to address these limitations, and to expand the use of 2DIR beyond conventional applications, especially to investigate biological materials which can be prepared with minimal purification. For example, the high sensitivity of 2DIR has been used to investigate protein secondary structures in lenses taken from human and pig eyes in an attempt to better understand cataract diseases[4]. Here, we join this scientific effort to apply 2DIR to investigate natural materials. We show that we can measure unpurified samples of silk produced by Bombyx mori caterpillars by using thin film samples. These silk samples are heterogeneous and contain both amorphous and crystalline regions, in which the silk proteins adopt different secondary structures that can vary upon humidity changes. Our preliminary 2DIR results confirm the presence of β-sheet structures in an untreated sample under ambient conditions. By changing the hydration state, we follow the effect of water on the molecular structure and dynamics.

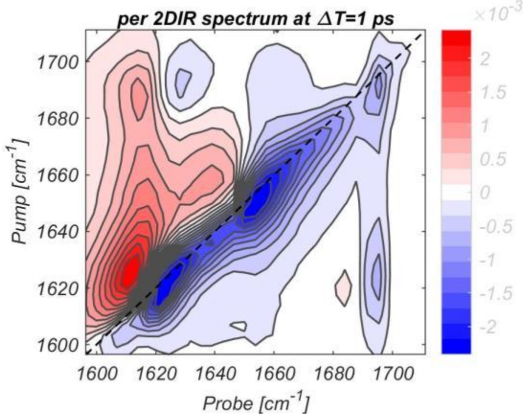


Figure 1: Example of a 2DIR spectrum recorded by measuring a dried film cast from the posterior section of a silk gland extract from a *Bombyx mori* silkworm.

Keywords:

2DIR; natural materials; silk

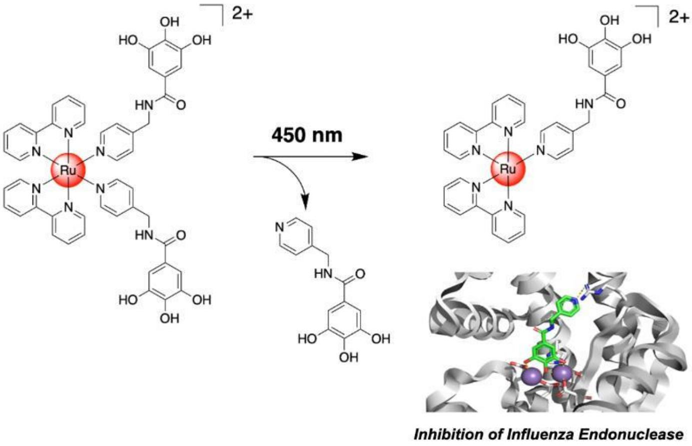
References:

[1] Fournier, J. A., Carpenter, W. B., Lewis, N. H. C. & Tokmakoff, A. Broadband 2D IR spectroscopy reveals dominant asymmetric H5O2+ proton hydration structures in acid solutions. *Nat. Chem.* **10**, 932–937 (2018).
[2] Petti, M. K., Lomont, J. P., Maj, M. & Zanni, M. T. Two-Dimensional Spectroscopy Is Being Used to Address Core Scientific Questions in Biology and Materials Science. *J. Phys. Chem. B* **122**, 1771–1780 (2018).
[3] Bakulin, A. A. *et al.* Real-Time Observation of Organic Cation Reorientation in Methylammonium Lead Iodide Perovskites. *J. Phys. Chem. Lett.* **6**, 3663–3669 (2015).
[4] Alperstein, A. M., Ostrander, J. S., Zhang, T. O. & Zanni, M. T. Amyloid found in human cataracts with two-dimensional infrared spectroscopy. *Proc. Natl. Acad. Sci. U. S. A.* **116**, 6602–6607 (2019).

Light Activated Release of a Metal Binding Pharmacophore from a Ru(II) Polypyridine Complex

Johannes Karges, Seth M. Cohen
Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California 92093, United States
E-mail address: jkarges@ucsd.edu

About 40-50% of all identified and characterised enzymes require a metal ion to perform their biological function. Despite comprising such a large space for drug development, less than 5% of recently approved therapies by the Food and Drug administration (FDA) target metalloenzymes, making them attractive and underrepresented pharmacological targets.[1] Metalloenzyme inhibitors typically coordinate to the active site metal ions and therefore contain ligands with charged or highly polar functional groups. While these groups may generate highly water-soluble compounds, this functionalization can also limit their pharmacological properties.[2] To overcome this drawback, drug candidates can be formulated as prodrugs. While a variety of protecting groups have been developed, increasing efforts has been devoted towards the use of caging groups, which can be removed upon exposure to light, as this provides spatial and temporal control over the treatment. Among these, the application of Ru(II) polypyridine complexes is receiving increased attention based on their attractive biological and photophysical properties.[3-4] Herein, a conjugate consisting of a metalloenzyme inhibitor and a Ru(II) polypyridine complex as a photo-cage is presented. The conjugate was designed using density functional theory calculations and docking studies. The conjugate is stable in an aqueous solution, but irradiation of the complex with 450 nm light releases the inhibitor within several minutes. As a model system, the biological properties were investigated against the endonuclease of the influenza virus. While showing no inhibition in the dark in an in vitro assay, the conjugate generated inhibition upon light exposure at 450 nm, demonstrating the ability to liberate the metalloenzyme inhibitor. The presented inhibitor-Ru(II) polypyridine conjugate is an example of computationally-guided drug design for light activated drug release and may help reveal new avenues for the prodrugging of metalloenzyme inhibitors.[5]



Keywords: *antiviral agents, photoactivation, photocage*

References:

[1] A. Y. Chen, R. N. Adamek, B. L. Dick, C. V. Credille, C. N. Morrison, S. M. Cohen, *Chem. Rev.* **2019,** *119* (2), 1323-1455.

[2] R. J. White, P. S. Margolis, J. Trias, Z. Yuan, *Curr. Opin. Pharmacol.* **2003,** *3* (5), 502-507.

[3] L. N. Lameijer, D. Ernst, S. L. Hopkins, M. S. Meijer, S. H. C. Askes, S. E. Le Dévédec, S. Bonnet, *Angew. Chem. Int. Ed.* **2017,** *56* (38), 11549-11553.

[4] T. Respondek, R. N. Garner, M. K. Herroon, I. Podgorski, C. Turro, J. J. Kodanko, *J. Am. Chem. Soc.* **2011,** *133* (43), 17164-17167.

[5] J. Karges, R. W. Stokes, S. M. Cohen, *Dalton Trans.* **2021**, *50*, 2757-2765.

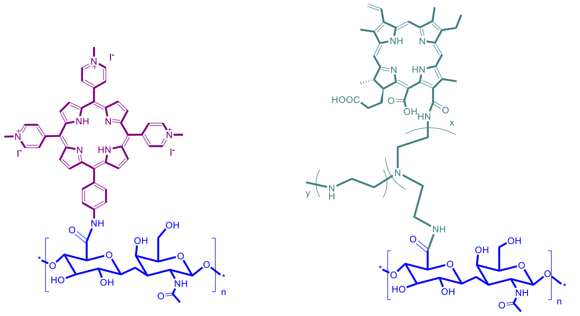
Antimicrobial photosensitizers and their formulations: A potential solution to current world scenario

Bhavya Khurana[a,b], Tan Ouk[a], Mathias O. Senge[b,c], Vincent Sol[a]
[a] *Université de Limoges, Laboratoire PEIRENE.*
[b] *School of Chemistry, Trinity Biomedical Sciences Institute, Trinity College Dublin, The University of Dublin.*
[c] *Medicinal Chemistry, Trinity Translational Medicine Institute, Trinity Centre for Health Sciences, Trinity College Dublin, The University of Dublin*
Email: khuranab@tcd.ie

In order to provide a long-lasting solution to infections affecting the current world scenario, photodynamic therapy (PDT) offers a means to destroy pathogenic microbes via formation of reactive oxygen species, promoting the damage of microbial targets such as nucleic acids (DNA or RNA), proteins, lipids, protein complexes, or by impeding the biofilm matrix.[1]

1

Thus, the main aim of the study is to design and synthesize photoactive moieties based on porphyrin and chlorin macrocycles and BODIPY dyes for antimicrobial photodynamic therapy (aPDT).[2] Furthermore, incorporating these photo-moieties into biopolymeric hydrogels as shown in Figure 1 for a variety of biomedical applications are targeted.



Cationic; 5-(4-Acetamidophenyl)-10,15,20- tris(4-N-methylpyridinium) porphyrin covalently bonded with hyaluronic acid polymeric platform

Purpurin-18 covalently bonded with hyaluronic acid polymeric platform

Figure 1. Photosensitizers incorporated in a hyaluronic acid hydrogel matrix for aPDT applications.

Porphyrin based cationic photosensitizers (PSs) were synthesized and a chlorin based PS was extracted from Spirulina maxima and modified to be included on a biopolymeric hyaluronic acid hydrogel platform. This platform was characterized spectroscopically and evaluated for antimicrobial photoactivity via microbial evaluation on different gram strains of bacterial species. Singlet oxygen production was determined as well to evaluate the photoactivity of this polymeric hydrogel platform.

Furthermore, BODIPY dye-based PS species have been synthesized and modified for their activity as aPDT agents. Several *N*-heterocyclic BODIPY-dyes have been positively charged or functionalized for incorporation into hydrogel platforms. These dyes exhibit good water solubility. A library of such *N*-heterocyclic BODIPY dyes was prepared and characterized and will be evaluated for photoactivity against microbes.

Keywords: *Photodynamic therapy, Antimicrobial, BODIPY, Hydrogel*

References:

[1] W.C. de Melo, P. Avci, M.N. de Oliveira, A. Gupta, D. Vecchio, M. Sadasivam, R. Chandran, Y.Y. Huang, R. Yin, L.R. Perussi, G.P. Tegos, J.R. Perussi, T. Dai, M.R. Hamblin, *Photodynamic inactivation of biofilm: taking a lightly colored approach to stubborn infection. Expert review of anti-infective therapy*, 2013, **11**, 669-693.
[2] A. Wiehe, J.M. O'Brien, M.O. Senge, *Trends and targets in antiviral phototherapy*, Photochem. Photobiol. Sci., 2019, **18**, 2565-2612.

Porphyrin-loaded acetylated lignin nanoparticles: preparation, characterization and antimicrobial activity

Nidia Maldonado-Carmona[a], Nicolas Villandier[a], Tan-Sothea Ouk[a], Mário J.F. Calvete[b], Mariette M. Pereira[b], Stéphanie Leroy-Lhez[a]
[a]PEIRENE Laboratory, Faculty of Sciences and Techniques, University of Limoges, Limoges, France
[b]Coimbra Chemistry Center, Department of Chemistry, University of Coimbra, 3004-535 Coimbra, Portugal
E-mail address: nidia.maldonado@etu.unilim.fr

Introduction. POLYTHEA project, has focused on "How light can save lives", during the last three years. One of the facets of the project aimed to develop antimicrobial alternatives based in Photodynamic Antimicrobial ChemoTherapy (PACT). **Methodology.** Part of the efforts poured into this project focused on the encapsulation of photosensitizers in acetylated lignin nanoparticles.[1] These nanoparticles were prepared through an antisolvent method, that lead to spherical nanoparticles with a wide size range. The obtained nanoparticles were physically characterized (dynamic light scattering, polidispersity index, transmission electron microscopy, environmental scanning electron microscopy), while the effect on the encapsulation on the photophysical parameter of the photosensitizers were also analyzed (UV-vis absorption, fluorescence emission and excitation, singlet oxygen production and photobleaching rate). **Results.** It was demonstrated that this is a suitable formulation for several kind of photosensitizers, maintaining its photophysical properties and enabling the eradication of Gram-positive bacteria (*Staphylococcus aureus, Staphylococcus epidermidis* and *Enterococcus faecalis*).[2] Furthermore, the antimicrobial effect is not obtained without evidence of photosensitizer leakage into the medium. Then, the bacterial eradication is explained through the intimate contact found between the nanoparticles and the bacteria. However, even when encapsulating cationic photosensitizers, our formulation was unable to decrease the bacterial survival of Gram-negative bacteria (*Escherichia coli*).[3] **Conclusions**. The use of acetylated lignin nanoparticles as a photosensitizers delivery system has been demonstrated. These nanoparticles are able to tightly interact with bacteria and efficiently eradicate Gram-positive bacteria. Further work is needed to achieve a formulation which enables the eradication of Gram-negative bacteria.

Keywords:

nanoobjects, photosensitizers, lignin valorization

References

[1] Marchand, G.; Fabre, G.; Maldonado-Carmona, N.; Villandier, N.; Leroy-Lhez, S. *Nanoscale Adv.* **2020**, *2* (12), 5648–5658. https://doi.org/10.1039/D0NA00615G.
[2] Maldonado-Carmona, N.; Marchand, G.; Villandier, N.; Ouk, T.-S.; Pereira, M. M.; Calvete, M. J. F.; Calliste, C. A.; Żak, A.; Piksa, M.; Pawlik, K. J.; Matczyszyn, K.; Leroy-Lhez, S. *Front. Microbiol.* **2020**, *11*. https://doi.org/10.3389/fmicb.2020.606185.
[3] Maldonado-carmona, N.; Ouk, T.; Villandier, N.; Calliste, C. A.; Calvete, M. J. F.; Pereira, M. M.; Leroy-lhez, S. **2021**, 1–26.

Synthesis and spectral properties of gem-dimethyl chlorin photosensitizers

Zoi Melissari[a,b], Harry C. Sample[a], René M. Williams[b] and Mathias O. Senge[a]
[a] School of Chemistry, Trinity Biomedical Sciences Institute, 152–160 Pearse Street, Trinity College Dublin, The University of Dublin, Dublin 2, Ireland
[b] Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, The Netherlands
E-mail address: melissaz@tcd.ie, z.melissari@uva.nl

Photodynamic therapy (PDT) is a developing non-invasive targeted therapy which involves systemic or topical administration of a photosensitizer (PS), which after irradiation of a specific wavelength of light reacts with the coexisting molecular oxygen. As a result, highly reactive singlet oxygen ($^1O_2$) and other reactive oxygen species (ROS) can be formed leading to specific apoptotic or necrotic cell death of the cancer cells.[1]

In this study we aim to develop novel non-toxic PSs, *i.e.*, chlorins which bear a *gem*-dimethyl group, attributing to their resistance to oxidation. These compounds have potential use as anticancer or antimicrobial agents and their photophysical properties are described herein.

Synthesis was performed following a method reported by Lindsey and co-workers.[2] A complete characterization of their spectral and photophysical properties (Φ_f, Φ_{isc}, Φ_{ic}, Φ_Δ, τ_S, τ_T, k_f, k_{ic}, k_{isc}, k_q) is accompanied by density functional calculations (DFT) and time dependent (TD) DFT to investigate the features of the frontier molecular orbitals. The metallochlorins exhibit high triplet state yields (Φ_{isc} = 0.80 – 0.90) and excellent singlet oxygen quantum yields in methanol and ethanol (Φ_Δ = 0.60 – 0.85) and the free base analogues exhibited suitable triplet state yields (Φ_{isc} = 0.70 – 0.80) and singlet oxygen quantum yields (Φ_Δ = 0.40 – 0.70). Results show that the chlorins can be potential PS candidates for PDT, given that they display high singlet oxygen quantum yields in polar solvents, modest fluorescence quantum yields (Φ_f = 0.03 – 0.14) and moderate triplet state lifetimes (τ_T = 150 – 220 ns) upon photoexcitation.[3]

Future work includes the optimization of the photophysical properties of the chlorins (red-shifted absorption, high triplet state yields, long triplet lifetimes and high singlet oxygen quantum yields) and enhancing the water solubility through modification of the periphery with a variety of substituents. Additionally, *in vitro* evaluation will be employed in future.

Keywords:

Singlet oxygen, photodynamic therapy, triplet photosensitizers

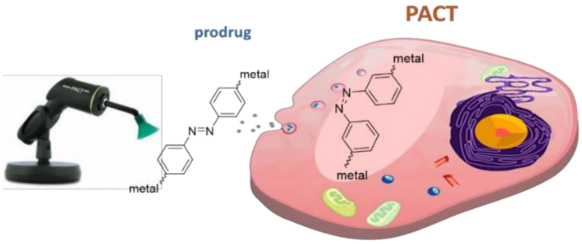
References:

[1] A. Wiehe, J. M. O'Brien and M.O. Senge, *Photochem. Photobiol. Sci.* 2019, **18**, 2565.
[2] M. Ptaszek, B. E. McDowell, M. Taniguchi, H. J. Kim and J. S. Lindsey, *Tetrahedron*, 2007, **63**, 3826.
[3] Z. Melissari, H. C. Sample, B. Twamley, R. M. Williams and M. O. Senge, *ChemPhotoChem*, 2020, **4**, 601.

Azobenzenes-based metal complexes photoisomerization: A new promising approach in PACT.

J.M. Herrero,[1,2] L. Cubo,[1] A.I. Matesanz,[1] I. Sánchez-Pérez[2] and A.G. Quiroga[1]
[1]Departamento de Química Inorgánica. Universidad Autónoma de Madrid.
[2]Instituto de Investigaciones Biomédicas Alberto Sols UAM-CSIC, Madrid, Spain
Email: jmherrero@iib.uam.es

Cisplatin is an antitumor metal complex known for its high activity and clinical use. However, its serious side effects have conducted research into new complex designs with less toxicity and greater antitumor efficacy. Currently, there are antitumor therapies that use irradiation as a method of activating chemical compounds to increase their activity and thus control them within the system. PhotoActivated Chemo therapy (PACT) is of particular interest, since it allows this control in drugs temporarily and spatially.[1] An alternative in the development of metal antitumor drugs is the formation of complexes containing ligands with "cis/trans" photochemical isomerization capacity due to the presence of the azo group (-N=N-).[2] This fact offers the possibility of a photochemical control in the antitumor activity of these types of compounds (Figure 1).



Within this frame, we have synthetized and characterized ligands which carry an azo group in their structures. We have also tested and studied the reactions of these ligands with platinum(II) salts to give the corresponding platinum complexes. The photochemical properties and the effect of the solvents on the structure of the azo compounds and the complexes have been studied by Nuclear Magnetic Resonance and UV-vis spectroscopy. The preliminary results evidence that the platinum complexes undergo trans-cis isomerization upon irradiation, and the cis isomers then undergo slow thermal isomerization back to the more stable trans isomers. Thus, this synthetic route and design could be a promising strategy to obtain photoactivable prodrugs to use in Phototherapy for cancer treatment.

Acknowledgements: This research was supported by a Spanish MINECO grant (PID2019-106220RB-I00) and MetDrugs network (RED2018-102471-T). We thank SIDI UAM for the support with the experiments and technologies: mass spectrometry and NMR.

Keywords:

PACT (PhotoActivated Chemotherapy), metallodrugs, azobenzenes

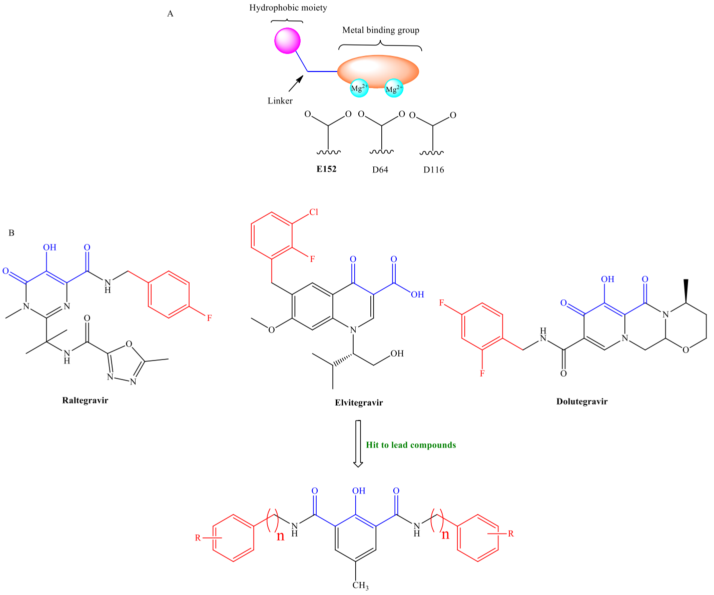
References:

[1] P. J. Sadler, C. Imberti, P. Zhang and H. Huang. *Angew. Chem*. **2020**, *132*, 61.
[2] E. Merino and M. Ribagorda. *Beilstein J. Org. Chem*. **2012**, *8*, 1071.

Structure-based Design of N^1,N^3-dibenzyl-2-hydroxy-5-methyl isophthalamides as novel antiviral agents

Arif Mermer
University of Health Sciences-Turkey, Experimental Medicine Research and Application Center, Uskudar, 34662, Istanbul, Turkey
arif.mermer@sbu.edu.tr

Human immunodeficiency virus is a spectrum of conditions caused by infection with the human immunodeficiency virus. In 2019, about 38 million people worldwide were living with HIV and 690,000 deaths had occurred in that year [1]. To date, for the treatment of HIV-1 disease, many compounds have been synthesized and some of them was approved by FDA. However, the use of these drugs has been limited due to reasons such as resistance caused by the misuse of drugs and bad side effects [2]. We describe herein designing 48 novel compounds as a potential inhibitor of HIV-1 integrase through in silico studies such as molecular docking, target analysis, toxicity prediction and ADME prediction. The online web-based platform, SwissADME, also predicts these molecules solubility, pharmacodynamics property and target accuracy.



Keywords:

SwissAdme, HIV-1 Integrase, Molecular Docking, In Silico Study

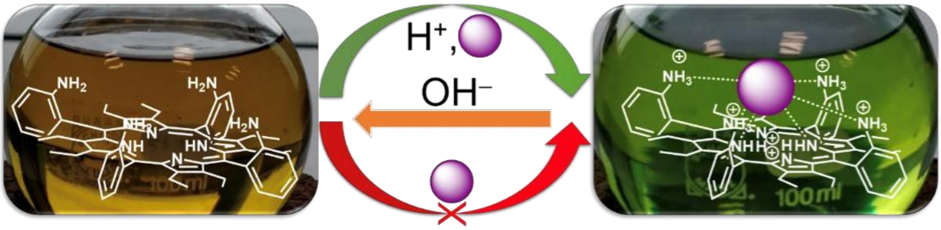
References:

[1] J. R. Thompho, T. H. Angela, M. Salerwe, V. Sandyvan, C. E. Mabel and L. B. Moira, *Bioorg. Med. Chem.*, 2020, **28**, 115210.
[2] P. Manoj, N. B. Narasimhulu, D. Ira, H. Helen, L. Zeyu, T. Brian, P. Tricia, K. Mark, J. Susan, P. Dawn, P. Chiradeep, R. Richard, M. Arvind, A. M. Nicholas and A. W. Michael, *Bioorg. Med. Chem.*, 2020, **28**, 115541.

Spectroscopic Analysis of Nonplanar Porphyrin Atropisomers with Specialized Binding Cavities

K. Norvaiša, Dublin/IRL, M. O. Senge, Dublin/IRL
Author affiliations: School of Chemistry, Trinity Biomedical Sciences Institute, Trinity College Dublin, the University of Dublin, Pearse Str. 152–160, Dublin
E-mail address: norvaiak@tcd.ie

The inner core system of metal-free (‘free base’) porphyrins has continually served as a ligand for various metal ions but only recently its highly tuneable basicity found its first application as an organocatalyst.[1] Highly conjugated porphyrin systems offer spectrophotometric sensitivity towards geometrical and/or electronic changes and thus, utilizing the porphyrin core for selective detection of substrates in solution offers significant potential for multitude of applications.[2] However, solvation and dilution drastically affect weak interactions by dispersing the binding agent to its surroundings. Thus, spectroscopic detection of N–H···X-type[3] binding in porphyrin solutions is almost impossible without specially designing the binding pocket. Here we present spectroscopic detection of the N–H···X-type interplay in porphyrins formed by weak interactions.[4] While a counter anion locks in the anion-selective inner core system it also reduces the proton exchange rate, generating static proton signals. This allowed an ideal case study in which porphyrin atropisomers can stand in rotation-restricted states for which high-resolution NMR is available. Performing 1D, 2D NMR spectroscopic analyses, we were able to characterize all four rotamers of the nonplanar 5,10,15,20-tetrakis(2-aminophenyl)-2,3,7,8,12,13,17,18-octaethylporphyirin as restricted H-bonding complexes. Upon detailed assignment of the chemical signals, symmetry operations, unique to porphyrin atropisomers, offered an essential handle to accurately identify the rotamers using NMR techniques only.[5]



Keywords:

Nonplanar, Porphyrin, 2D NMR, Sensing

References:

[1] a) M. Roucan, M. Kielmann, S. J. Connon, S. S. R. Bernhard, M. O. Senge, Chem. Commun., 2018, **54**, 26; b) M. Kielmann, N. Grover; W. W. Kalisch, M. O. Senge, Eur. J. Org. Chem., 2019, 2448.
[2] K. Norvaiša, M. Kielmann, M. O. Senge, ChemBioChem, 2020, **21**, 1793.
[3] M. Kielmann, M. O. Senge, Angew. Chem. Int. Ed., 2019, **58**, 418.
[4] K. Norvaiša, K. J. Flanagan, D. Gibbons, M. O. Senge, Angew. Chem. Int. Ed., 2019, **58**, 16553.
[5] K. Norvaiša, J. E. O’Brien, D. Gibbons, M. O. Senge, 2021, **27**, 331

Synthesis of New Bodipys for Photodynamic Therapy on Human Lung Cancer Cell Line H1299

Soraia Pedro[1], Juliana Araújo[2], Chrislaura Carmo[2], Mafalda Laranjo[3,4], Maria Filomena Botelho[3,4], Abílio J. F. N. Sobral[2]

[1] Department of Physics, University of Coimbra, P-3004-516 Coimbra, Portugal. [2] Department of Chemistry, University of Coimbra, P-3004-535 Coimbra, Portugal. [3]Institute of Biophysics and Coimbra Institute for Clinical and Biomedical Research (iCBR-CIMAGO), Faculty of Medicine, University of Coimbra, P-3000-548 Coimbra, Portugal. [4] Center for Innovation in Biomedicine and Biotechnology (CIBB), University of Coimbra, P-3000-548 Coimbra, Portugal.

E-mail: soraia.pedro@hotmail.com

Despite the existence of several therapeutic options, lung cancer remains the leading cause of cancer death and the most diagnosed worldwide for men and women. Therefore, the need for new and more effective therapies with fewer side effects is a concern. Photodynamic Therapy (PDT) relies on the administration of a photosensitizer that is subsequently activated by light of appropriate wavelength to produce reactive oxygen species (ROS) that lead to cell death[1,2]. The aim of this work was the development of new Boron-dipyrromethenes (BODIPYs) for PDT (Figure 1) and to evaluate them on the human lung cancer cell line H1299.

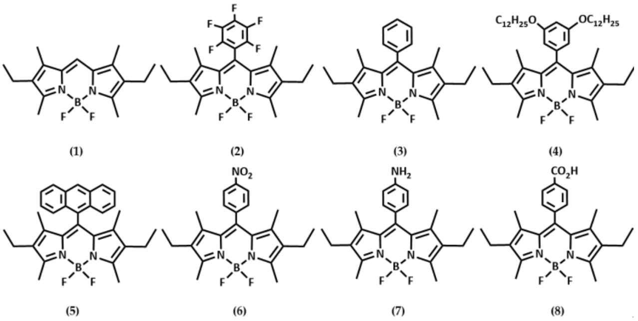


Figure 1. Structures of the Boron-dipyrromethenes synthesized and studied in PDT in this work.

Cell cultures were incubated with the BODIPYs in concentrations ranging 1 to 50 μM. 24h later cell culture medium was replaced by BODIPYs free media and irradiation with visible red light was performed. Metabolic activity and viability were evaluated by MTT and SRB assays, respectively 24 and 48h after treatment. Studies omitting the irradiation step were also performed. BODIPY 2, 3 and 5 based PDT led to a significant loss of cell viability. BODIPYs 2 and 5 are found as the most interesting photosensitizers.

Keywords:

Boron−dipyrromethenes; Photodynamic Therapy; Metabolic activity.

References:

[1] Costa, L. D., Silva, J. A., Fonseca, S. M., Arranja, C. T., Urbano, A. M., Sobral, A. J. F. N., *Molecules*, 2016, **21**, 1-12;

[2] Sobral, A. J. F. N., Eléouet, S., Rousset, N., Gonsalves, A. M. d'A. R., Le Meur, O., Bourré, L., Patrice, T., *Journal of Porphyrins and Phthalocyanines,* 2009, **06**, 456–462.

Acknowledgments: The authors thanks FCT and ChemMat Programme for the PhD research grant PD/BD/150440/2019 and Coimbra Chemistry Centre (CQC) through the project UIDB/00313/2020 and UIDP/QUI/00313/2020, co-funded by COMPETE2020-UE. Center for Innovative Biomedicine and Biotechnology (CIBB) us funded by FCT (UID/NEU/04539/2013) and COMPETE-FEDER (POCI-01-0145-FEDER-007440), through the Strategic Project UIDB/04539/2020 and UIDP/04539/2020.

Antimicrobial photodynamic therapy against clinical strains of *staphylococci* with the use of organic light emitting diode

Author name(s): M. Piksa[1], C. Lian[2], S. Persheyev[2], I. D. W. Samuel [2], K. Pawlik[1],
K. Matczyszyn[3]
Author affiliations: 1. Ludwik Hirszfeld Institute of Immunology and Experimental Therapy,
Polish Academy of Sciences, Poland
2. Organic Semiconductor Centre, School of Physics and Astronomy,
University of St Andrews, UK
3. Advanced Materials Engineering and Modelling Group, Faculty of Chemistry,
Wroclaw University of Science and Technology, Poland
E-mail address: marta.piksa@hirszfeld.pl

As we have shown in our latest publication *Staphylococcus aureus* may be efficiently killed via antimicrobial photodynamic therapy with the use of organic light emitting diode (OLED) as a light source.[1] The investigated microorganism was well-studied bacteria obtained from the Polish Collection of Microorganism, in case of which the efficiency of APDT was confirmed. However, if APDT destination is an outpatient use clinical strains should be also examined. For this purpose, we decided to collect medical specimens from diabetic patients with diagnosed diabetic foot ulcers and wounds and isolate *staphylococci* strains to evaluate their susceptibility APDT.

World Health Organization (WHO) identifies diabetes as one of the most common chronic diseases and one of the largest global health emergencies of the 21st century. The worldwide prevalence of both type 1 and type 2 diabetes is increasing and in 2014, there were 422 million adults worldwide diagnosed with diabetes.[2] One of the most traumatic and invasive diabetes complication is diabetic foot leading usually to amputation and increasing the mortality rate among diabetics. Bacterial infections are in this case particularly dangerous, especially when antibiotic-resistance bacteria occupied the wound. APDT seems to be a highly potential treatment or co-treatment.[3]

As a result of our research, we reached at least a 99% reduction of all isolated staphs strains showing the same that APDT may be an attractive alternative to fight infection caused by *staphylococci*.

Keywords:

APDT, antimicrobial photodynamic therapy, staphylococci, infections, diabetic foot, diabetis

References:

[1] C. Lian, M. Piksa, K. Yoshida, S. Persheyev, K. J. Pawlik, K. Matczyszyn and I. D. W. Samuel, *npj Flexible Electronics,* 2019, **3**, 1-6.

[2] T. Yamaguchi, S. Sato, S. Kawauchi, M. Terakawa, N. Shinomiya, D. Saitoh, H. Ashida, M. Obara, *Diabetes Res. Clin. Pract.*, 2017, **128**, 40-50.

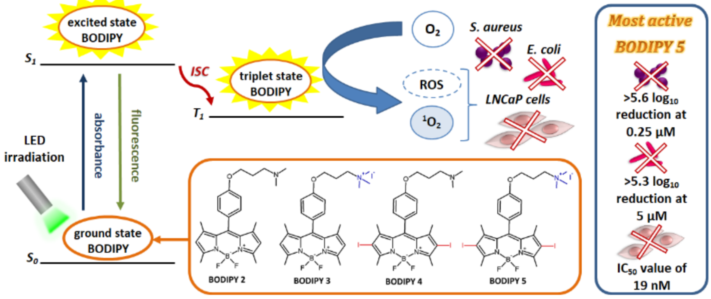
[3] B. A. Lipsky, A. R. Berendt, P. B. Cornia, J. C. Pile, E. J. G. Peters, D. G. Armstrong, H. G. Deery, J. M. Embil, W. S Joseph, A. W. Karchmer, M. S.Pinzur, E. Senneville, *Clinical Infectious Diseases*, 2012, **54**, 132-173

Novel BODIPYs with strong heavy atom effect as dual photosensitizers for antimicrobial and anticancer PDT

Weronika Porolnik[1], Malgorzata Kucinska[2], Jolanta Dlugaszewska[3], Marek Murias[2], Jadwiga Mielcarek[1], Jaroslaw Piskorz[1]
[1]Chair and Department of Inorganic and Analytical Chemistry, Poznan University of Medical Sciences, Grunwaldzka 6, 60-780 Poznan;
[2] Chair and Department of Toxicology, Poznan University of Medical Sciences, Dojazd 30 Street, 60-631 Poznan,
[3]Chair and Department of Genetics and Pharmaceutical Microbiology, Poznan University of Medical Sciences, Swieckiego 4, 60-781 Poznan, Poland
E-mail: w.porolnik@op.pl

Photodynamic therapy (PDT) is a promising regime successfully applied for the treatment of localized cancers and other premalignant or non-malignant dermal lesions, as well as microbial infections. PDT involves the use of a photosensitizer and light of appropriate wavelength to induce oxidative stress leading to the eradication of targeted cells[1]. Boron dipyrromethene (BODIPY) dyes exhibit a number of properties that make them suitable for exploration as PDT agents, including strong absorption coefficient, good stability, chemical robustness, and high structural tunability, which allows affecting their photophysical properties such as absorption and emission wavelengths, solubility and the rate of singlet oxygen generation[2].

Novel BODIPYs with dimethylaminopropoxyphenyl substituents and their cationic and iodinated derivatives were synthesized and characterized using mass spectrometry, UV-Vis spectrophotometry, and various NMR techniques. Subsequent photochemical studies allowed evaluating their absorption and emission properties and the singlet oxygen generation ability. *In vitro* photodynamic activity studies were performed on human androgen-sensitive prostate adenocarcinoma cells (LNCaP) and two bacterial strains (Gram-positive *Staphylococcus aureus* and Gram-negative *Escherichia coli*). It was found that the introduction of iodine atoms into the BODIPY core caused significant enhancement of singlet oxygen production, which is considered the main cytotoxic agent in PDT. BODIPY derivative possessing both a positive charge and iodine atoms revealed the highest activity towards all studied cells[3].



Keywords: *BODIPY, heavy atom effect, photodynamic therapy, photodynamic antimicrobial chemotherapy*

References:

[1] L. Benov, *Med Princ Pract,* 2015, **24**, 14–28.
[2] A. Kamkaew, S. H. Lim, H. B. Lee, L. V. Kiew, L. Y. Chung, K. Burgess, *Chem. Soc. Rev.,*2013, **42**, 77–88.
[3] J. Piskorz, W. Porolnik, M. Kucinska, J. Dlugaszewska, M. Murias, J. Mielcarek, *ChemMedChem,* 2021, **16**, 399–411.

This work was supported by the National Science Centre, Poland, under grant no. 2016/21/D/NZ7/01540

Developing Organic Light-emitting Diodes (OLEDs) for Photodynamic Therapy (PDT)

Mina Riahi, Hassan Hafeez, Saydulla Persheyev, Kou Yoshida, Cheng Lian, and Ifor D. W. Samuel

Organic Semiconductor Centre, School of Physics and Astronomy, University of St Andrews, St Andrews KY16 9SS, UK

mr287@st-andrews.ac.uk

Photodynamic therapy (PDT) is an effective, non-invasive method to treat human, animal and plant diseases[1–5]. However, its use has been restricted by the need for efficient and uniform light sources. Organic light emitting diodes (OLEDs) are attractive for PDT because they are wearable and can be easily attached to body parts[6]. They have been successfully used for ambulatory treatment of non-melanoma skin cancer[7]. However, increasing the size can cause several problems, such as luminance non-uniformity, power loss, and heat generation[8]. Due to the sheet resistance of the electrodes, the injected current decreases and the light emission distribution becomes non-uniform[9]. In this work, we show how improvements in contact design can give larger OLEDs with good uniformity.

Figure 4. Image of 28mm by 50 mm OLED

Keywords:

photodynamic therapy (PDT), organic light emitting diodes (OLEDs), uniformity

References:

[1] Issawi, M.; Sol, V.; Riou, C. Plant Photodynamic Stress: What's New? *Front. Plant Sci.* **2018**, *9* (May), 1–9. https://doi.org/10.3389/fpls.2018.00681.

[2] Fracarolli, L.; Rodrigues, G. B.; Pereira, A. C.; Massola Júnior, N. S.; Silva-Junior, G. J.; Bachmann, L.; Wainwright, M.; Bastos, J. K.; Braga, G. U. L. Inactivation of Plant-Pathogenic Fungus Colletotrichum Acutatum with Natural Plant-Produced Photosensitizers under Solar Radiation. *J. Photochem. Photobiol. B Biol.* **2016**, *162*, 402–411. https://doi.org/10.1016/j.jphotobiol.2016.07.009.

[3] Quirk, B. J.; Brandal, G.; Donlon, S.; Vera, J. C.; Mang, T. S.; Foy, A. B.; Lew, S. M.; Girotti, A. W.; Jogal, S.; LaViolette, P. S.; Connelly, J. M.; Whelan, H. T. Photodynamic Therapy (PDT) for Malignant Brain Tumors - Where Do We Stand? *Photodiagnosis Photodyn. Ther.* **2015**, *12* (3), 530–544. https://doi.org/10.1016/j.pdpdt.2015.04.009.

[4] Railkar, R.; Agarwal, P. K. Photodynamic Therapy in the Treatment of Bladder Cancer: Past Challenges and Current Innovations. *Eur. Urol. Focus* **2018**, *4* (4), 509–511. https://doi.org/10.1016/j.euf.2018.08.005.

[5] Ormond, A. B.; Freeman, H. S. Dye Sensitizers for Photodynamic Therapy. *Materials (Basel).* **2013**, *6* (3), 817–840. https://doi.org/10.3390/ma6030817.

[6] Jeon, Y.; Noh, I.; Seo, Y. C.; Han, J. H.; Park, Y.; Cho, E. H.; Choi, K. C. Parallel-Stacked Flexible Organic Light-Emitting Diodes for Wearable Photodynamic Therapeutics and Color-Tunable Optoelectronics. *ACS Nano* **2020**, *14* (11), 15688–15699. https://doi.org/10.1021/acsnano.0c06649.

[7] Attili, S. K.; Lesar, A.; McNeill, A.; Camacho-Lopez, M.; Moseley, H.; Ibbotson, S.; Samuel, I. D. W.; Ferguson, J. An Open Pilot Study of Ambulatory Photodynamic Therapy Using a Wearable Low-Irradiance Organic Light-Emitting Diode Light Source in the Treatment of Nonmelanoma Skin Cancer. *Br. J. Dermatol.* **2009**, *161* (1), 170–173. https://doi.org/10.1111/j.1365-2133.2009.09096.x.

[8] Lian, C.; Piksa, M.; Yoshida, K.; Persheyev, S.; Pawlik, K. J.; Matczyszyn, K.; Samuel, I. D. W. Flexible Organic Light-Emitting Diodes for Antimicrobial Photodynamic Therapy. *npj Flex. Electron.* **2019**, *3* (1), 0–6. https://doi.org/10.1038/s41528-019-0058-0.

[9] Neyts, K.; Real, A.; Marescaux, M.; Mladenovski, S.; Beeckman, J. Conductor Grid Optimization for Luminance Loss Reduction in Organic Light Emitting Diodes. *J. Appl. Phys.* **2008**, *103* (9). https://doi.org/10.1063/1.2907960.

Two- and multi-photon absorption photosensitizers[1]

E. Robbins [a, b], S. Leroy-Lhez [a], N. Villandier [a], and K. Matczyszyn [b]
Author affiliations: a) Universite de Limoges – Laboratoire PEIRENE, 123 Avenue Albert Thomas, 87060 Limoges, France. b) Advanced Materials Engineering and Modelling Group, Faculty of Chemistry, Wroclaw University of Science and Technology, Wybrzeze Wyspianskiego 27, 50-370 Wroclaw, Poland.
E-mail address: emma.robbins@pwr.edu.pl

For cancer treatment by photodynamic therapy (PDT), the ideal optical window is between 650 and 850 nm. Classic porphyrin derivatives do not reach this requirement ($\lambda_{max} \leq 650$ nm). To overcome this discrepancy, we utilise nonlinear optical properties, particularly two-photon absorption (TPA). TPA can be very valuable for PDT. It can reduce thermal photo-damage of surrounding tissue due to the low-energy NIR excitation (700-1100 nm) and allow for deeper tumour treatments.[2] However, TPA combined PDT is limited because of low TPA-cross sections, as observed for the commercially used Foscan® (28 GM).[3] Several studies have suggested the design of highly conjugated porphyrins to overcome this issue. Extension of the π–conjugated system leads to major photophysical modifications, including an increase of the TPA-cross section.[4] Recent studies (collaboration with PEIRENE Laboratory) highlight the potential of porphyrin dimers[5], as well as pyrimidines combined with porphyrins.[6] Analogous para-substituted compounds are in development based on previously synthesised meta-substituted pyrimidines. This presentation will have a focus on the theory behind TPA enhancement. As well as the synthesis of these new porphyrin systems developed to improve their TPA properties for singlet oxygen generation with potential applications in PDT.

Keywords:

porphyrins, photosensitizers, two-photon absorption, synthesis, photodynamic therapy

References:

[1] www.polythea.eu. "**POLYTHEA**: How light can save lives". This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement n°764837.
[2] Starkey, J. R., Rebane, A.k., Drobizhev, M. A., Meng, F., Gong, A., Elliott, A., Mclnnerney, K., Spangler, C. W. New two-photon activated photodynamic therapy sensitizers induce xenograft tumor regressions after near-IR laser treatment through the body of the host mouse. *Clin. Cancer Res*., 2008, **14**, 6564-6573.
[3] Hamed, B., von Haimberger, T., Kozich, V., Wiehe, A., Heyne, K. Two-photon cross-sections of the photosensitizers m-THPC and m-THPP in the 1.05–1.45 µm range. *J. Photoc. Photobio. A*, 2014, **295**, 53-56.
[4] Kim, K. S., Lim, J. M., Osuka, A., Kim, D. Various strategies for highly-efficient two-photon absorption in porphyrin arrays. *J. Photochem. Photobiol. C,* 2008, **9**, 13-28.
[5] Mazur, L. M., Roland, T., Leroy-Lhez, S., Sol, V., Samoc, M., Samuel, I. D., Matczyszyn, K. Efficient Singlet Oxygen Photogeneration by Zinc Porphyrin Dimers upon One-and Two-Photon Excitation. *J. Phys. Chem. B*, 2019, **123(19)**, 4271-4277.
[6] Jiblaoui, A., Brevier, J., Ducourthial, G., Gonzalez-Nunez, H., Baudequin, C., Sol, V., Leroy-Lhez, S. Modulation of intermolecular interactions in new pyrimidine–porphyrin system as two-photon absorbing photosensitizers. *Tetrahedron*, 2015, **71**, 2428-2434.

Utilization of the Tetraphenylethylene (TPE) Scaffold for the Generation of Photosensitizer Arrays

Harry C. Sample,[a] Ganapathi Emandi,[a] Brendan Twamley,[b] Nitika Grover,[a] Bhavya Khurana,[a,c] Vincent Sol,[c] Mathias O. Senge[a]
[a]H. C. Sample, Dr. G. Emandi, Dr. B. Twamley, Dr. N. Grover, B. Khurana, Prof. Dr. M. O. Senge
School of Chemistry, Chair of Organic Chemistry, Trinity College Dublin, The University of Dublin,
Trinity Biomedical Sciences Institute, 152–160 Pearse Street, Dublin 2, Ireland
[b]Dr. B. Twamley School of Chemistry, Trinity College Dublin, The University of Dublin. Dublin 2, Ireland
[c]B. Khurana, Prof. Dr. V. Sol, Université de Limoges, Laboratoire PEIRENE, EA 7500
8700 Limoges, France
E-mail address: sampleh@tcd.ie

Since the first exhibition of the phenomenon that is aggregation induced emission (AIE) in 2001,[1] molecules that demonstrate this property have been under the spotlight for myriad application.[2] One such motif is 1,1,2,2-tetraphenylethylene (TPE): facile in its synthesis and modification, it is currently an invaluable scaffold in materials chemistry.[3] Recently, the Senge group has shown the utility of boron dipyrromethene (BODIPY) photosensitizers in photodynamic therapy.[4] The subsequent combination of these two motifs would provide multiple photometric responses and subsequently a greater understanding of the systems into which they are placed. Herein we present the synthesis of two novel TPE-BODIPY arrays in which the distance between the TPE and BODIPY cores is varied, through the utilization of differing palladium-catalyzed cross coupling reactions. We find that in organic solvents, both arrays exhibit the expected locally excited BODIPY photometric response, however in THF/H_2O systems we observe an aggregation induced dual emission response from only one of the arrays. Furthermore, we have found that both of these arrays possess the ability to produce singlet oxygen. We propose that these arrays present themselves for applications including; light harvesting arrays, delivery of photosensitizers for photodynamic therapy, intracellular imaging, and the construction of porous materials.

Keywords:

Tetraphenylethylene, BODIPY, photosensitizer, array, aggregation induced emission

References:

[1] J. Luo, Z. Xie, J. W. Y. Lam, L. Cheng, H. Chen, C. Qiu, H. S. Kwok, X. Zhan, Y. Liu, D. Zhu, B. Z. Tang, *Chem. Commun.*, 2001, 1740;
[2] Y. Hong, J. W. Y. Lam, B. Z. Tang, *Chem. Soc. Rev.*, 2011, **40**, 5361; J. Mei, N. L. C. Leung, R. T. K. Kwok, J. W. Y. Lam, B. Z. Tang, *Chem. Rev.*, 2015, **115**, 11718; Z. Zhu, C. W. T. Leung, X. Zhao, Y. Wang, J. Qian, B. Z. Tang, S. He, *Sci. Rep.*, 2015, **5**, 15189;
[3] K. Li, Z. Li, D. Liu, M. Chen, S.-C. Wang, Y.-T. Chan, P. Wang, *Inorg. Chem.*, 2020, **59**, 6640;
[4] M .A. Filatov, S. Karuthedath, P. M. Polestshuk, H. Savoie, K. J. Flanagan, C. Sy, E. Sitte, M. Telitchko, F. Laquai, R. W. Boyle, M. O. Senge, *J. Am. Chem. Soc.*, 2017, **139**, 6282 ;S. Callghan, M. A. Filatov, H. Savoie, R. W. Boyle, M. O. Senge, *Photochem. Photobiol. Sci.*, 2019, **18**, 495.

Synthesis and characterization of a BODIPY dimer for photodynamic therapy

Leonardo F. K. Santos[a], Chrislaura Carmo[a], Juliana Araújo[a], Margarida Santos[b], Ana Clara B. Rodrigues[a], J. Sérgio Seixas de Melo[a], Abílio J. F. N. Sobral[a]
[a] Department of Chemistry, University of Coimbra, P-3004-535 Coimbra, Portugal
[b] Department of Physics, University of Coimbra, P-3004-516 Coimbra, Portugal
Email: leokleman@gmail.com

Since their discovery in 1964, the BODIPYs present themselves as an important line of research in chemistry, biochemistry, medicine, sensors and alternative energies, confirming the BODIPYs as a relevant organic class of compounds with a wide range of applications [1-3]. In this work we studied the synthesis and characterization of a BODIPY dimer obtained by the condensation of four molecules of an alfa-free-pyrrole (3-ethyl-2,4-dimethyl-1H-pyrrole) with one dialdehyde (terephthaldeyde) to produce the BODIPY dimer shown in Figure 1.

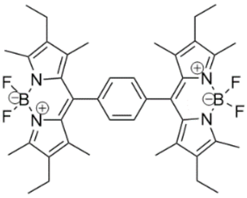


Figure 1: BODIPY (meso-phenyl-meso) dimer

We made an evaluation of the yield of the reaction based on variations of solvents, time of reaction and reagents stoichiometry. We also performed a photophysical characterization of the BODIPY dimer to determine its potential applications in medical studies of cancer therapy, namely on the photodynamic therapy of cancer.

Keywords:
bodipy, synthesis, fluorescence, dimer.

References:

[1] "BODIPY Dyes and Their Derivatives: Syntheses and Spectroscopic Properties", A. Loudet and K. Burgess, Chemical Reviews, Vol. 107 (2007) 4891-4932.
[2] "The chemistry of fluorescent bodipy dyes: versatility unsurpassed", Ulrich G, Ziessel R, Harriman A. Angewandte Chemie International Edition, Vol. 47 (2008) 1184-1201.
[3] "Synthesis, characterization and application of meso-substituted fluorinated boron dipyrromethenes (BODIPYs) with different styryl groups in organic photovoltaic cells", António Aguiar, Joana Farinhas, Wanderson da Silva, Mariana Emilia Ghica, Christopher M.A. Brett, Jorge Morgado, Abílio J.F.N. Sobral, Dyes and Pigments Vol. 168 (2019) 103-110.

Acknowledgments: The authors thank the ChemMat PhD program from the Fundaç. o para a Ciência e Tecnologia (FCT, MEC, Portugal) for their general financial support and the Coimbra Chemistry Centre (CQC) is supported by the FCT, through Projects (UIDB/00313/2020) and (UIDP/00313/2020)

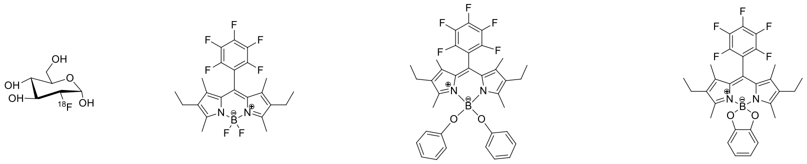
New BODIPYs for PET Diagnosis on the A549 Lung Cancer Cell Line

Margarida G. Santos[a*], Juliana Araújo[b], Chrislaura Carmo[b], Leonardo Santos[b], Maria Filomena Botelho[c,d], Mafalda Laranjo[c,d], Abílio J. F. N. Sobral[b]

[a] Department of Physics, University of Coimbra, P-3004-516 Coimbra, Portugal. [b] Department of Chemistry, University of Coimbra, P-3004-535 Coimbra, Portugal. [c] Institute of Biophysics and Coimbra Institute for Clinical and Biomedical Research (iCBR-CIMAGO), Faculty of Medicine, University of Coimbra, P-3000-548 Coimbra, Portugal. [d] Center for Innovation in Biomedicine and Biotechnology (CIBB), University of Coimbra, P-3000-548 Coimbra, Portugal.

**E-mail address of the presenting author: goncalvesmagy@gmail.com*

Cancer is the most prevalent disease in the world and since 1970 Nuclear Medicine has made an important contribution to the diagnosis and treatment of this pathology[1].
Positron Emission Tomography (PET) is used for diagnosis, based on the evaluation of cellular metabolic activity. Most PET radiopharmaceuticals are based on radioactive ^{18}F containing molecules like the ^{18}F-FDG (**1**).
BODIPYs (boron dipyrromethenes) have great structural versatility, intense absorption and fluorescence properties, can withstand large medium variations in polarity or pH, and have low self-aggregation in solution[2]. Furthermore, they can be radiolabeled by isotopic exchange (^{19}F to ^{18}F) on the boron center, which can lead to a faster procedure.



(1) (2) (3) (4)

Scheme 1- Structure of ^{18}F-FDG (**1**), BODIPY-*meso*-pentafluorinated (**2**), BODIPY-phenol **(3)** and BODIPY-catechol **(4)**.

In this communication, synthesis and biocompatibility of compounds **(2)**, **(3)** and **(4)** are shown. These were tested using the 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assay. The A549 cell line was submitted to concentrations between 1 and 100 µM and the results showed that cells metabolic activity tends to be above 80% for BODIPYs **(2)** and **(3)** at 1, 5, 10 and 25 µM, making these structures the best candidates for the next step of isotopic exchange.

Keywords:

PET;^{18}F; ^{19}F; MTT.

References:

[1] Eary, J. F. *Lancet,* **1999**, *354* (9181), 853–857.
[2] Vaquero, J. J.; Kinahan, P. *Annu. Rev. Biomed. Eng.,* **2015**, *17* (1), 385–414.
[3] Boens, N.; Verbelen, B.; Ortiz, M. J.; Jiao, L.; Dehaen, W. *Coord. Chem. Rev.,* **2019**, *399*, 213024.

Acknowledgements: The authors thanks Fundação para a Ciência e a Tecnologia (FCT) and ChemMat Programme for the PhD research grant PD/BD/150440/2019 and Coimbra Chemistry Centre (CQC) through the project UIDB/00313/2020 and UIDP/QUI/00313/2020, co-funded by COMPETE2020-UE. Center for Innovative Biomedicine and Biotechnology (CIBB) is funded by FCT (UID/NEU/04539/2013) and COMPETE-FEDER (POCI-01-0145-FEDER-007440), through the Strategic Project UIDB/04539/2020 and UIDP/04539/2020.

Radiolabelled Porphyrin Metalla-assemblies in Cellulose Nanocrystals as PDT Agents

João C. S. Simões[1,2,3], Sophia Sarpaki[2], Vincent Sol[3], Bruno Therrien[1], George Loudos[2]
[1]*University of Neuchâtel, Institute of Chemistry, Ave. de Bellevaux 51, CH-2000 Neuchâtel, Switzerland*
[2]*BioEmission Technology Solutions, Research & Development, Athens, Greece.*
[3]*University of Limoges, Laboratoire PEIRENE EA 7500, Limoges, France*
joao95simoes@gmail.com

The basic principle of photodynamic therapy (PDT) is the combination of oxygen, light, and a photosensitizing agent with the goal of destroying abnormal cells in cancer and other diseases.[1] Alongside treatment, early diagnosis undertakes a critical role for a successful outcome. Imaging, for example is an extremely intriguing tool since it allows not only for diagnosis but to follow treatment as well. Knowing this, we have synthesized and radiolabeled photo-responsive molecules in cellulose nanocrystals (CNCs), therefore creating agents that can be used not only for therapy but also for diagnostics. First, 5-(4-aminophenyl and 4-hydroxyphenyl)-10,15,20-tri(4-pyridyl)-21H,23H-porphine were prepared[2] and characterized. Due to their peculiar electronic resonance, these photo-responsive molecules give us the necessary properties for PDT. These were then used to construct metalla-assemblies through coordination with ruthenium dimers.[3] Next, these compounds were linked to CNCs,[4] for better solubility, targeting, and transport to biological targets. The resulting compounds were then radiolabeled with technetium-99m, allowing them to also be used as imaging probes. Their cytotoxicity and potential therapeutic effect were evaluated on a normal (HEK293T) and cancer (A2780) cell line. After, the radiolabeled derivatives were used for SPECT imaging in SCID (Severe combined immunodeficiency) mice. While the *in vitro* data confirmed that these multimodal agents are promising to be used in PDT; the *in vivo* experiments allowed us to image their biodistribution up to 24h. Currently, more studies are being performed to confirm that such molecules can be used for the diagnosis of cancer.

Keywords:

photodynamic therapy, theranostics, radiochemistry

References:

[1] Robertson, C. A.; Evans, D. H.; Abrahamse, H. Photodynamic Therapy (PDT): A Short Review on Cellular Mechanisms and Cancer Research Applications for PDT. Journal of Photochemistry and Photobiology B: Biology. 2009, 96, 1–8.

[2] Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. A Simplified Synthesis for Meso-Tetraphenylporphine. The Journal of Organic Chemistry. 1967, 32, 476.

[3] Mannancherril, V.; Therrien, B. Strategies Toward the Enhanced Permeability and Retention Effect by Increasing the Molecular Weight of Arene Ruthenium Metallaassemblies. Inorganic Chemistry. 2018, 57, 3626–3633.

[4] Chauhan, P.; Hadad, C.; Sartorelli, A.; Zarattini, M.; Herreros-López, A.; Mba, M.; Prato, M.; Prato, M.; Carofiglio, T. Nanocrystalline Cellulose–Porphyrin Hybrids: Synthesis, Supramolecular Properties, and Singlet-Oxygen Production. Chemical Communications. 2013, 49, 8525–8527.

New anti-inflammatory and pro-apoptotic photosensitizers against arthritis

Manuel Gallardo-Villagrán [a,b], Bertrand Liagre [b], David Léger [b], Bruno Therrien [a]
a) Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51, CH-2000 Neuchâtel, Switzerland
b) Laboratoire PEIRENE, Faculté de Pharmacie, Université de Limoges, EA 7500, F-87025 Limoges, France
Email: manuel.gallardo@unine.ch

Contrary to popular belief, rheumatoid arthritis (RA) is not a disease only associated with aging, since it can also affect young people.[1] It is an autoimmune pathology that, although mainly affecting joints, can also attack other organs such as kidneys, lungs or heart. If left untreated, it can lead to a serious prognosis.[2] The most common treatment remains synovectomy, which is an invasive treatment and involves long periods of postoperative rehabilitation. In recent years, promising results have been achieved using non-invasive treatments such as anti-tumor necrosis factor drugs, Janus kinase inhibitors, and especially photodynamic therapy (PDT).[3] The latter involves a photoactive compound, a photosensitizer (PS), and light activation. The simplicity and non-invasiveness make PDT an ideal treatment to alleviate the pain or disability caused by RA. Unfortunately, conventional PSs often have some drawbacks related mainly to their low solubility in biological media and undesirable side effects such as light hypersensitivity.[4] We believe that it may be possible to solve the poor water solubility of PSs using ruthenium metallacages. These metallacages are soluble in biological media and have an inner cavity in which the PS can lodge. Such ruthenium metallacages have already been tested *in vitro* on cancer cells, demonstrating their potential.[5]

We have now designed new ruthenium metallacages and tested them as PDT agents against RA. The *in vitro* activity of these PS carriers in human fibroblast-like synoviocytes cells (FLS) is promising. The proliferation assays are excellent and also, the anti-inflammatory show inhibition of COX-2 expression, being a promising result. Our most recent results will be presented.

Keywords:

Rheumatoid arthritis, metallacages, fibroblast-like synoviocytes, anti-inflammatory, ruthenium.

References:

[1] M.J. Stuart, J.A. Rand, *J. Bone Joint Surg*, **1988** 70, 84-87.
[2] H. Maradit-Kremers, C.S. Crowson, P.J. Nicola, K.V. Ballman, V.L. Roger, S.J. Jacobsen, S.E. Gabriel, *Arthritis Rheumatol*, **2005**, 52, 402-411.
[3] M. Gallardo-Villagrán, D. Y. Leger, B. Liagre, B. Therrien, *Int J Mol Sci*, **2019**, 20, 3339.
[4] G. Koderhold, R. Jindra, H. Koren, G. Alth, G. Schenk, *J Photoch Photobio B*, **1996**, 36, 221-223.
[5] F. Schmitt, J. Freudenreich, N.P. Barry, L. Juillerat-Jeanneret, G. Süss-Fink, B. Therrien, *J Am Chem Soc*, **2012**, 134, 754-757.

Index of presenting authors