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THE BOOK OF ABSTRACTS

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ŁUKASIEWICZ – PORT POLISH CENTER FOR TECHNOLOGY DEVELOPMENT

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PEROVSKITES

Solution-processed solar cells

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Makhsud Saidaminov is a Canada Research Chair Tier II in Advanced Functional Materials and an Assistant Professor at the University of Victoria, Canada. Grown up in Tajikistan, he received his Ph.D. from Lomonosov Moscow State University. Makhsud authored 100+ papers and was named 2021 Highly Cited Researcher by Clarivate Analytics.

In this talk, I will try to address three 'why' questions:

1) Why are we not happy with conventional solar cells?
2) Why halide perovskites can be a choice?
3) Why perovskite solar cells are not there yet?

Hybrid metal-halide perovskites under micro-Raman and photoluminescence spectroscopy: from fundamentals to applications

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The significant development of optoelectronic devices has been always accompanied by the access to materials with targeted and exceptional properties. Among these materials, hybrid organic-inorganic metal-halide perovskites (HOIPs) stand out with extraordinary optoelectronic performance in photovoltaics, LEDs and photodetectors. For the successful integration of these materials into devices it is key to better understand the relationship between crystal structure, optical properties and device performance. An effective way is to use micro-Raman spectroscopy as a non-destructive, accessible and powerful tool for monitoring and analyzing at the same time the structural changes in the rearrangement of the inorganic cage and organic cations of HOIPs, combined with photoluminescence (PL) spectroscopy. Here I will show the role of the organic cations within the inorganic framework on the structural and optoelectronic properties and on the modulation of the structural phase transitions.[1] To this aim, I will present two case studies using single crystals as an ideal material platform. The first one is focused on layered double HOIPs, demonstrating the influence of the organic cation and the reduction of the structural dimensionality.[2,3] The other deals with mixed-organic cation 3D HOIPs, using a mixture of organic cations to suppress and modify the phase-transition temperature.[4] Furthermore, micro-Raman and PL spectroscopy can be used to map the strain: (i) generated during the growth of single crystals[5] or (ii) engineered on-purpose by micro-patterning using 2D flakes leading to the formation of domes.[6] Both approaches result in the modulation of the bandgap and therefore in the device performance tuning without changing composition.

References:

[1] Spirito, D.; Asensio, Y.; Hueso, L. E.; Martín-García, B. Raman Spectroscopy in Layered Hybrid Organic-Inorganic Metal Halide Perovskites. *J. Phys. Mater.,* 5, **2022,** 034004.

[2] Martín-García, B.; Spirito, D.; Biffi, G.; Artyukhin, S.; Francesco Bonaccorso; Krahne, R. Phase Transitions in Low-Dimensional Layered Double Perovskites: The Role of the Organic Moieties. *J. Phys. Chem. Lett.,* 12, **2021**, 280–286.

[3] Martín-García, B.; Spirito, D.; Lin, M.; Leng, Y.; Artyukhin, S.; Tan, P.; Krahne, R. Low-Frequency Phonon Modes in Layered Silver-Bismuth Double Perovskites: Symmetry, Polarity, and Relation to Phase Transitions. *Adv. Opt. Mater.,* 10, **2022**, 2200240.

[4] Ray, A.; Martín-García, B.; Moliterni, A.; Casati, N.; Boopathi, K. M.; Spirito, D.; Goldoni, L.; Prato, M.; Giacobbe, C.; Giannini, C.; Stasio, F. D.; Krahne, R.; Manna, L.; Abdelhady, A. L. Mixed Dimethylammonium/Methylammonium Lead Halide Perovskite Single Crystals for Improved Structural Stability and Enhanced Photodetection. *Adv. Mater.,* **2022**, 2106160.

[5] Boopathi, K. M.; Martín-García, B.; Ray, A.; Pina, J. M.; Marras, S.; Saidaminov, M. I.; Bonaccorso, F.; Di Stasio, F.; Sargent, E. H.; Manna, L.; Abdelhady, A. L. Permanent Lattice Compression of Lead-Halide Perovskite for Persistently Enhanced Optoelectronic Properties. *ACS Energy Lett.,* 5, **2020**, 642–649.

[6] Spirito, D.; Barra-Burillo, M.; Calavalle, F.; Manganelli, C. L.; Gobbi, M.; Hillenbrand, R.; Casanova, F.; Hueso, L. E.; Martín-García, B. Tailoring Photoluminescence by Strain-Engineering in Layered Perovskite Flakes. *Nano Lett.,* 22, **2022**, 4153–4160.

Structural and spectroscopic study of cubic Nd^{3+}-doped $BaLaLiWO_6$ Double Perovskites - a New Candidate for Optical Transparent Ceramics

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Searching for new compounds which could be useful for the fabrication of new optical transparent ceramics, we were interested in $AA'BB'O_6$ perovskite-type tungstates, widely examined and applied for practical uses but not known in the form of sintered materials showing transparency. As potential candidates for transparent ceramics, they should possess highly symmetric crystal systems, $BaLaLiWO_6$ characterized by a cubic structure, which seems to be a candidate to realize this very difficult task.

A series of micro-crystalline samples activated by Nd^{3+} ion (0-20 mol%) was synthesized using a high-temperature solid-state reaction method. The Nd^{3+} dopant was chosen as the laser dopant and structural probe. Pure $BaLaLiWO_6$ matrix as well as Nd^{3+}-doped materials belong to cubic symmetry with space group $Fm\bar{3}m$. The crystal structure of $BaLaLiWO_6$ has been solved based on the small single crystal selected from micro-crystalline powder and has been reported for the first time. The powder diffraction patterns were also refined by the Rietveld method.

An originality of this research results from the unexpected substitution of divalent Ba^{2+} ions by small concentrations of trivalent Nd^{3+} ones till 7 mol% and above this value the replacement of both Ba^{2+} and La^{3+} ions.

Exchange of Ba^{2+} by Nd^{3+} ions leads to the formation of cationic vacancies due to the charge compensation effect: $3Ba^{2+} \rightarrow 2Nd^{3+} + \square$ (vacancy in lanthanum cation lattice), well-manifested in unit cell expansion which has also consequences in the spectroscopic properties.

Complementary techniques like XRD, SEM combined with low-temperature high-resolution spectroscopic ones helped to elucidate the main features of this promising optical material. A few Nd^{3+} non-equivalent symmetry sites and inhomogeneous Nd^{3+} ion distribution in the Ba^{2+} site, detected by site-selective laser spectroscopy at 77K, have been pointed out. The disorder of the structure manifests in broad absorption and emission bands even at low temperatures. First translucent micro-ceramics with quite high density were fabricated by Spark Plasma Sintering (SPS) method.

Acknowledgements:

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Low Dimensional Perovskite Scintillators

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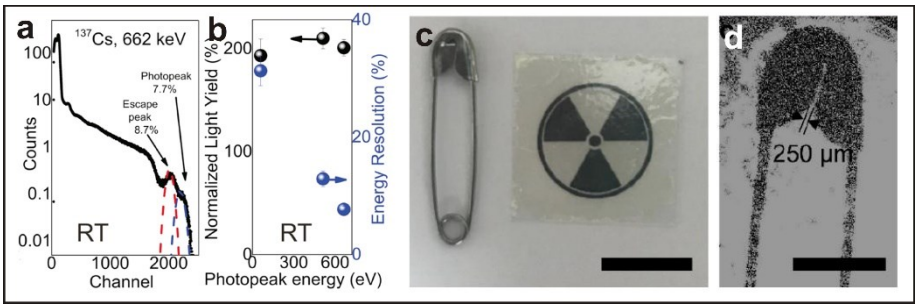
Hybrid organic-inorganic perovskites and perovskite quantum dots have shown remarkable properties as scintillators, which down-convert high energy radiation such as X-rays into visible light. Here, we show the emission properties of $CsPbBr_3$ perovskite QDs and two-dimensional (2D) perovskite crystals under excitation at high photon energies and particles, aimed at practical radiation detection applications.



$CsPbBr_3$-QDs have shown high light yield at room temperature up to 25,000 photons/MeV[1]. Here we also demonstrate the X-ray scintillation imaging application with microcolumn array for high-resolution imaging. 2D-perovskite crystals also show high light yield, in particular Lithium-doped phenylethyl-ammonium lead bromide (Li-PEA_2PbBr_4; 23,000 photons/MeV)[2] and butylammonium lead bromide (BA_2PbBr_4; 40,000 photons/MeV)[3]. The gamma-ray pulse measurement (Fig. 1a) shows sharp energy resolutions around 10 %, with Li- PEA_2PbBr_4 exhibiting the record of 7.7 % at 662 keV Fig 1b). The 2D-perovkites also show potential for imaging (Figs. 1c and d) and thermal neutron detection[2].

In conclusion, both perovskite QDs and crystals have great potentials for radiation imaging applications since both have strong emission responses from high-energy excitations. However, due to their good energy resolution with spectroscopy, 2D perovskite crystals have broader applications involving gamma-ray, alpha particle, and thermal neutron such as positron emission tomography, landmine detection, and oil lodging.

References:

1. Maddalena, F., et al., *Deterministic Light Yield, Fast Scintillation, and Microcolumn Structures in Lead Halide Perovskite Nanocrystals.* J. Phys. Chem. C, 2021. **125**(25): p. 14082-14088.
2. Xie, A., et al., *Lithium-doped two-dimensional perovskite scintillator for wide-range radiation detection.* Comms. Mater., 2020. **1**(1): p. 37.
3. Xie, A., et al., *Library of Two-Dimensional Hybrid Lead Halide Perovskite Scintillator Crystals.* Chem. Mater., 2020. **32**(19): p. 8530-8539.

High Filtering Efficiency of Electrospinning-based Nanofibers Membrane

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Current usage of disposable masks due to pandemic increases the undesired waste problem that leads to the environmental pollution.[1] The formation of nanofibers is promising to tackle the issue with its small dimension, wide surface area, good surface adhesion, low density and high porosity for high-performance air filtration. In this work, PAN/Ag/TiO_2 nanofibers membrane is utilized as an air filtration media with self-cleaning properties using the electrospinning methods.[2] Upon TiO_2 and Ag addition, the water contact angle measurement of nanofibers is 34.58°, indicating the surface become hydrophilic. SEM inspection demonstrates the diameter size of PAN/Ag/TiO_2 nanofiber membrane increased to 570 nm due to TiO2 intercalation. The band gap of PAN/Ag/TiO_2 nanofiber is shifted to visible light from 3.8 eV to 1.8 eV. The air filter performance efficiency of $PM_{2.5}$ can be obtained at 96.9%. This suggest that the filtering performance is outperformed the PAN nanofiber membrane, highlighting the future prospect for its implementation in air filtering media.

References:

[1] T. A. Aragaw, "Surgical face masks as a potential source for microplastic pollution in the COVID-19 scenario," *Mar. Pollut. Bull.*, vol. 159, no. July, p. 111517, 2020, doi: 10.1016/j.marpolbul.2020.111517.

[2] S. Hartati *et al.*, "Synthesis of Electrospun PAN/TiO2/Ag Nanofibers Membrane As Potential Air Filtration Media with Photocatalytic Activity," *ACS Omega*, vol. 7, no. 12, pp. 10516–10525, 2022, doi: 10.1021/acsomega.2c00015.

Radiation Detection using Lead Free (Sn and Mn) Hybrid Organic Inorganic Perovskite Crystals

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The potentialities of Sn and Mn-based perovskite crystals for X-ray scintillator have been studied [1-3]. Sn and Mn perovskites crystals show green and pink glows under UV irradiation (Figs. a-b). PL and time resolved PL spectra are recorded (Figs. c-f). Under excitation with a picosecond pulsed 355 nm laser, Mn-based perovskites show the location of PL peak changing from 604 to 581 nm with extra CH_2 in the chain, while Sn-based perovskite has PL peak at 498 nm. The Sn crystal has a lifetime of ~1 μs, while that of Mn crystals changes from ~4 to ~3 μs with additional CH_2. Relative to Sn crystal, the slow decay in Mn crystals is due to their smaller exciton radius, causing self-trapped exciton. Yet all crystals show low light yield due to thermal quenching and that in Sn crystal happens at higher temperature than Mn crystals. Although some properties may not be beneficial for scintillators, the small differences of properties in the crystals may provide direction for the new designs of high light-yield lead-free perovskite scintillators.

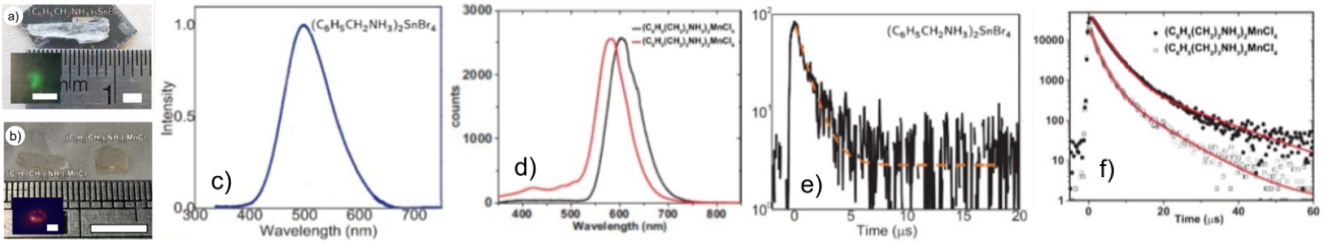

Fig. 1. a,b) Bright images of Sn and Mn crystals. c-f) PL spectra and time resolved PL decay curves of the samples.

References:

[1] Kaffah, S. *et al.*, Electronic and Optical Modification of Organic-Hybrid Perovskites. *Surf. Rev. Lett.,* Vol.28, No. 08, **2021**.

[2] Hardhienata, H. *et al.*, Optical and X–Ray Scintillation Properties of X_2MnCl_4 (X = PEA, PPA) Perovskite Crystals. *J. Phys. D: Appl. Phys.,* Vol. 53, No. 45, **2020**.

[3] Diguna, L. J. *et al.*, Scintillation in $(C_6H_5CH_2NH_3)_2SnBr_4$: Green-Emitting Lead-Free Perovskite Halide Materials. *RSC Advances,* Vol. 11, No. 34, **2021**.

Characterizations of LPCVD-grown Gallium Nitride Pine Tree-like Nanostructures

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Gallium nitride (GaN) pine tree-like nanostructures (PTLNs) were grown in low-pressure chemical vapor deposition (LPCVD) system using a combination of germanium and nickel catalyst [1]. Each nanostructure consists of straight nanowire-like stem and few layer-like lateral growths resembling "leaves". X-ray diffraction (XRD) and Raman measurements reveals the structure to be of wurtzite crystallinity. Upon 266nm laser excitation, the PTLNs emit photoluminescence (PL) at 3.65 ± 0.21 eV and 1.97 ± 0.19 eV. Absorption, X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS) and current-voltage (IV) measurements reveal the electronic structure of the PTLNs to be n-type.

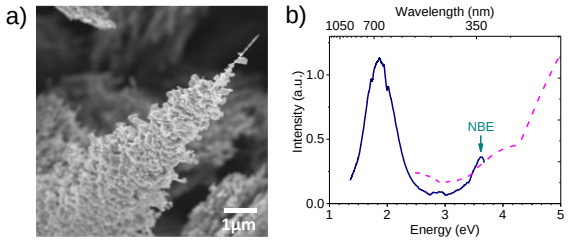

Figure 1. a) SEM image of a single GaN pine tree-like nanostructure; b) PL (solid line) and absorption (dashed line) spectra of GaN PTLNs.

References:

[1] Saleem, U.; Tjahjana, L.; Arramel; Ahmad, F.; Hardhienata, H.; Maddalena, F.; Birowosuto, M. D.; Hong, W., Electronic and Optical Modulation of Pine Tree-like Nanostructures of Gallium Nitride. *The Journal of Physical Chemistry C*, 125 (25), **2021** ,13917-13924. DOI: 10.1021/acs.jpcc.1c02819.

Visible Wavelength Photoluminescence from GaP Segments Grown on InP Nanowires

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Visible wavelength photoluminescence (PL) with peak at 540 nm is demonstrated from gallium phosphide (GaP) segments grown on indium phosphide (InP) nanowires (NWs) [1], which we call as GaP/InP NWs for simplicity. The EDS-TEM mapping of a single GaP/InP NW is shown in Figure 1(a). Moreover, PL mapping shows the 540 nm emission to be localized from the two GaP segments whereas 870 nm emission comes from InP parts outside the GaP segments. As shown in Figure 1(b), the GaP/InP NW also shows polarization dependence where the emission is polarized in parallel direction to the NW axis.

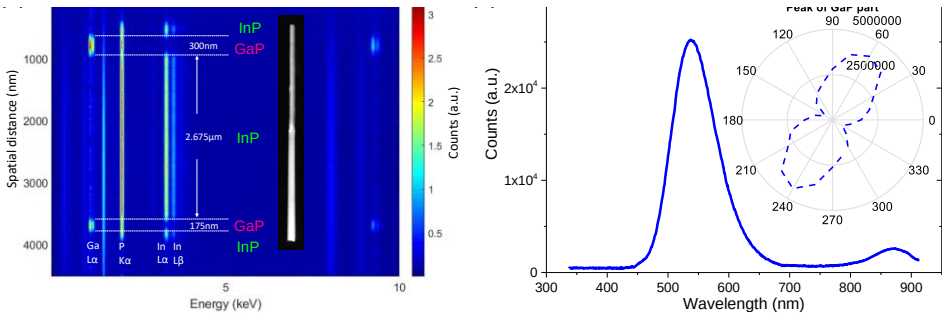

Figure 1. (a) EDS-TEM mapping of a single GaP/InP NW, (b) PL spectrum and polarization dependence of GaP/InP NW.

References:

[1] Tjahjana, L.; Olivier, A.; Herbani, Y.; Hardhienata, H.; Ahmad, F.; Arramel; Kowal, D.; Birowosuto, M.D.; Wang, H., Localized Visible Wavelength Photoluminescence from GaP/InP Heterostructure Nanowires. *The Journal of Physical Chemistry C*. doi: 10.1021/acs.jpcc.2c03597. Article ASAP.

Selected perovskite and spinel based materials for application as oxygen carriers for chemical looping combustion process

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Chemical looping combustion (CLC) is a promising technology of fuel combustion. Incineration in CLC process occurs without access to atmospheric air, which allows to reduce formation of thermal nitrogen oxides almost to zero. In a consequence, it allows to simplify process of purifying fumes and reduces the cost of capture of carbon dioxide, in comparison to conventional combustion methods. During the CLC process, oxygen for fuel combustion is released by a material called the oxygen carrier (OC). The oxygen carrier circulates between the two reactors (fuel and air reactor)[1]. Due to its working conditions, OC should exhibit not only a high oxygen transport capacity but also should be remained chemically and physically stable after numerous cycles of reduction and oxidation. Spinel and oxygen-deficient perovskites are considered promising materials for that role due to having such a properties [2].

In the presented research, perovskite and spinel-based oxygen carriers were synthesized using solid state reaction, then their oxygen transport capabilities were successfully demonstrated using thermogravimetric analysis. Crystal structures of both fresh and spent OCs were examined using X-ray diffractometry.

References:

[1] Adánez J, Abad A. Chemical-looping combustion: Status and research needs. Proc Combust Inst, **2019**, 37: 4303–4317.

[2] Ksepko E. Perovskite-type $Sr(Mn_{1-x}Ni_x)O_3$ materials and their chemical-looping oxygen transfer properties. Int J Hydrogen Energy, **2014**, 39: 8126–8137.

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Low dimensional perovskites: from chemical design to photonic applications

Daniele CORTECCHIA

Metal halide perovskites are attracting increasing interest for applications in photonics, light emitting devices and lasers. However, the need to overcome trapmediated non-radiative losses, increase the radiative recombination efficiency, improve the material stability, and find non-toxic alternatives to lead-based materials urgently call for the study of different perovskite structures. 2D perovskites are promising alternatives to improve the luminescence efficiency, grant increased environmental stability, block ionic diffusion, and relax geometrical constraints giving access to a wider range of lead-free compositions.

In this presentation, I will discuss how their exceptional chemical versatility allows to tune their optoelectronic properties on demand by modulating the chemical composition, structural properties, and quantum and dielectric confinement in structures with different dimensionalities. The use of optoelectronically active templating cations as well as of inorganic dopants further push the boundaries to create functional perovskites with unprecedented luminescence efficiency and tunability. Finally, I will discuss how the choice of the templating cation critically affects the structural rigidity, defectivity, photostability and morphology of the perovskite film determining its ability to sustain amplified spontaneous emission, thus providing fundamental synthetic guidelines to improve the coherent emission properties, and opening the way to the design and exploitation of a new class of two-dimensional perovskite lasers.

Flexible photonics: mechanically flexible optical systems

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As already done in electronics, passive and active photonic devices demand integration on flexible substrates for a broad spectrum of application ranging from integrated optics to sensors for civil infrastructure and environments, to coherent and uncoherent light sources and functionalized coatings for integration on biological tissue [1]. The fabricated systems should operate in several deformation conditions i.e. bending, folding, rolling, twisting, stretching and compression. To succeed in, the following steps are crucial: i) design and fabrication of appropriate flexible substrates and using the opportunities offered by the sol-gel technology to go beyond the standard polymers; ii) realization of planar waveguides and photonic crystals deposited on the flexible substrates reducing radiative losses and maintaining a constant adhesion under mechanical deformation; iii) understand the behaviour of the flexible glasses recently placed on the market. In this communication we will present some recent results concerning the fabrication of novel flexible optical layers by sol-gel and radio frequency sputtering deposition techniques. The perspective is to give a technological way to transform intrinsically rigid or brittle materials into a highly mechanically flexible and optically functional systems.

References:

[1] https://www.sciencedirect.com/journal/optical-materials/special-issue/10LJ4J18H61 and Optical Materials 129 (2022) 112555

POLYMERS

Polymeric sensors for pH and food monitoring

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Sensors are everywhere around us to monitor environmental conditions. Monitoring of pH is important for many applications such as protective equipment and clothing, food, agriculture and biomedicine.

This presentation will focus on the development of solid state sensors for pH and gases based on electrospun nanofibrous mats functionalized with halochromic dyes. These systems show a near instantaneous change of color when the solution pH is changed or when exposed to acid or base vapors as well as to biogenic amines. Dye functionalization of the nanofibers was achieved through blend electrospinning of a dye-functionalized copolymer with matrix polymers [1] via sol-gel electrospinning of tetraethoxysilane [2] as well as via a newly developed Plasma Dye Coating procedure where a dye functionalized with a radical sensitive group is covalent coupled to any polymer matrix, including Teflon and PE, under plasma irradiation [3]. The final part of the lecture will focus on detection of biogenic amines and thiols and demonstrate its use for continuous food monitoring applications [unpublished].

References:

[1] a) Steyaert, I.; Vancoillie, G.; Hoogenboom, R.; De Clerck, K. *Polym. Chem.* **2015**, *6*, 2685. b) Schoolaert, E.; Steyaert, I.; Vancoillie, G.; Geltmeyer, J.; Lava, K.; Hoogenboom, R.; De Clerck, K. *J. Mater. Chem. B* **2016**, *4*, 4507. c) Schoolaert, E.; Merckx, R.; Becelaere, J.; Rijssegem, S.; Hoogenboom, R.; De Clerck, K. *Adv. Funct. Mater.* **2021**, *32*, 2106859.

[3] Geltmeyer, J.; Vancoillie, G.; Steyaert, I.; Lava, K.; Hoogenboom, R.; De Buysser, K.; De Clerck, K., et. al., *Adv. Funct. Mater.* **2016**, *26*, 5987-5996.

[4] Vancoillie, G.; De Smet, L.; Minshall, P.; Lava, K.; Steyaert, I.; Schoolaert, E.; Van de Walle, E.; Dubruel, P.; De Clerck, K.; Hoogenboom, R., *Nat. Commun.* **2019**, *9*, 1123.

Bioinspired adaptive lubrication

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In nature, living organisms or moving tissues/organs evolve unique functional components and mechanics with extraordinary lubrication behavior. For example, natural articular cartilage shows ultralow friction even at high squeezing pressure. Biomimicking such robust wet-slippery interface has been and remains a grand challenge in the fields of materials science and engineering. Inspired by the unique structural features of the articular cartilage, as well as by its remarkable lubrication mechanisms, we have developed a series of cartilage-mimicking layered lubrication material by robustly entangling thick hydrophilic polyelectrolyte brushes into the subsurface of robust bio-based substrates. The topmost hydration layer provides effective aqueous lubrication, whereas the bottom robust layer used as a substrate delivers the load-bearing capacity. Their synergy is capable of attaining low friction coefficients under heavily loaded conditions in water environment, a performance incredibly close to that of natural articular cartilage. These results are theoretically explained and compounded by multi-scale mathematical simulations, opens innovative technology routes for developing cartilage-mimicking ultralow friction soft materials. Furthermore, some novel concepts of friction-control were proposed to reveal the fundamental relationship between hydration/contact mechanics and lubrication/adhesion properties. These novel materials, theory and concepts could be used for developing robust lubrication coatings for implantable devices.

References :

[1] Yunlei Zhang, Feng Zhou*, et al.,Nature Communications, 2022, 13: 377.

[2] Rongnian Xu, Feng Zhou*, et al., Advanced Materials, 2022: 2108889..

[3] Mingming Rong, Feng Zhou*, et al., Advanced Functional Materials, 2020, 30(39): 2004062.

[4] Shuanhong Ma, Feng Zhou*, et al, Advanced Materials, 2018, 30(50): 1803371.

Functional polymer coatings with designed interactions with water

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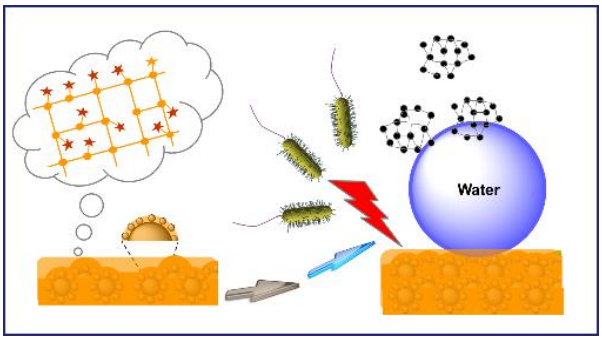
Polymer coatings with well-defined chemical composition and/or topography are commonly applied for protection but can also be used to fine-tune the materials performance towards a specific interaction with water and functionality.[1] Crosslinked polymer networks are particularly interesting for this purpose: 1) they provide sufficient robustness and the necessary cohesion and adhesion of the softer polymer layer onto a substrate; 2) they offer many possibilities to adjust the coating's surface characteristics via different polymer precursors, crosslinkers and crosslinking configurations.

I will present a few examples on how to design polymer networks and surfaces with low or high surface energy, *i.e.* (super)hydrophobic[2] or hydrophilic[3], which show extreme water repellence or attraction, respectively. This fine-tuning of the surface characteristics enables preparing self-cleaning, anti-fouling or highly lubricious coatings[2-4]. Furthermore, I will discuss how to incorporate self-healing strategies on the design of polymer networks, so that the surface functionalities can be spontaneously recovered upon damage, towards coatings with a high-performance level through an extended lifetime.[5]



Scheme: Schematic of functional coatings with designed interaction with water.

References:

[1] Functional polymer coatings: principles, methods and applications by Wu, L and Baghdachi, J; Wiley & Sons, **2015** (ISBN: 978-1-118-51070-4).

[2] Esteves, ACC.; Luo, Y.; van de Put, MWP.; Carcouët, CMC.; de With, G., Self-replenishing dual structured superhydrophobic coatings prepared by drop-casting of an all-in-one dispersion, *Adv Funct Mater*, 24, **2014**, 986.

[3] Albers, PTM.; Govers, SPW.; Laven J.; van der Ven LGJ.; van Benthem RATM.: de With G.; Esteves, ACC.; Design of dual hydrophobic–hydrophilic polymer networks for highly lubricious polyether-urethane coatings. *Europ Polym J,* 111, **2019**, 82.

[4] Jiménez-Pardo, I.; van der Ven, LGJ.; van Benthem, RATM., de With, G.; Esteves, ACC., Hydrophilic self-replenishing coatings with long-term water stability for anti-fouling applications, *Coatings*, 8, **2018**, 184.

[5] Esteves,ACC.; Self-healing functional surfaces, *Adv Mater Interf*, 5, **2018**, 1800293.

Multi-Functionalized Carbazole-Based Organic Luminescent Materials for Tunable Optoelectronic Properties

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Carbazole and its derivatives have been the most effective heterocyclic building blocks for material scientists. Carbazole-based organic luminescent materials are extensively used in optoelectronic applications especially organic-light emitting diodes (OLEDs) as emissive and hole-transporting layer which enjoys its high charge mobility. The optical and electrical properties of these materials can be finely tuned by multi-substitution of chromophores at C1, C2, C3, C6, C7, C8 and N9 positions of carbazole. [1] Additionally, its sufficiently high triplet energy offers its utility as suitable host materials in electroluminescent devices. It's self-emissive property, easy synthetic procedures, molecular rigidity and amorphous nature further proves its advantageous candidacy over other conventional fluorophores. [2]

Here, we have comprehensively examine the design, synthesis and optoelectronic properties of multi-functionalized carbazole-based functional materials. We have investigated the effect of the multi-substitution of carbazole unit on optical, electrochemical, thermal and electroluminescent properties. The characterization techniques help to successfully develop structure-property correlations among the materials. The bipolar carbazole derivatives showed a significant role of linking topology and nature of substituents attached in fine-tuning the optoelectronic properties. The utilization of the luminescent materials in fabricating efficient solution-processed OLEDs showed promising role of carbazole-based emitters.

References:

[1] Konidena, R. K.; Thomas, K. R.; Park, J. W., Recent Advances in the Design of Multi-Substituted Carbazoles for Optoelectronics: Synthesis and Structure-Property Outlook. *ChemPhotoChem,* **2022**, e202200059.

[2] Ledwon, P., Recent advances of donor-acceptor type carbazole-based molecules for light emitting applications. *Organic Electronics*, 75, **2019**, 105422.

Synthesis and Cell Interaction of Statistical -L-Arginine-Glycine-L-Aspartic Acid Terpolypeptides

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The arginine-Glycine-Aspartic acid (RGD) tripeptide sequence found in fibronectin and many other glycoproteins, is known to promote cell adhesion and cell proliferation. This tripeptide sequence is not easily accessible due to tedious and expensive preparation methods such as sequential peptide synthesis. Ring opening polymerization (ROP) of amino acid *N*-carboxyanhydrides (NCAs) offers a facile preparation of polypeptides with high molecular weights and similar properties of natural peptides. Understanding of copolymerization parameters of Glycine (Gly) NCA, *β*-Benzyl-L-Aspartate (Bz-Asp) NCA and N_{δ}-carbobenzyloxy-L-ornithine (*R'*) (Z-Orn) NCA may enhance the RGD sequence occurrence in terpolypeptides. The objective of the study was to prepare RGD containing terpolypeptides via ROP of Bz-Asp NCA, Gly NCA and Z-Orn NCA (*DGR'*). The *DGR'* sequence is the precursor to *DGR*, which is equivalent to RGD. However, in terpolymers the natural RGD sequence is referred as *DGR*, due to the mechanism of ROP of NCAs adapted in the study, which proceeds from *C*- to *N*- terminus whilst peptide sequences are listed from *N*- to *C*- terminus.

Binary copolymerizations of the three NCAs were investigated in order to understand copolymerization kinetics and 6 reactivity ratios were obtained. The reactivity ratios were used to model terpolymerizations of the NCAs and were found to define the terpolymerization of these NCAs. Hence, they were used in conjunction with statistical equations to maximize the probability of occurrence of the *DGR'* sequence in terpolymers. Subsequently, the ornithine (*R'*) units in the terpolymers were converted to arginine units and terpolymers with high probability of *DGR* sequences displayed improved cell proliferation and process formation when compared to natural polymers with the RGD tripeptide sequence.

Asymmetric organocatalysis under non-classical conditions

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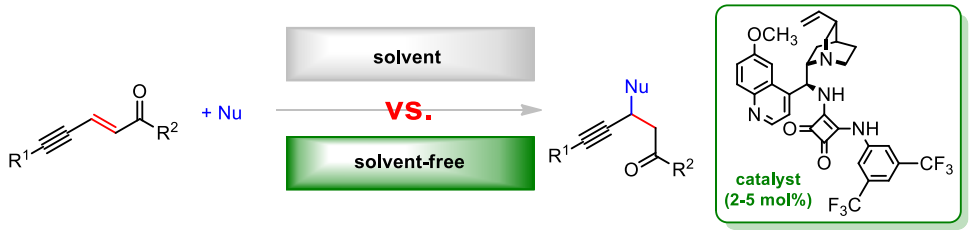
Molecules with conjugated double and triple bond are very useful class of substrates for pharmaceutical industry. After the Michael addition, the triple bond in the molecule is still available, what gives opportunities for further transformations leading to polycyclic adducts.[1] Those multi-functionalized compounds provide important scaffolds for organic chemistry that could be also found in natural molecules.[2] Conjugated carbonyl compounds react easily in thia-Michael addition [3], but are inert in reactions with carbon nucleophiles at room temperature. Another important aspect is a growing need for the development of more effective and greener alternatives to "classical" chemistry. Solvent-free reaction conditions in a ball mill can provide an improved enantioselectivity over the reaction in solution, due to lack of disruptive solvation of reagents.



Therefore, we investigated the reactivity of α,β,(γ,δ)-unsaturated carbonyl compounds in solvent-free nucleophilic addition reactions catalyzed by metal-free bifunctional hydrogen-bond donors. To our delight, solvent-free ball milling and 2-5 mol% of chiral *Cinchona* based squaramides provided products with higher yields and enantioselectivities than in the analogous reactions in a solution, and in several cases led to different product composition.

Acknowledgements:
We thank National Science Center (NCN) Poland for funding, grant No. 2016/22/E/ST5/00046.

References:

[1] Hack, D.; Chauhan, P.; Deckers, K.; Hermann, G. N.; Mertens, L.; Raabe, G.; Enders, D., *Org. Lett.* **2014**, 16, 5188-5191. [2] Liu, T.; Zhou, M.; Yuan, T.; Fu, B.; Wang, X.; Peng, F.; Shaoa, Z., *Adv. Synth. Catal.* **2017**, 359, 89–95. [3] Kowalczyk, R., Boratyński P. J., *Adv. Synth. Catal.* **2016**, 358, 1289-1295.

Functional metallic nanoparticles for antiviral applications

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Metallic nanoparticles exhibit broad-spectrum activity against bacteria, fungi and viruses. The antiviral activity of nanoparticles results from the multivalent interactions of nanoparticles with viral surface components that are the consequence of nanometre size of material and the presence of functional compounds adsorbed on nanomaterial surface. A key step in the virus infection process is docking and entry of virus into the host cell. This stage of the infection can be influenced by functionalized nanomaterials with exhibit high affinity to the virus surface and hence, can disrupt the infection process. Moreover, the affinity of virus to nanomaterial surface can be tuned by specific surface functionalization of nanomaterial.

The main purpose of this work was to determine the influence of the ligand type present on nanomaterial on the antiviral properties against herpes simplex virus type 1 and 2. The metallic nanoparticles (gold and silver) with different sizes (5 nm and 30 nm) were functionalized either with polyphenol (tannic acid) or sulfonates (ligand with terminated sulfonate groups). We found that the antiviral activity of nanoconjugates depends significantly on the ligand type present on nanoparticle surface. Moreover, we proved that HSV infection can be inhibited by blocking the viral entry receptors. Although, the HSV can follow different entry routes, e.g. i) fusion with the plasma membrane or ii) endocytosis, the infection always starts with the interactions between the viral envelope and the host cell membrane. Therefore, the development of effective anti-infection formulations as functional nanoparticles remains still the most effective approach in construction of antiviral agents.

This work was supported by the National Science Centre, Poland (UMO-2018/31/B/NZ6/02606).

More results about antiviral activity (HSV) of functionalized nanoparticles you can find on our team project page: https://www.researchgate.net/project/Functionalised-metallic-nanoparticles-for-antiviral-applications

YOUNG SCIENTISTS

Undoped and Ti-dopeds Sapphire crystals growth and optical characterization

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The need of large undoped and Ti-doped sapphire crystals with more and more advanced performance is a continuous request from frontier's experiments in elementary particles physics, gravitational waves (GW) detection and high power laser system based on chirped pulse amplification (CPA). Unfortunately, the multi-disciplinary nature of large size crystal growth technology, the different complex multi-parameter processes where ten or more growth parameters have to be compromised and optimized including the scaling problem have impeded the scientific development of this important domain. Yet, there are specific technical barriers that have limited the performance and the growth of large sapphire crystals (=400mm, L=300mm), and thus their wider adoption in the high technology applications. Technology experts and component designers agree that overcoming these technical barriers, such as bubbles defects, thermal stress, absorption and birefringence, chemical homogeneities and especially diameter increasing would open more applications. Therefore, emphasis was placed on the development and improvement of several crystal growth technologies to produce high quality sapphire single crystals. Among the problems encountered with sapphire there is its anisotropy that requires a good control of the thermal field during the crystal growth. Other properties that make sapphire difficult to grow are its high melting temperature (2050°C) and a relatively low thermal conductivity. A large temperature gradient can cause defects during crystal growth and expose crystals to high stress during cooling. Regardless of the growth process, a high density of defects (pores, bubbles, dislocation, voids, mosaic, vacancies, scattering, intergrowth, striations) is very often observed in the grown crystals. The larger diameters are associated with lower material yield due to higher sensitivity to defects. Quite often defects such bubbles are observed and do not allow the utilization of the entire ingot. Similarly, the composition of starting raw materials (impurities) also strongly affect the quality of sapphire. The problems are the same, with an additional complication due to the titanium doping of the material, for the Ti-doped sapphire crystals entering in the fabrication of the ultra-intense laser systems, which are presently considered in most of the largest international laser projects.

In this talk, we will present our resent progress on the development of performed large sapphire crystals grown from the melt under stationary stable regime and their optical characterization. The presence of Ti4+ is very detrimental to the laser performance of sapphire crystals, since it can create residual absorption band due to Ti3+-Ti4+ pair in the beginning of the emission band and therefore decrease the laser emission power. This is the reason why crystal usefulness is evaluated by their FOM (factor of Merit) which is the ratio of the absorption of Ti3+ at 532 nm to the absorption of Ti4+ at 800nm.

Acknowledgements.

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New approaches to determining the atomic-level structure of advanced materials

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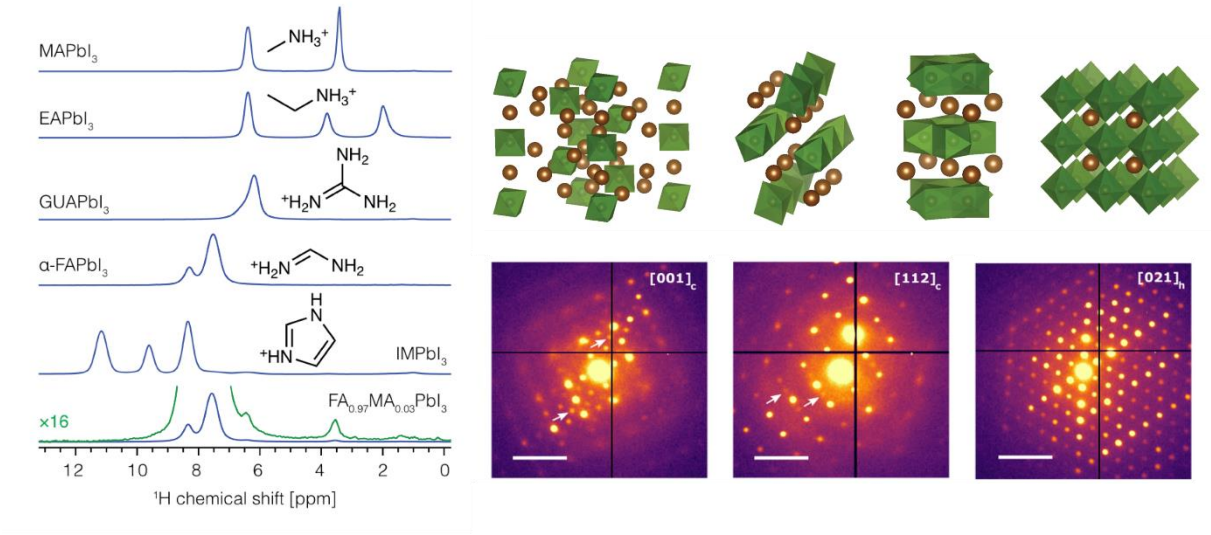
Determining the structure-property relationships at multiple length scales is one of the key tenets of rational design of new materials. While diffraction techniques offer insight into the long-range structure of solids, many properties are determined by local structure, which can be accessed using approaches based on, e.g., total scattering (PDF), XAFS, and magnetic resonance (NMR and ESR).

I will use the example of metal halide perovskites to discuss how we can determine the atomic-level structure of solids in an element-specific manner using solid-state NMR spectroscopy. The range of research problems includes quantifying dopant incorporation, phase segregation, decomposition pathways, passivation mechanisms, and structural dynamics [1]. I will also show how electron diffraction allows us to study structural phenomena inaccessible with X-rays [2].

I will then discuss my take on studying these multifaceted materials *in situ* and *operando* to elucidate the mechanism of structural transformations in fully assembled optoelectronic devices, especially under illumination. These strategies will be key to elucidating the performance-limiting factors in devices such as solar cells, light emitting diodes, and X-ray detectors.



References:

[1] Kubicki, D. J.; Stranks, S. D.; Grey, C. P.; Emsley, L. NMR Spectroscopy Probes Microstructure, Dynamics and Doping of Metal Halide Perovskites. *Nat. Rev. Chem.* **2021**, *5*, 624–645.

[2] Doherty, T.; Nagane, S.; Kubicki, D. J.; Jung, Y. K.; Johnstone, D. N.; Iqbal, A.; Guo, D.; Frohna, K.; Danaie, M.; Tennyson, E. M.; MacPherson, S.; Abfalterer, A.; Anaya, M.; Chiang, Y.-H.; Crout, P.; Ruggeri, F. S.; Collins, S.; Grey, C. P.; Walsh, A.; Midgley, P.; Stranks, S. D. Stabilized Tilted-Octahedra Halide Perovskites Inhibit Local Formation of Performance-Limiting Phases. *Science*, **2021**, *374*, 1598–1605.

Luminescent submicrometric polymer and sol-gel films – preparation, properties and future perspectives for application in photonics

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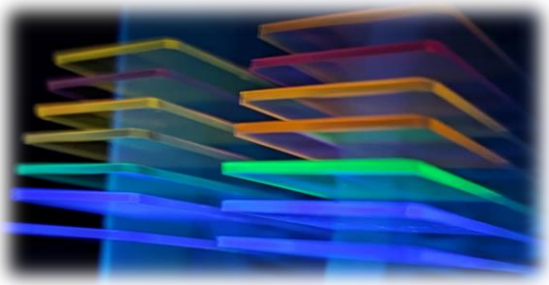
Thin sol-gel and polymeric films with controllable refractive index and thickness may be achieved by dip-coating method by means of proper selection of materials and preparation protocol. An important advantage is their low cost, facile fabrication and easy processing. They may find application as planar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



Photograph of dye activated polysulfone films on soda-lime glass (under UV light excitation)

We report fabrication of thin films based on SiO_2 or organically modified SiO_2 (ORMOSIL) and TiO_2 and such films activated with Rhodamine B. Preparation of polymeric films activated with various type of organic luminescent dyes is discussed as well. Influence of different preparation conditions on optical properties of sol-gel films and Rhodamine B activated films was studied. The refractive index and thickness of the films were evaluated using ellipsometry or/and profilometry. It was found that they can be controlled by adjusting the relative amount of SiO_2 and TiO_2 precursor, heat treatment conditions and withdrawal speed. Sol-gel films activated with Rhodamine B and dye activated polysulfone (polymer) films were characterized using absorption and emission spectroscopy. The optical transmission losses of selected planar waveguides were determined using scattered-light method. Moreover, simple approach of periodic structures fabrication in ORMOSIL based and polymeric thin films using nanoimprint technique was implemented. Preliminary studies on application of selected polymer materials in photonic devices is presented.

References:

[1] Horváth, R., Pedersen, H. C., Larsen, N. B., Demonstration of reverse symmetry waveguide sensing in aqueous solutions, Applied Physics Letters, 81 (12), **2002**, 2166–2168,

[2] Wang B., Hu. L., Optical and surface properties of hybrid TiO2/ormosil planar waveguide prepared by the sol-gel process, Ceramics International, 32, **2006**, 7–12

[3] Muñoz-Mármol R., Zink-Lorre N., Villalvilla J. M., Boj P. G., Quintana J. A., Vazquez C., Díaz-García M. A., Influence of Blending Ratio and Polymer Matrix on the Lasing Properties of Perylenediimide Dyes, The Journal of Physical Chemistry C, 122 (43), **2018**, 1-12

The research was co-financed by the Foundation for Polish Science from the European Regional Development Fund within the project POIR.04.04.00-00-14D6/18 "Hybrid sensor platforms for integrated photonic systems based on ceramic and polymer materials (HYPHa)" (TEAM-NET program). Ł.D. would like to thank the Ministry of Science and Higher Education in Poland for the Grant No. DWD/4/64/2020 in the frame of Implementation Doctorate Programme.

Bacteriophage protection from adverse conditions

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Bacteriophages are specific viruses that infect exclusively bacterial cells, while remaining harmless to protists, plants, animals and humans. Their exceptional specificity in host recognition makes them a perfect match for biosensors to detect pathogenic bacteria. However, as bacteriophages are made of biomolecules, they're sensitive to external conditions, including temperature, radiation, or long-term storage. These drawbacks can be overcome by using a proper stabilizing factor. During the presentation, the examples of phage stabilization against adverse conditions will be presented.

2D inverse opals made with self-assembled nanospheres for waveguide couplers

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Monodisperse nanospheres of diameter of hundreds of nanometers may serve for facile fabrication of 3D and 2D photonic crystals utilizing self-assembly phenomenon. 2D opals may act as gratings diffracting the light into colours. Opal-like and inverse opal structures may be obtained [1].

Self-assembly of nanospheres requires specific conditions, thus various techniques are used in order to find optimal conditions for fabrication of e. g. well-ordered 2D systems. Moreover, functionalization of nanospheres by luminescent dyes may require compatibility of the dye with the system, in order to control its concentration and to obtain uniform distribution in the nanosphere volume.

Experimental results on preparation of monodisperse PMMA nanospheres of various diameter and fabrication of 2D opals by different methods as e.g. Transfer from Air-Water Interface [2] and Confined Convective Assembly method [3] will be presented.

In the next step, 2D inverse opals were fabricated, from a sol-gel material, on a top of waveguiding film for the purpose of coupling of light into the film. Ability of coupling of monochromatic and white light was investigated.

The fabrication methods often lead to polydomain 2D opals, which show diversity of spatial period of the structures along arbitrarily chosen direction. This potentially allows for broadening of the range of acceptance angle and/or widening of the spectrum of the coupled light.

Acknowledgements:
This research was co-financed by the Foundation for Polish Science from the European Regional Development Fund under the project no. POIR.04.04.00-00-14D6/18 (TEAM-NET program).

References:

[1] Waterhouse, G. I. N.; Waterland, M. R., Opal and inverse opal photonic crystals: Fabrication and characterization. *Polyhedron* 26, **2007**, 356–368.
[2] Vogel N.; Goerres S.; Landfester K.; Weiss C. K., A Convenient Method to Produce Close- and Non-close-Packed Monolayers using Direct Assembly at the Air–Water Interface and Subsequent Plasma-Induced Size Reduction. *Macromol. Chem. Phys.* 212 (16), **2011**, 1719–1734.
[3] Kim M. H.; Im, S. H.; Park O. O., Rapid Fabrication of Two- and Three-Dimensional Colloidal Crystal Films via Confined Convective Assembly. *Adv. Funct. Mater.* 15(8), **2005**, 1329–1335.

Solid-state photoswitches based on transition metal nitro complexes

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Molecular switches are materials that undergo chemical transformations (isomerization, cyclisation etc.) upon some external stimuli. Photoswitchable solid-state materials may find various important real-life applications, including these in opto(bio)electronics, sensors, or in high-capacity storage devices. Among molecular switches, transition-metal complexes possessing ambidentate ligands (e.g. NO, NO_2, or SO_2) constitute a promising and readily modifiable group of compounds [1].

Hence here the latest achievements regarding the photoswitchable nitro transition-metal systems will be presented. It has appeared that most of the early reported systems were characterised by rather moderate conversion percentages to metastable linkage isomers and relatively low working temperatures. More recently a few compounds which undergo full conversion were reported, as well as the systems active under ambient conditions [2, 3] which is important regarding potential industrial applications. Among others, we have designed and introduced a series of effective nickel(II) nitro complexes differing by the type of the chelating (N,N,O)-donor ligand, which affects the Ni−NO_2 bond strength [4, 5]. This effect along with crystal packing and intermolecular interaction influence on the photo-induced isomerization will be discussed. New results dedicated to Co nitro complexes photoswitchable at room temperature and future prospects will be also presented. The isomerization was examined using solid-state infrared spectroscopy, photocrystallography and modelling.

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of Physics, UW, which was co-financed by the EU within the European Regional Development Fund (POIG.02.01.00-14-122/09).

References:

[1] Hatcher, L. E.; Raithby, P. R., Solid-state photochemistry of molecular photo-switchable species: the role of photocrystallographic techniques. *Acta Cryst. Sect. C* **2013**, *69*, 1448-1456.

[2] Warren, M. R.; Brayshaw, S. K.; Johnson, A. L.; Schiffers, S.; Raithby, P. R.; Easun, T. L.; George, M. W.; Warren, J. E.; Teat, S. J., Reversible 100% linkage isomerization in a single-crystal to single-crystal transformation: photocrystallographic identification of the metastable [Ni(dppe)(η1-ONO)Cl] isomer. *Angew. Chem. Int. Ed.* **2009**, *48*, 5711-5714.

[3] Brayshaw, S. K.; Deeth, R. J.; George, M. W.; Johnson, A. L.; Schiffers, S.; Teat, S. J.; Warren, A. J.; Warren, J. E.; Wilson, C. C.; Woodall, C. H.; Raithby, P. R., Solid-state interconversions: unique 100% reversible transformations between the ground and metastable states in single-crystals of a series of nickel(II) nitro complexes. *Chem. Eur. J.* **2014**, *20*, 5468-5477.

[4] Borowski, P.; Kutniewska, S. E.; Kamiński, R.; Krówczyński, A.; Schaniel, D.; Jarzembska, K. N., Exploring photoswitchable properties of two nitro nickel(II) complexes with (N,N,O)-donor ligands and their copper(II) analogues. *Inorg. Chem.* **2022**, *61*, 6624-6640.

[5] Kutniewska, S. E.; Krówczyński, A.; Kamiński, R.; Jarzembska, K. N.; Pillet, S.; Wenger, E.; Schaniel, D., Photocrystallographic and spectroscopic studies of a model (N,N,O)-donor square-planar nickel(II) nitro complex: in search of high-conversion and stable photoswitchable materials. *IUCrJ* **2020**, *7*, 1188-1198.

Dye-doped opals for angle-dependent emissive colour

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The history of photonic crystals known to today's scientists began with the work of Yablonovitch [1] and John [2]. Photonic crystals are remarkably interesting and deeply-studied group of modern optical materials, because of their periodical arrangement of the forming elements, which gives such effects as chromatic dispersion of diffracted light or Bragg reflection [3]. Nowadays, artificial opals consisted of monodisperse polymeric nanospheres are relatively easy to synthesize. Possibility of doping photonic crystals with various types of materials makes it possible to obtain compounds with unique optical properties. The use of photonic crystals allows, among others on designing completely new, hard-to-counterfeit features of originality.

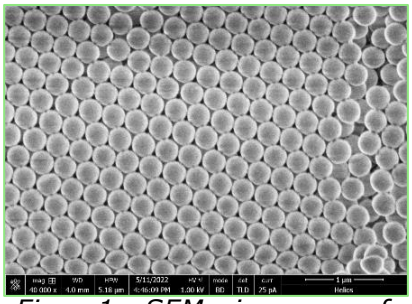

Fig. 1 SEM images of PMMA colloidal crystals

We synthesized a series of colloidal photonic crystals undoped and doped with organic dyes. Dyes were chosen with respect to different emission range and high quantum efficiency (POPOP, DCM, coumarin 6). Size of the nanospheres forming the synthesized opals was determined by SEM (Fig. 1) and optical Bragg reflection band position. The size of the nanospheres of the photonic crystals was optimized in order to cover the emission range of the dye by the reflection band of the photonic crystal. For this purpose, we performed full spectroscopic characterization of the fabricated luminescent opals, including characterization of angle-dependent emission of light at the output of the photonic crystal. The fabricated luminescent opals showed unusual angle-dependent emission spectrum, covering three different spectral ranges. Use of these materials allows to design completely new and difficult to counterfeit security features.

References:

[1] Yablonovitch E., "Inhibited Spontaneous Emission in Solid-State Physics and Electronics," *Phys. Rev.*, vol. 58, **1987,** 2059–2062.
[2] John S., "Strong Localization of Photons in Certain Disordered Dielectric Superlattices Lett, *Phys. Rev.*, vol. 58, **1987**, 2486-2489.
[3] Armstrong E., O'Dwyer C., Artificial opal photonic crystals and inverse opal structures – fundamentals and applications from optics to energy storage, *J. Mater. Chem. C*, vol. 3 **2015**, 6109.
These studies were supported by the National Centre for Research and Development (Poland) within the framework of the 12th edition of the LIDER programme – project contract no.LIDER/39/0203/L-12/20/NCBR/2021.

Development and characterization of graphene/hBN-based MEMS varactor.

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Recent development of the mm-wave and terahertz technologies creates a need for the development of new passive components such as varactors which allow to electrically tune the system properties. Inspired by the [1], we have developed a ***MEMS*** architecture of varactor using 2D metamaterials (*see* ***Fig. 1a***). The cross-sectional view (*see* ***Fig. 1b***) illustrates a varactor's principle of operation. Graphene (***GR***) and hexagonal boron nitride (***hBN***) are used as a top electrode and insulator, respectively. ***GR*** and ***hBN*** are transferred upon etched trenches, bottoms of the trenches are metallized forming the bottom electrode. Voltage applied between the ***GR*** and bottom electrode causes electrical force that results in ***GR*** bending. Owing to the electrical interaction between the electrodes, the distance (***D***) is reduced thus changing the capacitance. We present the characterisation of the metamaterial layers used in our device. The measurements are complemented by the electrical I-V and C-V characterisation, which reveal linear behaviour of the varactor. Capacitance tunability is confirmed to be of the order of few hundreds pF/V.

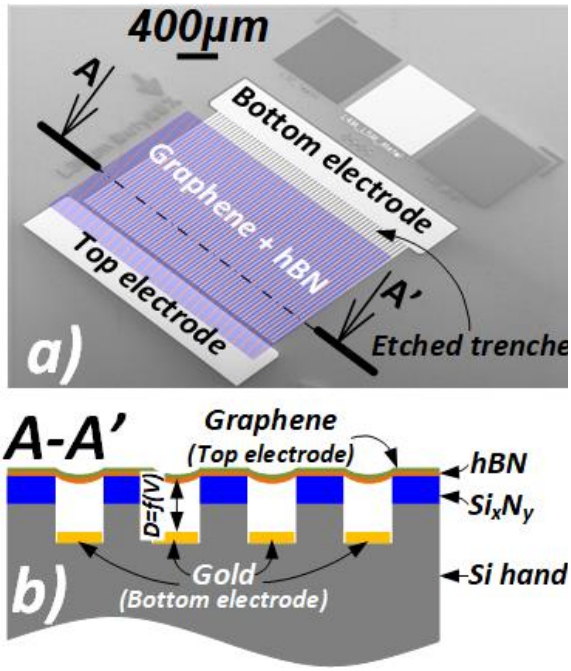

Fig. 1 a) ***SEM*** monograph of a ***GR***/***hBN***-based varactor; **b)** cross-sectional view along A-A' cutline emphasizing the top-to-down materials stack.

References:

[1] Generalov, A. A.; Anoshkin, I. V.; Ermandis, M.; Lioubtchenko D. V., J.; Ermandis, M.; Ovchinnikov, V; Räisänen, A. V., Carbon nanotube network varactor. *Nanotechnology,* Vol. 26, **2015,** 045201.

Spectroscopic properties of nano-crystalline Nd^{3+}-doped $GdPO_4$ obtained by ionic liquid and oleic acid assisted methods

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We report the detailed analysis of both structural and spectroscopic investigation of monazite-type Nd^{3+}-doped $GdPO_4$ nano-powders obtained *via* three wet synthesis methods *i.e.* ionic liquid assisted hydrothermal (IL HT) and microwave method (IL MW) as well as oleic acid assisted hydrothermal method (OA HT). PXRD technique confirmed that obtained $GdPO_4$ nano-powders crystallize in monoclinic system ($P2_{1/n}$) and no other phase has been detected. Electron microscopy techniques *i.e.* SEM and TEM were used to demonstrate the differences in the morphology and grain size of nano-materials, which brings the consequences in the physico-chemical properties. Gd^{3+} ion is easily substituted by Nd^{3+} one due to their similar ionic radius, so that high-resolution low-temperature absorption and emission spectra did not show any structural distortion. The $^4F_{3/2}$ excited level decay times recorded at 77 K have also shown an abnormal temporal behavior of Nd^{3+} photoluminescence similar as it was already observed for YPO_4 and $LuPO_4$ tetragonal orthophosphates [1].

References:

[1] J. Pawłów, K.A. Prokop, M. Guzik, Y. Guyot, G. Boulon, J. Cybińska, Nano/micro-powders of Nd^{3+}-doped YPO_4 and $LuPO_4$ under structural and spectroscopic studies. An abnormal temporal behavior of f-f photoluminescence, *J. Lumin.*, 236, 2021, 117997

Acknowledgements:

The research was financed by the National Science Centre Poland Fund within the project HARMONIA 9 UMO-2017/26/M/ST5/00563. J.P. would like to thank the Ministry of Science and Higher Education in Poland for the Grant No. DWD/5/0361/2021 „Design and synthesis of materials for use in optical temperature sensors" in the frame of Implementation Doctorate Program.

Optimization of the thickness of the graded AlGaN:Mg layer to obtain low resistivity ohmic contact in deep UV emitters

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AlGaN layers with high Al content are the basic materials for deep UV applications like sterilization of medical equipment, sensing, water and air purification [1,2]. AlGaN-based light-emitting diodes have many advantages over mercury lamps such as: low toxicity, the possibility of tuning the emitted wavelength, small size and long working time. The only drawback is the low emission efficiency of such devices, which arise from e.g. low hole concentration of p-AlGaN layer. One approach to improve p-doping properties in (Al)GaN-based materials is using a method called polarization doping by growing the graded AlGaN:Mg layers.

In our study, p-AlGaN contact layers with different thickness of the graded layer were deposited by metalorganic vapour phase epitaxy. The grown samples were investigated by X-ray photoelectron spectroscopy, X-ray diffraction and Hall measurements to study the influence of the thickness of the graded AlGaN:Mg layer on the structural as well as the electrical properties of the whole grown structure. Our findings reveal that the highest hole concentration (1.2×10^{18} cm^{-3}) was obtained for the structure with a gradient layer thickness of 50 nm while maintaining low sample resistance (84.9 kΩ) and resistivity (1.42 Ω cm). This project was financed by the National Science Centre (NCN) Poland [2020/37/N/ST3/02248].

References:

[1] Kneissl, M.; Rass, J., *III-Nitride Ultraviolet Emitters: Technology and Applications*, Springer, **2015**.
[2] Nagasawa, Y.; Hirano, A., A Review of AlGaN-Based Deep-Ultraviolet Light-Emitting Diodes on Sapphire, *Appl. Sci.* 8, **2018**, 1264.

PHOTONIC, 2D MATERIALS

High-resolution dispensing of functional inks for microfabrication of optoelectronic devices

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We demonstrate the Ultra-Precise Deposition (UPD) technology [1], which is an additive manufacturing technique for microfabrication. In the printed electronics landscape, UPD is an intermediary approach between printing 2D planar structures and free-standing 3D architectures. Therefore, we will focus on the results that are hard-to-achieve by other printed electronics technologies. This includes fabrication of micrometer-size interconnections that map the topography of the substrate, redistribution layers (RDL) on chips, as well as filing micro-vias in semiconductor devices.

We provide an in-depth discussion of the mechanics of the UPD technology and the means to control the process. UPD allows maskless deposition of micrometer-size conductive structures on complex substrates: highly-concentrated paste based on metallic nanoparticles (silver or copper) is directly extruded from a nozzle with diameter in the range from 0.5 to 10 μm. This gives the printed feature size from 1 to 10 μm with the electrical conductivity up to 40% of the bulk value.

References:

[1] Łysień, M.; et al.; High-resolution deposition of conductive and insulating materials at micrometer scale on complex substrates. *Scientific Reports,* Vol. 12, **2022,** 9327.

Designing Switchable Chromophores and Fluorophores

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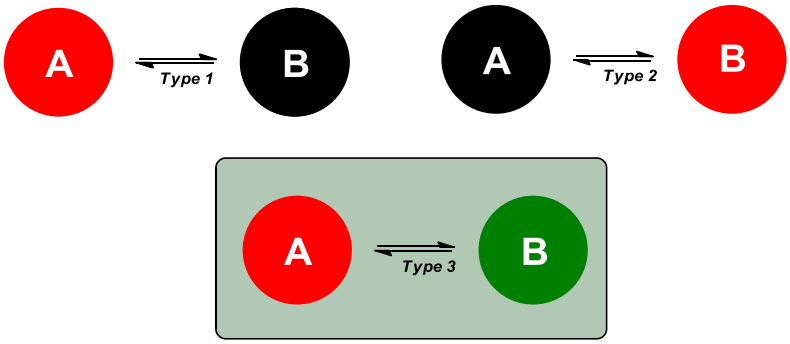
An interaction of organic matter with the electromagnetic irradiation remains a key factor used for the analysis of newly synthesized derivatives allowing understanding performed processes but also to monitor the progress along with a detailed description of novel systems.

A special place has been given to molecules showing a noticeable interaction with a visible region of electromagnetic irradiation by absorption (chromophores) end emission (fluorophores) leading to dyes applicable in several fields from medicine to contemporary electronics. Both aspects of interaction can be derived from specifically constructed organic molecules where the extension of π-conjugation allows a modulation of the energy of transition eventually showing the absorption and/or emission in different region starting from the blue light to near red and eventually far red absorption. Construction of such systems usually requires a precise formation of well-defined derivative containing a specific size (number) of π-electrons cloud precisely tuned to desired HOMO-LUMO gap. The significant limitation of such approach is derived from the covalent formation of the final derivatives that do not show any possibility for modulation of the final outcome. An alternative for such construction of a covalently bound systems is imprinting in the final molecule a specific trigger allowing switching from state A to state B with a different spectroscopic behaviour eventually leading to control of the optical response.



Switching between two (or more) available states leads to different spectroscopic picture and should be possible to be performed with a fundamental process based on e.g. protonation/deprotonation or a simple redox modulation. The later one can also lead to switching from aromatic to antiaromatic conjugation that also deeply influence the optical response. In a trivial case the change within the designed derivative allows a switching-off the emission and shifting the absorbance (***Type 1*** and ***2***), nevertheless several examples of modulation of the properties with shifting the absorbance and emission between two active states (***Type 3***) have been also reported.

The specific design and synthetic approach for formation of switchable chromophores/fluorophores based on the π-extended and strongly conjugated derivatives will be presented and fully discussed supporting the conclusions with the spectroscopic and structural data.

Towards an integrated chiral photonics: design, realisation and polarization control of chirowaveguides

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The planar optics' symmetry implies that only the two linear TE/TM polarizations are able to propagate without deformation. This linear birefringence (LB) behaviour of the guided modes, known as early as in graduate school, makes all the photonics based on the planar waveguides ruled by these two polarizations. It is a strong limitation of integrated optics because the polarization, the direction in which light vibrates, may provide a lot of informations on the objects it interacts with, from the magnetic field of stars to the molecules in living bodies. As a consequence, any application requiring other polarizations, such as circular polarization (the key polarization in chiral sensing), cannot take advantage of integrated photonics technology, in terms of miniaturization, robustness, etc. . . One way to overcome this linear birefringence limitation, is to use waveguides made of chiral materials having circular birefringence (CB), known as chirowaveguides.

Here, we present the realization as well as the theoretical and experimental study of channel chirowaveguides having polarization eigenmodes other than TE/TM. Using the coupled mode theory, we show that these waveguides have elliptically polarized eigenmodes whose ellipticity is proportional to the CB/LB ratio. For a given CB related to the chiral material, we can therefore modulate the ellipticity of the eigenmodes by varying the LB. PDMS-based imprint lithography method on the sol-gel material has been developed to produce high quality channel waveguides. With this method, we were able to fabricate in a simple way, channel waveguides of different geometries and, consequently, any eigenmodes with polarization varying from linear to quasi-circular. Furthermore, we put into evidence the extreme sensitivity of the sol-gel derived material to humidity. Our experimental results demonstrate that the integrated photonics is no longer limited to the linear TE and TM polarizations modes.

One-step and effective change of material properties - Direct Laser Interference Patterning

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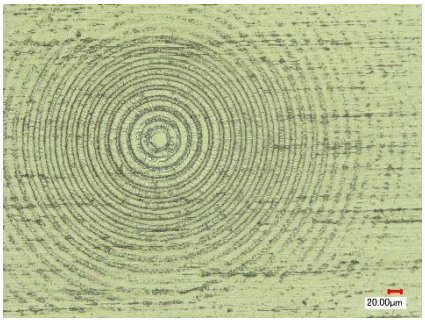
The outer layers of engineered materials are often modified to induce specific surface properties. This can be achieved by polishing, chemical etching, thinning, lithography etc. Here, a method of Direct Laser Interference Patterning (DLIP) available at Łukasiewicz - PORT, is presented. DLIP can be used to create repetitive patterns on the surface of materials with an optical stamp. The photo on the left shows a microscopic image of microstructure created on stainless steel by DLIP in one laser shot.



Through creation of the microstructure on materials' surface, changes in the tribological, optical, biological and other properties can be achieved. Interestingly, by observing the solutions that nature has developed (shark skin or the lotus flower effect), it is possible to create extreme wetting conditions for water or oil by such modifications, and also it may lead to the self-cleaning, reduced icing, reduced susceptibility to bacterial biofilm on the modified area [1-2].

A system based on a picosecond laser will be presented, thanks to which it is possible to easily and quickly generate patterns repeated on virtually any material along with the possibilities of its use - both potentially and already obtained.

References:

[1] Müller, Daniel Wyn, et al. Applying ultrashort pulsed direct laser interference patterning for functional surfaces., Scientific reports 10.1 (2020): 1-14.

[2] Peter, Alexander, et al. "Direct laser interference patterning of stainless steel by ultrashort pulses for antibacterial surfaces." Optics & Laser Technology 123 **2020**: 105954.

Laser lift-off as a method for manufacturing transparent electrodes

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Transparent electrodes are present in many daily applications such as displays, solar panels, smart windows, or windscreen heaters. [1,2] Among different types of transparent electrodes we can distinguish those in the mesh–shaped where the transmittance and resistance of the electrode can be controlled by line width and spacing. Finding the balance between those two parameters is a key to design transparent electrode for the appropriate application. [3] One of the manufacturing method that allow to anticipate and reproduce the designed pattern is laser lift-off method. [4,5] It uses polymer layer, spin-coated on a transparent solid substrate, as a disposable mask which can be structured by the laser beam, used in evaporation chamber and then dissolved in water. Two polymers were tested and also different sensitizers were examined as an addition to the polymer to reduced laser beam power required to structure the layer. The most prominent results was obtain for poly(vinylpyrrolidone) mixed with antimony tin oxide sensitizer giving reduction from 1.3 to ~0.3 W for a UV laser line irradiation. Finally, and most importantly, the key step of this method, the development step that includes the removal of a polymer mask, was carried out in water, instead of other environmentally hazardous solvents (e.g. toluene) usually use in this kind of processes. Consequently, this method paves the way for other applications requiring patterned semitransparent electrodes made in a sustainable process.

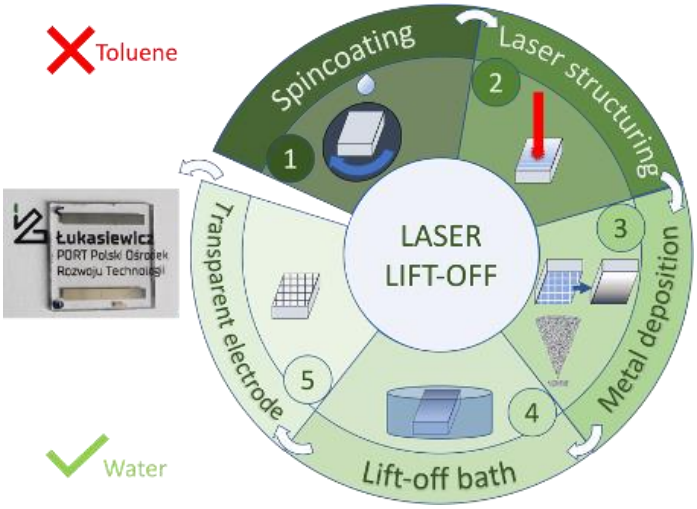

Figure 1. Scheme presents laser lift-off process as method for manufacturing semitransparent electrodes.

References:

[1] Layani, M.; Kamyshny, A.; Magdassi, S. Transparent Conductors Composed of Nanomaterials. Nanoscale **2014**, 6, 5581– 5591.

[2] He, W. W.; Yan, X. H.; Liang, Y. M.; Long, Y. F.; Pan, C.; Zhao, J. L.; Chen, L.; Xiong, W.; Liu, Q. X. Scalable and Cost-Effective Ag Nanowires Flexible Transparent Electrodes. RSC Adv. **2018**, 8, 12146– 12151.

[3] Anand, A.; Islam, M. M.; Meitzner, R.; Schubert, U. S.; Hoppe, H. Introduction of a Novel Figure of Merit for the Assessment of Transparent Conductive Electrodes in Photovoltaics: Exact and Approximate Form. Adv. Energy Mater. **2021**, 11, 2100875.

[4] Yeo, J.; Hong, S.; Lee, D.; Hotz, N.; Lee, M.-T.; Grigoropoulos, C. P.; Ko, S. H. Next Generation Non-Vacuum, Maskless, Low Temperature Nanoparticle Ink Laser Digital Direct Metal Patterning for a Large Area Flexible Electronics. PLoS One **2012**, 7, e42315.

[5] Ślusarz, A. M.; Komorowska K., Baraniecki T., Zelewski S. J., Kudrawiec R. Transparent Metal Mesh Electrodes Microfabricated by Structuring Water-Soluble Polymer Resist via Laser Ablation. ACS Sustainable Chem. Eng. **2022**, 10, 25, 8196–8205.

Towards chiroptoelectronics: development of functional electro- and photoactive chiral materials

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Since many decades, scientists are trying to reach Nature's proficiency in creating new materials. One common feature of materials created by Nature is their intrinsic chirality *i.e.* their structure do not possess elements of mirror symmetry. Chirality is a fundamental property which determines many biological functions by stereoselectivity of non-covalent interactions [1]. Importantly, just as molecules can exist in left-handed (LH) and right-handed (RH) mirror image pairs (enantiomers), light can feature either LH or RH circular polarization. Bioinspired materials comprising chiral structures, like helices, reveal particularly interesting properties when interacting with light, *e.g.* selective reflection of circularly polarized light (CPL) of the handedness similar to the screw sense of the helix [2] or the CPL emission [3]. Recently, we have observed a growing interest not only in organic chiroptics [4], but also in spin-selective effects in electronic transport [5].
In this lecture, I will present result of studies related to control of the morphology of supramolecular polymers based on triphenylene-2,6,10-tricarboxylicamide (TTA) derivatives. After deposition on surface, the TTA polymers possess a helical topology, with preferred handedness. As a result, their implementation in the optoelectronic devices will convey added value in form of stereo-selectivity in light-matter interactions. The development of functional materials exploiting molecular and supramolecular chirality will push forward the realization of three-valued logic: CPL(LH), CPL(RH) and 0 (no light).

References:

[1] Karabencheva, T.; Christov, C., *Adv. Prot. Chem. Struct. Biol.,* 80, **2010,** 85-115.

[2] Wang, L.; Urbas, A. M.; Li, Q. *Adv. Mater.,* 32, **2018,** 1801335.

[3] Han, J.; Guo, S.; Lu, H.; Liu, S.; Zhao, Q., *Adv. Optical Mater.,* 6, **2018,** 1800538.

[4] Albano, G.; Pescitelli, G.; Di Bari, L., *Chem. Rev.,* 120, **2020,** 10145-10243.

[5] Naaman, R.; Paltiel, Y.; Waldeck, D. H., *Nat. Rev. Chem.,* 3, **2019,** 250-260.

Influence of silica-titania layers doping with lanthanides on their waveguide properties

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Binary oxide systems SiO_x:TiO_y are very good matrices for lanthanide ion incorporation. They allow to gain control over parameters such as refractive index, thickness, crystallite size, surface roughness, solubility of lanthanide ions, material composition, etc. which allows for obtaining for individual applications [1]. Silica-titania films SiO_x:TiO_y doped with lanthanide ions are an interesting and promising material in various fields such as photonics, sensing, displays, optical amplifier, lasers, fluorescent sensing, including medical diagnostics [2,3]. Lanthanide doped films can be produced using physical vapor deposition (PVD) or chemical methods, including chemial vapor deposition (CVD) and sol-gel method [4].

The presentation will show lanthanide-doped silica-titania SiO_x:TiO_y waveguide films fabricated using the sol-gel method and dip-coating technique. In particular, will be presented relationships between a withdrawal speed and film parameters: their thickness and refractive index. The optical properties of lanthanide-doped silica-titania films were investigated with aid of UV-Vis spectrophotometry. The surface roughness were examined by AFM. The optical transmission losses of lanthanide doped waveguide films were determined using the scattered-light measurement method.

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References:

[1] J.MM. Buargue et.al, *Mat. Res. Bu*., **2018**, 107, 295-307.
[2] M. Pal et. al., *Nanoscale Research Letters,* **2012**, 7:1.
[3] J.A. Perez et.al., *Vacuum* **2019**, 169, 108873.
[4] J.D.B. Bradley et.al. *Laser Photonics Rev.* **2011**, 5,3, 368-403.

Pitfalls and Blessings in Reduced Rare-Earth Metal Halide Chemistry

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Rare-earth metal trihalides, RX_3 (R = Sc, Y, La-Lu), are known comprehensively with one exception, EuI_3. One of the prolific ways to produce trichlorides and tribromides is the ammonium halide route [1]. Following this process, oxygen can easily enter or is preserved as oxide-halide, ROCl, in the raw product. In subsequent reduction processes, either via conproportionation or metallothermic routines, the oxide may be retained, e.g., as in $\{OSm_4\}Cl_6$. Other light elements may also be incorporated in cluster-like halides, an important historic pitfall, as the examples of $\{H_xGd\}Cl$, $\{NGd_2\}Cl_3$, or $\{C_4OR_9\}I_9$ (R = Y, Ho, Er, Lu), may show. To turn these pitfalls into a blessing, a large number of the elements of the periodic table have been tested as endohedral atoms Z *aka* interstitials in rare-earth metal "clusters", of non-metallic and metallic elements alike. These "clusters", $\{Z_zR_r\}$, with r between 3 and 8 for the individual unit, are not really clusters in Cotton's sense, as there is hardly any bonding interaction between the cluster atoms R. Rather, bonding between the endohedral atom (or atom group) Z and the surrounding R atoms is mandatory.

Transition metal atoms, $Z = T$, especially of the 5d row, have turned out to be excellent endohedrals owing to their voluminous 5d orbitals that interact with the 5d electron of the R atoms [2, 3]. One of the most prolific compound type is $[\{ZR_6\}X_{12}]R$ with the number of examples decreasing in the sequence X = I, Br, Cl. There are thermodynamic reasons for this observation as the ionicity and therefore the lattice energy increases within this sequence and, thus, the stability of the trihalides, RX_3, increases. This is also the reason why fluorides with clusters are hardly known.

What seemed like another pitfall was the observation that transition/rare-earth metal, T/R, intermetallics like $Ru_{11}Lu_{20}$ were observed, here as a by-product during the attempt to synthesize $[\{RuLu_6\}Cl_{12}]Lu$. Meanwhile, there are examples of T/R intermetallics with all rare-earth elements known—preferably on the low T/R ratio side—with the exception of those R's = Nd, Sm, Eu, Dy, Tm, Yb that are known to form stable divalent states. So far, T:R ratios of 1:3 to 1:6 were employed in conproportionation reactions, for example targeting $\{AuTb_3\}Cl_3$ but yielding $AuTb_2$ + $TbCl_3$. Quite obviously there is a thermodynamic competition between the formation of a cluster complex halide and an intermetallic compound. Here, $TbCl_3$ acts as an "innocent" (molten salt) solvent rather than a reactant. Other innocent solvents may be halides like NaCl. Metallic melts, such as of tin, take part in the formation of intermetallics as we have recently shown in a case study for the Pt/Sn/Nd system. In a rather narrow region, eight ternary intermetallics have been discovered, PtSnNd, $Pt_{0.21}Sn_2Nd$, $PtSn_2Nd$, $Pt_{1.33}Sn_2Nd$, $Pt_{1.73}Sn_{2.27}$, Pt_3Sn_2Nd, $Pt_{1.5}Sn_{5.16}Nd_2$, and $Pt_3Sn_5Nd_{1.84}$, a true blessing!

References:

[1] G. Meyer, The Ammonium Ion for Inorganic Synthesis. In: *Advances in the Synthesis and Reactivity of Solids* (T. E. Mallouk, ed.), JAI Press, Greenwich, Connecticut, USA, **1994**, *2,* 1-26.

[2] G. Meyer, Rare-Earth Metal Cluster Complexes. In: *The Rare Earth Elements: Fundamentals and Applications* (D. Atwood, Ed.) John Wiley & Sons, Chichester, UK, **2012**, 415-436.

[3] G. Meyer, Symbiosis of Intermetallic and Salt: Rare-Earth Metal Cluster Complexes with Endohedral Transition Metal Atoms. In: *Handbook on the Physics and Chemistry of Rare Earths* (J.-C. G. Bünzli, V. K. Pecharsky, Eds.) Elsevier **2014**, *45*, 111-178.

POSTERS SESSION

PHOSPHORESCENCE PHENOMENON IN SiO_2-BASED GLASSES DOPED WITH DYES FROM CHALCONE GROUP

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Chalcones belong to a large group of bioflavonoids found in plants. They are precursors in the biosynthesis of all classes of flavonoid compounds. Their structure of α,β-unsaturated bicyclic natural ketones have a broad spectrum of activity depending on the type of substituents attached to the aromatic rings [1]. These compounds have been extensively used for various optical applications including lasers, photorefractive polymers or photo-alignment layer of liquid crystal displays [2].

Glasses based on SiO_2 were synthesized by the sol-gel method described by Zdończyk *et al*. [3]. The material was then doped with dyes from the chalcone group. The material obtained in this way was aged and then annealed in a furnace. After annealing, phosphorescence was observed, occurring in some cases after excitation with a UV lamp with a wavelength of 364 nm. We present the glass synthesis method doped with various chalcone dyes and phosphorescence duration dependent of type of substituent attached to chalcone skeleton.

The *Hybrid sensor platforms of integrated photonic systems based on ceramic and polymer materials* project is carried out within the TEAM-NET program of the Foundation for Polish Science financed by the European Union under the European Regional Development Fund.

References:

[1] Potaniec, B.; Żarowska, B.; Kozłowska, J.; Anioł, M., Synthesis and anti-microbiological properties of chalcones oximes, New Biotechnology, Vol.33, **2016**;

[2] Gaber, M.; El-Daly, S.A.; Fayed, T.A.; El-Sayed, Y.S., Photophysical properties, laser activity and photoreactivity of a heteroaryl chalcone: A model of solvatochromic fluorophore, *Optics & Laser Technology*, Vol.40, **2008**, 528-537;

[3] Zdończyk, M.; Potaniec, B.; Fiedot-Toboła, M.; Baraniecki, T.; Cybińska, J. Concentration-Dependent Emission of Annealed Sol-Gel Layers Incorporated with Rhodamine 19 and 6G as the Route to Tunable High-Temperature Luminescent Materials. Gels **2022**, 8, 408.

Hydrophobic Composite Coatings with Low Ice Adhesion as a Passive Anti-icing System

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Anti-icing systems prevent to form the ice on the protected surface. The most common systems include: heating the surfaces or spraying on them liquid (e.g. propylene glycol or ethylene glycol). Passive anti-icing system preparation is crucial for many industry and life aspects. Mentioned solution doesn't need electrical energy to work. Reduction of ice adhesion to the substrate and thereby ice formation prevention is a serious issue, which hasn't been sufficiently addressed.

For this reason in this work hydrophobic epoxy resin coatings with low ice adhesion have been presented. Chemical structure of epoxy resins has been modified using different kind of organic fluorinated compounds. It has been shown that the obtained coatings delayed the ice formation on their surfaces. They were characterized by low ice adhesion and their efficiency didn't change upon exposure to climate tests. The resistance of obtained coatings to atmospheric conditions is important factor. The research results have strong application potential for wind energy industry.

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References:

[1] Bressler, A.H.; Castano, C.E.; Fergusson, C.P; Mohammadi, R., Superhydrophobic graphite-like amorphous carbon coatings - innovative and eco-nomically expedient approach for the atmospheric icing and biofouling preven-tion, Appl. Surf. Sci. 390, 2016, 452-460.

[2] Piłkowski, M.; Morgiante, G.; Myśliwiec, J.; Kuchowicz, M.; Marczak, J., Environmental testing of hydrophobic fluorosilane-modified substrates, Surf. Interfaces, 23, 2021, https://doi.org/10.1016/j.sur-fin.2021.100987.

EVANESCENT WAVE EXCITATION OF REDUCED GRAPHENE OXIDE ON SILICON-ON-INSULATOR WAVEGUIDES

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Silicon photonics is one of the most widely used photonic integration platforms. The very high refractive index contrast and the availability of well-developed silicon-based electronics fabrication technologies allow the making of photonic circuitry in large scale.

Because of the very high refractive index contrast between silicon and its oxide (or air), single-mode strip waveguides can have very small bending radius[1]. This allows for extremely compact tracks on the substrate's surface, maximizing the covered area exposed to the evanescent field originated from the light confined in the waveguide's core.

Reduced graphene oxide can exhibit Anti-Stokes white light emission when excited by NIR laser radiation[2]. However, the emission area is usually limited to the point of incidence of the excitation radiation.

Therefore, here we present a possible alternative to the excitation method used to generate the white light emission in graphene. With the deposition of reduced graphene oxide onto the surface of silicon-based waveguides, we can transmit the NIR wavelength through the waveguide tracks and excite the reduced graphene oxide throughout the entire area of the substrate covered by the photonic structures.

References:

[1] W. Bogaerts et al., Laser & Photonics Reviews, 6, 1, (2011)

[2] W. Strek et al., Sci. Rep. 7, 41281 (2017)

Control of oligocarbamate shapes through stereochemistry

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Three-dimensional structure and folding of biomacromolecules are determined by their primary structure [1]. The order of amino acid units regulates protein shape at the molecular level and induces the functions properties. The folded motifs in proteins, existing due to specific interactions, are critical features to determine three-dimensional conformation of biomacromolecules [2]. In turn, the control over macromolecule shape is crucial for tunning its functionalities. To program advanced functions of abiotic polymers materials it is critical to understand sequence-single chain folding relationship [3]. In this work, we synthesized a library of oligocarbamates stereoisomers and investigated the effect of stereocenters on their conformation. We established methodology relying on NMR and vibrational spectroscopy technics to observe single chain folding. Experimental data combined with DFT calculations revealed existing conformations for each diastereoisomer, their stability depends on the sequence. Presented work is a step forward programming functionalities of macromolecules.

Acknowledgement:

The authors are highly grateful to the Polish National Science Centre (2018/31/D/ST5/01365) and Lukasiewicz Centre (4/Ł-PORT/CŁ/2021) for financial support.

References:

[1] B. Legrand and L. T. Maillard, α,β-Unsaturated γ-Peptide Foldamers, *Chempluschem*, 86., **2021**, 629–645.

[2] J. Jumper *et al.*, Highly accurate protein structure prediction with AlphaFold, *Nature*, 596., **2021**, 583–589.

[3] Z. Deng, Q. Shi, J. Tan, J. Hu, and S. Liu, Sequence-Defined Synthetic Polymers for New-Generation Functional Biomaterials, *ACS Mater. Lett.*, 3., **2021**, 1339–1356.

Selected biomass of plant origin samples technical analysis

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Increasing demand for energy sources leads to a necessity of search for new, renewable energy sources. One of promising energy carriers, considered by the European Union as a renewable is a plant biomass. Biomass combustion could be one of key factors for achieving carbon neutrality, but according to the European Commission, biomass fuels could meet certain criteria like coming from agricultural wastes or from non-recyclable residuals. Biomass combustion should also deliver at least 65% fever greenhouse gases than conventional fuels. It could be done with combining biomass combustion with efficient Carbon Capture and Storage (CCS) technologies [1] or emerging combustion technologies..

Technical biomass analysis is a first step for determining biomass quality for application as a fuels. In the presented research, technical analysis of some biomass coming from agricultural wastes was performed. According to the ISO standards content of ash, volatiles and total moisture was determined. The analysis of total heat combustion was also performed.

References:

[1] European Commission, Joint Research Centre, Camia, A., Giuntoli, J., Jonsson, R., et al., The use of woody biomass for energy production in the EU, Publications Office, 2021, https://data.europa.eu/doi/10.2760/831621

Analysis of different Polish coals for possible energy application

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Despite shifting away from combustion of fossil fuels, coal still accounts for about 20% of total energy production in EU and 35% of global energy production. Although the primary application of coal in energy is direct burning in coal-fired powerplants, it could be also converted to gas and liquid fuels [1]. Basically, all types of coal could be applied for electricity generation, but depending on the properties of certain coals, different conditions of the burning process could be required. For coals of poor quality they could be suitable for coal gasification, as an example [2].

Technical analysis of coal is a first step for evaluation of quality of the fuel for energetic applications. In the presented research, evaluation of total moisture, volatiles, ash content and heating value of different polish coals was performed, according to Polish standards.

References:

[1] European Commission, Joint Research Centre, Miranda Barbosa, E., Peteves, E., Vázquez Hernández, C., et al., EU coal regions : opportunities and challenges ahead, Publications Office, 2018,

[2] Song HJ, Lee J, Gaur A, Park JJ, Park JW. Production of gaseous fuel from refuse plastic fuel via co-pyrolysis using low-quality coal and catalytic steam gasification. J Mater Cycles Waste Manag 2010 124, 12: 295–301.

Anodic oxidation of naphthalene

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Organic semiconductors have attracted much interest because of their promising electronic and optical properties. The latter can be tailored by the possibility of controlling the width of band gap of these materials, e.g. by introducing functional groups to the polymer chain. Substituted polynaphthalenes have potential use in flexible electronic or as blue light sources in OLED diodes [1]. Polymers of naphthalene and of naphthalene derivatives can also potentially play a role in the conversion of solar into chemical energy. Naphthalene as the smallest acene is a very interesting precursor to many types of synthesis. Large acenes and non-linear polycyclic aromatic hydrocarbons (PAHs) can be understood as graphene strings and graphene dots respectively [2].

Our recent research show that conductive polymers with an band gap about 2eV can be obtained by anodic oxidation of naphthalene. The results of imaging by electron microscopy has shown that deposits adhere tightly to the electrode surface. Electronic properties of obtained polymers have been studied by cyclic voltammetry and impedance spectroscopy. The influence of the electrode material, precursor concentration and water content will be discussed.

References:

[1] K. Samanta, G. S. Kumar, U. K. Ghorai, U. Scherf, S. Acharya, and S. Bhattacharya, "Synthesis of High Molecular Weight 1,4-Polynaphthalene for Solution-Processed True Color Blue Light Emitting Diode," *Macromolecules*, vol. 51, no. 20, pp. 8324–8329, Oct. 2018, doi: 10.1021/acs.macromol.8b01057. O.

[2] A. Shinkarenko, R. A. Safonov, A. S. Kolesnikova, J. K. Al-Alwani Ammar, M. v. Pozharov, and E. G. Glukhovskoy, "Naphthalene condensation as a means of producing nanostructured graphene," *Applied Surface Science*, vol. 424, pp. 177–183, Dec. 2017, doi: 10.1016/j.apsusc.2017.02.256.

Oligocarbamates vs. peptides, how to induce unnatural bioactivity in synthetic polymers?

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The natural, uniform macromolecules such as proteins of perfectly, sequence-defined structures have been inspiring polymer chemists for years. Proteins are an extremely important elements of all living organisms which act as antibodies, enzymes, signaling and transport molecules or are the building blocks of various structures. Performing all these functions is possible thanks to the strictly defined sequence of monomers in the chain, which determines the three-dimensional structure of macromolecules. In spite of many efforts, man-made materials are still far away from functions that are displayed by natural matter. [1] To reach for complex properties achieved by native biological polymers sequence programmability of the synthetic polymers seems to be a promising tool. Oligocarbamates in which the monomers are linked by a urethane bond analogous to the peptide bond deserve special attention. They can be obtained by iterative synthesis in solution using amino alcohol monomers without the need for functional group blocking. The commercial availability of amino alcohols with a structure analogous to amino acids opens the door to the synthesis of oligocarbamate biomimetics. Here, we evaluated synthetic strategy that was developed before [2] to obtain peptidomimetics with analogus site chains which contain methyl, benzyl, isopropyl and isobuthyl side chains similarly to alanine, phenylalanine, valine and leucine.

Acknowledgement:

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References:

[1] Lutz, J. F.; Lehn, J. M.; Meijer, E. W.; Matyjaszewski K., *Nat Rev Mater*, 5, **2016**, 1-14.

[2] Forysiak, W.; Kozub, S.; John, Ł.; Szweda, R., *Polym Chem*, 13, **2022**, 2980-2987.

Studies of sequence-dependent properties of stereocontrolled polyurethanes in solution

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Since decades scientists have been interested in natural polymers with a specific monomeric sequence, such as proteins and nucleic acids. This is because of the numerous sequence-function correlations that have been discovered [1]. Remarkably, the function of an entire protein can be altered by changing or removing just one amino acid from a polypeptide chain. Over the last years, efforts have been made to create synthetic polymers that can take their cue from nature and have qualities as natural macromolecules – sequence-defined structures. This would enable the production of polymers with precisely designed properties and functionalities, which are expected to have a wide range of applications in advanced materials such as storage media, information encryption, catalysis and drug delivery systems [2]. In this work, we investigated solution behaviour of sequence-defined oligocarbamates of controlled chirality. The library of different sequences have been obtained by using solution synthesis process [3]. Their properties in different solvents were studied by circular dichroism and NMR spectroscopy to learn about their folding to secondary structures.

Acknowledgment

The authors are highly grateful to the Polish National Science Centre (2018/31/D/ST5/01365).

References:

[1] Lutz, J.-F., Defining the Field of Sequence-Controlled Polymers, *Macromol. Rapid Commun*., **2017**, 38(24), 1700582

[2] Aksakal, R., Mertens, C., Soete, M., Badi, N., Du, F., Applications of Discrete Synthetic Macromolecules in Life and Materials Science: Recent and Future Trends. *Adv. Sci*. 8, **2021**, 2004038.

[3] W. Forysiak, S. Kozub, Ł. John, R. Szweda, *Polym. Chem*., **2022**, 13, 2980-2987

Intermolecular binding: modulating interaction strength via stereochemical center changes

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Intermolecular non-covalent binding is a key part of molecular recognition and signaling, which is present in proteins. They, as macromolecules capable of adopting a specific spatial form, can specifically bind to other molecules. However, developing the strategy to rationally design the efficient receptor characterized by high binding constant and selectivity is very challenging. Taking proteins as a model, we have created abiotic macromolecules that share with proteins the features of monodispersity and specific arrangements of monomers called sequence-defined polymers [1]. We have studied the effect of changes in stereochemical center arrangement on their affinity for the target ligand - bisphenol A. The binding energy was evaluated theoretically using the Molecular Dynamics approach and experimentally based on fluorescence measurements [2].

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References:

[1] E. Laurent, R. Szweda, and J. Lutz, *Synthetic Polymers with Finely Regulated Monomer Sequences: Properties and Emerging Applications*. 2022.

[2] J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, vol. 33, no. 1. 1956.

Deep-level defects in transition metal diselenides $(W,Mo)Se_2$ and their electrical properties

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Transition metal dichalcogenides (TMDs), especially in two-dimensional (2D) form, belong to the new family of materials with desirable properties for device applications. However, device performance can be hindered by the presence of defects, such as vacancies, interstitials, adatoms or substitutional impurities. These defects could act as efficient trapping centers for electrons or holes and thus play an important role in tailoring their electrical and optical properties.

In this work, we report electrical investigations of WSe_2 and $MoSe_2$ bulk crystals. The current-voltage (I-V) and capacitance-voltage (C-V) characteristics, measured on the Schottky barrier contacts in a broad temperature range (100-450K), indicate n-type behaviour of the studied TMDs crystals. By combining state of the art experimental and computational approaches we were able to determine formation energies and charge transition levels of defects in bulk TMDs. The deep level transient spectroscopy (DLTS) measurements revealed the existence of three deep-level traps in the upper half of the band gap. Finally, the density functional theory (DFT) calculations allowed for identification of the origin of experientially found defect levels. We found that chalcogen vacancies (V_{Se}) are the most stable defects in the studied TMDs crystals and that the selection of transition metal has only little effect on their position in the band gap. The other two deep-levels were attributed to metal vacancies (V_0, V_{Mo}) and antisites (Se_W, Se_{Mo}), respectively. This work may aid in properly designing and fabricating TMD-based device applications.

Leuco dye-based thermochromic systems for application in temperature sensing

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Leuco dye-based thermochromic systems are classified as intelligent materials because they exhibit thermally induced color changes. Usually two components, a color former and a developer are needed to produce a system with irreversible color change. The color former is an electron donating (proton accepting) compound such as fluoran leuco dye. The developer is an electron accepting (proton donating) compound such as organic carboxylic acid. When the developer melts, the color former - developer complex is created and the termochromic system becomes colored. Typically, the melting point of the applied developer determines the temperature at which the color change occurs. Since the color former and the developer are often solid, they can be incorporated into polymer films to facilitate their practical use in industry.

The objective of this research was to fabricate a leuco dye-based termochromic system that will irreversibly change color after reaching the temperature of 100°C. For this purpose, benzofluoran leuco dye (as color former) and phenoxyacetic acid (as developer with a melting point of 100°C) were introduced into the polymer films during the drop casting process. The film preparation process was optimized in order to obtain thin films with appropriate properties such as transparency, flexibility and homogeneity. The selected films, containing benzofluoran leuco dye and phenoxyacetic acid, were combined by mild heat treatment. Structural characterization of single and combined films was carried out by FTIR spectroscopy, morphological analysis was performed by SEM, phase transitions were investigated by DSC, color and emission changes were studied by UV-Vis and photoluminescence spectroscopies.

The resulting thermochromic system is colorless at room temperature, but after reaching 100°C, the developer melts and the system turns irreversibly pink. Therefore, it could be used as an additional sensor to warn against boiling of water in power plants using water cooling. Currently used electronic temperature indicators are prone to faults and unwanted third-party actions. The sensor constructed in this work is transparent, thanks to which it can be unnoticed by an outsider and constitute a reliable reference for the person responsible for the apparatus.

Development of the sol-gel layers doped with organic dyes synthesis using different pH values

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Sol-gel technology is an important and relatively simple synthesis method for producing inorganic or hybrid materials. In this study, selected material is silica doped with organic dyes. This synthesis method can be successfully implemented for the synthesis of active materials with high chemical stability. High stability observations, origins of Alfred Nobel, who observed that explosive nitroglycerin adsorbed in silica is much more stable, which allows for safer transportation and storage [1].

In chemistry, chromism is a process that induces a change, often reversible, in the colors of compounds, based mostly on changes in molecule stated. Organic dyes are an excellent example of a molecule that exhibits this effect. Spectroscopic properties of them are tunable in case of used pH factor or solvent. In this poster presentation, we used Rhodamines as active substances (dopants). In another work, we investigated their concentration effect in bulk materials [2], while in this work we show spectroscopic properties and the synthesis of thin films with the use of different pH catalysts.

For this, a synthesis was performed, starting in both cases with TEOS (tetraethyl orthosilicate) with an alcoholic Rhodamine 800 solution (c = 0.05mg / mL). The factor that differs in both cases is the catalyst used - in the case of the first synthesis, it is acidic (HCl), and in the second, it is basic (NH_3 x H_2O). Thin layers were obtained with the use of a dip or spin coater. Their spectroscopic properties have been investigated.

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References:

[1] Ciriminna R., Fidalgo A., Pandarus V., Beland F., Ilharco L., Pagliaro M., Chemical Reviews, *113,8,* ***2013,*** 6592–6620

[2]Zdonczyk M., Potaniec B., Fiedot-Toboła M., Baraniecki T., Cybińska J., Gels 8,408 **2022**, 1-11

The effect of preparation conditions such as sol-gel solution pH, Cu doping, and calcination temperature on the phase composition and crystallinity of TiO_2-based photocatalysts.

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A series of Cu-modified TiO_2 photocatalysts were successfully obtained through the two–steps preparation procedure consisting of (1) sol-gel synthesis followed by (2) a thermal treatment [1]. Two sol-gel solutions at pH=1.5 and 3 were obtained. The crystalline powders were achieved by calcination of the gel at various temperatures: 400, 450…650°C for 1h in an air atmosphere. The nomenclature of the example products obtained and the parameters of the preparation process are listed in Table 1.

Table 1. The preparation conditions of the example samples.

Sample	Sol-gel	Calcination		Phase composition [%]			Crystallites size [nm]		
	pH	temperature [°C]	time [h]	anatase	rutile	brookite	anatase	rutile	brookite
I-400	3	400	1	67	-	33	9	-	9
I-650	3	650	1	26	73	1	70	172	13
II-400	1.5	400	1	42	27	31	10	20	6
II-650	1.5	650	1	1	99	-	29	61	-

Doping Cu into TiO_2 caused a shifting of the absorption edge to the visible region and a significant reduction in band-gap energy. Low pH of a sol-gel solution, such as pH 1.5 favored the formation of rutile during calcination and caused slower growth of the crystallites with increasing temperature of calcination in comparison with sol-gel prepared at pH 3.

References:

[1] Tryba, B.; Orlikowski, J.; Wróbel, R.J.; B Przepiórski, J.; Morawski A.W., Preparation and Characterization of Rutile-Type TiO_2 Doped with Cu. *Journal of Materials Engineering and Performance*, Vol. 24, **2015,** 1243-1252.

Engineering of synthesis of polyurethanes with programmable monomeric sequence towards high-molar mass products

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Sequence-defined polymers are a new type of macromolecule materials that have been gaining interest in recent years [1]. That is due to the fact, that by controlling the monomeric sequence inside a polymer, myriad of characteristic can be imparted on polymers and make them applicable in various fields e.g. data storage, tagging of products and in vivo tagging of implants [2-3]. Two different approaches to synthesis of SDPs can be differentiated: solution synthesis [4] and synthesis on solid support [3]. However, reported methods still demand optimisation to be applied on industrial scale. Recently synthesis of sequence-defined polyurethanes in one pot by using two reactions: (I) activation of alcohol and (II) coupling with amino alcohol was reported [5]. Here, one-pot synthesis of sequence-defined polyurethanes was investigated to find the most optimal conditions for iterative activation and coupling reactions, the developed protocol could be used to scale up the process and adapt it for large scale manufacturing.

Acknowledgements:

The authors are highly grateful to the Polish National Science Centre (2018/31/D/ST5/01365) and Łukasiewicz Centre (grant PolyProbe: 4/Ł-PORT/CŁ/2021) for funding.

References:

[1] Solleder, S. C., Schneider, R. V., Wetzel, K. S., Boukis, A. C., Meier, M. A. R., Recent Progress in the Design of Monodisperse, Sequence-Defined Macromolecules, Macromol. Rapid Commun. 2017, 38, 1600711.

[2] Gunay US, Petit BE, Karamessini D, Al Ouahabi A, Amalian JA, Chendo C, et al. Chemoselective Synthesis of Uniform Sequence-Coded Polyurethanes and Their Use as Molecular Tags. Chem. 2016 Jul 7;1(1):114–26

[3] Karamessini D, Simon-Yarza T, Poyer S, Konishcheva E, Charles L, Letourneur D, et al. Abiotic Sequence-Coded Oligomers as Efficient In Vivo Taggants for the Identification of Implanted Materials. Angew Chem Int Ed. 2018 Aug 13;57(33):10574–8.

[4] W. Forysiak, S. Kozub, Ł. John, and R. Szweda, 'Discrete oligourethanes of sequence-regulated properties – impact of stereocontrol', Polym. Chem., vol. 13, no. 20, pp. 2980–2987, May 2022.

[5] Szweda, R.,Walencik, P., Cwynar, P., Turski, M., no. 2021 PCT/IB2021/057872.

Synthesis and crystal structure analysis of perovskite and spinel based oxygen carries

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Oxygen carriers (OC) used in Chemical Looping Combustion technology are materials suitable for accepting and releasing oxygen due to changes in oxygen partial pressure in their working environment or due to direct contact with a fuel. Released oxygen is later used for fuel combustion. That approach allows fuels to burn under conditions similar to oxy-combustion technology (combustion with pure oxygen) but without the necessity of using costly oxygen separators. CLC is an emerging technology; one of important factors to apply it in practice is to lower cost of oxygen carriers. It could be done both with the reduction of the cost of OCs synthesis and the increase of their mechanical stability [1].

Monophasic spinel and perovskite based materials are considered as durable and efficient oxygen carriers for CLC application. A very promising route of obtaining those OCs is solid state synthesis with a mechanical mixing and calcination. In mechanical mixing, metal oxides and/or carbonates are used as precursors, which makes it much more cheaper and environmentally friendly comparing to other methods like sol-gel where precursors like metal nitrates are used.

The materials were obtained using solid-state synthesis from metal oxygen and metal carbonate precursors. The quality of obtained OCs was examined using X-ray diffractometry, while Rietveld refinement was applied to determine crystal structure and phase composition.

References:

[1] Ksepko E, Lysowski R. Extremely Stable and Durable Mixed Fe–Mn Oxides Supported on ZrO_2 for Practical Utilization in CLOU and CLC Processes. Catal 2021, Vol 11, Page 1285, 2021, 11: 1285.

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Luminescent Binary Fluorides and Graphene Oxide Nanocomposites via Ionic Liquid

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Graphene-based nanocomposites have been attracting tremendous attention for various applications including optoelectronics, photocatalysis, imaging, solar cell and so on.[1,2] However, very limited literatures related to rare-earth (RE^{3+})-doped binary/ternary fluorides and graphene/graphene derivatives-based nanocomposites are available.[2] Herein, RE^{3+}-doped binary fluorides and graphene oxide (GO)-based nanocomposites are synthesized using environmentally benign 1-butyl-3-methylimidazolium tetrafluoroborate ($[C_4mim][BF_4]$) IL–assisted hydrothermal method. IL is employed as a source of F^- ions, reaction medium as well as capping/templating agent that is, "all three in one". No solvent except water is used as solvent for the synthesis of nanocomposites. It is noticed that GO has played pivotal role not in controlling the size of as-prepared nanoparticles but also has governed the excitation and emission spectra of the nanocomposites. Furthermore, $GdF_3:Tb^{3+}$ nanoparticles and $GdF_3:Tb^{3+}$-GO nanocomposites have revealed significantly high magnetization (e.g., 6.676 emu g^{-1} at 300 K and 184.449 emu g^{-1} at 2 K in the applied magnetic field from +50 to −50 kOe) and promises their future uses in bio-imaging etc..[2]

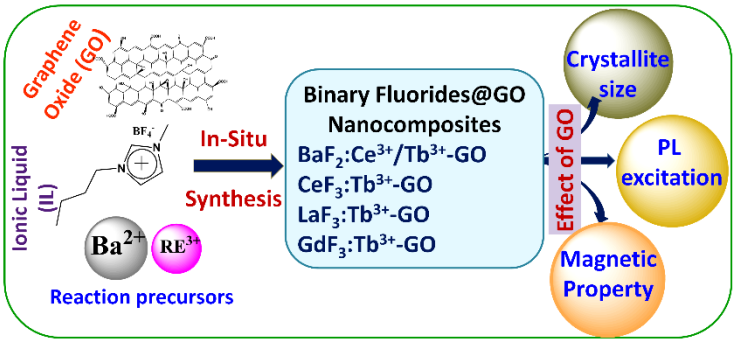

Figure 1. Schematic representation of nanocomposites synthesis

References:

[1] Chang, H., Wu, H., Graphene-based nanocomposites: preparation, functionalization, and energy and environmental applications, *Energy Environ. Sci.*, 6, **2013**, 3483-3507.

[2] Sharma, R. K., Ghora, M., Chouryal, Y. N., Ganguly, T., Acharjee, D., Mondal, D. J., Konar, S., Nigam, S., Ghosh, P., Multifunctional Lanthanide-Doped Binary Fluorides and Graphene Oxide Nanocomposites Via a Task-Specific Ionic Liquid. *ACS Omega*, 7, **2022,** 16906−16916.

Electron beam patterning of sol-gel-based films

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The increasing demands imposed on electronic and photonic devices have been stimulating the development of new materials as well as new micro- and nanopatterning techniques. One of the promising patterning methods is focused electron beam direct writing (FEB DW), which allows for very precise micro- and nanofabrication directly in a layer of selected material [1]. The choice of a material for FEB DW is crucial, as it should provide desired properties either for electronics or photonics. In this work, we present a detailed study on electron beam structuring of titania sol-gel layers. This kind of material is very attractive for photonics [2] and we show that we are able to produce well-defined and high-resolution gratings by FEB patterning of it. Moreover, we demonstrate preliminary results for FEB structuring of ionogels which are combinations of sol-gels and ionic liquids.

Acknowledgements:

The research was co-financed by the Foundation for Polish Science from the European Regional Development Fund within the project POIR.04.04.00-00-14D6/18 "Hybrid sensor platforms for integrated photonic systems based on ceramic and polymer materials (HYPHa)" (TEAM-NET program).

References:

[1] Lee, S.W.; Sankaran, R.M., Direct writing via electron-driven reactions. *Materials Today*, Vol. 16, **2013**, 117-122.

[2] Fu, M.; Zheng, Y.; Li, G.; Yi, W.; Qi, J.; Yin, S.; Li, X.; Guan, X., Ultra-compact titanium dioxide micro-ring resonators with sub-10-μm radius for on-chip photonics. *Photonics Research*, Vol. 9, **2021**, 1416-1422.

Modified ionic liquid-assisted synthesis routes to obtain well-crystallized Yb^{3+}-doped $LuPO_4$ and spectroscopic analysis

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Rare earth-doped orthophosphates establish a considerable family of compounds characterized by different physico-chemical properties. Their high thermal stability, high insolubility, relatively cheap synthesis, and the fact that they are good host lattices for RE^{3+} ions make them a new promising matrix for inorganic luminescent materials. Among the lanthanides ions, Yb^{3+} is an optically active ion for laser applications. In addition, the possibility of obtaining effective luminescence in the NIR region makes it attractive also from the bio-imaging point of view. Basic research on the influence of the synthesis route on structural and spectroscopic properties of obtained materials is crucial for proper modelling of new efficient optical materials for potential applications.

So, taking advantage of the Yb^{3+} ion as a structural probe, here we present a detailed analysis of both structural characterization and high-resolution spectroscopic properties of Yb^{3+}-doped $LuPO_4$ in the form of nano/micro-crystalline powders crystallizing in a zircon-type tetragonal system. A series of fine nano-crystalline samples (0.5 – 5 mol%) was obtained by ionic liquid-assisted hydrothermal synthesis. This protocol allowed to fabrication of fine nano-size powders exhibiting desired well-crystallized single-phase phosphate nano-materials. For comparative research, a series of micro-materials obtained via high-temperature solid-state reaction was used. The correlation between the three synthesis routes and unexpected spectroscopic properties in nano and micro-crystalline Yb^{3+}-doped $LuPO_4$ was shown. Only one, symmetry site is occupied by Yb^{3+} ion in $LuPO_4$, however, unusual emission from both 5 and 6 levels of $^2F_{5/2}$ excited state, which are in thermal equilibrium was detected.

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Synthesis and thermal characteristic of stereocontrolled discrete oligourethanes

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Polymer thermal characteristic is one of the critical measurements important for their future applications. One of the very interesting approaches for the regulation of polymer thermal properties is the control of monomer composition and order in macromolecule chains. Therefore, it is intriguing to what extent we can manipulate the properties of polymer materials by altering their sequence and stereochemistry. Recent progress in polymer chemistry concerns methods of synthesizing uniform polymers with a well-defined monomer sequence [1]. However, the synthesis of sequence-defined polymers has still a lot of drawbacks that hinder studies on the sequence-properties relationship. Here, we developed an optimized protocol for solution synthesis of sequence-defined oligourethanes. Obtained oligourethanes were used as models to study how sequence and stereocontrol influence the thermal properties of these materials [2].

Acknowledgements:

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

References:

[1] J.-F. Lutz , M. Ouchi, D. R. Liu, M. Sawamoto, Science, 2013, 341, 1238149-1238149.

[2] W. Forysiak, S. Kozub, Ł. John, R. Szweda, Polym. Chem., 2022, 13, 2980-2987

High-yielding and scalable method for synthesis of sequence-defined polyurethanes

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Sequence-defined polymers (SDPs) are discrete macromolecules with controlled monomer order. Control of the monomer sequence and their stereochemistry allow to mimic features of biomacromolecules. These novel polymer materials possess unique properties useful for a wide range of applications such as: data storage, information encryption, foldamers, catalysis, sensing, drug delivery systems [1]. However, the synthesis with structural control as precise as proteins or nucleic acids is still a challenge. SDPs are currently being synthesized through multi-step processes that results in various limitation, e.g. low yield, high reagents consumption, small synthesis scale, and complicated protocols. The limitations arise mainly from a necessity of purification after each synthesis step that is needed to obtain perfectly sequence-defined macromolecules [2,3]. Here, we investigated one-pot approach for the solution synthesis of sequence-defined oligourethanes. We used cascade of two chemoselective reactions: activation of alcohol by N,N'-disuccinimidylcarbonate (DSC) and chemoselective coupling of amino alcohol monomers [4]. Terminal amine of obtained oligourethanes is protected with tert-butyloxycarbonyl group (Boc) that might be easily removed under acidic conditions. The lack of purification between steps makes this process more green thanks to the reduced consumption of solvents. The one-pot strategy for synthesis of SDPs is advantageous due to its simplicity, scalability and high yields. While the oligomers synthesized via one-pot can be used as 5-mer building blocks for the synthesis of longer sequence-defined polyurethanes.

References

[1] Aksakal, R., Mertens, C., Soete, M., Badi, N., Du, F., Applications of Discrete Synthetic Macromolecules in Life and Materials Science: Recent and Future Trends. Adv. Sci. 8, 2021, 2004038.
[2] Solleder, S. C., Schneider, R. V., Wetzel, K. S., Boukis, A. C., Meier, M. A. R., Recent Progress in the Design of Monodisperse, Sequence-Defined Macromolecules, Macromol. Rapid Commun. 38, 2017, 1600711.
[3] Laurent, E., Szweda, R. and Lutz, J.-F. (2022). Synthetic Polymers with Finely Regulated Monomer Sequences: Properties and Emerging Applications. In Macromolecular Engineering (eds N. Hadjichristidis, Y. Gnanou, K. Matyjaszewski and M. Muthukumar)
[4] Szweda, R.,Walencik, P., Cwynar, P., Turski, M., no. 2021 PCT/IB2021/057872.

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Antiviral activity of metallic nanoparticles functionalized with sulfonates vs. polyphenols

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One of the most common human pathogens nowadays is HSV which is the name of two viruses: herpes simplex virus type 1 (HSV-1), associated with orofacial infections and encephalitis and herpes simplex virus type 2 (HSV-2) causing genital infections. The symptoms of HSV infection are already well-known to most people and include cold sores of the mouth and keratitis, but HSV may also cause life-threatening diseases in immunodeficiency persons, including newborns, patients with human immunodeficiency virus (HIV), or patients undergoing immunosuppressive treatment. There are several ways to fight against HSV virus. Most of the currently available antiviral therapies rely on the mechanism of inhibition of viral DNA polymerase. Although those antiviral drugs can be highly effective, they require strict patient compliance and can have harsh side effects. Nanomaterials have the potential to overcome these obstacles and offer opportunities for developing novel broad-spectrum nano-therapeutic platforms to combat viral infections.

Based on the considerations above, the goal of this study was to prepare and compare the inhibitory effect of two types of nano-conjugates known for its anti-HSV activity: sulfonate-conjugated metallic nanoparticles and tannic acid-conjugated metallic nanoparticles.

This work was supported by the National Science Centre, Poland (UMO-2018/31/B/NZ6/02606).

More results about antiviral activity (HSV) of functionalized nanoparticles you can find on our team project page: https://www.researchgate.net/project/Functionalised-metallic-nanoparticles-for-antiviral-applications.

Quadrupole-structure pyrrolo[3,2-b]pyrroles as a new class of red-emitting functional dyes

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1,2,4,5-tetraarylpyrrolo[3,2-b]pyrroles (TAPPs) are a group of functional dyes, which was discovered in 2013 as a result of multicomponent reaction between aromatic aldehydes, anilines and butane-2,3-dione [1]. These dyes exhibit various photophysical properties which are beneficial for many applications in optoelectronics or cellular imaging. Although many TAPPs are known, red-emitting non-expanded examples were not synthesized before. In this work we present a new subgroup of TAPPs, contains 2,1,3-benzoxadiazoles or 2,1,3-benzothiadiazole moieties and as a result exhibits red fluorescence. These compounds have acceptor-donor-acceptor structure provides to excited-state symmetry breaking in polar solvents and solvatofluorochromism (**Figure 1**) as a result. Such "intelligent compounds" may be applied in detection of environmental changes. Investigated TAPPs have also unusual photophysical properties in solid state, which are correlated with torsion angle between pyrrolo[3,2-b]pyrrole core and acceptor moiety. Studies on behaviour of these compounds in solid state may shed a new light on structure-properties relationship.

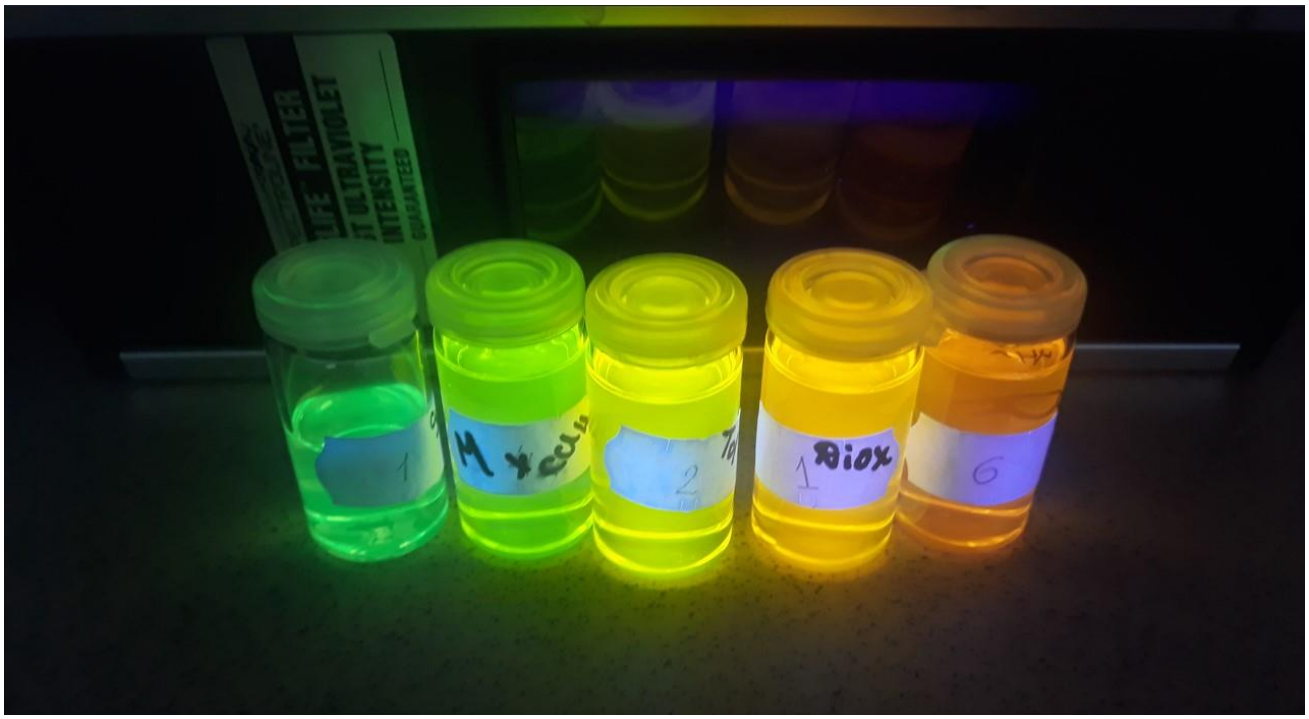

Figure 1. Samples of one of synthesized TAPPs, exhibits large solvatofluorochromism. From left to right in cyclohexane, carbon tetrachloride, toluene, 1,4-dioxane and dichloromethane. Batochromic shift in polar solvents is visible.

References:

[1] Janiga A., Głodkowska-Mrówka E., Gryko D.T., Synthesis and Optical Properties of Tetraaryl-1,4-dihydropyrrolo[3,2-b]pyrroles. *Asian J. Org. Chem.,* Vol. 2, **2013,** 411-415.

Analogous Ni(II) and Pd(II) nitro complexes with a (N,N,O)-donor supporting ligand – structural and photoswitching properties.

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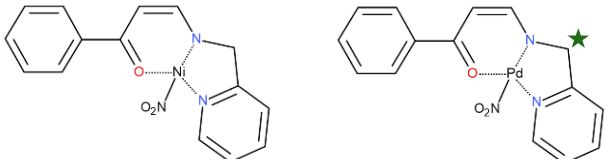
Photo- and thermoswitchable chemical systems can be applied in various fields, e.g.: photovoltaics or photonics. Hence, the primary aim of this project was to examine properties of two new potentially (photo)switchable compounds in the solid state. The N,N,O-donor square complexes with an ambidentate NO_2 ligand bound to the metallic center, **1a-Ni** and **1a-Pd** were synthesized according to the literature procedure [1]. Schematic representation of both studied compounds is shown in Scheme 1 below.



Scheme 1 - Schematic representation of the studied systems.

Crystallization of **1a-Ni** and **1a-Pd** was carried out with the use of various solvents. It turned out that the studied compounds crystallize differently depending on the solvent and crystallization method. In the case of the Pd(II) complex it was possible to obtain solvatomorphs containing DCM or $CHCl_3$ in the crystal structure and also a non-solvent crystal structure when crystallized from ethyl acetate or acetonitrile. Moreover, when crystallized from DMF the carbon atom marked with a green star in *Scheme 1* is oxidized to carbonyl atom. All crystal structures were investigated using single-crystal X-ray diffraction method and profoundly analyzed. Additionally, bulk samples of both complexes were studied using solid-state IR spectroscopy regarding photoswitchable properties. Based on structural examination the Ni(II) system exhibits higher photoswitchable potential which was confirmed by both, the IR spectroscopic and single-crystal X-ray diffraction results [2]. Almost full nitro-to-nitrito photoisomerization occurs with the 530 nm LED light at 100 K. In turn, **1a-Pd** does not exhibit photoswitchable properties in the solid state form.

The Wrocław Centre for Networking and Supercomputing (grant No. 285) is gratefully acknowledged for providing computational facilities. The in-house X-ray diffraction experiments were carried out at the Department of Physics University of Warsaw on Rigaku Oxford Diffraction SuperNova diffractometer which was co-financed by the European Union within the European Regional Development Fund (POIG.02.01.00-14.122/09).

References:

[1] Dabrowski, J.; Krówczyński, A. Ni(II) complexes with bis(β-acylvinyl)amines and (8-quinolyl-β-acylvinyl)amines. *Z. Naturforsch.* **1977**, *32b*, 62– 67

[2] Kamiński, R.; Jarzembska, K.N.; Kutyła, S.E.; Kamiński, M.A. portable light-delivery device for in situ photocrystallografic experimets at home laboratory. J. Appl. Crystallogr. **2016**, 49, 1383-1387.

Waveguide structures for refractive index sensing on a low-cost Silica–Titania optical platform

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In the poster possible integrated optical waveguide structures for refractive index sensing applications on a low-cost Silica-Titania (SiO_2:TiO_2) material platform [1] are proposed and reviewed. Also a preferred fabrication method is given [2]. The presented structures consist of subwavelength grating structures (SWGs) [3], ring resonators (RR) [4] and 1D photonic crystals (1D-PhC) [5]. The possibility of multichannel operation and serial operation is investigated.

References:

[1] Karasiński, P.; Tyszkiewicz, C.; Piramidowicz, R.; Kaźmierczak, A., "Development of integrated photonics based on SiO2:TiO2 sol-gel derived waveguide layers: state of the art, perspectives, prospective applications," Proc. SPIE 11364, Integrated Photonics Platforms: Fundamental Research, Manufacturing and Applications, 1136414 (2 April 2020).

[2] Kazmierczak, A.; Butt, M. A.; Zięba, M.; Tyszkiewicz, C.; Karasiński, P.; Piramidowicz, R., "Towards the most convenient configuration of integrated photonic sensor for implementation in SiO2:TiO2 sol-gel derived waveguide film technology," Proc. SPIE 12139, Optical Sensing and Detection VII, 1213908 (17 May 2022).

[3] Butt, M. A.; Tyszkiewicz, C.; Wojtasik, K.; Karasiński, P.; Kaźmierczak, A.; Piramidowicz, R., "Subwavelength Grating Waveguide Structures Proposed on the Low-Cost Silica–Titania Platform for Optical Filtering and Refractive Index Sensing Applications." International Journal of Molecular Sciences 2022, 23, 6614 .

[4] Butt, M. A.; Kaźmierczak, A.; Tyszkiewicz, C.; Karasiński, P.; Piramidowicz, R., „Mode Sensitivity Exploration of Silica-Titania Waveguide for Refractive Index Sensing Applications.” Sensors. 21. 7452. 2021

[5] Butt, M. A.; Tyszkiewicz, C.; Karasiński, P.; Zięba, M.; Hlushchenko, D.; Baraniecki, T.; Kaźmierczak, A.; Piramidowicz, R.; Guzik, M.; Bachmatiuk, A., "Development of a low-cost silica-titania optical platform for integrated photonics applications," Opt. Express 30, 23678-23694 2022

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