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Foz do Iguaçu - Brazil

PROCEEDINGS OF THE XXII INTERNATIONAL SYMPOSIUM OF BIOLUMINESCENCE & CHEMILUMINESCENCE/ XX INTERNATIONAL SYMPOSIUM OF LUMINESCENCE SPECTROSCOPY

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SUMMARY

ANALYTICAL, CLINICAL AND MEDICAL APPLICATIONS OF LUMINESCENCE

Bioluminescence biosensing platforms for One Health: from paper sensors to thread-based analytical devices

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Bioluminescence (BL) is a fascinating phenomenon in which photons are emitted as byproduct of a chemical reaction occurring in living organisms, including bacteria, fireflies, and several marine species.BL systems possess remarkable features, such as high quantum yield and no need for an external light source, that render them highly valuable bioanalytical tools for developing portable biosensors for monitoring molecules, cells, and bioactivities with applications spanning from agro-food to clinical fields. Therefore, bioluminescent biosensors have a great potential to support the "One Health" approach, to guarantee health to humans, pets, wildlife and our environment. Here we report the development of novel BL tools and strategies which can be used to improve the analytical performance of paper-based smartphone biosensors. BL showed suitable to develop highly sensitive biosensing paper platforms enabling the detection of target analytes down to the ppb levels in complex biological matrices such as environmental and clinical samples. Cell-biosensors, enzyme biosensors and cell-free systems were implemented on paper using the smartphone as detector. The stability of these biosensors has been increased by the obtainment of bio-nanocomposites relying on nanomaterials (metal-organic framework, MOF), thus improving the robustness of the analytical platforms.Moreover, we explored the combination of bioluminescence biosensing with microfluidic thread-based analytical devices (μTADs), which represent a sustainable and low-cost alternative to paper based biosensing, especially to handle very low volumes of samples (less than 5 μl), showing great potential also for multiplex analysis in combination with chemiluminescence. We report a proof-of-principle application of bio-chemiluminescence biosensing on cotton threads and, to prompt future applications in point-of-care and point-of need settings, we exploited smartphone detection enabling easy detection of the bio-chemiluminescent signal directly on the thread. The implementation of artificial intelligence (AI) algorithms to smartphone-based bioluminescence detection is also reported for the first time. We developed a paper-based

toxicity smartphone biosensor which provides, thanks to an Android AI mobile app, quantitative and user-friendly information.

Keywords: bioluminescence, paper biosensor, smartphone, artificial intelligence, microfluidic thread-based analytical devices

Autoluminescence in germination - applications

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Living beings do spontaneously emit (ultra-weak) light in the visible range whose parameters can be related to the metabolic state and/or environment perturbations. By using dedicated photon-counting chambers, the germination of seedlings can be monitored in real time, non-invasive, with applications in agronomy, toxicology and chronobiology to be explored. We will present some ofthe LaFA/FT-UNICAMP results in these area, with brief view of other goals of our group.The sources of biological auto-luminesnce (BAL) in seedlings can be found, as in other organisms, among the by-products of the metabolic activity where reactive chemical species take part, mainly the ones involving radical-oxygen species (ROS) that are electronically excited, and that can occur inside living cells and tissues, such as triplet excited carbonyls and singlet oxygen species, most released during enzymatic reactions. ROS would react with biomolecules and give unstable intermediates as results – such as dioxetanes and tetroxides – that further would form triplet excited carbonyls and/or singlet oxygen, in forms able to further emit photons in the visible range. In effect, BAL occurs for organisms evolving under normal, optimal conditions as well as in response to chronic or acute stressing conditions, physical or chemical.

Keywords: luminescence, germination, toxicology

BESIDES: a lab-in-space for life biomarkers detection in astrobiology investigations

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The search for biomolecules thought to be biomarkers of life is a topic of increasing scientific interest in the field of astrobiology, especially now that the exploration of the Solar System has gained further momentum. At present, significant ambiguities remain in the identification of specific organic chemical species with currently widely used in situ detection methods (i.e., mass spectrometry). The goal of the BESIDES (BiomolEcular SIgnature DEtection System) project, funded by the Italian Space Agency (ASI), is to develop a highly integrated multiparametric miniaturized platform to be used in future planetary exploration missions. BESIDES offers the *in-situ* analysis of organic molecules with state-of-the-art analytical techniques for the specific detection of target molecules.BESIDES leverages Lab-on-Chip technology and uses natural and artificial recognition elements to detect biogenic compounds. The payload will integrate in a single Lab-on-Chip 1) a microfluidic network for handling analytes and reagents; 2) a set of detection sites dedicated to immuno-, enzyme- and nanoMIP (nano Molecular Imprinted Polymers)-based assays, which exploit magnetic microspheres as a solid phase and bio/chemiluminescence (BL/CL) detection; 3) an array of hydrogenated amorphous silicon (a-Si:H) thin-film photosensors for the detection of the BL/CL analytical signal. The BESIDES analytical system also includes signal read-out electronics characterized by a high signal-to-noise ratio, a control subsystem and auxiliary subsystems for sample and

reagent dispensing, the user interface for system control, programming and data management.Bio/Chemiluminescence is recognized as a very advantageous detection technique for Lab-on-Chip devices, offering high detection in small volumes, high specificity, and simple instrumental requirements. In addition, exploitation of magnetic beads as a solid phase to perform analyses provides, compared to the more conventional approach of immobilizing the recognition elements in microfluidic channels, the advantage of making the system reusable in order to perform a greater number of analysis cycles. The proposed analytical approach has a unique ability to exploit specific antibodies, enzymes, and nanoMIPs to selectively recognize structurally related target molecules, extracted from the samples of interest, to provide a powerful tool for the sensitive and multiplex detection of organic molecules of biological origin (e.g., nucleotides, proteins, alkaloids, lipids and pigments), of fundamental importance for the confirmation of present or past life on a planet (or planetary body).

Keywords: Lab-on-Chip, Microfluidics, Life biomarkers, Multiplex bioassays

Bile Salt Hydrolase: a new effect-based bioluminescent fecal bioassay at the crossroads between gut microbiota and human health

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Bile salt hydrolases (BSH) are a family of microbial enzymes that play important roles in a wide range of host metabolic processes. They catalyze the hydrolysis of amide bonds in conjugated primary bile acids (BAs), resulting in the release of free amino acids (glycine or taurine) and deconjugated primary BAs. Once deconjugated, free primary BAs can be metabolized to secondary BAs, involved in different intestinal pathologies such as colorectal cancer (CRC). To uncover BSH abundance and its activity in the gut microbiota, a few methods such as biochemical assays and metagenomic analysis are currently used; however, these approaches have several limitations. In this context, we developed a rapid and cost-effective bioluminescence (BL) bioassay for the screening of BSH activity in human feces using an amino luciferin" caged" with the primary BA chenodeoxycholic acid (aLuc-CDCA), thus mimicking the conjugated CDCA with glycine [1]. Since aLuc- CDCA isn't a substrate for the luciferase enzyme being "caged" by the amidation, the reaction occurs after the BSH-catalyzed hydrolysis that allows the release of the "free" amino luciferin that in turn induces the BL reaction in the presence of luciferase and ATP. Firstly, we investigated *in vitro* the deconjugation level of aLuc-CDCA (50 µM) in the presence of pure BSH (range 0-10 µg/mL) using different exposure times (15, 30, and 60 min) at 37°C. The BL reaction was triggered, adding in the solution the firefly luciferase (0.5 mg/mL) in Tris-HCl 0.1 mM, pH 7.5, supplemented with Mg_2SO_4 (80 mM) and ATP (40 mM). Kinetic profiles showed a linear correlation between BL emission intensity and increased amount of BSH, with an R^2 of 0.92

after 60 min of incubation (LOD:0.8 µg/mL; LOQ: 1.6 µg/mL). Next, we moved to real human feces, but the light output decreased markedly probably due to interferents in the fecal material that affect the luciferase activity. To address this issue, we exploited the possibility of using a whole cell-based BL assay in which human colorectal adenocarcinoma cells (Caco2) genetically encoded with a firefly luciferase (*Amydetes vivianii*), were exposed to solutions containing aLuc-CDCA (50 µM) previously incubated with pure BSH (range 0-100 µg/mL) for 60 min at 37°C. This approach enables the protection of the luciferase enzyme by cell membranes, obtaining a good correlation between BL signal intensity and BSH amount with a LOD of 2.6 µg/mL. As a proof of concept, the whole cell-based assay has been successfully employed for quantifying BSH activity in intact fecal stools (1mg/1ml) obtained from healthy volunteers and patients with adenoma and CRC diagnosis, thus demonstrating the possibility of using BSH as a potential biomarker for CRC prevention and treatment.*1. Roda, A. et al. Chemosensors 2021, 9(6), 122.*

Keywords: caged-amino Luciferin, bile salt hydrolase (BSH), bile acids, gut microbiota, fecal samples

Bioluminescence for the Screening of Colon Cancer: the role of Notch signaling and the gut microbiota

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Colorectal cancer (CRC) is the second cause of death due to cancer worldwide and its incidence is estimated to increase by 60% in 2030 in developing countries. The stage at diagnosis is the most important indicator of survival, so predictive biomarkers are highly demanded. Recent studies suggest a pivotal role of epigenetic factors, such as "aberrant" Notch signaling activation and secondary bile acids (BAs) formation. To evaluate Notch signaling activation, a recombinant protein that combines the extracellular domain (ECD) of the Notch high affinity mutated form of the selective Notch ligand Jagged 1 (Jag1) with a Red emitting firefly luciferase (FLuc) was developed to understand if Jag1-FLuc binding with Notch correlates with CRC progression. Once a good linear correlation between the BL signal and the concentration of Jag1-FLuc protein was obtained up to 10 µg/mL in a cell-free system, we moved on to human colorectal adenocarcinoma cells Caco-2. Under the optimized conditions, we observed that BL signal increase was proportional to the Notch expression, with a linear range from 0.1 to 50 µg/mL of Jag1-FLuc obtaining a LOD and LOQ of 0.8 ± 0.2 and 6.0 ± 0.2 µg /mL, respectively. Next, BLI experiments were performed to examine the light output of Jag1-FLuc construct on Caco-2 cells and ex vivo on human biopsies derived from patients with different pre-CRC stages. Secondary BAs derive from the hydrolysis of amide bonds in conjugated primary BAs as a first step, a reaction catalyzed by microbial bile salt hydrolases (BSH) enzymes in gut microbiota. To uncover BSH abundance and its activity in human stools, we developed an

effect-based BL bioassay based on an amino luciferin" caged" with chenodeoxycholic acid (aLuc-CDCA), thus mimicking the conjugated primary BA with glycine. Since the reaction occurs after the BSH-catalyzed hydrolysis that allows the release of the "free" amino luciferin, we investigated in vitro the deconjugation level of aLuc-CDCA (50 µM) in the presence of pure BSH (range 0-10 µg/mL) using different exposure times at 37°C. Kinetic profiles showed a good linear correlation between BL emission intensity and increased amount of BSH, after 60 min of incubation (LOD:0.8 µg/mL; LOQ: 1.6 µg/mL). To overcome the decrease in light output due to interferents in fecal matrices, we then exploited the possibility of using a whole cell-based BL assay in which Caco2 cells were genetically encoded with the firefly luciferase Amydetes Vivianii. This approach enables the protection of the luciferase by cell membranes, obtaining a good correlation between BL signal intensity and BSH amount with a LOD of 2.6 µg/mL, and has been successfully employed for quantifying BSH in human stools. These effect-based BL bioassays can represent new tools for the screening of pre-neoplastic CRC lesions and possible therapeutic approaches.

Keywords: Bioluminescence; Recombinant protein; Notch pathway; Colorectal cancer; Imaging, "caged" amino luciferin, bile salt hydrolase, bile acids, gut microbiota

Bioluminescence in Point-of-Care Diagnostics

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This presentation will focus on the design and development of bioluminescence-based point-of-care diagnostics methods. Specifically, we will discuss laboratory methods, as well as point-of-care (POC) testing that have been developed by us based on the bioluminescence detection principle. These diagnostic methods are designed for monitoring infectious diseases. Examples of POC methods employed to address an unmet need regarding the diagnosis of urinary tract infection (UTI) - antimicrobial resistance (AMR) and COVID-19 will be discussed. Emphasis will be on the simple design principles and improving the performance/stability of bioluminescent proteins to enhance their utility in POC method development. Rapid bioluminescence assays were developed and evaluated for the detection of UTI using intact lyophilized cells of *Photobacterium leiognathi* ATCC 33981™. Further, using ATP-based assay antimicrobial resistance was detected. UTI-AMR detection was performed using a microtiter-based, hand-held luminometer, and POC adaptor-cartridge-based detection. To improve the usage of bioluminescent reporters in POC devices, we prepared an encapsulated, stable bioluminescent fusion protein, Tamavidin-Gaussia luciferase (TA2-Gluc) in a ZIF-8 metal-organic framework (MOF). Tamavidin-2 is a group of avidin-like high-affinity biotin-binding protein and Gluc is a small *Renilla-type* luciferase that yields high bioluminescent intensity. This bioluminescent reporter produces light upon the addition of the substrate coelenterazine. We evaluated the stability of the ZIF-8 encapsulated TA2-GLuc at various temperatures (25° C, 4° C, and room temperature) and demonstrated that we can preserve this fusion protein in all of the tested temperatures for at least 6 months. Further, we designed a highly sensitive bioluminescent assay for detecting the SARS-CoV-2 spike antigen using ZIF-8 encapsulated TA2-Gluc.

Keywords: Bioluminescence, diagnostics methods, SARS-CoV-2

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Construction of self-powered nanomotors and its application

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We report here the concept and operation of a self-powered, target-triggered DNA motor constructed by engineering a DNAzyme to adapt into binding-induced DNA assembly. Binding of a target molecule to the two ligands induced hybridization between the DNAzyme and its substrate on the AuNP that are otherwise unable to spontaneously hybridize. The binding-induced association of the DNAzyme with the substrate on the AuNP activated the DNAzyme, initiating the cleavage of the substrate and the autonomous movement of the DNAzyme along the tracks on the AuNP. A simple addition or depletion of the cofactor Mg^{2+} enabled fine control of the DNAzyme motor. A single binding event resulted in the movement of the motor by more than one hundred steps. The binding-induced association of the DNAzyme with the substrate on the AuNP activated the DNAzyme, initiating the cleavage of the substrate and the autonomous movement of the DNAzyme along the tracks on the AuNP. A simple addition or depletion of the cofactor Mg^{2+} enabled fine control of the DNAzyme motor. A single binding event resulted in the movement of the motor by more than one hundred steps. Simply altering the ligands enabled the motor to specifically respond to any target proteins, DNA or MiroRNA.

Keywords: nanomotors, DNAzyme, proteins, AuNP

Engineering and biocatalysis of luciferases and related systems for sustainability

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Our group interests are in the broad areas of enzyme catalysis, enzyme engineering, systems biocatalysis, metabolic engineering and synthetic biology. This talk will highlight our contributions on creation of new luciferins and luciferases using enzyme engineering and biocatalysis approach. The first topic is the development of Flavin Luciferase from Vibrio campbellii (Vc) for Mammalian Cell Expression (FLUXVc) by engineering luciferase from Vibrio campbellii (the most thermostable bacterial luciferase reported to date) and optimizing its expression and reporter assays in mammalian cells which can improve the bioluminescence light output by >400-fold as compared to the non-engineered version. We found that the FLUXVc reporter gene can be overexpressed in various cell lines and showed outstanding signal-to-background in HepG2 cells. The second topic is the use of rational and computer-assisted protein engineering approach to enhance Fluc stability. We successfully generated two thermostable variants of Fluc with superior biochemical properties than the wild-type enzyme. These variants could be expressed in HEK293T and exhibited greater light signals than that of the native enzyme. For the last topic, we will discuss enzymatic cascades employing flavin-dependent dehalogenase or monooxygenases to catatalyze one-pot reactions to synthesize various new luciferins. We have developed Luminescence-related Method for Specific detection (LUMOS) which can be used for detection of pesticides and metabolites of pesticides in food, environmental, and biological samples called. LUMOS technology provides high sensitivity of detection in a range of ppt levels with the accuracy comparable to the gold standard methods of using HPLC-MS. We have used LUMOS technology in local communities

in northern Thailand as a surveillance tool to detect pesticide contamination in food and environmental samples.

Keywords: luciferase, luciferin, luminescence, pesticide, enzyme engineering

Engineering of firefly luciferase for cell line-based applications

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Firefly luciferase (Fluc) is widely used as bioreporter genes for monitoring gene expression or studying cellular signaling in living cells or organisms. However, Fluc is not very stable upon a long-term storage. In this work, we employed rational and computer-assisted protein engineering approach to enhance Fluc stability. We successfully generated two thermostable variants of Fluc, exhibiting enhanced half-lives ($t_{1/2}$) at 37 ^{o}C. Specifically, for VISTEC1, the improvement is 3.5-fold compared to the native enzymes, while for VISTEC, it is 2.8-fold. The two variants which showed superior biochemical properties than the wild-type enzyme could be expressed in HEK293T and exhibited greater light signals than that of the native enzyme, up to 4.2-fold compared to the native Fluc. Furthermore, we also demonstrated the use of engineered Fluc as cell-line bioreporter applications to measure inhibitors and activators activities of the cell signalling pathways. Therefore, our results indicate that these variants with improved properties are suitable for applications as reporter genes in mammalian cells.

Keywords: Firefly luciferase; Thermostability; Protein engineering; Reporter genes; Cell signaling

Enhancing Targeted Drug Delivery Systems through the Integration of BODIPY Fluorescent Probes in Nanocomposites for Theranostic Applications in Lung Cancer

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Introduction: BODIPY (boron-dipyrromethene) fluorescent dyes represent a versatile class of molecules that have significantly impacted various fields, including biotechnology, materials science, and chemical biology. In drug delivery systems, conjugating BODIPY dyes to carriers enables the monitoring of drug release kinetics, intracellular transport, and enhances the overall efficiency and specificity of drug delivery. **Objective:** Improve a nanocomposite with fluorescent probe BODIPY as a theranostic tool for lung cancer. **Materials and Methods:** The synthesis of the BODIPY nucleus starts with an aldehyde precursor. Following three reaction steps involving oxidation and complexation, the BODIPY nucleus is achieved with an overall yield ranging from 40% to 45%. Large unilamellar vesicles (LUV), composed of 1-palmitoyl-2-oleoyl-glycero-3-phosphocholine (POPC), a negatively charged lipid 1-palmitoyl-2-oleoyl-sn-glycero-3-phospho-(1'-rac-glycerol) (POPG), and cholesterol (Chol) were prepared by extrusion through polycarbonate filters. Dynamic Light Scattering Measured LUVs diameter and zeta potential in a Zetasizer Nano 317. The iron oxide nanoparticles, and the aptamers were prepared using standard procedures. Fluorescence was measured in a Hitachi F 7000 fluorimeter. internalization of bodipy in cells was observed using an EVOS FLoid Imaging System. The toxicity of the compounds was determined by MTT assay in HL60 cells. **Results:** The integration of BODIPY fluorescent into liposomes was assessed using fluorescence analysis. The fluorescence spectra of BODIPY (excited at 440nm) exhibited a peak at 515nm. Upon addition of LUV (large unilamellar vesicles), the emission intensity increased without altering the peak wavelength. This observation confirmed the interaction between LUV and BODIPY, enabling the generation of binding isotherms for this interaction. The internalization of BODIPY into HL-60 cells was evaluated, demonstrating that both free BODIPY and BODIPY conjugated to liposomes were capable of internalizing into the cells. Liposomes and BODIPY, at concentrations of 20mM and 0.01mM, respectively, did not exhibit toxicity after

48 hours of incubation with cells. Furthermore, when all four components were combined at the same concentrations, no toxicity was observed for HL-60 cells. **Conclusion:** our work has resulted in the successful development of a stable nanocomposite equipped with an embedded fluorescent probe. This achievement holds great potential as a versatile theranostic tool.

Keywords: Bodipy; Liposome; Theranostic.

Firefly luciferase implication in discrimination of programed cell death modalities

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Programed cell death modalities like apoptosis, pyroptosis and necroptosis are crucial for homeostasis and implicated in several human disorders like cancer and neurodegenerative diseases. Development of high-throughput assays which evaluate distinct cell death modalities are critical to identify potential therapeutic agents that control these cellular responses. Split luciferase complementary assays have been widely developed for assessing protein- protein interactions (PPI) in regulated cell death due to their simplicity, sensitivity, and known chemistry. Split luciferase reconstitution assays have been used to probe role of Apaf-1 structure and the regulation of apoptosome formation in apoptosis. Similar approaches were used to probe the interactions of NLRP3 and ASC in inflammasome formation, which occur in pyroptosis, as well as components of necrosome complex involved in necroptosis. Multiplex bioluminescence platforms which simultaneously distinguish between the various cell death phenomena will be discussed. We also highlight the recent technological achievements of bioluminescent tools within European Commission granted networks (EPIC and VIDEC).

Keywords: Luciferase, Cell death, Split luciferase, Apoptosome, Inflammasome

Luminescence spectroscopy of lanthanides in selected inorganic nanomaterials and its innovative applications

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Luminescent nanomaterials doped with lanthanide ions have attracted considerable attention and due to their unique properties allow for applications in various areas, e.g. optoelectronics, display panels, solar cells, sensors. This lecture presents selected nanomaterials based on inorganic matrices (e.g.: fluorides, vanadates, borates, etc.) doped with luminescent lanthanide (Ln) ions, characterized by efficient emission properties. As application materials, they show: phase purity, high crystallinity and homogeneity, small particle size and narrow particle size distribution, and should not be agglomerated. Examples of effective nanoluminophores (NL) and up-converting (UCNL) doped with Ln^{3+} (or Ln^{2+}) ions and their surface functionalized, by coting with organic compounds, hybrid systems for sensing and analytical applications are discussed in detail. Nanoparticles (NPs) functionalized with organic compounds have proven to be very useful for analytical and biomedical and purposes. We have developed new highly sensitive and highly selective fluorescence methods [1-2] based on energy transfer from the analyte ion to the Tb^{3+} ion, or Eu^{3+} ion NPs for the (sensing) determination of metal species (e.g. Cu^{2+}, Al^{3+}) in real water samples. The presentation shows and discusses examples of effective luminescent nanoparticles doped with Ln^{3+} (Tb^{3+} or Eu^{3+}) ions in systems functionalized with the desired organic ligand molecules, e.g.: LaF_3: Tb^{3+}, Ce^{3+} @SiO_2-NH_2 nanoparticles with acetylsalicylic acid (aspirin) coated on the surface [3], or ligand sensitized: 2,6-Pyridine dicarboxylic acid capped-LaF_3:Eu^{3+} and adenosine capped-SrF_2:Eu^{3+} nanoparticles (NPs) [3], showed high hemocompatibility and therefore can be successfully used in biomedical research. In this lecture also present examples of selected Ln-doped NLs or UCNLs that can be successfully used as optical sensors, capable of measuring temperature and/or pressure for (nano)-thermometry or/and (nano)-manometry [4]. **References** [1] V. N K.

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Keywords: luminescence, lanthanides, nanoluminophores, sensing, analytical and biomedical applications

Novel Luciferins synthesis and their applications for pesticide detection

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Pesticide contamination in food and environment is a major problem in Thailand and many countries around the world because it can cause long-term negative effects on human health. We have developed an enzymatic cascade reaction to degrade various pesticides and change them into firefly luciferin derivatives (~51% yield) which are widely used in detection applications. We have shown that the bioluminescence of novel luciferins is red-shifted with maximum emission at 663 nm (5',7'-dimethoxy luciferin, 5',7'-DiOMeLH$_2$). Reactions of 5'-methyl luciferin (5'-MeLH$_2$) and 5',7'-dimethyl luciferin (5',7'-DiMeLH$_2$) with various beetle luciferases provide higher light intensity than that of natural D-luciferin. Remarkably, the novel 5',7'-DiOMeLH$_2$ and 5',7'-DiMeLH$_2$ give steadily light emission with a slower rate of light decay (3.2-fold) than D-luciferin. These novel luciferins thus can provide substantially stronger bioluminescence that the natural D-luciferin, making them useful and suitable for various applications including real-time bioluminescence imaging. Moreover, we have developed the enzymatic reaction to detect pesticide contamination in food, environmental, and biological samples called Luminescence-related Method for Specific detection (LUMOS). LUMOS technology provides high sensitivity of detection in a range of ppt levels with the accuracy comparable to the gold standard methods of using HPLC-MS. We have used LUMOS technology in local communities in northern Thailand as a surveillance tool to detect pesticide contamination in food and environmental samples.

Keywords: bioluminescence, luciferin, luciferase, pesticide, environment, analytical

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Keywords: bioluminescence, luciferin, luciferase, pesticide, environment, analytical

Portable luminescence-based biosensors for space health science and astrobiology applications

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NASA currently has plans to return humans on the Moon and eventually land crewed missions on Mars. However, these challenging goals are unachievable unless we can ensure the safety and health of the astronaut crew and other terrestrial biology on those missions. Biosensors can play several roles in this context, such as evaluating astronauts' health, monitoring environmental and food safety, assessing the impact of deep space conditions on biological systems, and investigating the traces of past or present life in extra-terrestrial environments, thus evaluating their potential habitability.Chemiluminescence (CL)-based biosensors are a very promising approach, offering high specificity and detectability, and amenability to miniaturization. In addition, the increasing development of extremely compact systems relying on microfluidics, commonly known as lab-on-chip devices, has gained much attention thanks to their favourable characteristics in terms of reduced size and weight, very low sample and reagent consumption, reduced analysis time and, often, superior achievable performances in terms of limits-of-detection. Chemiluminescence-based lab-on-chip devices are extremely suitable for space missions. The recent and ongoing research activity in the development of CL-based lab-on-chip devices for space life science investigations will be presented. An integrated, easy-to-use, and portable analytical instrumentation is under development and will be tested onboard the International Space Station (ISS) for the CL immunoassay-based analysis of salivary biomarkers of immune system impairment in astronauts. Furthermore, autonomous analytical platforms are being developed, suitable for CubeSat missions, aimed at evaluating the combined effect of microgravity and ionising radiation on prokaryotic and eukaryotic bioluminescent cells and on fluorescent microbial biofilms. Additional activity regards the development of a CL lab-on-chip-based autonomous device, suitable searching of past and present life in robotic and human space exploration missions, based on the enzyme-, antibody- or molecular imprinted polymer-mediated recognition of organic molecules and molecular biosignatures related to the processes of life.The highly interdisciplinary activity performed in collaboration with several Italian and European institutions and companies will be presented.

The strengths and future development opportunities for CL biosensors in Space life science applications will be highlighted.The ALCYONE project is supported by the European Union's Horizon Europe programme under grant agreement No. 101082679; the APHRODITE project is supported by the Italian Space Agency (ASI) through the Contract n. 2021-4-R.0, (CUP F35F21002690005, CIG 850065633F); the BESIDES project is supported by ASI through the Contract n. 2023-3-E.0 (CUP F43D23000130005); the BOREALIS project is supported by ASI through the Contract n. 2024-2-I.0 (CUP F33C24000040005, (CIG A0277F7460).

Keywords: Chemiluminescence; Bioluminescence; Lab-on-chip; Astrobiology

Smartphone-based bioluminescent tissue on-a-chip for multiplexed biosensing

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Living cells used as sensing systems have proved to be valuable tools for prediction of the physiological response to drugs, chemicals, and samples in complex matrices, which toxic effects and specific biological activities can be evaluated in a straightfo rward manner. Thanks to their predictivity, 3D cell models (i.e. spheroids, organoids and microtissues) are replacing conventional 2D cell cultures, enabling to recapitulate the extracellular matrix and cell cell interactions, creating an architecture that reflects native morphology of organs and tumors. Bioluminescent reporter assays represent the gold standard for high throughput screening assays employed in drug discovery and BL proteins showed a formidable tool for elucidating the biological mechanisms underlying morphogenetic and pathogenetic processes and for unravelling molecular pathways involved in the etiopathogenesis of several diseases.According to the three key pillars of the organ on a chip technology, we developed a bioluminescent tissue on a chip with different cell lines (i.e., human embryonic kidney (HEK293T), human cervical cancer (HeLA)) genetically engineered with newly developed luciferase mutants emitting at different wavelengths and characterized by high stability, implemented in a mi crofluidic system for multiplexed biosensing. Thanks to 3D printing technology a cell cartridge and an adaptor were developed to provide a mini dark box interfaced with portable light detectors for BL signal acquisition.The proposed biosensing platform could become a useful tool for multiple bioactivity analysis, for on-site screening of toxic substances, prioritizing samples for more accurate chemical analyses.

Keywords: bioluminescence, 3D models, tissue-on-a-chip, smartphone-based biosensor

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THE NICHE ROLE OF ANALYTICAL BIO-CHEMILUMINESCENCE FOR PLANETARY HEALTH

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Several holistic and interdisciplinary approaches exist to safeguard health and the most influential concepts are One Health evolving to Planetary Health. These approaches promote the underlying assumption of humans and other animals sharing the same planet and the same environmental challenges. The diagnostic devices representing 70-80% of healthcare decisions produce waste accounts for a tenth of all medical waste. Billions of lateral flow tests have been used worldwide during the COVID-19 pandemic. Single-use, disposable, point-of-care diagnostic devices carry great promise for planetary health, including meeting urgent needs for testing and diagnosis in places, usually under developing Countries with limited laboratory facilities. Point-of-care (POCT)devices are manufactured from unsustainable polymeric materials derived from fossil sources. Yet, in the absence of government regulatory frameworks, safe and sustainable waste management for these medical devices is often left unaddressed. We propose solutions available to point-of-care test developers to start embedding sustainability at an early stage in their design, and to reduce their non-renewable plastic consumption. On the frame of eco-sustainability, as a proof of concept, I will present portable cellulose based device including LFIA characterized by extremely simplicity and robustness, with no power source, electronics, miniaturized to minimize reagents and chemicals, easily to use and at low cost. Chemiluminescence based tests are the more popular in clinical chemistry automated analyzer demonstrating the exceptional performance of the CL based detection using different system i.e. acridinium esters, (iso)uminol. as a labels. CL offers combination of high detectability with fast, accurate and simple instrumentation. The technology transfer from clinical setting to POCT or lab on a chip demonstrated a high analytical performance not fully paralleled by commercial success. The principle of the device is the same of a LFIA , but nitrocellulose and the other pads are replaced by a single cellulose paper and the immunoreagents , The size of the strip is further miniaturized i.e. 2X80 mm . The sample (2-5ul) is added like in LFIA device and travel along the paper pad by capillarity. In the test and

control area the CL reagent absorbed on a paper pad are over posed for the CL reaction. Under the pad is placed in contact a light sensitive instant film Fuji or Polaroid or mini self-developing dental film for X ray radiography which are highly sensitive also to light and require a simple pull on the top to start the instant developing process. Using this analogic approach, we eliminate the use of electronics, CMOS, and power supply. The detectability of the used film is similar to conventional smartphone CMOS with B/W or color detection. So no micropumps, microfluidics and the reagent movement is driven and controlled by capillarity according the structure of the material used. In the case of CRET or BRET on multiplex test format with different luciferases the color film offer a quite useful opportunities . If instruments were adapted or redesigned to operate with smaller volumes of blood, it would result in a corresponding reduction in the amount of reagent required. Multiplex format are consider particularly for simultaneous detection of biomarkers in man, animal and environment including air particulate and soil.

Keywords: One health, analytical chemiluminescence, biosensors, sustainability

Functionalized nitrogen and lanthanides co-doped carbon dots with strong photoluminescence for cellular bioimaging

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Metal–organic frameworks (MOFs), also known as porous coordination polymers, are innovative functional materials characterized by a wide variety of framework architectures. Among them, nanoMOFs have emerged as nanomaterials with nanosized pores that can be significantly modified due to confinement and chain extension, improving physical and chemical properties when compared with bulk materials. For analytical chemistry, the synthesis of nanoMOFs with controllable pore size, structure and luminescent properties has driven to the development of novelty sensing platforms. The specific pore size and host-guest interaction ensure the selectivity of the designed sensor to detect small molecules or metals [1]. These excellent properties, the possibility to be used in membranes technology and their low toxicity are the main driven forces towards the development of nano-MOFs based food sensors. In this regard, food safety is one of the most concerning issues at this time. Food degradation during storage and commercialization in terms of microbiological and physicochemical properties is quite variable, it depends of the conservation procedure and type of food. Some compounds, that can be used as degradation markers, are biogenic amines (BAs). BAs appear because of the metabolic activities of microorganisms in food and they can be present in all types of foods with high protein or free amino acid content, such as fish, meat or wines [2].As stated before, the combination of nanoMOFs properties and and amines as food safety markers could be an alternative in the development of non-invasive sensors to be implemented in smart packaging. In this work, we have designed and tested a luminiscent based Cu-nanoMOF to detect and quantify Biogenic Amines (BAs) in food. This alternative will be evaluated as a food safety strategy to be included in smart packages. This proposal try to develop a luminescent nano-MOF to detect volatile BAs. For this purpose, the changes in luminescence properties of the fluorescent copper MOF (CuDOBCD) when exposed to different amines, including cadaverine and putrescine, have been studied. The optical behaviour of the nano MOFs varies depending on the amine, and a fluorescence quenching is observed at different reaction times, making

possible the design of a "turn off" and non-invasive fluorescence sensor. PVC and Cu nano-MOF membranes were designed and after exposing these nanoMOF membranes to different BAs colourimetric changes (from green to brown) and fluorescence quenching were observed. After chemical development a portable and miniaturized device has been tested to confirm food safety status in field.

Keywords: Carbon Dots, Fluorescence; Bioimaging, Multimodal imaging

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Lanmodulin as a Novel Reagent for Lanthanide-Based Diagnostics

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Lanthanides have unique luminescence properties with sharp emission bands and long luminescence lifetimes. Lanmodulin, (LanM) is a newly discovered protein that binds to lanthanides in the picomolar range, making it ideal as a reagent in the development of imaging technologies. To image the cancerous tissues that are well discerned from the rest of the body, the contrast agent must preferentially concentrate in the cancerous tissue. This can be achieved using tumor specific targeting moieties. We have used lanmodulin along with a tumor-specific targeting moiety as a tool for cancer imaging. Specifically, we have designed a diagnostic test for $HER2^+$ breast cancer by employing a human epidermal group factor receptor 2 (HER2)-specific antibody mimetic fused to lanmodulin as the imaging reagent that targets and binds the HER2 receptors, which are overexpressed in $HER2^+$ breast cancer. For this purpose, we prepared a novel fusion protein, DARPin/LanM, by genetically fusing the gene for the HER2-specific designed ankyrin repeat protein (DARPin) to the gene for lanmodulin. HER2 negative and positive breast cancer cell lines were studied to assess the targeting ability of the DARPin/LanM reagent and its toxicity. We envision that our newly developed reagent has the potential to be translated into a series of nanomedicine diagnostic tools and find applications both in in vitro diagnostics and in vivo imaging technologies.

Keywords: Lanmodulin, diagnostics, imaging

Nano Metal-Organic Frameworks based Fluorescent sensors for food freshness control

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Metal–organic frameworks (MOFs), also known as porous coordination polymers, are innovative functional materials characterized by a wide variety of framework architectures. Among them, nanoMOFs have emerged as nanomaterials with nanosized pores that can be significantly modified due to confinement and chain extension, improving physical and chemical properties when compared with bulk materials. For analytical chemistry, the synthesis of nanoMOFs with controllable pore size, structure and luminescent properties has driven to the development of novelty sensing platforms. The specific pore size and host-guest interaction ensure the selectivity of the designed sensor to detect small molecules or metals [1]. These excellent properties, the possibility to be used in membranes technology and their low toxicity are the main driven forces towards the development of nano-MOFs based food sensors. In this regard, food safety is one of the most concerning issues at this time. Food degradation during storage and commercialization in terms of microbiological and physicochemical properties is quite variable, it depends of the conservation procedure and type of food. Some compounds, that can be used as degradation markers, are biogenic amines (BAs). BAs appear because of the metabolic activities of microorganisms in food and they can be present in all types of foods with high protein or free amino acid content, such as fish, meat or wines [2].As stated before, the combination of nanoMOFs properties and and amines as food safety markers could be an alternative in the development of non-invasive sensors to be implemented in smart packaging. In this work, we have designed and tested a luminiscent based Cu-nanoMOF to detect and quantify Biogenic Amines (BAs) in food. This alternative will be evaluated as a food safety strategy to be included in smart packages. This proposal try to develop a luminescent nano-MOF to detect volatile BAs. For this purpose, the changes in luminescence properties of the fluorescent copper MOF (CuDOBCD) when exposed to different amines, including cadaverine and putrescine, have been studied. The optical behaviour of the nano MOFs varies depending on the amine, and a fluorescence quenching is observed at different reaction times, making

possible the design of a "turn off" and non-invasive fluorescence sensor. PVC and Cu nano-MOF membranes were designed and after exposing these nanoMOF membranes to different BAs colourimetric changes (from green to brown) and fluorescence quenching were observed. After chemical development a portable and miniaturized device has been tested to confirm food safety status in field.References[1] Liu Y., et al.., Strategies to fabricate metal–organic framework (MOF)-based luminescent sensing platforms, Journal of Materials Chemistry C, 2019, 7(35),10743-10763. http://dx.doi.org/10.1039/C9TC03208[2] Wunderlichová, L. *et al.* Formation, degradation, and detoxification of putrescine by foodborne bacteria: a review. Comprehensive Reviews in Food Science and Food Safety, 2014,13(5), 1012-1030. https://doi.org/10.1111/1541-4337.12099

Keywords: food safety, quenching luminiscence, nanomaterials

Photodithazine-nanoclay composites to improve antimicrobial activity.

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Advanced nanomaterials for drug delivery systems are the main focus of numerous research groups and, its application on drug resistance problem is probably the biggest challenged faced by scientists in the field. Indeed, in 2018, WHO declared the antimicrobial resistance as '(…) *one of the top 10 global public health threats facing humanity*', along with a similar problem in cancer treatment: the chemotherapeutic drug resistant cells. In both cases, photoinactivation systems and photodynamic therapy (PDT) can overcome the problem of drug resistance when compared to the traditional approaches. For PDT, which has been shown to be efficient against some Gram (-) and (+) bacteria, more robust and efficient molecules that can act as photosensitizers (PS) are still needed for the improvement of the technique. In this work, the second-generation PS derived from chlorophyll, photodithazine (PDZ), was submitted to a set of physiochemical variations (pH 2, 5, 7 and 10, and concentrations of 2.5, 6, 12, 16, 22, and 25 µg/mL) to promote new aggregation states with the aim of improving its antimicrobial activity. The aggregated states of PDZ were characterized by photoluminescence and photoluminescence excitation spectroscopies, showing different conformations at basic and at acidic pH, but not changing significantly with the increase in concentration. The acidic forms, which showed higher activity against both bacterial strains, were used to build composites with halloysite nanoclays, which showed a significant improvement in antimicrobial activity against *S. aureus* and decreased the growing rate of *E. coli* cells. The effect of the composites will be discussed in light of the photophysical behavior of PDZ and the near field effect.

Keywords: PDI, Nanoclays, photoluminescence

Photophysics stability of gold nanoparticles as membrane markers.

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Metallic nanoparticles involve metallic atoms arranged in a way that distinct and very interesting characteristics, such as specific electronic structure (local density of states) and quantum confinement properties, will appear, enabling their use in the most varied applications, from drug delivery systems to membrane markers. The development of biomaterials based on metallic nanoparticles for makes it possible to combine the properties of the biomolecule of interest with properties of the nanoparticles, going from modifications in thermal and mechanical characteristics (when incorporated into polymeric matrices), up to changes in the aggregation states, photophysical properties, biocompatibility, non-toxicity, and transport of molecules of interest for controlled release. However, for these devices to be efficient, it is essential that the development of biomaterials is carried out in such a way that neither the nanoparticle manufacturing processes nor the strategies for incorporating the biomolecule of interest are capable of promoting structural changes in such a way as to compromise their effectiveness. Thus, the success of developing advanced biomaterials depends on conformational studies of the molecules of interest that will be incorporated into the nanoparticles, considering physicochemical changes that the preparation processes may cause in their surroundings. In this sense, we have been working on the photophysical characterization, using photoluminescence (PL) and photoluminescence excitation (PLE), of the interactions between gold nanoparticles synthesized with poly(ethylene glycol) dithiol 8000, $PEG(SH)_2AuNP$, and the lipid phosphatidylserine labelled with NBD (N-(7-nitro-2- 1,3-benzoxadiazol-4-yl) in three different positions: 18:1, 18:6 and 18:12. We will discuss the conformation and aggregation of NBD in several concentrations and the changes in NBD conformation when the $PEG(SH)_2AuNP$ are titrated into NBD solution. In a nutshell, our results showed, so far, that microenvironment of the polar heads undergo the same changes whether in buffer or in nanoparticle solution, suggesting that the NBD- $PEG(SH)_2AuNP$ interaction is through the nonpolar tails and not the polar heads.

Keywords: Gold nanoparticles, photoluminescence, photoluminescence excitation, NBD

Title: Application of nanoparticles with generation of singlet oxygen in macrophage cells

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Singlet oxygen is a reactive oxygen species, as its chemical reactivity derives from its characteristic electronically-excited state. This species has attracted researches in the last years because of the involvement of singlet oxygen in many important atmospheric, physical, chemical, biological, and therapeutic processes. Currently, nanoparticles that present upconversion (UC) luminescence have become a research field, related to the potential for application in biological images, which has led to the search for intensifications in the signals emitted by upconversion.This work presents an efficient route for emission of singlet oxygen from the upcoversion process and subsequent application of the nanomaterial in the murine macrophage cell line, RAW 264.7.The hexagonal phase NaYF4:TR3+ nanoparticles are synthesized by the coprecipitation method, TRCl3, NH4F and NaOH as precursors to the matrix and doping ions. This work included the synthesis of nanoparticles in the core-shell form of β-NaTRF4:TR3+ @β-NaYF4 with different concentrations of the doping ion(s) to obtain the maximum emission in different regions and the interaction of NPs with different concentrations of photosensitizers for the generation of singlet oxygen, detected by spectroscopy at 1270nm and subsequent incubation of macrophages in the presence of nanoparticles and assessment of cell viability after exposure to singlet oxygen.

Keywords: singlet oxygen, RAW macrophages, upconversion

Use of a novel pH-sensing luciferase to determine pH changes associated with the switch from mitochondrial respiration to glycolysis in colon cancer cells

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Cancer cells generally exhibit increased glycolysis for ATP generation (the Warburg effect) due in part to mitochondrial respiration injury and hypoxia, which are frequently associated with resistance to therapeutic agents. This switching induces cancer cells to plunder more glucose than normal ones from microenvironment, thus secreting more lactic acid to meet energy requirements (doi: 10.1016/j.gendis.2017.02.003). During this process, at the initial stage a large amount of protons is produced, so mechanisms to expel protons from the cell are activated to keep an alkaline intracellular pH (doi: 10.1038/nrd3554). As a result, the tumor microenvironment (TME) becomes acidic. Furthermore, extracellular acidic pH and intracellular alkaline pH of cancer cells are known to induce malignant behaviors, such as increased invasion and metastasis, multi-drug resistance, and suppression of immune surveillance. To investigate the pH changes associated with the switching to glycolysis in cancer cells, we used a novel pH-sensing luciferase reporter gene (AmyLuc), which is thermally more stable at 37°C, and intentionally broke down mitochondria respiration in human *colorectal adenocarcinoma cells (*Caco-2) and monitored the intracellular pH by measuring the ratio of red and green light intensities. Considering that this luciferase emits more red light in an acidic environment while at an alkaline pH produces more green light, we measured BL spectra of AmyLuc transfected Caco-2 cells seeded in cells media at pH 6.0 and 8.0, and determined the BL spectral peaks (pH 6.0: 593 nm; pH 8.0: 548 nm). Based on the BL peak at these two pHs, we then calculated the red/green light intensity ratio, allowing to estimate the intracellular physiological pH of Caco2 cells and to monitor the intracellular acidification or

alkalinization upon different treatments. Indeed, the AmyLuc transfected cells were treated with the mitochondrial uncoupler FCCP (10 µM), the respiratory chain inhibitor antimycin (10 µM), and the proton antiporter K+/H+ nigericin (2 µg/mL). Upon treatment with these drugs, the BL spectra showed a gradual increase of the ratio red/green light intensities during the first 20-30 min, indicating an acidification of the cytoplasm, especially in the case of antimycin, and then a slower decrease of this ratio indicating recovering of buffering capacity. Such initial intracellular acidification upon mitochondria respiratory chain inhibition or uncoupling could be caused by the switch from mitochondrial respiratory catabolism to fermentative glycolysis, which initially results in a burst of lactate production, temporarily acidifying the cytoplasmic environment. Altogether, these results indicate that the *Amydetes vivianii* color-tuning luciferase could be a new promising bioimaging tool to investigate the switch from aerobic respiration to anaerobic glycolysis in cancer cells.

Keywords: Bioluminescence, mitochondrial inhibitors, FCCP, Antimycin

APPLICATION OF CHEMILUMINESCENCE AND BIOLUMINESCENCE TO NANOMATERIALS

Functionalization of NiO Thin Films with His-Tag Proteolytic and Bioluminescent Enzymes for Sensor Applications

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Immobilization of enzymes on films, nanoparticles, and liposomes is largely used to produce reusable catalysts and sensors. In the present study, a new system of enzyme immobilization was developed to take advantage of the well-known affinity of histidine to divalent metal ions. Therefore, a thin film of Ni was deposited by the evaporation technique (Prest Vacuo model PV0450) of Ni flake 99.99% on glass substrates. Ni film was oxidized upon entering air in the vacuum chamber immediately after the deposition. The NiO films were calcinated using a tubular furnace (Thermo Scientific, Lindberg Blue M) open to the atmosphere at 400◦C for 3 h. Micro-Raman spectroscopy (Horiba-Jobin-Yvon model T64000 spectrometer) was carried out to identify the vibrational properties of the NiO thin film. The morphology of the NiO films was studied by scanning electron microscopy (SEM) using a JEOL JSM-6010LA microscope. Two potentially applicable sensing and diagnosis enzymes were chosen for immobilization and expressed with a tail of six histidine residues (His-tag). The bioluminescent green-blue emitting Amydetes vivianii firefly luciferase (Amy-WT) linked with the N-terminal ZZ portion of protein A (chimeric ZZ-Amy) and the neuronal enzyme prolyl oligopeptidase (POP) were dispersed on the NiO films and incubated for two hours. The film surfaces were rinsed with water to remove unlinked protein. The binding of the chimeric ZZ-Amy and POP on the NiO surface was characterized by Fourier Transform Infrared (FTIR), which evidenced the enzyme binding in a concentration-dependent manner. The functionalized films exhibited the finger-print protein bands amide I (1600-1800 cm^{-1}), amide II (1470-1570 cm^{-1}), amide III (1250-1350 cm^{-1}), and amide A (3300-3500 cm^{-1}). These results show NiO films as a promising platform for enzyme immobilization and application based on the His-tag affinity for coordinated metal ions.

Keywords: his-tag, NiO, luciferases, prolyl oligopeptidase, sensor

Plasmon-induced Increased Absolute Activity of *Amydetes* and chimeric ZZ-Amy Firefly Luciferases bound to PEG(SH)$_2$- and Cys-Functionalized Gold Nanoparticles

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The novel bioluminescent fusion protein, which was formed by the green-blue emitting *Amydetes vivianii* firefly luciferase (Amy-WT) linked with the N-terminal ZZ portion of protein A (chimeric ZZ-Amy), has been efficiently applied in immun blots for detection of SARS-CoV-2 nucleoprotein. The chimeric ZZ-Amy displays a slightly higher and more sustained luminescent signal when compared to commercial cheiluminescent HRP-labeled secondary antibodies. The increase of *Pyrearinus termitilluminans* (PyLuc) and *Phrixotrix* red emitting (RELuc) luciferases stability when associated with gold nanoparticles (AuNPs) capped with dithiol polyethylene glycol (PEG(SH)$_2$AuNPs) inspired similar Nano/Bio construction for Amy-WT and chimeric ZZ-Amy luciferases. The association of the enzymes with the PEG(SH)$_2$AuNPs did not affect the enzymatic structure, as attested by FTIR analysis and bioluminescence spectra. Scanning electron microscopy images showed 10 nm AuNPs aggregated in a dense PEG(SH)$_2$ corona that became rarefied in the presence of Amy-WT. Contrary to the observed for PyLuc and RELuc, Amy-WT and chimeric ZZ-Amy associated with PEG(SH)$_2$AuNPs exhibited a significant luminescence increase (absolute activity) with a slight stability increase. The spectral overlap of luciferases with the absorption band of the 10 nm AuNPs maximizes the effect of confined plasmons on the optical density of states near the emission peaks of Amy-WT and ZZ-Amy. The Nano/ZZ-Amy construction improves the detection limits of the bioluminescence for several practical applications.

Keywords: luciferases, gold nanoparticles, plasmon resonance, ZZ-Amy.

BIOLUMINESCENCE DIVERSITY, ECOLOGY AND APPLICATIONS IN CONSERVATION

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Adapting to a Warming World: Modeling the Future Distribution of Marine Bioluminescent Species in Response to Climate Change

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Bioluminescence is a natural phenomenon characterized by the emission of light from living organisms due to a chemical reaction. Although bioluminescent species exist both on land and in marine environments, they predominantly inhabit the ocean's deeper layers. This phenomenon plays a crucial role in the marine ecosystem, aiding in defense against predators, facilitating communication, and attracting prey. Research into bioluminescence has revealed its benefits and applications in fields such as Biotechnology, Medicine, and Engineering. However, despite their significance, bioluminescent species face threats from climate change and ocean pollution, which directly impact their behaviors and the marine ecosystem. The conservation of these species is vital to prevent ecosystem collapse, underscoring their importance in the food chain, carbon and nitrogen cycles, and biodiversity. Here, we modeled the distribution of marine bioluminescent species, focusing on the effects of changes in temperature, precipitation, and other abiotic marine conditions that affect species occurrence. We modeled the species distribution of 10 species, from distinct Classes, across three time periods (current, 2050, and 2100), based on less (ssp126) and more (ssp585) catastrophic environmental scenarios following the SSP (Shared Socioeconomic Pathways) diagnoses. For 2050, the conditions appeared not to be alarming; however, we observed a distribution shift towards the northern part of the globe. By 2100, many species showed a concerning reduction in distribution of 30%-40% relative to their current distribution. These results may indicate an increase in temperature in the tropics and near the North Pole, as well as changes in marine currents, which directly affect the distribution of these species. Such analyses illuminate the dynamics of bioluminescent species and their relationship with the environment. They aim to understand how these species are adapting to or facing challenges due to climate change. This information is crucial for informing conservation policies and adaptation strategies to promote the sustainability of ocean ecosystems for future generations.

Keywords: Bioluminescence, Climate Changes, Conservation, Species distribution modelling

New insights on the rhythmicity and sensing of light of the bioluminescent fungus *Neonothopanus gardneri*

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Bioluminescent fungi emit green light peaking at 530 nm. The biochemical mechanism and the genes involved in fungal bioluminescence have been recently described. The emission of light is one of the products of the so-called Caffeic Acid Cycle (CAC), wherein caffeic acid is firstly converted into hispidin in a reaction catalyzed by hispidin synthase (HispS), followed by its hydroxylation by hispidin-3-hydroxylase (H3H), giving rise to the fungal luciferin (3-hydroxyhispidin). Then, a luciferase (Luz) catalyzes the addition of molecular oxygen from the luciferin, yielding an endoperoxide as high-energy intermediate, whose decomposition leads to the formation of oxyluciferin (caffeylpyruvate) and light emission. In the last step, oxyluciferin is recycled to caffeic acid by caffeylpyruvate hydrolase (CPH), restarting the cycle. Despite metabolites and genes of CAC having been characterized, the molecular regulation and ecological functions of the fungal bioluminescence for the mycelium remain poorly understood. Previous work from our group has demonstrated that the bioluminescence of *Neonothopanus gardneri*, a fungus that can be found in Babaçu Forest in Brazil, is controlled by a temperature-compensated circadian clock. Based on the transcriptome and genome obtained by our group from *N. gardneri* mycelium, we have identified candidate genes for the biological clock and other ones acting as light sensors. We have developed reference genes for RT-qPCR assays that allow us to explore the regulation of light emission at the level of transcription. In this context, we investigate whether the expression of transcripts of CAC genes and other candidates to the biological clock and light sensors is responsive to light in *N. gardneri's* mycelium. With this in mind, the mycelium was cultivated in liquid medium at 25ºC for *i)* 5 days in constant darkness (DD) and *ii)* subjected to 1-hour of light after constant darkness. After 5 days, the mycelium

was macerated in liquid N_2, and submitted to RNA extraction, and the expression of target transcripts was assessed by RT-qPCR. Preliminary results indicate that some genes involved in fungal bioluminescence show a decrease in transcripts production after 1-hour of light exposure. We also incubated *N. gardneri* mycelium in a 12h-light/dark cycle at 25ºC and sampled it every 4h over 48h. HPLC-MS was used to quantify intermediates, and RT-qPCR was used to analyze the time-dependent expression of CAC genes at the transcript level. Results showed that CAC intermediates production peaked during subjective night periods, indicating a circadian rhythm. This study can contribute with new cues and insights on the regulation of transcripts related to the bioluminescence in fungi as well as the molecular aspects of the circadian regulation of the fungal bioluminescence.

Keywords: fungal bioluminescence, circadian rhythm, caffeic acid cycle, light response

New insights on the rhythmicity and sensing of light of the bioluminescent fungus *Neonothopanus gardneri*

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Bioluminescent fungi emit green light peaking at 530 nm. The biochemical mechanism and the genes involved in fungal bioluminescence have been recently described. The emission of light is one of the products of the so-called Caffeic Acid Cycle (CAC), wherein caffeic acid is firstly converted into hispidin in a reaction catalyzed by hispidin synthase (HispS), followed by its hydroxylation by hispidin-3-hydroxylase (H3H), giving rise to the fungal luciferin (3-hydroxyhispidin). Then, a luciferase (Luz) catalyzes the addition of molecular oxygen from the luciferin, yielding an endoperoxide as high-energy intermediate, whose decomposition leads to the formation of oxyluciferin (caffeylpyruvate) and light emission. In the last step, oxyluciferin is recycled to caffeic acid by caffeylpyruvate hydrolase (CPH), restarting the cycle. Despite metabolites and genes of CAC having been characterized, the molecular regulation and ecological functions of the fungal bioluminescence for the mycelium remain poorly understood. Previous work from our group has demonstrated that the bioluminescence of *Neonothopanus gardneri*, a fungus that can be found in Babaçu Forest in Brazil, is controlled by a temperature-compensated circadian clock. Based on the transcriptome and genome obtained by our group from *N. gardneri* mycelium, we have identified candidate genes for the biological clock and other ones acting as light sensors. We have developed reference genes for RT-qPCR assays that allow us to explore the regulation of light emission at the level of transcription. In this context, we investigate whether the expression of transcripts of CAC genes and other candidates to the biological clock and light sensors is responsive to light in *N. gardneri's* mycelium. With this in mind, the mycelium was cultivated in liquid medium at 25ºC for *i)* 5 days in constant darkness (DD) and *ii)* subjected to 1-hour of light after constant darkness. After 5 days, the mycelium

was macerated in liquid N_2, and submitted to RNA extraction, and the expression of target transcripts was assessed by RT-qPCR. Preliminary results indicate that some genes involved in fungal bioluminescence show a decrease in transcripts production after 1-hour of light exposure. We also incubated *N. gardneri* mycelium in a 12h-light/dark cycle at 25ºC and sampled it every 4h over 48h. HPLC-MS was used to quantify intermediates, and RT-qPCR was used to analyze the time-dependent expression of CAC genes at the transcript level. Results showed that CAC intermediates production peaked during subjective night periods, indicating a circadian rhythm. This study can contribute with new cues and insights on the regulation of transcripts related to the bioluminescence in fungi as well as the molecular aspects of the circadian regulation of the fungal bioluminescence.

Keywords: fungal bioluminescence, circadian rhythm, caffeic acid cycle, light response

Unveiling the hidden glow: contributions to the biodiversity, conservation, and evolutionary studies of bioluminescent fungi in Brazil

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More than 125 known species of fungi, all part of the Agaricales order, can spontaneously emit light. Currently, they are distributed across five distinct lineages: Armillaria, Omphalotus, Mycenoid, Lucentipes and the latest discovered Eoscyphella. All bioluminescent fungi share the same mecanism: the light emission results from the oxidation of a luciferin derived from caffeic acid by oxygen under the action of the enzyme luciferase. Since 2018, our group has been collecting over than 100 bioluminescent fungi specimens at the area surrounding the Alto do Ribeira Touristic Park, located at the Atlantic Rainforest biome in Brazil (Iporanga and Apiaí, São Paulo state). In a collaborative effort including researchers from São Paulo (Brazil) and California (USA) we have been working on the morphological and molecular analyses from these specimens, contributing with the understanding on the ecology, evolution, and biodiversity of the bioluminescent fungi occurring in Brazil. One of our latest collections led to the discovery of a fifth and new lineage of bioluminescent fungi in 2023: *Eoscyphella*, the tiniest glowing mushroom ever seen. Combined with the morphological description of the specimens, fungal DNA barcoding, including the assessment of ITS (Internal Transcribed Spacers) and the rRNA gene encoding the large ribosomal subunit (LSU), has led to a fast specimens' identification and providing the genetic data for phylogenetic studies. Furthermore, recent evidences have suggested the need of obtaining additional genetic data to resolve the phylogeny of certain groups. For instance, studies of phylogenetic replacement are being conducted from the DNA- and RNA-seq data for the species initially classified as *Mycena lucentipes* and *Gerronema viridilucens* which actually belongs to the same genus. We also have successfully isolated pure cultures from 36 different bioluminescent fungal species, which makes our group the main holder of bioluminescent fungi in the world. In addition to provide us biological material for routinely laboratory experiments, this collection is also extremely relevant for the conservation of biodiversity and fungal genetic resources. Thus way, the initiatives above mentioned effectively contribute with relevant information on fungal

biodiversity as well as with further studies focusing on the origin and evolution of fungal bioluminescence.

Keywords: Bioluminescence, ITS, LSU, fungal systematics, evolution.

Unveiling the richness and ecological significance of bioluminescnt lifeforms in Brazil

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Bioluminescence, the production of light by living organisms, stands as an enthralling phenomenon observed across a diversity of species, serving various ecological purposes. In this detailed abstract, we delve into the realm of bioluminescent life forms within Brazil, rich and varied natural habitats for most of the species. Highlighting species ranging from the fireflies and luminescent fungi to the alluring marine dinoflagellates and fish, Brazil presents an impressive (and unknown) spectrum of bioluminescent biodiversity. By examining the distribution and new discoveries based on taxonomy and molecular data, we gain insights into the evolutionary adaptations and ecological roles of these organisms. Nonetheless, challenges such as habitat degradation, climate variations, and light pollution threaten their existence. The adoption of conservation strategies, fostering of cross-disciplinary efforts, and implementation of environmentally friendly lighting solutions are vital for their protection. Future research directions should include the discovery of unique species, investigation of the environmental variables affecting bioluminescence, and the formulation of effective preservation tactics. With the support of cross-disciplinary collaboration, state-of-the-art technology, and enhanced financial backing, Brazil has the opportunity to explore the intricacies of its bioluminescent wildlife, further scientific knowledge, and safeguard these mesmerizing species for future generations.

Keywords: Bioluminescent, Biodiversity, Conservation, Ecological roles

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The chemistry between *Neonothopanus gardneri* and Babassu palm: Real symbiosis or an interesting metabolite?

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The bioluminescent fungi *Neonothopanus gardneri* grows only in the base of the babassu palm tree, in Brazil. It is the biggest bioluminescent mushroom of the region and also has the highest light emission. Fungi-plant association is world-widely seen and known for giving the plant an enormous advantage in nutrient gathering through different approaches, therefore this symbiosis may lead the plant to have an advantage against the others in the ecosystem.This way of thinking is supported by the fact that the babassu palm is the main large plant of the palm forest biome, highly overcoming moriche and carnauba palms.To discover if there is symbiosis between *N. gardneri* and babassu and if it gives the plant some advantage we must test growing the plant in the presence and in the absence of the fungi and see its roots under microscope.Germinating the embryo using different combinations of plant growth hormone and creating calluses directly from a plant seedling collected in the wild are two of the strategies being tested in our lab, results have yet to come due to the long wait reality of the techniques.Another test planned to the laboratory made seedlings is to compare *N. gardneri* infected and control plants metabolome, for the plant may produce a specific molecule that is necessary for the fungi.With this work we expect to elucidate the first relationship between a plant and a bioluminescent organism.

Keywords: Bioluminescence, Fungi, Plant tissue culture

ENVIRONMENTAL APPLICATIONS OF LUMINESCENCE

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Algae delayed luminescence dynamics altered by Zinc stress - preliminary data

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This study compares a standard ecotoxicological method - algae colony growth (*Raphidocelis subcapitata*) over 72 hours - with a photonic technique: the delayed luminescence (DL) analysis, developed by Katsumata *et al.*., by evaluating its decay profile and comparing data from control and stressed samples, with results as fast as 1 hour after inoculation. The method demands less consumables and work-hours than the long, standard growth tests. The test procedure is: preparation of the oligo medium (10L) for stock and erlenmeyer flasks (50mL), followed by washing and sterilization of the material to be used and preparation of the inoculum; inoculation of the algae samples with hazard to be tested, and flaks completed with oligo solution and sterilized water (20mL for erlenmeyer flasks and 10mL for test tubes), all flasks are kept on a shaking table with constant light and temperature. The DL test is run using a photon counting chamber immediately after inoculation (0h), and at 1, 3, 6, and 24 hours after it; the standard test (ie. light absorption of algae sampels) are run after 72 hours, using a spectrophotometer.In this work, solutions of Zinc sulfate heptahydrate (ZnSO4.7H2O) were tested. It is an inorganic salt and very toxic to aquatic organisms. Thus, the concentrations used were: 0 (control), 0.05, 0.1, 0.25, 0.5 and 1 mg/L, and DL measured by a dedicated dark chamber (PMX6100 (IR), Hamamatsu Photonics KK), with the sample being exposed to controlled light excitation (white LED for 30s + IR@700nm for 1s), and immediately after (< 50ms) the photon counting is performed for the next 60s, counts every 0.1s, forming a characteristic curve for the control samples: rapid decay followed by the formation of a peak and then a slow decay. By comparing the DL time profile of stressed and control samples, it is possible to determine the inhibition of the DL curve (iDL) and correlate it with the toxicity of the solution.This DL is based on the combined response of two systems: the photosyntetic I and the photosyntetic II, with charge recombination and electron transport: the initial electron receptors are the quinones QA and QB, near the primary donor chlorophyll molecule at PS-II (P680), giving so the decay rapid component; subsequently, electron carriers such as the plastoquinone, the plastocyanin and the ferredoxin at PS-I, located further away, giving the the slow component of DL (slow decay). Some substances - NaCl, diuron, flumetralin, and ametryn

- have already been tested, showing satisfactory results when compared to the conventional method. For the zinc salt discussed here, a noticeable larger peak was observed for the control group and for the lowest concentration of zinc sulfate just few hours after inoculation.

Keywords: luminescence, algae, toxicology, rapid testing.

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Simultaneous determination of atenolol and pindolol by a synchronous fluorescence method. Application to Senegal natural waters

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In recent years, the presence of pharmaceutical residues, such as β-blockers, in the environment raised significant concerns on their potential risks to the ecosystem and human health. Therefore, sensitive and selective analytical methods are needed to determine β-blockers in environmental samples. The fluorescence spectrometric method is often applied to the determination of beta-blockers which generally exhibit natural fluorescence. However, the selectivity of fluorescence is often poor and can yield problems for the simultaneous determination of multi-component samples with broad bands and overlapped emission spectra. Therefore, synchronous fluorescence can be used for mixture analysis by removing the overlapping of individual fluorescence spectra. A synchronous fluorescence method is described for the simultaneous determination of atenolol (AT) and pindolol (PIN) in mixtures. This method can resolve the overlapping conventional fluorescence spectra of both compounds. The simultaneous fluorescence detection of AT and PIN is based on a single scan at 288 nm and 317 nm, corresponding to AT and PIN, at $\Delta\lambda$ = 60 nm, respectively. Different experimental conditions that affect synchronous fluorescence, including $\Delta\lambda$ and diluent solvent are optimized. The result shows that the ranges of linear calibration curves for both drugs are comprised between 25 and 1000 ng/ml in methanol. The limit of detection (LOD) for AT and PIN are 1.5 ng/ml and 1.8 ng/ml, respectively. The proposed method is successfully applied to the simultaneous determination of AT and PIN in spiked samples in tap and natural waters, by using the liquid-liquid extraction (LLE) procedure and standard addition with good recovery values of 102 to 105% for AT and 96 to 102% for PIN.

Keywords: atenolol, pindolol, pharmaceutical residues, synchronous fluorescence

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Simultaneous determination of naproxen and ibuprofen by synchronous fluorescence spectroscopy (SFS) in cyclodextrin and micellar media

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Despite their positive effects, drugs represent a major source of pollution for the aquatic and terrestrial environment. Concentrations in the environment generally range from ng/L to µg/L. The worldwide presence of these drugs threatens the survival of many living species, including fish and aquatic plants. Chromatographic methods are mainly used for drug determination. However, other highly sensitive and accessible alternative methods have made drug detection possible. These include simple, rapid and highly sensitive fluorimetric methods. Various experimental parameters (solvent type, $\Delta\lambda$ selection, influence of CTAC micellar organized media and β-CD cyclodextrins) affecting the performance of the proposed SFS method were optimized. Optimal conditions for both drugs were an aqueous solution of β-CD cyclodextrins (6×10^{-3} M) with a $\Delta\lambda$ = 80 nm. Interesting limits of detection and quantification were found, respectively equal to 0.008 and 0.02 ng/mL for naproxen; 0.31 and 1.039 ng/mL for ibuprofen. This method was applied to tap water collected from Marne la Vallée in France, natural water samples (sea water), STEP effluent samples from Senegal and real pharmaceutical drug samples using the standard addition method. The recovery rates obtained were satisfactory, ranging from 72.79 to 109.80 % for ibuprofen and 85.27 to 109.87 % for naproxen. DSR values are relatively low, ranging from 0.18 to 0.40 % for naproxen and from 1.37 to 2.17 % for ibuprofen. This very interesting result, compared with those obtained in the literature, makes SFS a good alternative for the simultaneous determination of pollutants in the environment, particularly NSAIDs drug residues

Keywords: naproxen, ibuprofen, synchronous fluorescence spectroscopy (SFS), quantification, natural waters

Bioluminescence tests using *Pyrocystis lunula* (Schutt, 1896) under effect of anionic surfactants contamination

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The bioluminescence of the dinoflagellate *Pyrocystis lunula* is an excellent indicator for observing the effects of different contaminants on organisms in the marine environment. In this study, standardized tests were applied in *P. lunula* from the Aidar & Kutner Microorganism Bank of the Oceanographic Institute of the University of São Paulo. The cultivation medium was Guillard F/2 medium. The culture was exposed to photoperiod of 12h night/12h day. The anionic surfactants used were sodium dodecyl sulfate ($C_{12}H_{25}OSO_3Na$ – SDS) and sodium dodecylbenzene sulfonate ($CH_{12})_{11}C_6H_4SO_3Na$ - LAS). These components commonly used in detergents and differ by the presence of benzene. The mother culture had around 11,700 cells mL^{-1} and the experimental design followed ABNT standards for ecotoxicological testing with marine microalgae (ABNT). In the bioassay, 250 mL Erlenmeyer flasks with 50 mL of the mother culture in 100 mL of Guillard medium formed 150 mL of solution with a concentration of 4,000 cells.mL^{-1}. Three different treatments were performed: *i*) dodecyl sulfate sodium (SDS), *ii*) sodium dodecylbenzene sulfonate (LAS) and *iii*) both. Different concentrations were used besides the control. They are: 5 mg, 10 mg, 25 mg and 50 mg of surfactants. The exposure lasted 24h and 48h. The Tecan Infinite® luminometer was used to measure bioluminescence. Cell density was measured in a Sedgewick-Rafter. Cells were counted under Leica® optical microscope model DME with 40x magnification. Chlorophyll was measured by spectrophotometry. Exposure to SDS was lethal to cells, with the inhibition of light emission from the dosage of 25 mg.L^{-1}, representing their mortality. High emission values of light in 24 and 48h, at a dosage of 5 mg.L^{-1}, indicate a first degree of damage to cells, as they are associated with the rupture of scintillon membranes. These organelles contain the luciferin-luciferase enzyme complex and its breakdown results in an increase in light emission, the increases observed in dosages of 5 mg.L^{-1}, and subsequent decrease at 10 mg.L^{-1} of exposure may be related to the denaturation of this membrane. A lethality was observed at 25 and 50 mg.L^{-1} was

corroborated by observation of dead cells in the Sedgewick-Rafter chamber presented anomalies, such as the encysted and extroverted nucleus and the cellular membrane damaged associated with the entry of surfactant into the cell. In turn, exposure to LAS was characterized as less harmful. In low dosage (5 $mg.L^{-1}$), light emission was greater than in the control, even with greater light emission even after 48 hours, also related to the rupture of the scintillons. At dosage of 10 $mg.L^{-1}$, the light emission were lower compared to samples exposed to SDS at the same dose. From 25 $mg.L^{-1}$, inhibition was observed of bioluminescence, with values close to zero at 50 $mg.L^{-1}$.

Keywords: Bioluminescence, dinoflagellate, surfactants, toxicity

Bioluminescent microbial-electronic modules for the detection of buried explosives

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Landmines and explosive remnants of war pose a global humanitarian problem which claims numerous casualties long after the conflict has ended. Current approaches for the location of landmines, such as metal detection, which require physical presence at the minefield, involve high risk to personnel; these methods are also costly, time consuming, and have a high rate of false positive results. No currently viable technology allows the remote detection of buried explosive devices. A possible solution may be provided by the use of genetically engineered *E. coli* strains, molecularly "tailored" to emit a bioluminescent signal in the presence of trace explosives escaping for the landmine and accumulating in the soil above it. The emitted bioluminescence then serves to generate a physical map of the mines' location. The optical signal emitted by the sensor bacteria in response to the presence of trace explosives in the soil below them is imaged and quantified by one of two means: (a) Imaging from a remote location, such as by a drone; (b) A network of bioelectronic modules, incorporating the sensor bacteria and harboring all the necessary electronics and optics. The latter system will be described, along with the synthetic biology approaches employed that significantly enhanced the major performance parameters: higher signal intensity, faster response time, and lower detection threshold of the target explosives.

Keywords: Bacterial whole-cell biosensors, buried explosives, bioluminescence, landmines, optoelectronics, synthetic biology

Effect of ytterbium ions on broadband anti-stokes visible emission

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The Laser Induced White Emission (LIWE) phenomena has received much attention in recent years, however, the mechanism behind this process is still not entirely understood. LIWE of $Y_{2(1-x)}Yb_{2x}SiO_7$ nanocrystallites was observed upon excitation with CW infrared laser diode. The visible broad emission centered at 600-700 nm was dependent on concentration of Yb^{3+} and it increased exponentially with excitation power density. It was detected blue shift of the LIWE emission with increase in Yb3+ concentrations. Increase in the Yb^{3+} concentrations leads to rise in the LIWE absolute intensity. It was shown that the N order parameters of LIWE process increase from 3 to 7 with increase of Yb^{3+} concentration from 1 at.% to 5 at.% while the further increase leads to saturation and reach a magnitude 8 for fully concentrated nanocrystals. The laser induced photocurrent assisting generation of visible broad band emission was measured. It increased exponentially with applied excitation power and concentration of Yb^{3+} ions. The increase in the concentration of Yb^{3+} ions to 5 at.% leads to small increase in the photocurrent, while the further increase lead to significantly rise in the photocurrent. The avalanche ionization process in Yb^{2+}/Yb^{3+} mixed valence pair was proposed as a tentative model of LIWE phenomenon. The ionization process occurs due to the cooperative energy transfer from several Yb^{3+} ions to Yb^{2+}/Yb^{3+} mixed valence pair followed by the ejection of electron.

Keywords: white light source, nanocrystals,

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Fluorescent microbial biosensor for environmental monitoring

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Environmental monitoring is a major challenge for modern society. Most of the methods currently in use are based on physico-chemical analytical principles. Although they are very powerful for determining specific parameters of an environment (such as pH, specific molecules, etc.), they do not allow us to assess biological parameters such as the fate of molecules in the environment, or their impact on the biosphere. Also, over the last few decades, several teams around the world have proposed solutions to this challenge. However, the question of representativeness remains unresolved. These biological parameters are the result of a close relationship between one (or more) molecule(s) and a target (organism, community, ecosystem). However, the metrological approaches proposed are very often based on monospecific approaches using a single biological sensor (such as the ISO 11348 standard toxicity test based on Aliivibrio fischeri) or on complex, uncontrolled communities (OECD 209, 301). In this context, the data interpretation can be complex and the results transposition to an environmental context can appear hazardous, because of the lack of representativity.In order to increase the representativity of biological approaches, the GEPEA laboratory has been developing fluorescent biosensors based on multi-specific approaches using several bioreporters. To achieve this, the choice of biological sensors is at the heart of the metrological strategy and is based on in-depth knowledge of the target ecosystem. This type of approach has been deployed in response to a number of issues (assessing the persistence of molecules, estimating toxicity) and in different environments (maritime coastline, domestic WWTP, industrial WWTP).

Keywords: Fluorescence, biosensor, environment, bioelectronic tongue, biodegradation, toxicity, multisensorial approach

Raman spectroscopy of living samples: from the cell to field applications

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Raman spectroscopy offers a promising technique for rapid and non-destructive analysis in several domain of applications. The main approaches showing the use of Raman spectroscopy as biosensor will be presented in this study. Some examples of application have been selected to show the ability of Raman spectroscopy to identify the toxic effects of effluents on living cells and its potential to monitor the physiology of cells under complex environment of production. In all cases, the obtained Raman spectra reflect the molecular composition of the biological samples without any extensive preparation or the use of chemical reagents. Regardless of the advantages offered by this technique, many challenges remain for its field applications. In fact, the analysis of living cells is very complex because microorganisms are evolving continuously over time and their compositions are very depending to the experimental conditions. This characteristic of biological samples induces high variability and a complexity in the obtained spectral information that cannot be explored by conventional methods. Consequently, complex statistical exploration is always necessary to understand the data. Nowadays, the main challenges will be the automation of the whole approach, including the chemometric models, to simplify its use by an unqualified user. Reducing the prices of spectrometers is also very important to help this technology to become widely used and transferred to other biocontrol domains.

Keywords: Biosensor, Raman spectroscopy, Chemometrics, Living cells, Monitoring

EXCITED STATE DYNAMICS AND ULTRAFAST PROCESSES

Lanthanide-based Materials Emitting at Telecom Wavelength: challenges and perspectives for photonic and quantum techologies

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Optical and photonic systems are nowadays at the heart of modern technology towards sustainable and energy-efficient devices for computing, communication, data security, including photonic integrated circuits and the newly emerging frontier of quantum optics. The high color pure and long lived emission delivered by the lanthanide f-f transitions establishes a unique value for the realization of such devices, which require efficient near-infrared (NIR) optical output (1 μm to 2 μm), to match with the silicon window in photonic integrated circuits and silica in telecom optical fibers. Nonetheless, recently, wavelength tunability allowing for signal multiplexing is becoming a much sought-after property to expand the potentialities of these technologies.Nanomaterials doped with lanthanide ions (Ln) offer countless possibilities for tailoring the optical output towards the desired functionality and at the same time deliver high processing potential by mild solution methods for the fabrication of optical devices. However, the emission intensity achievable in such materials remains low due to the poor absorption of these ions resulting in an inefficient photosensitization. For this reason, dye-sensitized lanthanide fluoride nanoparticles, where photosensitization is achieved through an organic light-harvesting unit, have become increasingly popular in the last years. On the other hand, the energy transfer at the organic-inorganic interface and the energy propagation within the nanoparticle is severely subjected to losses due to the presence of external and uncontrolled channels for the deactivation of the photoexcited states resulting in a dramatic lowering of the quantum yield. Ultra-fast transient absorption (TA) spectroscopy combined with time-resolved photoluminescence (PL) reveals the mechanisms and the short-lived intermediates at the organic-inorganic and Ln-Ln interfaces in dye-sensitized Ln^{3+}-doped fluoride nanoparticles. By adopting a “molecule on a particle approach” where the energy donor and acceptor units are spatially confined into a precise core-shell architectural design of the nanoparticle and by selecting suitable small-sized (sub nm) dye molecules, it is possible to achieve exceptional sensitization efficiencies close to 100%.More recently, Ln-doped lead halide perovskite nanoparticles are also emerging as alternative materials to achieve highly efficient emission. In

such systems, the large absorption cross section (10^{-14} – 10^{-13} cm^2) of the perovskites for light with a photon energy above the LHP band gap, greatly facilitates the harvesting of the energy needed to excite the dopant ions. Perovskite materials offer enhanced absorption cross sections, high excitation densities and semiconducting properties. Extremely high quantum yield, exceeding 100% at ~1 µm, can be reached in Yb^{3+} doped $CsPbCl_3$ nanocrystals which in turn can be exploited to achieve outstanding intense and long lived emission from Er^{3+} at 1.5 µm, creating novel perspectives for developing Ln-based optical devices operating in the near-infrared window.

Keywords: lanthanides, energy transfer, luminescence, nanoparticles

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The femtosecond transient absorption spectroscopy of a lanthanoid(1,3-diketonate): Energy transfer mechanisms, rates and efficiency

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The bright luminescence of lanthanoid complexes (including enolates) is intrinsically related to the ligand-to-metal energy transfer processes, which are, in turn, dependent on the lifetime of the ligand excited states. Such lifetimes are in itself somewhat challenging to measure through emission spectroscopy when the efficiency of these energy transfer processes are high, and the excited states of the organic moiety are thus almost completely quenched (as is the case of europium(III) 1,3-diketonates). In this context, the femtosecond transient absorption (fs-TA) spectroscopy is a powerful technique which can probe these states even in the presence of energy transfer processes, and that has been gaining attention over the past years in the area of lanthanoid spectroscopy. However, there is still a lack of kinetic data for the most prevalent lanthanoid (III) 1,3-diketonate complexes, such as S_1/T_1 lifetimes, and intersystem crossing/energy transfer rates. In order to fill this gap, we've chosen the tetraethylammonium salts of tetrakis(2-thenoyltrifluoroacetonato)europate(III), $Et_4N[Eu(tta)_4]$, and tetrakis(2-thenoyltrifluoroacetonato)lanthanate(III), $Et_4N[La(tta)_4]$, as candidates to determine the lifetimes/kinetic constants. These organic salts are thermodynamically more stable than the tri-coordinated counterpart $[Ln(tta)_3(H_2O)_2]$ (Ln: lanthanoid(III) ion) in acetonitrile solution and are a reliable source of $[Ln(tta)_4]^-$ anions. The compounds were prepared following the standard procedure from the literature and characterized via single-crystal X-ray diffraction. The fs-TA measurements showed a S_1 lifetime of ~200 fs followed by the vibrational cooling of the excited T_1 state in ~10 ps in both Eu^{3+} and La^{3+} complexes. These lifetimes agree with the ones obtained from the fs-TA of the free anionic ligand in the potassium 2-thenoyltrifluoroacetonate. This excited state was confirmed to be a triplet as it outlived the duration of the femtosecond-TA experiment (3.3 ns) in the Ktta and $Et_4N[La(tta)_4]$ solutions. In contrast, the excited T_1 state

absorption rapidly decayed in the $[Eu(tta)_4]^-$ complex with a lifetime of ~320 ps, decay which is attributed to the intramolecular energy transfer process involving the T_1 and the excited states of the $4f^6$ configuration. From these data, we approximate the energy transfer rate ($W_{ET} \sim 3 \times 10^9\ s^{-1}$) and calculate the lower limit for the energy transfer efficiency at $\eta_{ET} \geq 98\%$. These results demonstrate the power of the femtosecond transient absorption spectroscopy in the analysis of the energy transfer processes in lanthanoid(III) chelates. Furthermore, future measurements of ns-TA (Flash Photolysis) will allow a more precise determination of the W_{ET} and η_{ET} and, together with emission quantum yield values, make the calculation of the $S_1 \rightarrow T_1$ intersystem crossing rate possible. The values of these rates are important given that the 2-thenoyltrifluoroacetone ligand is among the most widely used in Eu^{3+} chelates and these rates are paramount to the theoretical modelling and future development of such complexes.

Keywords: Transient Absorption, Energy Transfer, Luminescence, Lanthanides

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Different emission sensitization pathways in Ln^{3+} chelates with O_8, O_6N_2 and O_8N_2 chemical environments

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Lanthanide (Ln^{3+}) compounds are of great interest due to their special luminescence properties and their various applications for technological purposes. Ln^{3+} luminescence is associated with transitions within the *4f* subshell. Due to the small value of the molar absorption coefficient, Ln^{3+} emission requires sensitization. One way involves the so-called antenna effect, i.e. the use of organic ligands with strong absorption, which transfer excitation energy to the excited levels of Ln^{3+} via intramolecular non-radiative energy transfer (IET). It is important to know the paths and mechanisms of IET as well as the impact of structural modification on the sensitized emission of the Ln^{3+} ions. Knowledge of these issues is helpful in designing Ln^{3+} coordination compounds with specific luminescent properties. We provide insights into the different pathways and mechanisms of IET for two series of Ln^{3+} coordination compounds with N-phosphorylated sulfonyl- and carboxamides, which were designed as UV to Vis converters. We will show that the pathways and mechanisms of IET are also affected by slight changes in the crystal structure of the chelates in the second coordination sphere, such as counter ions or solvent molecules. We will analyze the influence of the ligand-to-Ln charge transfer state (LMCT), which, by depopulating the ligand singlet state (S_1), dramatically reduces the sensitization efficiency of the Eu^{3+} emission while changing the dominant mechanism of IET. The key role of the $^7F_5$ state of Tb^{3+} in IET will be proved, as well as the dominance of IET through the S_1 state for Tb^{3+} coordination compounds with 2,2'- bipyridine and 1, 10-phenanthroline as the co-ligand. We will also demonstrate how proper ligand design, combined with stiffening of the crystal structure of the coordination compound by introducing alkali metal

cations into the first coordination sphere, affects IET efficiency and the intensity of sensitized emission. The above examples provide new insights into the sensitization processes of Tb^{3+} and Eu^{3+} coordination compounds.

Keywords: lanthanide, luminescence, energy transfer, crystal structure, N-phosphorylated amides

FIELD-INDUCED LUMINESCENCE IN ORGANIC AND INORGANIC MEDIA, OLEDS, AND LEDS

Luminescent films of Eu^{3+} dinuclear complex embedded in PMMA as candidates for application in PC-LED lighting devices

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Luminescent materials based on phosphors or complexes containing rare earth ions are intensively explored by the scientific community due to their applicability as cell markers and biological thermometers, in solar concentrators, as anti-fraud reagents, in imaging devices, in screens and lighting devices, more recently, of the type of LEDs and OLEDs. Aiming the application in lighting devices, this study focuses on the synthesis and characterization of films produced by the drop-casting method containing the red-emitting [$Eu(dbm)_3$-μ-(bpm)$Eu(dbm)_3$] complex (Hdbm = dibenzoylmethanate; bpm=2,2'-bipyrimidine), using polymethyl-methacrylate (PMMA) as polymeric matrix. The [$Eu(dbm)_3$-μ-(bpm)$Eu(dbm)_3$] complex was synthesized without any coordinated water molecule and its structure and its features were elucidated by FTIR, TGA, UV-Vis, and photoluminescence spectroscopy. Focusing on the optical behavior, the synthetized Eu^{3+} dinuclear complex exhibited the expected narrow emission bands within the orange-red spectral region due to the Eu^{3+} $^5D_0 \rightarrow {}^7F_J$ (J = 0-4) set of transitions. From the kinetic point of view, it was found that the lifetime of the $^5D_0$ excited state of the Eu^{3+} complex via ligand excitation was 0.377 ms, exhibiting an intrinsic quantum yield of 29.6%. These values are higher than those of the mononuclear [$Eu(dbm)_3H_2O$] complex (0.05 ms and 3.3%). The gain in the dinuclear architecture is relevant, in addition to the fact that these data indicate the absence of coordinated water molecules, agreeing with the proposed structure. Furthermore, the band related to the $^5D_0 \rightarrow {}^7F_2$ transition of the dinuclear complex exhibited a similar profile of the *tris*, in terms of position of the maximum and in the number of components, indicating a structure with low symmetry, as expected. Finally, to produce the luminescent films, the proportion of the complex [$Eu(dbm)_3$-μ-(bpm)-$Eu(dbm)_3$] in PMMA were varied as being 0.1, 0.25, 0.5, 0.75, 1 or 2 % by weight, yielding films completely transparent up to 1 wt%. They also exhibited the characteristic Eu^{3+} luminescence within the orange-red spectral region due to the $^5D_0 \rightarrow {}^7F_J$ (J = 0-4) transitions. So, it is possible to conclude that the films produced based on the dinuclear complex express very promising

characteristics to be used in the manufacture of red PC-LED prototypes or even as a red component in the PC-WLED architecture.

Keywords: Luminescence, Lanthanides, Solid State Lighting

Novel sub-eutectic engineering for luminescence and photoconversion control in $Tb_3Al_{5-x}Sc_xO_{12}$:Ce crystals

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A comprehensive evaluation of the structural and property relationships in $Tb_3Al_5O_{12}:Ce^{3+}$ upon partial substitution of Al with Sc atoms was conducted. The inherently thermodynamically unstable $Tb_3Al_5O_{12}$ in the form of single crystal readily decomposed into a mixture of secondary phases [1]. However, Sc incorporation demonstrably enhanced the stability of the resulting $Tb_3Al_{5-x}Sc_xO_{12}$:Ce phase, enabling its successful crystallization from the melt [2]. Systematic variation of the Sc concentration in $Tb_3Al_{5-x}Sc_xO_{12}$:Ce crystals enabled the precise control of the composition and morphology of the secondary phase inclusions. At low Sc concentrations, these inclusions were primarily composed of $TbAlO_3$:Ce. As the Sc concentration increased, the secondary phase composition transitioned to $TbScO_3$:Ce. This observation suggested that Sc ions effectively replace Al ions in the secondary phase lattice, leading to a progressive compositional shift and forming garnet-perovskite sub-eutectic composition. Temperature dependence studies revealed that the rate of the energy transfer processes between Tb^{3+} and Ce^{3+} was governed by Sc^{3+} ions concentration [3]. This modulation of Sc concentration enabled the tailoring of photoconverting parameters, including correlated color temperature (CCT), color rendering index (CRI), and luminous efficacy (LE). Sc incorporation also influenced the thermal stability of Ce^{3+} ions luminescence [4]. **References:**[1] S. Ganschow, D. Klimm, et al., Cryst. Res. Technol. 34 (1999) 615–619. [2] O. Zapadlík, J. Pejchal, et al., J. Lumin. 263 (2023) 119984. [3] O. Zapadlík, J. Pejchal, et al., Cryst. Growth Des. 21 (2021) 7139–7149. [4] A. Markovskyi, K. Bartosiewicz, et al., Mater. Sci. Eng. B 273 (2021) 115395.

Keywords: single crystal, photoconversion parameters, Energy transfer modulation, Garnet-perovskite eutectic

LUMINESCENCE IN EDUCATION

Chemiluminnescence reations modified for children

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In many countries, including Germany, conducting chemical experiments in schools has become challenging due to financial constraints, lack of equipment, or, as observed in Germany, excessive safety concerns. Despite these hurdles, children, especially the younger ones, are deeply fascinated by experiments that provide immediate, tangible results. To bridge this gap, the German city of Jena hosts a 'Long Night of Sciences' biennially, inviting the public to explore scientific institutions. During this event, our Institute of Organic Chemistry welcomes hundreds of families, including very young children, to demystify chemistry through hands-on experiments. In my laboratory, we specialize in various forms of luminescence, such as fluorescence, triboluminescence, and chemiluminescence, tailoring our experiments to be safe yet captivating for children. These experiments, some of which are derived from research projects by upper-grade scholars, are designed to ensure even the youngest participants can successfully engage in chemiluminescence reactions without raising safety concerns. If possible, I will present some of these experiments on-site, showcasing the enchanting beauty of chemiluminescence.

Keywords: chemiluminescence, safety, education

LUMINESCENCE SPECTROSCOPY OF MACROMOLECULES AND BIOMOLECULES

Bioinspired fluorescent dyes: lessons from biofluorescent plants

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In this presentation, we will delve into the intriguing phenomenon of biofluorescence observed in plants, specifically focusing on structures that are not directly exposed to light. This area of study not only broadens our understanding of plant biology but also offers insights into the adaptive roles of fluorescence in subterranean environments. We will explore how simple chemical modifications to the fluorescent secondary metabolites in plants can pave the way for the development of innovative bio-inspired systems. These systems are tailored for the transfer of electrons, energy, and information, reflecting the sophisticated mechanisms evolved by nature.Our discussion will include a detailed examination of biocompatible dyes, which have been engineered to interact harmoniously with biological tissues, thereby minimizing any potential cytotoxic effects. Additionally, we will present a novel superoxide generator that allows for the real-time monitoring of reactive oxygen species, providing valuable data for oxidative stress research. Furthermore, we will introduce a bioinspired self-assembling chiral system, drawing inspiration from natural molecular assemblies, which demonstrates exceptional proficiency in specific information transfer, offering potential applications in the fields of materials science and nanotechnology.

Keywords: betalains, plants, biofluorescence, electron transfer, energy transfer

Influence of vibrational quenching on NIR lanthanide luminescence and strategies to reduce it in lanthanide molecular materials

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Near-infrared (NIR) lanthanide luminescent molecular materials are of interest for their wide applications such as lasers, optical telecommunication, bioimaging, quantum technologies. Due to the forbidden nature of the f-f transitions, it is difficult to directly excite lanthanide ions due to their low molar absorption coefficients. To overcome this problem, organic molecules are used to form molecular complexes, where the organic moiety acts as an antenna, absorbing light and undergoing energy transfer to nearby lanthanide ion. On the other hand, the gain of a more efficient excitation of lanthanide ions comes at the cost of having shorter emission lifetimes and lower quantum yields as a consequence of vibrational quenching phenomena by strong oscillators such as C-H and O-H groups present in the coordination environment. First, we will present a quantitative study of vibrational quenching in a series of NIR-luminescent beta-diketonate complexes. We elucidate the influence of the number, orientation and donor-acceptor distance of C-H and O-H groups on quenching and propose a semi-empirical predictive model based on the Förster's resonance energy transfer (FRET) theory of general validity for NIR-emitting lanthanide complexes. Second, we propose the use of 3d complexes as metalloligands to afford d-f heterometallic molecular materials. This strategy allows for reducing the proximity of the high energy oscillators such as C-H, N-H and O-H groups to the lanthanide center and, at the same time, obtain efficient dual emitters in the Visible and NIR region thanks to the combined properties of transition metal and lanthanide ions.

Keywords: Lanthanide, NIR, Luminescence, Quenching

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Spectroscopy and chemometrics analysis of antibiotic in milk serum

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Determining the residual amount of antibiotics in whey using the most cost-effective method is of interest to most dairy companies. The chemical composition of milk is of interest to the manufacturer of cheese and casein whey. The serum contains the main protein fractions (immunoglobulins G and serum albumins). Colostrum differs in composition from regular milk, being particularly high in fat, protein, ash and whey proteins. The latter contain immunoglobulins (Ig), necessary to provide immunity to newborns, and are transferred to the calf with colostrum.In this work, milk whey was studied using electron absorption and luminescence spectroscopy with the addition of a fluorescent probe to develop a determination of antibiotic residues.Modern requirements for the quality of medicines characterized by a tendency to obtain new or additional data on physicochemical properties antibiotics using spectral-luminescent methods, which have not yet become widespread in pharmaceutical analysis and production process control. At the same time about there is only scattered information on the spectroscopic properties of these molecules and their complexes. Studying the dependence of spectral and luminescent properties on the structure of antibiotics is of great importance for the development of luminescent methods and will make it possible to further use these data for analysis. The report will discuss the following problems: experimental and quantum chemical study of the spectral and luminescent properties of erythro- and threo-isomers of chloramphenicol, streptomycin sulfate, sulfaguanidine, mafenide, sulfadoxine, oxacillin, ampicillin, azlocillin, and their complexes with water molecules; interpretation of the nature of electronically excited states of the molecules under study; experimental study of the spectral and luminescent properties of antibiotics with fluorescent markers in various environments, including whey.

Keywords: Spectral luminescent properties, electron absorption and luminescence spectroscopy, pharmaceutical analysis

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SPECTROSCOPY AND CHEMOMETRICS FOR ANALYSIS OF ANTIBIOTIC LIQUIDS AFTER IRRADIATION

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Luminescence occurs as a result of thermal, optical or radiation-induced stimulation. During exposure, radiation energy accumulates and is stored in the object under study. Radiation-induced luminescence should be distinguished from other luminescent phenomena, such as photoluminescence, phosphorescence, etc., which do not depend on the dose of exposure. The study aimed to interpret the content of transformation products of aqueous solutions of sulfaguanidine and chloramphenicol under UV light and an electron beam using UV-Vis absorption and luminescence spectroscopy. We also analyzed COD and total organic carbon (TOC) by physicochemical methods. Many chemical measurements are subject to international guidelines and regulations. We carried out TOC measurements using Folin reagent at 740 nm. Sulfonamides are among the most commonly consumed veterinary antibiotics in the EU: they are used for the prevention and treatment of diseases in livestock. Chloramphenicol shows good solubility in water and is therefore used for parenteral use as a broad-spectrum antibiotic. However, it has a number of adverse effects: dose-dependent irreversible aplastic anemia. dose-dependent reversible bone marrow suppression in newborns. Following their administration, significant amounts may be excreted from the body as parent compounds and/or metabolites and released into the environment during grazing or spreading of manure. Moreover, the released acetyl conjugates can be cleaved back to the parent compound and can be transported to surface and groundwater.To prevent further environmental contamination and adverse effects of antimicrobial agents, understanding the fate of these compounds in the environment is necessary. To assess the mobility of pollutants in the environment, knowledge of their photostability is crucial. Our experiments showed that the studied sulfaguanidine and its

photoproducts have greater photostability than chloramphenicol. We found that the relatively high COD value and high content of phenolic compounds after UV irradiation indicate that the transformation of the parent compounds leads to a set of organic compounds, possibly more toxic. The presence of organic substances in aqueous solutions of antibiotics after the electron beam must be taken into account. Total organic carbon has proven to be very useful in obtaining quantitative and qualitative information on both the absolute value and the trend of the original antibiotic molecule after electron beam treatment. As a promising technology, indeed, due to the advantages of no chemical additives, electron beam treatment can be widely popularized and become a mature technology in the pre-purification stage of water from organic impurities.

Keywords: Luminescence, COD, electron beam, UV irradiation

LUMINESCENT MATERIALS FOR IMAGING, SENSORS AND THERANOSTICS

The charming role of chiral and luminescent lanthanide-based complexes in both technological and biomedical fields

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In the present contribution, a journey around the possible optical and chiroptical applications of chiral luminescent lanthanide-based complexes is described, with particular attention to the technological and biomedical fields. We will focus our attention on luminescent ions, such as Eu(III), Tb(III) and Yb(III) and chiral ligands containing oxygen and nitrogen donating atoms. The design of the best ligand/metal ion couple to obtain a satisfying thermodynamic stability of the complex and an efficient luminescence in the visible and Near Infrared (NIR) spectral region will be discussed. Also, we will see how to play with the ligand chirality to obtain a good chiroptical emission (Circularly Polarized Luminescence). Finally, the potential role of the discussed complexes in some emerging chiroptical applications in the aforementioned fields will be presented (i.e. the investigation of chiral molecular interactions in living cells and the use of the circularly polarized emission for the production of advanced security inks).

Keywords: lanthanide complexes, Chirality, Chiroptical activity, antenna effect

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Advancements and Outcomes in Optical Pressure Sensing: Strategies and Results

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Pressure is a fundamental physical parameter in the description of nature. Precise determination of pressure value remains a challenging process, especially for non-standard systems or under extreme pressure conditions. Inorganic materials doped with optically active ions (such as lanthanides or transition metals) represent some of the most promising materials for accurate pressure value determination without direct contact. Their physical stability allows for their utilization in various pressure conditions, ranging from partial vacuum to high-pressure conditions in the GPa range. Luminescence properties investigations under high-pressure conditions are carried out using the Diamond Anvil Cell (DAC), with the ruby R1-line shift serving as a conventional high-pressure indicator. Investigations at low pressure (partial vacuum) are possible in vacuum chambers equipped with vacuum pumps and standard manometers. Investigation of novel, advanced optical pressure sensors enables contactless monitoring of the pressure variations in extreme conditions.The internal crystal structure of materials undergoes changes (plastic or elastic deformation) under high-pressure conditions. The unit cell volume and inter-ionic distances decrease, leading to alterations in the local surroundings of optically active ions and resulting in changes in their excited energy levels. Such degenerations manifest as observed changes in photoluminescence properties, *e.g.*, blue/red emission band shift, variations in band intensity ratio, changes in the luminescence color, modifications of the bandwidth, or alteration in luminescence lifetime under varying pressure conditions [1]. On the other hand, in low pressure (partial vacuum), the intensified laser-induced heating of materials (light-to-heat conversion) occurs, resulting from impeded convection caused by a reduction in the number of air molecules and boosted thermalization of excited states [2]. Here, we present the different strategies and current results in contactless pressure sensing with the use of luminescence properties of inorganic materials doped with f-

or d-block ions. The utilization of novel, optical manometers can be determined and compared with other potential luminescent manometers by calculation of the two main manometric parameters *i.e.*, absolute sensitivity (S_a) and relative sensitivity (S_r) [3]. The development of luminescent pressure sensors, *i.e.*, optical, contactless manometers, offers new possibilities for monitoring changes in the spectroscopic properties of materials under extreme pressure conditions (from vacuum to high-pressure), thereby enabling remote determination of pressure value in the investigated systems. This research opens up new possibilities in advanced technologies for nano-scale and extraterrestrial research.References:[1] P. Woźny, et. al., *J. Lumin.*, 2019, 209, 321-327.[2] M. Runowski, et. al., *J. Mater. Chem. C*, 2021, **9**, 4643-4651.[3] Ł. Marciniak, et. al., *Coord. Chem. Rev.*, 2024, 507, 215770.

Keywords: optical sensors, luminescent manometers, lanthanides, high-pressure

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Bifunctional lanthanoid-based molecular materials: exploring opto-magnetic properties of a mononuclear Yb complex

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Multifunctional molecular materials are a type of compounds that mix various physical or chemical properties in one molecule. Among the various multifunctional systems, much attention has been given to the design of magnetic molecular materials with additional capabilities. This interest changed the direction of the field of molecular magnetism with the discovery of the first single ion magnet (SIM) in 2003, the terbium bis-phthalocyanine complex [$Tb(Pc)_2$], which demonstrated that mononuclear lanthanoid complexes can show slow relaxation of magnetisation. In addition, complexes based on trivalent lanthanoid ions exhibit specific luminescence covering a broad spectrum, from the visible to the near-infrared, with outstanding features such as narrow emission, long lifetimes and high luminescence. Despite these useful properties, the number of these compounds studied spectroscopically remains small. Hence, the first study reporting the coexistence of slow relaxation of magnetisation and luminescence based on lanthanoids was published in 2009.The first study linking relaxation dynamics and light emission was published in 2012, while an inductive effect between magnetic fields and luminescence was demonstrated in 2016. Consequently, interest in bifunctional molecular materials that combine luminescence with magnetic properties has grown. Lanthanoid-based magneto-luminescent complexes are promising for a variety of applications, such as molecular spintronics devices, single molecule detection and quantum readout. Among the lanthanoid ions, Dy^{3+} is commonly used to design luminescent single-molecule magnets (SMMs) due to its unique properties. Yb^{3+} is also investigated, but few examples of mononuclear Yb SIMs have been spectroscopically analysed. In addition, the temperature

dependence of luminescent properties in Yb-based materials remains underexplored, despite their potential for optical temperature sensors. Considering these data and our ongoing research on lanthanoid coordination chemistry, we have examined the opto-magnetic properties of a mononuclear Yb complex with a planar pentadentate ligand (H_2L), detailed in this study.The mononuclear complex [Yb(L)Br(EtOH)] (**1**) was isolated and structurally characterised. The opto-magnetic properties of **1** were investigated, showing that this complex is a bifunctional compound. Consequently, **1** reveals two coexisting functionalities: single-molecule magnetic behaviour induced by an external field (H_{dc}=1000 Oe), and temperature-dependent (11-361 K) Yb^{3+} centred NIR luminescence. The magnetic relaxation in this complex is of the Orbach-Raman-QTM type with a barrier to magnetisation reversal of 55.82 K (38.80 cm^{-1}).

Keywords: Multifunctional molecular materials, Lanthanoids, Single-ion magnets, Luminescent Thermometer

Bioluminescence color detection of Cadmium Made Simple with Mobile Technology

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The increasing portable imaging technological developments enables numerous discoveries across various research areas, making the researcher's work somewhat simpler. An example of such technology is the mobile phone application for bioluminescence and chemiluminescence analysis proposed some years ago (Roda et al., 2014). Utilizing a smartphone's camera, we previously showed that it was possible to estimate cadmium contamination of water based on visual and photodetection of bioluminescence color tuning using *Amydetes* firefly luciferase for educational purposes (Viviani et al., 2023). To increase analytical applicability of such method *hands on* field biosensors, here we developed a cell phone based applicative to analyze cadmium concentration based on bioluminescence color discrimination. The application has proven to be efficient with high precision, relying on reference values also inserted into the analyzed sample. The light emitted in a dark box by the luminescent colorimetric analysis is captured by the smartphone's camera, which, using computer vision, automatically finds the positioning of the samples and classifies them, delivering a visual result. In addition to making the process of quantifying Cadmium contamination as fast as taking a photo, this application, is potentially appliable to other luminescent color tuning sensors, with the convenience of a smartphone in the palm of one's hands.**Financial support:** FAPESP 2022/04800-0; CNPq 401.050/2021-1

Keywords: photodetection, biosensors, cell phone,

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Characterization and optimization of ZZ-AmyLuc for bioluminescent immunoassays

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ZZ-AmyLuc is a fusion protein consisting of the ZZ-domain of protein A and *Amydetes vivianii* (Amy) firefly luciferase, which was designed for use in bioluminescent immunoassays and Western Blotting. ZZ-AmyLuc offers a more sensitive and stable alternative to chemiluminescence methods based on HPR for detecting primary antibodies against specific antigens, including anti-SARS-COV-2 nucleoprotein. The goal of this study was to characterize the physical-chemical properties of ZZ-AmyLuc, and to improve its sensitivity and stability for bioluminescent immunoassays. For this purpose, *E. coli* BL-21 bacteria transformed with pCold-ZZ-AmyLuc cDNA were used for heterologous expression, and ZZ-AmyLuc was extracted and purified by Nickel-agarose affinity chromatography. The kinetics and spectra properties of the purified fusion protein were characterized and the immunoassay conditions optimized. The fusion protein had an optimum pH ~ 9.0, which is higher than that of the Wild-type AmyLuc (WT). The KM for ATP (22 µM) and luciferin (30 µM) increased in relation to the wild-type Amy-Luc (WT), corroborating the slower and more sustained luminescent kinetics of the phusion protein, which can be advantageous for immunoassays. Furthermore, ZZ-AmyLuc showed a *k*cat of 1.5 . 10-4 *cps*), slightly higher than the value found for WT (1.09 . 10-4 *cps*), but its catalytic efficiency was slightly lower (6.8 c.s-1.µM-1 for ATP and 5.0 c.s-1.µM-1 for luciferin) when compared to WT luciferase (12.1 c.s-1.µM-1 for ATP and luciferin). The fusion protein BL spectrum overlapped with that of the WT luciferase (λmax=549 nm), and showed similar pH-sensitivity. The immunoassays in the current format detected up to 0.5 ng of SARS-CoV-2 nucleoprotein, highlighting the need for further studies to increase the detection limit, such as engineering this fusion protein and changing the composition of the assay solution. Thus, ZZ-AmyLuc fusion protein shows great potential to be used as an efficient and sensitive alternative for large-scale IgG-based immunoassays and Western Blotting.

Keywords: Amydetes vivianii, bioluminescence; luciferase; ZZ-domain

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Chemiluminescence biosensors for H_2O_2 and oxidases substrates quantification based on peroxidase-like activity guanosine self-assembled hydrogel

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Chemiluminescence (CL) is widely used for hydrogen peroxide detection, mainly exploiting the highly sensitive peroxidase-luminol-H_2O_2 system. Hydrogen peroxide plays an important role in several physiological and pathological processes and is produced by oxidases, thus providing a straightforward way to quantify these enzymes and their substrates [1]. Recently, biomolecular self-assembled materials obtained by guanosine and its derivatives and displaying peroxidase enzyme-like catalytic activity have received great interest for hydrogen peroxide biosensing [2]. These soft materials are highly biocompatible and can incorporate foreign substances while preserving a benign environment for biosensing events. In this work, a binary guanosine hydrogel prepared using a mixture of guanosine and guanosine 5′-monophosphate in the presence of K^+ ions are loaded with a CL reagent (luminol) and a catalytic cofactor (hemin), to produce a functional material showing peroxidase-like activity to the CL reaction of luminol with H_2O_2. The hydrogel is then functionalized with a specific oxidase enzyme to enable marker biosensing: the hydrogen peroxide produced by analyte oxidation reacts, in the presence of the self-assembled guanosine/hemin gel mixture, with luminol to produce photon emission. The biosensor takes advantage of both the features of CL detection, offering high detectability and amenability to miniaturization, and of the 3D porous structure of hydrogel, as providing increased stability and catalytic activity even in alkaline and oxidizing conditions of incorporated enzymes. In this work, we show the development of four guanosine hydrogel – based biosensors for the detection of glucose, xanthine, uric acid and lactate by simple incorporation of corresponding oxidases: glucose oxidase (GOx) [3], xanthine oxidase (XOD), urate oxidase (UO) and lactate oxidase (LOx). Exploiting 3D printing technology, smartphone-based portable devices for CL biosensors were developed, verifying the applicability to quantify biomarkers of clinical interest at the point-of-care (POC). The photon emission from the CL reaction was detected using a portable device that employs a smartphone's CMOS (complementary metal oxide semiconductor) camera for CL emission detection. **References**[1]

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Keywords: guanosine-based hydrogel; enzyme mimic; G-quadruplex; supramolecular chemistry; chemiluminescence; biosensor; hydrogen peroxide; point of care

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Combination of lanthanides luminescence with second harmonic generation (SHG) in polycrystalline materials for temperature sensing, optical coding and anti-counterfeiting

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Optically active luminescent materials, based on lanthanides attract significant attention due to their unique spectroscopic properties, non-linear optical (NLO) activity and possibility of application as contactless sensors, in anti-counterfeiting and optical coding. NLO spectroscopy may be a powerful tool for sensing of various intrinsic properties of materials and different state functions of the system. Materials exhibiting diverse non-parametric and parametric NLO processes, such as up-conversion luminescence (UCL) and second harmonic generation (SHG), respectively, are essential in areas such as nanophotonics, optical information processing, and biomedical imaging. However, the polycrystalline, micron- and nano-sized materials employed for such diverse applications to date are efficient only for one type of non-linear optical activity.

Here we show the feasibility of simultaneous employing the luminescence of lanthanides, both down-shifting and/or UCL, combined with SHG in different polycrystalline materials, including micron- and nano-sized inorganic particles and metal-organic-framework (MOF) materials.[1-3] In the first case we used $BaTiO_3:Ln^{3+}$ (Ln = Yb, Er, Ho) micron-sized powder for optical temperature sensing, following the thermal evolution of SHG and UC emission bands (intensity ratios). Moreover, we showed that this strategy can be utilized for detection of phase transitions from non-centrosymmetric to centrosymmetric systems, and *vice versa*.[1] In the case of Ln-doped MOF (Ln = Er^{3+} or Yb^{3+}/Er^{3+}) materials the SHG signals could be easily collected exciting the materials in a broad NIR spectral range, from ≈800 to 1500 nm, resulting in the intense color of emission, observed in the entire visible spectral region. Moreover, upon excitation in the range of ≈900-1025 nm, the materials also exhibit the

NIR luminescence of Er^{3+} ions, centered at ≈1550 nm. Taking the benefits of different thermal responses of the mentioned effects, we have developed a non-linear optical thermometer based on the lanthanide-MOF materials. Our study provides a groundwork for the rational design of readily-available and self-monitoring NLO-active Ln-MOFs with the desired optical and electronic properties.[2] Finally, we developed the multi-modal, NLO active nanomaterials based on lanthanide-doped $LiNbO_3$ nanoparticles that simultaneously exhibit unprecedentedly efficient SHG and THG, as well as UC photoluminescence. These dielectric nanoparticles retain their high non-linear optical conversion efficiency both as powder and as aqueous colloidal solution. We used them for fabrication of optically active biocompatible microfibers and polymer-based 3D-printable objects, as well as for fingerprint detection. Finally, we demonstrate the first 8-bit coding platform purely based on multi-modal non-linear optical activity originating from different parametric and non-parametric processes, show-casing the technological potential of these materials for anti-counterfeiting and advanced optical information processing.[3]References:[1] Zheng, T. et al. Advanced Optical Materials, 9, 2100386 (2021)[2] Runowski, M. et al. ACS Applied Materials & Interfaces 15, 3244–3252 (2023)[3] Runowski, M. et al. Advanced Functional Materials. 34, 2307791 (2024)

Keywords: Luminescence; up-conversion emission, SHG and THG; non-linear optics; optical thermometers; optical coding, anticounterfeiting, nanomaterials; nanoparticles, MOF materials

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Combining Luminescence with Indium-Tin Oxide Nanoparticles for Biomedical Applications at the Third Biological Window

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Certain optically-triggered nanoparticles (NPs) greatly facilitate the light-into-heat conversion in a region of interest, thus serving for photoacoustic imaging (PAI) and photothermal therapy (PTT), which are attractive in vivo biomedical applications both requiring local and controlled delivery of heat. More specifically, plasmonic NPs with their optical extinction engineered to lie within the third near-infrared window (NIR-III, 1500-1800 nm) allow higher penetration depth into tissues and fewer side-effects (e.g. heating of non-targeted regions) than those working in the NIR-II (1000-1350 nm). That is because of the minimal absorption and scattering of the excitation beam at NIR-III wavelengths when propagating through tissues. Moreover, beyond the use of such plasmonic NPs to build an all-optical system achieving local heat release for PAI and PTT, the combination of luminescent and plasmonic NPs can form an integrated system combining detection and therapy (so-called theranostic). Currently, the broadly extended use of luminescent NPs with excitation in the first (NIR-I, 750-950 nm) and emission within NIR-II, respectively, leaves NIR-III available for optical-triggering of plasmonic NPs for the previously mentioned applications (PAI and PTT).This work addressed the lack of NPs working exclusively in such NIR-III range by preparing indium oxide plasmonic NPs doped with tin (ITO), purposedly tuning their optical extinction to the 1600-1800nm range. Furthermore, these ITO NPs show a heat-conversion-efficiency (HCE) value above 80% under irradiation at 1700 nm. Remarkably, a potential theranostic system was straightforwardly mimicked by mixing the ITO NPs with luminescent Nd-doped $NaGdF_4$ NPs -nowadays a widely used workhorse for NIR-II in vivo imaging and temperature sensing. Spectra obtained after excitation of the nanofluid at 800 nm showed a minimum spectral distortion and very low reduction in Nd-doped NP emission intensity. Hence, it demonstrates the minimal interference from ITO absorption over the information-carrying emission from those Nd-doped NPs acting as imaging agents/sensors and located nearby. The spectral profile of ITO NPs´ optical

extinction and their high HCE value make them ideal candidates for PAI and PTT and as a novel tool to be combined with other (luminescent) NPs for an integrated theranostic platform.

Keywords: Nanoparticles, plasmonic, luminescence theranostic, biological window

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Design and Construction of Novel Chiral Covalent Organic Framework-Based Fluorescent Sensors

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Chiral recognition of molecules holds significant importance in numerous fields including analytical chemistry, food chemistry, and biotechnology. Chiral fluorescence spectroscopy has the advantages of simple operation, low cost, and high analytical flux, but it requires highly sensitive chiral optical probes. Compared with small molecular probes, chiral covalent organic framework (COF) probes have large specific surface areas, easily regulated structures, and can be reused.Two C=C bond-linked chiral COFs were synthesized by Knoevenagel polycondensation of chiral tetrabenzaldehyde of dibinaphthyl-22-crown-6 with 1,4-phenylenediacetonitrile or 4,4'-biphenyldiacetonitrile. Reduction of olefin linkages of the as-prepared chiral COFs produces two C–C bond-linked frameworks, which retain high crystallinity and porosity as well as high chemical stability in both strong acids and bases. Compared to the C=C bond-linked chiral COFs, the C–C bond-linked COFs display blue-shifted emission with enhanced quantum yields and fluorescence lifetimes, while the parent C=C bond-linked COFs exhibit higher enantioselectivity than the reduced analogs when be used as fluorescent sensors to detect chiral amino alcohols via supramolecular interactions with the built-in crown ether moieties (*J. Am. Chem. Soc.* **2021**, *143*, 369).The chiral memory effect was investigated for the first time during the dynamic transformation from porous organic cages to COFs. A total of six 2D chiral COFs constructed by entirely achiral building blocks were successfully synthesized by the transformation of amine bond-linked chiral cages. The prepared chiral COFs exhibited high enantioselectivity as fluorescence sensors and can be utilized for the sensing of chiral amino alcohols and amino acids. To microscopically elucidate the host-guest interactions between chiral COFs and enantiomers and reveal the mechanism of chiral COF-based fluorescence sensing system, preliminary investigations were conducted into the host-guest interactions using energy-minimized density functional theory (DFT) calculation (*J. Am. Chem. Soc.* **2024**, *146*, 7594).Consequently, these studies underscore the significant potential of employing chiral COFs as luminescent sensors. Evidence suggests that COF-derived fluorescent probes display superior fluorescence properties, pronounced

enantioselectivity, and excellent reusability. Moreover, the well-ordered crystalline framework of COFs allows for the investigation of chiral recognition processes at an atomic level, a feat that is not readily achievable with conventional probes.

Keywords: Fluorescent sensors, Chiral recognition, covalent organic framework, Enantiorecognition

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Development of reporter resistant bacteria strains to assess *in vivo* and *in vitro* infection using bioluminescence imaging

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Antimicrobial resistance is on the rise, set to surpass the major causes of death for humans by 2050. Two bacterial species, *Escherichia coli* and *Pseudomonas aeruginosa*, are becoming highly antibiotic resistant, being important pathogens in nosocomial infections. The aim of our project is to generate reporter bacterial strains with genomic integration of genes for expression of a luciferase (either CBG2 or NanoLuc) and a fluorescent tag (either miniSOG or mKate2) to be used as a sensitive method *in vitro* and *in vivo* for antimicrobials efficacy assessment. Plasmids containing either reporter genes were generated using Gibson Assembly. The promoter J23119 was chosen to enhance the expression of both proteins in the final constructs. Plasmids containing the homology arms for the 16s locus of the bacteria will be used as donor DNA plasmid for the CRISPR/Cas9 gene editing technology. Lambda/Red recombination strategy will facilitate the integration in both species (ATCC25922/Niessle 1917 strains for *E. coli* and ATCC27853/PA01 strains for *P. aeruginosa*). CBG2/NanoLuc expressing bacteria have been imaged using the IVIS Spectrum Imager (PerkinElmer) after incubation of D-Luciferin, Naphtyl-Luciferin (CBG2) and Furimazine (NanoLuc). MiniSOG/mKate2 fluorescence has been visualized using the microscopes DM5500 B and SP8 DLS (Leica). Our preliminary results demonstrate that a series of constructs for the dual expression of CBG2/NanoLuc and miniSOG/mKate2 has been successfully assembled in gram negative bacteria for CRISPR/Cas9 integration. All reporter proteins were correctly expressed and bacteria may be applied for different assays for the testing of antimicrobials in vitro and in vivo using optical readouts.

Keywords: Bacteria, Antimicrobial Resistance, Fluorescence, Reporter

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Employing an iridium^{III} complex in luminescent thermometry: a multiparametric thermal sensing and multiple regression approach

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In the past decade, luminescence thermometry has made significant advancements, approaching current measurement technologies. Typically, a thermometer performance is evaluated based on the relative thermal sensitivity (S_r) and temperature uncertainty (dT). Some thermometric parameters (Δ) of a single emitting center can be explored and combined, such as emission intensity, spectral positions of absorption and emission bands, emission bandwidth, anisotropy, luminescence decay time, and relative intensity between two emission bands (ratiometric systems). However, in the literature there are few works that explores thermometry in Ir^{III} complexes. In Ir^{III} complexes, the emission comes from the ^{3}LC-^{1,3}MLCT hybrid state, with triplet ^{3}MLCT being dominant at high temperatures. This emission experiences strong temperature dependence due to the rigidochromic effect. Therefore, we report the synthesis of an Ir^{III}-complex and thermometry studies based on the performance of a multiparametric luminescent thermometer. To make this possible, the synthesis consisted of the preparation of a μ-chlorobridged cyclometalated Ir^{III} dimer $[Ir(Fppy)_2(\mu\text{-}Cl)_2Ir(Fppy)_2]$, followed by the insertion of the ancillary ligand pdc to form the heteroleptic complex $[Ir(Fppy)_2pdc]$, where Fppy = 2-(2,4-difluorophenyl) and pdc = 2,4-pyridinedicarboxylic acid, resulting in a yellow solution with a strong green emission under UV irradiation. After slow evaporation of solvents, the crude product was purified by column chromatography with silica gel. The complex $[Ir(Fppy)_2pdc]$ was obtained as a yellow powder. Yield: 87%. Quantum yield ($\Phi_{DMSO\ solution}$): 47%. The emission spectrum of the complex $[Ir(Fppy)_2pdc]$ (l_{max} = 553 nm) at RT, exhibited a broadened band with an unstructured profile, indicating a greater ^{3}MLCT character. Emission spectra were acquired varying the temperature from 11 to 320 K, revealing spectral changes as the temperature decreased. At lower temperatures, bands appeared at 485 nm and 513 nm, attributed to the emission of ^{3}LC vibronic splittings, which exhibit practically invariable energies with increasing rigidity. However, it is notable that the ^{3}MLCT band is strongly

influenced by temperature, with the rigidochromic effect destabilizing it, resulting in a shift to lower energies as the temperature increases. The thermally coupled nature of the ^{3}LC/^{3}MLCT levels enabled us to utilize the ratiometric approach, resulting in a maximum S_r of 1.25% K^{-1} within the 11 – 125 K temperature range. By using the ^{3}MLCT band shift parameter (18507 – 17410 cm^{-1}), it was possible to obtain a maximum S_r of 0.033% K^{-1} in all temperature range. Finally, using the lifetime Δ, a high sensitivity of 4.40% K^{-1} (11 – 125 K) was found. Thus, these results place the multiparametric approach using the luminescence of Ir^{III} complexes at the center of attention in luminescence thermometry, demonstrating new paths for thermometry.

Keywords: Luminescence thermometry, Ir(III) complexes, ratiometric approach, multiparametric luminescent thermometer

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Luminescent iridium^{III} complexes with N-Oxide ligands: synthesis and characterization

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The Ir^{III} ion readily forms coordination compounds with various classes of cyclometalating ligands, exhibiting attractive luminescent characteristics such as high quantum yields (Φ), modulation of both absorption and emission, as well as modulation of excited state lifetime. These complexes have promising applications in optoelectronics such as OLEDs, DSCs, LEECs, and several other optoelectronic devices. Additionally, they find application in the biological field, including oxygen sensing, bioimaging and agents in photodynamic therapy. Thus, this work describes the synthesis and spectroscopic characterization of two novel Ir^{III} complexes with N-oxide bridging ligand (N^O). The syntheses consisted on the preparation of the cyclometalated Ir^{III} dimer $[Ir(Fppy)_2(\mu\text{-}Cl)_2Ir(Fppy)_2]$, followed by the preparation of heteroleptic mononuclear $[Ir(Fppy)_2pzdc]$ and dinuclear $[Ir(Fppy)_2(\mu\text{-}pzdc)Ir(Fppy)_2]$: Fppy = 2-(2,4-difluorophenyl) and pzdc = 2,3-pyrazinedicarboxylic acid. Both complexes were structurally characterized by ^{1}H-NMR, elemental analysis, and FTIR-ATR. FTIR-ATR (υ_{max}/cm^{-1}): 1632 $(\upsilon C{=}O)_{pzdc}$, 1600, 1570, 1557 $(\upsilon C{=}N, C{=}C)_{fppy}$, 1333 $(\upsilon COO)_s$, 1108 $(\upsilon C{=}N, C{=}C)_{pzdc}$. Coordination through the N^O site of the pyrazine is indicated by infrared spectra, wherein the pyrazine stretching bands disappear in the complex. Calculated CHN (found) for the structure $IrC_{28}H_{23}N_4O_8F_4$: C, 41.43% (41.50%); H, 2.86% (3.02%); N, 6.90%. Absorption and photoluminescence spectra were obtained in several solvents: DMSO, DCM, ACN, and MeOH. The complexes exhibited high molar absorptivity, attributed to singlet and triplet metal-to-ligand charge transfer (MLCT) and ligand-centered (LC) transitions, which were observed in the UV-Vis spectra. Excitation spectra showed a broad band with a similar profile for all tested solvents, for both complexes. In the emission spectra for each solvent tested, broad emissions ranging from yellow-orange to red were observed. Notably, the mononuclear complex exhibited emission maxima at approximately 510 and 617 nm in DMSO, 612 nm in DCM, 622 nm in ACN, and 630 nm in MeOH. Conversely, the dinuclear complex showed

emission maxima at approximately 616.5 nm in DMSO, 624.5 nm in DCM, 617.5 nm in ACN, and 673.0 nm in MeOH. This difference in emission maxima is attributed to the solvatocromic effect that leads to structural differences, which influence the energy levels of the excited states. Additionally, the presence of two iridium centers in the dinuclear complex may lead to interactions between the metal centers, altering the electronic properties and resulting in a red-shifted emission compared to the mononuclear complex. The Φ for the mononuclear complex was determined: DMSO (7.7%), DCM (9.2%), ACN (6.9%), and MeOH (1.2%). Their photophysical properties indicate potential for applications in photonics, particularly notable for their high molar absorptivity and tunable emission in different solvents.

Keywords: irIII Complexes, luminescent properties, N-Oxide ligands, photophysical characterization.

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Modified matrices of gellan gum doped with lanthanide ions for the production of photonic devices

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The study of new materials based on gellan gum (GG), a natural polysaccharide derived from bacteria, allows the production of modified and biocompatible hydrogels and films to suit different applications. In this work, GG was combined with network-forming molecules, such as sericin (SS), a protein extracted from silkworm cocoons aiming for a material with better optical and greater mechanical resistance. The SS material showed interesting mechanical and optical properties for a functional composite, with the ability to reproduce patterns on its surface film through the soft lithography process and periodic micropatterns with angle-dependent iridescent colors (Figure 1-left), structurally induced in the film by a mold, which aims applications such as sensors, random lasers, and structural color systems. Preliminary studies indicated reduced energy transfer rate between GG and lanthanide ions, which are important in the development of photonic devices due to their distinguished luminescent properties. The modified system, with sensitizing groups, was doped with Eu^{3+} showing an interesting sensitization effect (Figure 1-right), resulting in an increased emission intensity with longer lifetime of the excited state by the presence of SS. This effect enables these new materials to be studied as sensors printed on supports to produce intelligent packaging, either by suppression or enhancement of luminescence, for example.

Keywords: gellan gum, sericin, lanthanide, photonic

Nanomanometers: Engineering Luminescent Copper Indium Sulfide Quantum Dots

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Keywords: Luminescent nanoprobes, nanomanometers, copper indium sulfide, quantum dots, mechanical forces in biology

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Plasmonic Heating Monitored Through Luminescent Nanoparticles

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Between the technological interests of plasmonic nanoparticles is their ability to transform light into heat. This fact can be used in biomedical applications (photothermia), promotion of chemical reactions at the nanoscale or water remediation. All those applications, though, take place in aqueous environments, which is not totally transparent to the excitation beam (typically in the visible or near-infrared ranges). In the biomedical case, besides water, the environment may also have additional components, such as melanin, haemoglobin, lipids, etc. which may also absorb or scatter the light beam. This composition of the environment implies that there is not a good accuracy on the illumination that really reaches the plasmonic nanoparticles, thus uncontrolled heating doses are delivered. This fact calls for the development of *in situ* temperature measurements.Our approach to this problem starts developing and optimizing a specific luminescent nanomaterial: CaF_2:Nd^{3+}, Yb^{3+}. It has been precisely designed to work (both regarding excitation and emission) in the wavelength ranges in which typical biological media attenuates light the least. Following a thorough spectroscopy study, required due to the complex optical-sites characteristics of the material, we have designed the best thermometry approach it allows.Afterwards, we have tested its performance in the biological environment, triggering heat optically through plasmonic nanoparticles. We have developed measurement strategies to guarantee the accuracy of the measurements. Given the heterogeneous and optically dense nature of biological tissues, this second part is a challenge, as the interaction of the emitted light with the tissue may involve a deformation of the luminescent spectrum, and thus create inaccurate thermal readings.

Keywords: luminescence, plasmonics, thermometry, optical sensor, optical heating, biological environments

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Pushing boundaries: dysprosium complex as a novel magneto-luminescent molecular material

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Multifunctionality represents a pivotal objective in the realm of smart materials, offering enhanced versatility and performance. Within this context, the field of magneto-luminescent molecular materials has garnered considerable attention and interest due to its potential for a wide array of applications. A significant challenge in this field is the development of single molecule magnets (SMMs) with temperature-dependent luminescence, enabling them to function as in situ thermometers.The ability to continuously monitor temperature in SMMs with temperature-dependent luminescence is invaluable, ensuring the preservation of magnetic behavior across varying thermal conditions. This capability is crucial for applications requiring consistent magnetic properties, such as molecular spintronics and quantum readout systems.Despite recent progress, several challenges remain unresolved. One such challenge is the development of air stable SMMs with high blocking temperatures (T_b). While milestones like the 80 K achieved with metallocenes are noteworthy, their practical utility is hindered by their air instability. Therefore, there is a need for further research to explore air-stable alternatives. In this way, recent efforts have focused on synthesizing air-stable SMMs with improved properties. For instance, a dysprosium azafullerene with a 45 K blocking temperature shows promise. However, the current record for unencapsulated SMMs is 36 K, pointing to the necessity for additional improvements.In this way, we introduce a novel molecular magnet setting a new T_b record of up to 43 K for air-stable unencapsulated SMMs. This material exhibits

luminescence thermometry capabilities below the blocking temperature, representing a significant advance in air-stable bifunctional nanomaterials development.Overall, our findings contribute to ongoing efforts to improve multifunctional molecular materials, paving the way for broader applications across various technological and scientific domains. Our air-stable hexagonal bipyramidal complex $[DyL(OSiPh_3)_2](BPh_4)\cdot 1.5CH_2Cl_2$ (**1**$\cdot 1.5CH_2Cl_2$) serves a dual purpose as both a luminescent thermometer and a single ion magnet (SIM), boasting an impressive energy barrier of 1528 K. However, its robust QTM contributes to a lower T_b. Similarly, our diluted complex $[Dy_{0.09}Y_{0.91}L(OSiPh_3)_2](BPh_4)\cdot 1.5CH_2Cl_2$ (**1@Y**$\cdot 1.5CH_2Cl_2$) functions simultaneously as a magnet and thermometer. It operates as a SIM with a blocking temperature of up to 43 K, the highest reported among air-stable unencapsulated SMMs. Consequently, **1@Y**$\cdot 1.5CH_2Cl_2$ stands at the cutting-edge of a dual-role as a model of a bifunctional SMM and luminescent thermometer, facilitating temperature monitoring within its magnetic operational range. Importantly, this material showcases superior magnetic properties (U_{eff} and T_b) compared to any other documented SMM luminescent thermometer.

Keywords: Multifunctional materials, Single molecule magnets, Luminescent thermometry, Temperature sensing

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Quinolones as sensitizers of visible emitting lanthanide(III) ions

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This work presents a detailed study of lanthanide ions (Eu^{3+}, Gd^{3+}) with nalidixic acid and flumequine ligands as binary complexes and as ternary complexes with phenanthroline (phen) and triphenylphosphine oxide (tppo) as co-ligands.When it comes to forming complexes with lanthanides, the choice of ligands plays a crucial role. Both flumequine and nalidixic acid because of their structures (Fig. 1) coordinate with metal ions in a bidentate fashion, utilizing the oxygen atoms from both their carbonyl (quinolone) and carboxylic groups. This not only allows to formation of stable complexes but also enhances the spectroscopic properties of lanthanide by displacing water molecules from the inner coordination sphere which might cause unwanted nonradiative quenching of luminescence. Both chosen ligands belong to a first generation quinolone antibiotics which makes them perfect ligands. Their anti-microbial properties have been thoroughly tested which expands the possibility of use their compounds in the biological and biolabeling areas and as ligands they are readily available at very reasonable cost. Introducing to the complexes co-ligands is aimed at increasing the luminescence properties of complexes. In order to characterize the structure of the compounds, carbon analysis, thermogravimetry and infrared spectroscopy (FTIR) were used. The strong red luminescence arises from the $^5D_0 \rightarrow {}^7F_2$ transition which indicates efficient energy transfer from ligand to metal ion. Furthermore, decay times, the overall and intrinsic quantum yields were used to determine a contribution of the radiative and non-radiative paths to the excited state deactivation and to estimate the efficiency of ligand-to-metal energy transfer. Luminescent properties indicate a high application potential of the tested compounds, especially when introduced into polymeric materials such as films or beads.

Keywords: luminescence, europium, quinolones

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Selection and engineering Color tuning luciferases: from mammalian cell pH indication to smartphone based luminescent biosensors

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We recently have shown that firefly luciferases pH-sensitivity can be harnessed for intracellular pH indication and for heavy metal sensing in water samples. We have also shown that different luciferases display distinct heavy metal selectivities. However, there are drawbacks that need to be addressed to bring this technology to practical uses, such as the red-shifted spectra of most firefly luciferases at high temperatures which limit the application for mammalian cells, and the broad selectivity for different metals such as Zn, Cd, Hg. These issues can be addressed by selection of new luciferases and also by engineering the proton/metal binding sites. We show that AmyLuc™ color tuning luciferase, was the best option among firefly luciferases tested for mammalian cells pH-sensing, and also a promising tool for BL color tuning detection of cadmium, being successfully applied for educational purposes to demonstrate the effect of heavy metals and pH on enzyme function. To be effective for *hands on* field biosensor, however, such methodology must be associated to easy, cheap and portable photodetection devices associated to quantification programs. Based on the previously demonstrated applicability of smartphone technology for bioluminescence assays (Roda et al., 2014), and the availability of cell phones with increasingly sensitive CCD cameras, we recently developed smartphone based applicative for luminescent colorimetric analysis of cadmium contamination of water. The methodology can be harnessed not only for metal sensing, but also for intracellular pH sensing.

Keywords: cadmium sensing, pH-indications,

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Synthesis and effect of the shell thickness of monodispersed bright $NaYbF_4:Tm^{3+}@NaYF_4$ core/shell upconversion nanoparticles for bioimaging applications

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Lanthanide-based upconversion nanoparticles (Ln^{3+}-UCNPs) can convert near-infrared (NIR) photons into higher energy ultraviolet-visible (UV-Vis) light.[1] These nanoparticles are characterized by sharp luminescence peaks, long luminescence lifetimes, and tunable luminescence emissions across the UV-Vis-NIR region.[2] Such optical properties lead to reduced autofluorescence and enhanced penetration depth, rendering UCNPs ideal for advanced biomedical luminescence imaging.It has been recently recognized that β-$NaYbF_4$ is the most efficient host material for constructing multiphoton upconversion nanoparticles (UCNPs).[3] This host provides a high concentration of Yb^{3+} sensitizers that increase the absorption cross-section of the nanoparticles to maximize excitation light utilization. However, energy migration (EM) back to the surface is the main limitation of this host, therefore an optically inactive protective shell is necessary. The synthesis and precise size control of β-$NaYbF_4$ nanoparticles, along with the appropriate thickness for the inactive shell, remain areas for further exploration.Here we present the synthesis, surface modification, cell viability assays, and bioimaging application of $NaYbF_4:Tm^{3+}@NaYF_4$ core/shell UCNPs.The protection of the 27.2 nm $NaYbF_4:Tm^{3+}$ core UCNPs and the increase in the shell thickness (and core/shell nanoparticles size) from 1.4 to 5.9 nm (from 30.1 to 38.9 nm) using a layer-by-layer shell growth strategy resulted in a concomitant increase in the upconversion luminescence intensity, lifetime, and quantum yield.

After surface modification using poly(acrylic acid) polymer, the nanoparticles demonstrated excellent colloidal stability when redispersed in water, borate buffer, and biological media. The cell viability assays demonstrated the low cytotoxicity of our nanoparticles to 3T3 and MDA-MB-231 cell lines. Preliminary bioimaging experiments revealed successful internalization of the nanoparticles by MDA-MB-231 cells, highlighting their potential as candidates for bioimaging applications.References:1) Y.E. Serge-Correales, C. Hazra, S. Ullah, L. Roncalho, S.J.L. Ribeiro. *Nanoscale Adv.* **2019**, 1, 1936–1947.2) Y.E Serge-Correales, S. Ullah, E. P. Ferreira-Neto, H. D. Rojas-Mantilla, C. Hazra, S.J.L. Ribeiro. *Mater. Adv.* **2022**, 3, 2706–2715.3) S. De Camillis, P. Ren, Y. Cao, M. Plöschner, D. Denkova, X. Zheng, Y. Lu, J. A. Piper. *Nanoscale* **2020**,12, 20347-20355

Keywords: Upconversion nanoparticles, monodisperse core/shell nanoparticles, layer-by-layer shell growth, bioimaging, biocompatibility.

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Tb^{3+} Doped LaOBr - Persistent or Photostimulable Phosphor - or Both - and Why?

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X-rays were invented in 1895 by observing luminescence excited by this radiation. By the next year, $CaWO_4$ powder screens were introduced and dominated the medical X-ray diagnostics markets until 1970s – *for 75+ years*. A new phosphor, Eu^{2+} doped *BaF*(Cl,*Br*,I) took then gradually over and the *X-ray excited Photoluminescence* emitted by $CaWO_4$ shifted to *Photostimulated Luminescence* (PSL) of Eu^{2+}. At the same time, the process became much more complicated, though. The X-ray image was now possible to be *stored for up to weeks* by trapping energy in defects of the host lattice. Other improvements took place as well: strong Eu^{2+} band band emission replaced the weaker emission of $CaWO_4$ and, more important, the considerable afterglow of $CaWO_4$ causing blurring of the X-ray images was removed. The change of phosphors occurred without much struggle though the Tb^{3+} doped LaOBr (*structurally isomorphic to matlockite PbFCl*) was initially considered as well. The candidate of Fuji Corp. (BaF(Cl,Br,I:Eu^{2+}) overcame finally in 1990s (*money talks*). As the chemical formula of the new phosphor suggests, the extensive substitution of Cl with Br and even I would mean that the defect structure of this *BaFCl* phosphor is quite complex. In this report, the preparation, thermal stability and PL/PLE/PSL/TL luminescence of LaOBr:Tb^{3+} are described to solve the defect structure, luminescence, PSL/TL properties as well as the luminescence mechanisms in detail.The LaOBr:Tb^{3+} powders were prepared by heating La_2O_3:Tb^{3+} with *55 %* excess of NH_4Br @ 800 C. Annealing at 1000+ C *in air* leads to a *partial substitution of bromide* (Br^-) *by oxide* (O^{2-}). To achieve the global *neutrality of the doped compound*, the *charge compensation* (CC) of *excess negative* charge due to the said substitutions is *compulsory and was* carried out by *oxidation of* Tb^{3+} *to* Tb^{IV} which changed the material's color from white to yellow. Despite the faint colouring of the material, the anionic substitution enabled the compulsory formation of negatively charged traps which are capable to trap holes (h^+). On the other hand, the Tb^{IV} *in the* Tb^{3+} *site, acts as a positively* charged trap which is capable to trap

electrons (e^-). As a result, the oxidation of Tb^{3+} resulted in an unexpected change in the Tb^{3+} emission: the blue emission from the $^5D_3$ levels was seriously quenched changing the emission colour from bluish green to green composed essentially of the emission from the $^5D_4$ levels, The quenching mechanisms include the self-absorption by the Tb^{IV} impurities at energies above 2.5 eV (500 nm). Alternatively, the cross-relaxation between the $^5D_3$ and $^5D_4$ as well as the $^7F_6$ and $^7F_0$ levels has a similar effect, The structural effects of doping and defect formations are studied and the exact PersLum and PSL mechanisms will be eventually studied.

Keywords: Persistent Luminescence, Photostimulated Luminescence, Charge Compensation, Trap formation

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[Eu(tta)$_3$(PIB)] Incorporated Castor-Oil Based Film: Characterization and Evaluation of Thermometric Performance

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With the increasing demand for more precise and small-scale temperature sensors, lanthanide ion-based compounds have gained prominence due to their high dependence of luminescence on temperature. These compounds offer the potential for miniaturization of temperature measurement tools, down to the nanoscale, enabling precise temperature measurement even in cellular environments. Notable applications include industrial systems and electronic circuit boards. An accurate method for evaluating temperature via luminescence involves using the ratio between two emissions of different levels in a ratiometric system. This method eliminates errors associated with electrical fluctuations, background noise, and sample concentration. Luminescent complexes based on lanthanide ions coordinated to organic ligands and inserted into a polymeric matrix are promising for several applications. In this study, the complex [Eu(tta)$_3$(PIB)] was used as a luminescent component in a castor oil-based film prepared via the Sol-Gel route, at 0.25% complex concentration. The complex before and after incorporation into the film was monitored via FTIR, and the successful synthesis of the complex was verified by detecting Eu-O and Eu-N stretches, between 400 cm^{-1} and 600 cm^{-1}, as well as the absence of band at 2,250 cm^{-1} (n_{NCO}) in the film, indicating polymer formation. Furthermore, the luminescence behavior before and after film formation was studied via photoluminescence spectroscopy (PLS). Furthermore, the luminescent film had its thermometric performance evaluated in the range between 13 K and 325 K. The developed system exhibited an ideal working window between temperatures of 125 K and 282 K, achieving a maximum relative thermal sensitivity (S_m) of 1.8% K^{-1} at 270 K, with a minimum temperature uncertainty (dT) of

5 K at 225 K. The values obtained are considered suitable for further in-depth investigations regarding application in luminescent thermometry.

Keywords: Luminescent thermometer, Eu(III)-Complex, polymeric luminescent film

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Beyond the single parametric thermal sensing: Unifying thermometric parameters to improve the performance of Eu^{III}-based luminescent thermometers

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The physical quantity that measures the thermal energy of a body is one of the definitions of temperature, which is the most fundamental thermodynamic state variable. Its fluctuations are central to myriad natural and man-made operations, such as life-sustaining cellular processes and networked devices. In these domains, the traditional contact temperature reading becomes inefficient, as the accuracy of a thermometer is limited by its size. Consequently, remote temperature readings have emerged to meet this need, where luminescence thermometry excels in the pursuit of highly sensitive and accurate thermometers. This field depends on temperature-induced changes in the spectroscopic properties of an ensemble of probes. However, thermal sensitivity may vary substantially depending on the chosen spectroscopic property. Therefore, this study aims to unify the traditional ratiometric approach and the thermal dependence of the emission lifetime to harvest higher sensitivities and lower uncertainties through dimensionality reduction. Accordingly, the principal component analysis (PCA) was employed, a technique often used for dimensionality reduction in machine learning. As a proof-of-concept, the SrY_2O_4:$Tb^{III/IV}$(2at.%),Eu^{III}(5at.%) phosphor was selected, synthesized by the Pechini modified method at 1100 °C/5 h under a partial CO atmosphere. Notably, the $Tb^{III/IV}$ was used as a co-dopant to distort the host lattice and amplify the intensity of Eu^{III} emission bands because Tb^{IV} is spectroscopically inert in the visible region. The XPS analysis confirmed our hypothesis, revealing a 35/75% Tb^{III}/Tb^{IV} ratio, being this small amount not detectable in the emission spectrum. To further avoid any Tb^{III} emission, the sample was excited in the $^5D_2 \leftarrow {}^7F_0$ (464 nm) Eu^{III} 4*f* transition. Examining the emission spectrum of the phosphor, the characteristic $^5D_0 \rightarrow {}^7F_{0\text{-}4}$ emission bands were detected, in addition to the $^5D_1 \rightarrow {}^7F_2$ Eu^{III} band (541 nm). The 5D0/5D1 pair's thermally coupled nature enabled the development of a ratiometric temperature probe, yielding a maximum relative sensitivity (S_r) of 0.95% K^{-1} in the 380-470 K range. By switching to the $^5D_0$ lifetime using the $^5D_0 \rightarrow {}^7F_2$ (612 nm) emission, and $^5D_2 \leftarrow {}^7F_0$ (464 nm)

excitation, maximum values of 0.42% K^{-1} for S_r were obtained in the same interval. Both values involve individual thermometric approaches, which raises the question of whether joining them would imply an improvement in sensitivity. In this sense, dual-parametric S_r was accomplished by PCA. The overall S_r values reached the 2.5% K^{-1} limit in the 350-460 K temperature range, representing a nearly 2.5-fold gain. Furthermore, a temperature uncertainty of 0.006 K was fostered when the dual-parametric approach was employed. Such low uncertainty allows accurate readouts at high temperatures. Hence, these outcomes demonstrate that enhanced sensitivities can be achieved through data analysis rather than solely relying on materials design.

Keywords: Data analysis, Dual-parametric thermal sensing, Dimensionality reduction

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Charge Compensation and Persistent Luminescence: Make a Virtue of Necessity

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Persistent luminescent (PersLum) materials are composed of an emitting center, host and supplementary/optional co-dopant which may act as an emitting centre. Research of these materials is still often focused on emission centre, host's properties are neglected while co-dopants' role is based on speculation. Emission centres' properties are well-known, mostly the same as for the conventional phosphors studied since 1960s. However, times change, and study of charge compensation (CC) arose from the cost of phosphors. The price of R^{3+} dopants is not anymore the decisive factor due to low amount and recycling of the dear phosphor part(s). Now the host must be as cheap as possible lest, at the same time, jeopardize the performance of the dopant.The *R^{3+} dopants* are efficient and stable luminescence sources and inexpensive at low concentrations. That said, even the Eu^{3+} content was decreased because of austerity measures. $R^{2+/3+}$ *hosts* are now *excluded*, cheaper phosphors are based on *solid solutions* (SS) between M^{2+} (Ca^{2+}, Sr^{2+}, Ba^{2+}) hosts and $R^{2+/3+}$ dopants. This evolution requires *new emphasis* to Materials Science/Engineering. The basic rule on compounds' neutrality - presently forgotten - must be rigorously respected. The size and charge constrains based on Vegard's rules – including structures of solid solutions' end members - must be reconsidered. Formation of compounds must be studied in detail to account for their *Lewis acid-base behavior* - valid *in solid state*, as well, not only in gas phase or solutions. Brute *breaking bonds* to achieve compound's neutrality is *not any more a reply – vacancies* are *forbidden* by *Thermodynamics*. Instead, *Crystallography* must find means to *include, not exclude* ions in the host with enough space available.Trivial examples of *charge compensation* (CC) include cancelling excess positive charge due to doping with *inclusion* of *an anion* (F^-), or *two as a divalent ion* (O^{2-}) creating/using R^{3+}- O^{2-} - R^{3+} bridges. Smarter solutions are available to circumvent the powerful Vegard's charge rule: $Na^+ + R^{3+} = Ca^{2+} + Ca^{2+}$. Changing the oxidation state(s) of host's species ($Ti^{IV} \rightarrow Ti^{3+}$) will be routine in the future to compensate the excess/deficit charge due to doping.

Let the (un)successful CC be voluntary or accidental, it creates traps for electrons & holes. Kröger-Vink notation can help understand the processes and species: Ti'_{Ti}, $Ti^{\bullet}_{Ti}$, *and* $Ti^{\times}_{Ti}$ are the electron (e^-) or hole (h^+) traps for the Ti^{2+}, Ti^{IV} and Ti^{3+} species, respectively, in regular Ti^{3+} site, to name a few.Finally, after identification of traps and their properties, the ultimate conundrum remains: How to obtain *trap depths*? *Bond valence model* (BVM) calculations based on structural data yield the **trap depths** and information on **structural stability** Trap energies which matching thermoluminescence curves are obtained easily. **Full-scale design of PersLum materials is now possible!**

Keywords: Persistent luminescent, solid solutions, charge compensation

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Development of Coelenterazine Analogues for High-Brightness Multicolor Bioluminescence

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Marine bioluminescence emits light through an enzymatic reaction where the enzyme (luciferase) catalyzes the oxidation of the bioluminescent substrate, coelenterazine (CTZ). Due to the absence of drawbacks such as excitation light-induced interference, phototoxicity, photobleaching, and high background, it enables highly sensitive and non-invasive imaging. Furthermore, various applications in bioassays and bioimaging have been reported by artificially modifying and optimizing luciferases and CTZ. Our research group has successfully developed artificial marine bioluminescence systems such as bioluminescent probes that emit light upon stimulation by specific ligands and multicolor bioluminescence systems using CTZ analogues. However, these artificial bioluminescence systems have several issues. It has been observed that the bioluminescence intensity significantly decreases in multicolor bioluminescence systems that cover a range from blue to red (400-650 nm). Therefore, in this study, we focused on exploring chemical structures that exhibit high brightness and multicolor bioluminescence.We have designed and synthesized new CTZ analogues. We performed bioluminescence evaluations of these CTZ analogues with various marine luciferases. The characterization revealed that CTZ analogues luminesce with blue to orange-colored bioluminescence spectra with marine luciferase. Furthermore, they demonstrated high bioluminescence intensity with various marine luciferases, leading to the successful development of a high-brightness and multicolor bioluminescence system.

Keywords: Marine Bioluminescence, Coelenterazine, Multicolor

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Development of efficient far-red emitting *Phrixotrix* railroadworm luciferase combinations using amino-luciferin analogs

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Beetle luciferases are very useful for bioimaging purposes, such as monitoring metastasis, bacterial and viral infections in cell cultures or animal models. In mammalian tissues, red-emitting luciferases are preferred, due to low absorption by hemoglobin, myoglobin or melanin. Among beetle luciferases, red bioluminescence is produced naturally only by *P. hirtus* railroadworm luciferase (PxRE) and also by some engineered luciferases. Recently, new red-emitting luciferin analogues have been synthesized, which in combination of engineered luciferases, emit far-red (FR) or near-infrared (NIR) light. Departing from the principle that PxRE luciferase is a better starting point to produce more efficient red emitting luciferases, our group has previously developed a system combining an engineered luciferase (RE-R215K) and the analogue 6′-(1-pyrrolidinyl)luciferin (N5), which emits FR light (650 nm) with very high efficiency. The aim of this work was to further improve this FR emitting system by engineering RE-R215K luciferase in combination with N5. Site-directed mutagenesis using PhusionTM High-Fidelity DNA Polymerase (Thermo Fisher) was performed, the luciferase mutants were expressed in *E. coli* BL-21 and purified by affinity chromatography using Ni-NTA-Agarose, and their kinetics, bioluminescence and thermostability properties were characterized. Double mutants were produced with improved properties, including higher thermostability (4 times increase of half-life at 37 ºC); ~10 nm red-shifted BL spectra (658 nm) using the N5 luciferin analogue in relation to the original mutant (650 nm), and 28 nm red-shifted in relation to D-luciferin, and a much higher bioluminescent activity with N5 analogue in relation to D-luciferin. The K_M value for N5 luciferin analogue were also very low ($\leq$ 1 μM), whereas the KM values for D-luciferin and ATP were quite high (300 and 250 μM, respectively). Compared to firefly luciferases and wild-type PxRE luciferase, this new FR mutant showed improved *in vivo*

bioluminescence signal when expressed in monkey COS-1 fibroblasts. Considering that intracellular concentrations of ATP range from 2-8 mM depending on the cell, the higher K_M for ATP makes this luciferase an interesting option to measure physiological intracellular changes of this molecule. Altogether, these results show that this new FR emitting luciferase combination constitutes a promising reporter gene option for bioimaging purposes in mammalian tissues.

Keywords: Far-red luciferase; Bioimaging; Luciferin analogue.

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Evaluation of Luminescence Properties of Novel Luciferin Analogues with Heterocyclic

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[background/purpose]Firefly bioluminescence is caused by the reaction of luciferin, a luminescent substrate found in fireflies in nature, with luciferase, a luminescent enzyme.Firefly bioluminescence has a very high luminescence quantum yield due to its high energy efficiency and almost no heat loss.Due to these characteristics, it is applied in a wide range of technologies such as biological imaging.However, since the wavelength of light emitted by natural fireflies is 560 nm, it is absorbed by hemoglobin and other biological substances in the body. Therefore, its light could not visualize deep tissues, making it difficult to put it to practical use as a biological imaging technique. To solve this problem, we have been working on modifying the structure of the luminescent substrate, the luminescent enzyme, or both, to achieve longer wavelengths.In addition, in recent years, analogs with heterocyclic rings, such as TokeOni and seMpai, which are highly water soluble, Akasuke, which emit light with high brightness, and KinPachi, which emit light at the world's longest wavelength, have attracted attention.However, since there are few synthetic examples of analogues with heterocycles, a correlation between luminescence activity has not yet been established. Moreover, the scarcity of synthesized analogs with heterocyclic rings has hindered the establishment of luminescence activity correlations. Therefore, in this study, I synthesized novel luciferin analogs A and B with heterocyclic rings and measured their luminescence to evaluate their luminescence properties.[Results/Discussion]Measurements of luminescence intensity showed that both new luciferin analogs A and B were greatly reduced compared to the natural substrate. As for the emission wavelengths, analog A and B were found to have wavelengths of λ_{max} = 580 nm and λ_{max} = 730 nm, respectively. Analog A has a wavelength comparable to that of the natural substrate, D-luciferin, and analog B has a wavelength 170 nm longer than the natural-type substrate.In this presentation, we will discuss the wavelength variation using DFT calculations.

Keywords: Bioluminescence, Firefly ,NIR, Heterocyclic

Feel the Heat: Exploring Luminescence Nanothermometry for Next-Generation Thermal Imaging

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The emergence of luminescent nanothermometry during the last decade opened the possibility ofmeasuring thermal flows at spatial scales below 1 μm, unreachable by conventional electrical methods.Diverse phosphors capable of providing remote detection through their light emission properties havebeen examined, e.g., polymers, DNA or protein conjugated systems, organic dyes, quantum dots, andtrivalent lanthanide (Ln^{3+}) ions incorporated in organic-inorganic hybrids, multifunctional heater-thermometernanoplatforms, upconverting, downconverting and downshifting nanoparticles.In recent years, luminescence nanothermometry has entered a more mature stage. Although new classesof thermographic phosphors continue to be reported (e.g., covalent organic frameworks and single-ionmagnets) we are perceiving a gradual shift in the emphasis of the technique. The research efforts are nowfocused on establishing comprehensive theoretical backgrounds and standardization procedures (both indata acquisition and processing and in measurement methodologies), discussing the reliability,repeatability, and reproducibility of the technique, and developing new applications.The lecture will give a general perspective of the work done on luminescence nanothermometry since theexplosion of the field one decade ago, emphasizing the potential of the technology with recent examplesinvolving upconverting nanoparticles for advancing thermal imaging.

Keywords: luminescence nanothermometry

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HIGH-TEMPERATURE LUMINESCENT THERMOMETERS BASED ON LANTHANIDE COMPLEXES

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Luminescent thermometry is not only one of the most accurate methods of temperature measurement, but is also indispensable for non-contact temperature measurement. One of the most important applications of luminescent thermometry is the measurement of high temperatures, for example, engine parts and gas pipeline walls, where almost the only measurement method is non-contact luminescent thermometry. In addition, it allows for continuous real-time measurements and even mapping. Inorganic materials are usually used as luminescent thermometers at high temperatures. Despite the low intensity of their luminescence, they are stable up to very high temperatures, while the thermal stability of brightly luminescent coordination compounds (CCs) is insufficient. However, metal-organic frameworks (MOFs) based on lanthanide aromatic carboxylates are often stable to temperatures of 400-600 °C, sufficient for a number of thermometric applications, and exhibit very intense luminescence.We proposed using heterometallic aromatic lanthanide carboxylates as high-temperature fluorescent thermometers in composite films based on transparent heat-resistant polymer materials. We proposed an analytical description of a four-level system for luminescent thermometry, including one main and three excited states, which include Tb-Eu complexes with an organic ligand, and demonstrated a strategy for creating such systems to increase temperature sensitivity. Based on this study, new approaches to increasing sensitivity due to a complex design have been proposed.We have conducted a number of studies of highly stable complexes as emitters for high-temperature luminescent thermometry, studied the stability of complexes under simultaneous exposure to UV excitation and heating, as well as the features of the formation of composite films with polymers of different classes. As a result, materials capable of operating up to 400 °C in both the visible and NIR ranges were obtained. We have also demonstrated, both mathematically and experimentally, that mixtures of monometallic complexes are more sensitive than the corresponding bimetallic compounds.

Keywords: thermometry, MOF, lanthanides, bimetallic complexes

How can we plan the composition of europium complexes to modulate the surface charge, cytotoxicity, and luminescence of red-emitting nanoprobes?

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Red light-emitting contrast agents have been developed for applications in bioimaging, biosensing, and thermometry, based on europium complexes, however, their low water solubility and photostability issues limit their application, which can be overcome by their covalent anchoring on silica nanoparticles (SNP). Yet, the bioapplication depends on several factors, with the surface charge being a key factor in the toxicity and internalization of nanoparticles by cells. Herein, we evaluated the modulation of the surface charge on SNP by anchoring Eu-complexes of different structures, combining the ligands *pamba* (4-(Aminomethyl)benzoic acid) and *tta* (2-thenoyltrifluoroacetone), a carboxylic acid and a b-diketone, respectively, and their impact on the toxicity of the hybrids towards Huh 7.5 cells. For this, 50 nm-SNPs decorated with carboxylic acid (COOH) were produced, then, Eu^{3+} ions were coordinated to the carboxylate groups, and their coordination sphere was completed using *pampa* or *tta*, separately or combined, resulting in three samples, NPS⁻[Eu(COO^-)$(pamba)_x(H_2O)_y$] (*hybrid A*), NPS⁻[Eu(COO^-)$(tta)_x(H_2O)_y$] (*hybrid B*), and NPS⁻[Eu(COO^-)$(pamba)_x(tta)_z(H_2O)_y$] (*hybrid C*). The ligands sensitized the europium ion, which then emits in the red region with high color purity. Hybrids B and C showed the best, and similar, photophysical properties such as higher excited state lifetimes and intrinsic quantum yields, indicating that *tta* works as a better sensitizer for Eu^{3+} ions than *pamba*. The surface charge of the SNPs changed according to the charge of the complexes, with zeta potential values of +18, ⁻13, and ⁻39 mV observed for hybrids A, C, and B, respectively. The presence of the NH_3^+ group in *pamba* induces positive charge values in hybrid A while *tta*, which contains a negative charge, induces the opposite effect in hybrid B. The combination of the two ligands produced an intermediate charge in hybrid C. The change in charge directly influenced the toxicity of the hybrids analyzed through the MTT assay. The more negative the surface charge, the more toxic the hybrid was. IC_{80} values of 3.13, 25, and 50 µg/mL were obtained for hybrids B, C, and A,

respectively. Although europium complexes are promising in bioimaging assays, the application of their hybrids must be carefully investigated, as the surface charge plays an important role in the toxicity of the materials.

Keywords: silica nanoparticle, hybrid, bioimaging, Eu3+

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Innovation of NIR luciferin analogues using firefly bioluminescence for in vivo imaging

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We have developed near-infrared (NIR) luciferin analogues that exhibit firefly bioluminescence, including compounds dubbed “TokeOni” and “seMpai,” which are now commercially available. In this conference, I will present the characteristics of NIR luciferin analogues.Firefly bioluminescence, a process whereby light is emitted with high efficiency, has found widespread use in life science applications. Notably, NIR light is suitable for use in *in vivo* imaging because deep tissues are highly permeable to light in the relevant wavelength range (650–900 nm). However, the wavelength of light emitted *via* firefly bioluminescence is usually yellow–green (560 nm). We performed studies on the structure–activity relationship of compounds producing firefly bioluminescence in order to synthesize luciferin analogues emitting NIR light. Thus, AkaLumine, a luciferin analogue that produces light at 675 nm wavelength, was developed. This compound was shown to yield useful results when applied to the *in vivo* imaging of mice. We have improved the characteristics of AkaLumine to optimize this compound for use in *in vivo* imaging, thus obtaining the compounds dubbed TokeOni and seMpai. Recently, Akaluc, an artificial enzyme that specifically catalyzes the light-producing oxidation of TokeOni, has been developed. As a result, it became possible to *in vivo* imaging for larger animals than mice like micro pig and marmoset. In this way, bioluminescence imaging technology is undergoing constant innovation, and we continue to develop NIR luciferin analogues that can be used as imaging tools. In the present study, we aimed to develop bioluminescent systems emitting light at wavelengths over 700 nm; we thus synthesized luciferin analogues and evaluated their bioluminescence light.In this conference, I will present the characteristics of recently developed NIR luciferin analogues including the synthesized luciferin analogs showed over 750 nm emission of light “GeKiaka” and “KinPachi”.

Keywords: Firefly, Bioimaging, NIR, Luciferin

Lanthanide doped nanostructured materials as Theranostic Platforms

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The application of light and light-based technologies is now widespread in a significant number of human activities and leads to research in many technological areas. The development of photonic materials has not only revolutionized the area of Information and Communication Technology but has influenced widely in strategic global areas such as health, environment, lighting and energy. Our recent work on photonic and theranostic applications will be discussed, specifically, concerns about the synthesis and optical properties of rare earth doped nano and microstructured inorganic materials based on fluoride and oxides as theranostic agents for glioblastoma multiforme. Spheres, hollow spheres, cubes, rods, nanoparticles prepared by different methodologies will be presented, demonstrating high visible upconversion (UC) or near infrared (NIR) emission intensity after NIR excitation at transparent biological windows, radioluminescence, photoacustic features for multimodal imaging. In vitro assays of UC nanoparticles have been performed, and cell viability has been evaluated for gliobastoma cells, making them promising materials for bioimaging and photodynamic therapy using as an excitation source near infrared radiation. Ensemble and Single Particle were evaluated as primary nanothermometer with relatively high thermal sensitivity.References [1] L.F. Dos Santos, J.C. Martins, K.O. Lima, L.F.T. Gomes, M.T. De Melo, A.C. Tedesco, L. D. Carlos, R.A.S. Ferreira, R.R. Gonçalves. Physica B: Physics of Condensed Matter, 624, 413447, 1-11 (2022); [2] F. H. Borges, J. C. Martins, F. J. Caixeta, R. R. Pereira, L. D. Carlos, R. A. S. Ferreira, R. R. Gonçalves. Journal of Sol-Gel Science and Technology, **102**, 249–263 (2022); [3] K. De O. Lima, L. F. Dos Santos, R. Galvão, A. C. Tedesco, L. De S. Menezes, R. R. Gonçalves. Frontiers in Chemistry **9**, 1-13 (2021).

Keywords: rare earth, luminescence, particles, theranostic

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Light-controlled drug release of MOF nanoparticles influenced by upconversion nanoparticles

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Cancer treatment remains a formidable hurdle in medicine, prompting exploration into innovative materials like Metal-Organic Frameworks (MOFs) for drug delivery and up-conversion nanoparticles (UCNPs) for bioimaging. This study aimed to develop a core-shell material using NaYF4:Yb^{3+}, Er^{3+} up-conversion nanoparticles (UCNP) modified with polyacrylic acid (PAA) and ZIF-8, evaluating their potential for controlled antitumor drug release. Physicochemical analyses confirmed unchanged MOF and UCNP structures post core-shell formation. Luminescence spectra revealed emission in green and red regions, respectively, upon excitation at 980 nm by Yb^{3+} and Er^{3+} ions. UCNP @ZIF-8 particles had an average size of 75 nm with a 20 nm-thick ZIF-8 shell and encapsulation efficiency of 68% for doxorubicin. Notably, drug release was significantly higher in acidic (PBS pH 5.0) and laser-stimulated (980 nm; 5 min; 0.8W/cm^2) conditions compared to neutral medium (PBS pH 7.4) without laser, indicating the influential role of laser in enhancing drug release. This suggests potential for targeted drug delivery and tumor microenvironment-responsive release. In vitro assays showed cell viability above 70% in MCF-7 and MCF10A cell lines at 0.1 mg. mL^{-1} concentration after 48 h incubation, confirming UCNP@MOF potential as theranostic materials, with reduced viability post 980 nm laser stimulation. Laser application led to decreased cell density, more detached circular structures, and cell shrinkage, indicating enhanced cell death. In conclusion, multifunctional UCNP@MOF materials hold promise for cancer treatment and imaging, with laser stimulation significantly augmenting drug release efficacy.

Keywords: metal-organic framework, up-conversion nanoaprticle, drug delivery nanoparticle, theranostic

Light-controlled enhanced drug release: MOF nanoparticles influenced by upconversion nanoparticles

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Cancer treatment remains a formidable hurdle in medicine, prompting exploration into innovative materials like Metal-Organic Frameworks (MOFs) for drug delivery and up-conversion nanoparticles (UCNPs) for bioimaging. This study aimed to develop a core-shell material using NaYF4:Yb^{3+}, Er^{3+} up-conversion nanoparticles (UCNP) modified with polyacrylic acid (PAA) and ZIF-8, evaluating their potential for controlled antitumor drug release. Physicochemical analyses confirmed unchanged MOF and UCNP structures post core-shell formation. Luminescence spectra revealed emission in green and red regions, respectively, upon excitation at 980 nm by Yb^{3+} and Er^{3+} ions. UCNP @ZIF-8 particles had an average size of 75 nm with a 20 nm-thick ZIF-8 shell and encapsulation efficiency of 68% for doxorubicin. Notably, drug release was significantly higher in acidic (PBS pH 5.0) and laser-stimulated (980 nm; 5 min; 0.8W/cm^2) conditions compared to neutral medium (PBS pH 7.4) without laser, indicating the influential role of laser in enhancing drug release. This suggests potential for targeted drug delivery and tumor microenvironment-responsive release. In vitro assays showed cell viability above 70% in MCF-7 and MCF10A cell lines at 0.1 mg. mL^{-1} concentration after 48 h incubation, confirming UCNP@MOF potential as theranostic materials, with reduced viability post 980 nm laser stimulation. Laser application led to decreased cell density, more detached circular structures, and cell shrinkage, indicating enhanced cell death. In conclusion, multifunctional UCNP@MOF materials hold promise for cancer treatment and imaging, with laser stimulation significantly augmenting drug release efficacy.

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Multicolor bioluminescence imaging across scales: novel tools and developments

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Biological imaging across scales can reveal dynamics of complex processes such as cancer metastasis, immune function, host-microbiome interation, connections of neurons and leads to a better understanding of physiology. Imaging modalities are applied as separate niches in biomedical research, where optical microscopy and mesoscopy focus on subcellular, cellular and tissue slice imaging and nuclear and MR imaging are applied to living subject. Bioluminescence imaging which can generate bright signals and high signal to noise ratios can nowadays be applied for microscopy, mesoscopy and mascroscopy imaging.This lecture will discuss recent developments from my laboratory on bioluminescence microscopy imaging of single cells and engineered tissues on chips, mesoscopic imaging in intact ex vivo tissues and organs and on multiplexed bioluminescence imaging in small and large animals to elucidate cancer-immune cells and host-microbiome interactions. In particular, cancer cell based sensors based on multicolor bioluminescent readouts and how novel unmixing algorithms and detectors can improve resolution of multiplex bioluminescent signals will be highlighted.

Keywords: Multicolor bioluminescence; imaging; BL cell based sensors

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MULTIFUNCTIONAL METAL-DOPED PHOTOLUMINESCENT NANOPARTICLES AS PROMISING NANOTOOLS FOR TARGETED BIOIMAGING AND FOOD SAFETY CONTROL

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Nanotechnology has significant promise for improving the generation of novel and beneficial imaging nanoprobes. Compared to traditional molecular-scale contrast agents, use of nanoparticles (NPs) as imaging probes has several benefits. These include: (1) high loading capacity, which allows the concentration of the imaging agent to be controlled within each nanoparticle during the synthesis process; (2) tunable surface, which may allow the contrast agent to be targeted to specific locations in the body or extend its circulation time in the blood; or (3) multimodal imaging capacities, which result from NPs' ability to combine two or more contrast properties and be used in multiple imaging techniques simultaneously.Nowadays, strong research efforts are drawn to the development of NPs with multiple capabilities (e.g., photoluminescent and magnetic resonance) because of their enormous potential to revolutionize biomedical imaging technology. A promising new class of optical contrast agents, colloidal metal semiconductor nanocrystals, or quantum dots, or QDs, have a large surface area for additional functionalization, strong resistance against photobleaching, adjustable emission colors, and broad absorption bands. Fluorescent QDs such as these can be used for in vivo imaging, but their use is limited by tissue auto-fluorescence, which causes low signal-to-noise ratios that make it difficult to identify them in biological contexts and lower contrast and clarity in the resulting image. There are several approaches to getting around this restriction. The creation of metal nanoparticles with NIR-spectrum excitation and emission is a strategy with strong potential. These innovative fluorescent labels hold great promise for bioanalysis since they combine the benefits of both QDs and NIR light. An alternative method involves incorporating transition metals, such as manganese (Mn), a chemical element that is also necessary for life, into nanocrystals. This provides the crystals with properties that are typical of phosphorescent emitters, such as longer luminescent lifetime and longer Stokes shift between excitation and emission wavelengths. Time-resolved photoluminescence (PL) studies offer the benefit of straightforwardly differentiating the luminescent emission from Mn-doped QDs from

the sample's background fluorescence thanks to the ensuing phosphorescent emission. Furthermore, some of the potential doping ions—like Mn, for example—may be paramagnetic, making them good MRI contrast agents. Consequently, doping the photoluminescent nanocrystals with such components gives the QDs more MRI contrast capabilities. Because of their immense potential to revolutionize biomedical imaging technologies, research on the production of NPs with both optical and magnetic resonance functions is appealing. An overview of some of the cutting-edge research on this innovative kind of QDs for biomedical applications will be provided in this talk.

Keywords: Metal-Nanoparticles, Quantum dots, bioimaging, sensing, multimodal contrast capabilities

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Near-infrared persistent luminescent materials functionalized with europium β-diketonate complex for optical imaging

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Over the past few years, research towards novel and efficient near-infrared (NIR) emitting persistent luminescent materials makes use of surface sensitizers to incorporate organic dyes and tune light emission within the first and second biological windows, using activators such as transition metals and rare-earth ions (*e.g.* Cr^{3+}, Nd^{3+}) [1,2]. In this work, $Zn_xMg_ySnO_4:Cr^{3+}$ NIR-emitting phosphors were prepared *via* ceramic method and microwave-assisted solid-state synthesis, which were later functionalized with the $[Eu(tta)_3(H_2O)_2]$ complex by microwave-assisted surface silanization. These materials showed high crystallinity in the results of both powder X-ray diffraction and electron microscopy experiments, where SnO_2 by-product formation with increasing Mg content was observed. Luminescence spectra registered intense NIR emission of Cr^{3+} ions, assigned to the allowed $^4T_2(t^2e) \rightarrow {}^4A_2$ transition under a weak crystal-field environment. Interestingly, in functionalized materials, a similar response was registered under direct Eu^{3+} excitation, revealing intrinsic europium-to-chromium energy-transfer processes in single-shell phosphors. Said mechanism was further studied in materials functionalized with a double-shell, where Eu^{3+} red emission was observed in the visible range alongside the Cr^{3+} NIR emission. Additionally, NIR persistent luminescence under band-gap excitation was studied by vacuum-ultraviolet spectroscopy, where Cr^{3+} emission was recorded up to 10 min after excitation. Finally, X-ray fluorescence, X-ray absorption near edge structure, and X-ray excited optical luminescence spectroscopy experiments were carried out at the Carnaúba (Coherent X-ray Nanoprobe) beamline of the Brazilian synchrotron (Sirius). Site-selective luminescence was investigated and correlated with local chemical composition, where the results showed intense NIR emission under X-ray excitation related to the Cr K-edge and the Eu L-edge in functionalized materials. Hence, the results obtained in this work outline an important understanding of energy-transfer mechanisms and their role in promoting NIR emission utilizing β-diketonate complexes as sensitizers in Cr^{3+}-doped persistent phosphors

which are widely studied for optical imaging applications.References:[1] F. Zhao et al., *Laser Photonics Rev*. 16 (2022) 2200380.[2] X. Zhu et al., *ACS Materials Lett*. 4 (2022) 1815.

Keywords: Persistent luminescence, Near-infrared, β-diketonate

Neodymium(III) molecular species for thermometry in the near-infrared region operating in the physiological temperature range.

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Due to its electronic structure, which presents thermally coupled levels, and their absorption/emission bands that lies in the biological windows, neodymium(III) cation possesses advantages to be used in luminescent thermometry for bio-applications. This cation has been used in several materials, such as nanoparticles, glasses or MOFs, proving its optimal characteristics.In the present work, a novel family of neodymium(III) based molecular compounds will be presented, covering from synthesis, characterization up to luminescent thermometry in the NIR region. Macrocyclic motifs were used, together with different anions that were selected to impart different coordination geometries. The analysis is focused to the molecular point of view, by analysing the coordination environments of the cation in the different species and its influence in the spectroscopies properties. The thermometric properties were studied exciting in the first biological window and analysing emission in the second biological window, analysing its temperature dependence in the physiological temperature range. The most intense band was c.a. 1065nm, which presents different splitting in agreement with the present of other coordination environments. By deconvolution it was possible to identified each components, in order to analyse its temperature dependency. The spectroscopic characteristic and the present of different component in each sample was confirmed by theoretical calculations. Among all samples, an hexanuclear complex highlights due to the higher sensibility of Sr of 3.7 %K-1 at 293 K, and more important because luminescence intensity ratio of two components of the 1065 nm transition was achieved.

Keywords: neodymium(III), NIR-thermometry, molecular compounds

Novel strategies towards optical thermometers based on single-molecule magnets

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The application of lanthanide(3+) (Ln) ions for optical thermometry gained enormous attention in the last decade due to the possibility of temperature sensing via the emission signal originating from their f-f electronic transitions located in the wide vis-to-NIR window (C. D. S. Brites et al. *Adv. Opt. Mater.* **2019**, *7*, 1801239). Strong and tunable temperature-variable emission characteristics enable the contactless use of such thermometers in various aspects of industry and medicine. On the other hand, the development of Ln(III)-based single-molecule magnets (SMMs), i.e., magnetic entities showing a magnetic hysteresis loop at the level of a single paramagnetic center or single molecule, makes them promising in future high-performance data storage tools, quantum computing, and spintronic devices (D. N. Woodruff et al. *Chem. Rev.* **2013**, *113*, 5510). The conjunction of SMM behavior and optical thermometry based on Ln(III) complexes emerged a few years ago, as a method to develop future SMM-based technology with a self-monitoring temperature mechanism (R. Marin et al. *Angew. Chem. Int. Ed.* **2021**, *60*, 1728). This aim stems from the large sensitivity of SMM performance, such as the blocking temperature and the related magnetic relaxation times, on the temperature of the system. Up to now, different Ln(3+) ions have been tested in this aspect, starting from Dy(3+), the best-performing center for the construction of SMMs, and Yb(3+), well-known for its efficient near-infrared-centered f-f emission. In this field, we focused on the development of luminescent SMMs built of less common lanthanide centers, such as Ho(III) and Tb(III). Both of them show prominent SMM performance if only employed in the crystal field of proper symmetry. On the other hand, the Tb(III) is recognized for its use in luminescent thermometers when combined with Eu(3+) ions; however, its application for a single-center thermometry is quite limited, while Ho(III)-based systems show rather small potential as efficient solid-state luminophores. As the result of proper design, we discovered unique strategies to generate high-performance optical thermometers based on SMMs for those centers, which include luminescence re-absorption effect for Ho(III) complexes diluted in a luminescent matrix (J.

Wang, J. J. Zakrzewski, et al. *Chem. Sci.* **2021**, *12*, 730), and generation of high-symmetry Tb(III) centers by the desolvation of a rigid Tb^{III}–$[Co^{III}(CN)_6]^{3-}$ inorganic framework (J. Wang, J. J. Zakrzewski, et al. *Angew. Chem. Int. Ed.* **2023**, *62*, e202306372).

Keywords: optical thermometry, lanthanides, magnetic properties, photoluminescence

Organic electroluminescent devices: OLEDs and beyond

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The research in organic semiconductors is a key element to boost the development of new devices enabling new commercial applications in the field of Organic Electronics (OE), such as the production of cold light for lighting environments and car panels, transistors, photovoltaic cells, sensors, and flexible devices. OLEDs, that derive their name from the organic molecules used to produce light through the phenomenon of electroluminescence, have been developed to the point that they have become a mainstream display technology for mobile devices and televisions. However, organic electroluminescence can also be used for applications beyond the more fascinating world of displays. Organic Up-converter Devices (OUDs), for example, have attracted considerable research interest due to potential applications in optical communications, biomedical applications, night vision, biological imaging, telemetry and security. The OUD consists in a tandem structure with NIR sensitive organic photodetector (OPD) stacked in an efficient visible OLED. In the dark the device is in the off-state. When NIR light is absorbed by the PD, electron-hole pairs are formed. Under the appropriate bias, holes are driven into the OLED where they recombine with electrons injected from the cathode, thus leading to light emission. OLEDs can be used also as flexible and biocompatible light sources for photodynamic therapy (PDT). The PDT mechanism is non-invasive treatment for surface lesions, such as human skin, which uses visible light to excite a photosensitizer (PS), which is a photosensitive drug. The PS molecule in its ground state can absorb a photon and pass to its excited state and, at the end of this process, reactive oxygen species, mainly singlet oxygen, are produced. The oxygen produced is reactive and can destroy nearby cells such as bacteria, fungi, and tumor cells. In this presentation, we will describe the challenges and opportunities in the OLEDs applications described above.

Keywords: Ciloca electrochemiluminescence, Leeds, photodynamic therapy, Leds

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Practical applications of versatile highly luminescent beta-diketonate tetrakisTb3+/ Eu3+ complex doped in polymeric matrices as light-converting molecular devices and optical thermometer

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Concerning photophysical properties, trivalent lanthanide ions (Ln^{3+}) are unique among the periodic table elements due to their intrinsic electronic configuration. Features such line-like absorption and emission bands, large Stoke shifts and long-lived emission decay times, besides monochromatic emissions from visible to NIR spectral range also make these ions a current alternative to organic dyes, avoiding practical disadvantages like photobleaching and re-absorption process. In fact, Eu^{3+} and Tb^{3+} are by far, the most common Ln^{3+} ions in terms of visible light, with red and green monochromatic emissions, respectively. Such applications include photonics, biomarkers, temperature sensors, hybrid materials, luminescent solar concentrators (LSCs) and downshifting layers (DSLs) to name a few. Another feature in which the Ln^{3+} ions can be significantly helpful is the search for micro and nano scale thermometers that have been significantly growing in the last decades. Such approach allows overcome limitations of more traditional temperature measurements *e.g.* liquid-filled bulbs or stems and thermocouples and allows even cellular level monitoring. The measurements are focused mainly on three methodologies *i.e.* i) the spectral shift of a given transition, ii) the integrated intensity of one or two transitions (in case of doped systems) and iii) lifetime measurements. It is noteworthy that the measurement based on integrated intensity ratio has been one of the most promising ones due to the short response time, self-calibration, high precision, and reliability. It is noteworthy, however, that Ln^{3+}- complexes can show features such as low photo and thermal stability besides poor mechanical and conductive properties, that poses practical limitations for some of their direct applications. Thus, the engineering of hybrid materials containing Ln^{3+}- complexes have been arising in the past twodecades as an alternative to such drawbacks and are generally denoted as lanthanide-based luminescent hybrid materials. Such

materials usually present synergistic effects associating features such as flexibility, transparency and relatively ease of production of the polymer with the remarkable photonic properties of the Ln^{3+}-complexes. In this way, this work reports the synthesis, characterization, and optical-thermal study of a tetrakis Tb^{3+}/Eu^{3+}- complex with thenoyltrifluoroacetone (tta) containing tetraethylammonium (Et_4N) as counterion. In addition, the complex was doped at 1% in weight in PMMA and PVA polymeric matrices. The complex present general formula $Et_4N[Tb_{0,999}Eu_{0,001}(tta)_4]$ and was fully characterized via elemental and thermal analysis, mass spectrometry, infrared absorption spectroscopy, X-ray diffraction analysis. The complex and the doped polymeric materials, showed a remarkable excitability either in the NUV-Vis range (even far beyond 400 nm) and under sunlight exposure (mainly for the PMMA film). The thermometric parameters of the $Et_4N[Tb_{0,999}Eu_{0,001}(tta)_4]$ complex determining the ratio between the integrated intensities of the $^5D_4 \rightarrow {}^7F_5$ (Tb^{3+}) and $^5D_0 \rightarrow {}^7F_2$ (Eu^{3+}) transitions and the relative thermal sensitivity (S_r) and the temperature uncertainty (δT), were discussed.

Keywords: Lanthanides, photoluminescence, LCMDs, optical thermometry, polymers, PMMA, PVA

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Precision temperature sensing in cryogenic environments: harnessing Eu^{3+} in multisite luminescent thermometry

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Temperature is the most fundamental thermodynamic state variable, which demands meticulous monitoring across various fields. Its precise measurement holds increasing significance in cutting-edge futuristic technologies such as superconductors and quantum information processing via quantum computing. In these domains, temperature plays a critical role, with the most efficient devices operating close to or slightly above the liquid nitrogen temperature (77 K). Consequently, thermometers capable of measuring such temperatures with low uncertainty are highly attractive. Because of such demand, luminescence thermometry has emerged to fulfill this need, leveraging the thermal dependence of electronic transitions to enable contactless temperature measurement. Thus, we propose a luminescent thermometer with low uncertainty that is tailored for cryogenic temperatures (close to liquid nitrogen). This thermometer based on SrY_2O_4:Eu^{3+}(2,4,6,8 at.%) phosphor was synthesized using the modified Pechini method. The procedure employed stoichiometric proportions of the metallic nitrate solutions, $Sr(NO_3)_2$, and $RE(NO_3)_3$ (RE = Y^{3+}, Eu^{3+}), citric acid, and D-sorbitol to form a polymeric resin. This resin underwent pre-calcination at 350 °C/3 h, followed by annealing the precursor charcoal at 1100 °C/5 h. Analysis of the diffraction patterns via X-ray Diffraction (XRD) confirmed compatibility with the orthorhombic SrY_2O_4 matrix as the majoritary phase, validating the success of the synthesis method. Examination of the emission spectra at low (10 K) and room (298 K) temperatures revealed that the 4 at.% sample excelled among the others due to its higher relative intensity values. Interestingly, the $^5D_0 \rightarrow {}^7F_0$ band split into two components, implying that at least two sites with C_n, C_{nv}, and/or C_s symmetry were replaced by Eu^{3+}. Consequently, several components were observed for the most intense $^5D_0 \rightarrow {}^7F_2$ band. This band exhibited a nonlinear pattern with temperature, as one of the components, namely Γ_1, gained intensity at higher temperatures, while the other component (Γ_2) reduced. This observation enabled us to use the ratiometric approach to construct a luminescent thermometer. The maximal relative sensitivity (S_r) reached values of 0.25% K^{-1} in the 70 – 120 K temperature

range. Despite the reasonably low value of S_r, one can have an extremely sensible thermometer but poor thermal accuracy and resolution, which can mislead the readout. In this sense, in the same temperature range, the uncertainty (δ_T) assumed values of 0.12 – 0.32 K. These are reasonably low values, where the first is comparable to δ_T obtained from multiparametric or dimensionality reduction approaches. Hence, the low uncertainty in the measurement yields high thermal resolution, implying that the proposed thermometer has potential for measuring temperatures in the cryogenic realm.

Keywords: modified Pechini method, thermometers, luminescence

Seleno-BODIPYs: synthesis and application of new fluorescent sensors for detection and quantification of analytes of environmental and biological interest

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The development of new fluorescent compounds has been attracting the attention of researchers due to various possibilities of application including cellular biomarkers, fluorescent sensors for analytes of environmental or biological interest, or even in the construction of OLEDs. In this context, BODIPY appears as a class of compounds that, in general, presents excellent properties such as large extinction coefficients, high fluorescence quantum yield, and narrow emission and absorption bands. The insertion of chalcogenated groups into a chromophoric core causes a quenching on the compound's fluorescence, being a strategy that allows these compounds to be used as fluorescence sensors in a turn-on fluorescence process.In this work, we present a combination of our latest results on the synthesis and application of new Se-BODIPYs as fluorescent sensors showing the versatility of the new obtained compounds. The general synthetic route to obtain the new BODIPYs is composed by 3 formal steps, consisting of an alkylation of the hydroxyl group of 4-hydroxibenzaldehyde, followed by reaction with pyrrole, and then the *N*-assisted complexation with boron, introducing the BF_2 fragment. The selenium post-functionalization of the fluorescent core was conducted in two ways. The first strategy consisted of a bromination step, giving rise to a tetrabrominated compound followed by a

selenilation step, using PhSeH, generated *in situ*, from Ph_2Se_2 and $NaBH_4$. This method allowed to obtain BODIPYs containing 2 "Br" and 2 "SePh" groups directly connected to the chromophoric core in the final structure. The second strategy was conducted through the selenylation reaction of the BODIPY core, without previous halogenation, using Ph_2Se_2, benzoyl peroxide, and *p*-toluenesulfonic acid. This method allowed to obtain BODIPYs containing four "SePh" groups in the final structure. A screening with different analytes, including amino acids, biothiols, anions, reactive sulfur species, and some oxidants was conducted by absorption and emission spectra. Four main different applications for the new chalcogenated compounds as fluorescent probes were studied. 1) Se-BODIPY as a fluorescent sensor for selective detection, quantification, and distinction of biothiols (including cysteine (Cys) and glutathione (GSH)), resulting in low detection limits, fast response time, and high fluorescence quantum yield for the products. Cell bioimaging using HeLa cells was also conducted. 2) Se-BODIPY as fluorescent sensor to distinguish Cys/Hcy from GSH using different excitation wavelengths. Kinetic study was conducted allowing to differentiate Cys from Hcy. The sensor was also applied to the quantification of these analytes in urine samples, obtaining good recovery values. Tests using discs of paper were also carried-out, making possible visualization of color variation, without organic solvent. 3) Se-BODIPY as a fluorescent sensor for selective detection of CN^-, OH^- and F^- by fluorescence. 4) BODIPY-doped polymer films and particles were obtained, using PMMA and TPU, for fluorometric detection of NH_4OH and thermometric applications.

Keywords: BODIPY, fluorescent sensor, biothiols, polymers

Spectroscopic studies of $NaYF_4$, YVO_4,and AuNRs/NPs for multifunctional superparticles

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The quest for materials exhibiting orthogonal properties, termed multimodal/multifunctional systems, is driving the development of novel synthesis methodologies aimed at achieving precise morphological and structural control. An appealing alternative to complex core@shell systems is the controlled aggregation of diverse nanoparticles into submicrometric structures called superparticles. Given the increasing demand in nanomedicine for materials capable of locally monitoring temperature (luminescent nanothermometry) and inducing controlled localized heating under light (phototherapy), the combination of luminescent and plasmonic particles is attractive for theranostic applications. Prior to controlled aggregation steps, precise tuning of surface and spectroscopic characteristics of individual luminescent and plasmonic particles is mandatory. In this context, we have prepared several rare-earth-based nanoparticles (RE NP) with different excitation wavelengths (λ_{exc}), and AuNRs/AuNPs. $NaYF_4$:Yb, Er and $NaYF_4$:Nd, Yb, Er exhibited Er^{3+} emission in the green ($^2H_{11/2} \rightarrow {}^4I$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$) and red ($^4I_{13/2} \rightarrow {}^4I_{15/2}$) regions with λ_{exc} of 980 and 808 nm, respectively, and both exhibited β-$NaYF_4$ crystal structures. Tetragonal YVO_4:Eu^{3+} particles displayed high-intensity Eu^{3+} emissions ($^5D_0 \rightarrow {}^7F_n$, n= 1, 2, 3 and 4) under λ_{exc} = 270 nm. Additionally, AuNRs were synthesized using the seed-mediated growth method, and AuNPs were prepared using the classic Turkevich method. The upconversion emission of $NaYF_4$ resulted in thermal sensitivities (S_R) ranging between 0.2 and 1.8% K^{-1} for both samples. The individual NPs showed promising properties for further combination into superparticles for thermometry and thermal therapy. Additional studies will further comprise the control of the aggregation processes using light to initiate crosslinking between the capping agents on the particle surfaces.

Keywords: Spectroscopy, Rare Earth, Nanothermometry, Theranostic, Superparticles.

Synthesis and application of new fluorescent probes based on Seleno-BODIPYs for bioimaging and selective detection of biothiols in urine samples

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Biothiols like Cysteine (Cys), Homocysteine (Hcy), and Glutathione (GSH) are compounds with essential physiological functions involved in redox homeostasis in living organisms. Due to their biological importance, the development of new fluorescent sensors for the detection, distinction, and quantification of these analytes has been attracting great attention. Although there are many fluorescent sensors capable of detecting biothiols, the distinction between them remains a challenge, due to their similar structures. In this work, we present the synthesis of two new seleno-BODIPYs for distinction and selective detection of biothiols, through colorimetric and fluorometric analysis, with high fluorescence quantum yields, fast response time, ratiometric response, and low detection limits, in a turn-on fluorescence process. The general procedure to obtain the new compounds started from 4-hidroxibenzaldehyde, and, after 3 reactional steps resulted in the desired BODIPY core, in reasonable overall yields (42-45%). The selenium post-functionalization of the BODIPY core was conducted through a bromination step, using *N*-bromosuccinimide, resulting in tetrabrominated compound in 69% yield, followed by a selenilation step, using PhSeH, generated *in situ* from Ph_2Se_2 and $NaBH_4$ (50-

60% yield). The final chalcogenated compounds present a polyethylene glycol (PEG) substituent, and the main difference between these two new compounds is the chain size of this portion.The first compound obtained was successfully applied to the selective detection of Cys and GSH against 21 analytes through colorimetric and fluorometric analysis. The new probe presented low detection limits (18.4 nM for Cys and 0.42 uM for GSH), high fluorescence quantum yields (31.8% for GSH and 88.1% for Cys), high sensitivity, and fast response time. Mechanistic investigation was conducted allowing to conclude that the reaction with Cys results in a monosubstituted amino-product while the reaction with GSH results in a double substituted thiol-product, by replacing the Se-containing portion. Due to the difference in the reactivity, it is possible to distinguish and detect Cys and GSH simultaneously at different wavelengths. This new compound was also applied for bioimaging in HeLa cells, acting as a fluorescent cell biomarker. The other Se-BODIPY synthesized was applied to selective detection of Cys, Hcy and GSH, in a similar way. It was possible to distinguish Cys/Hcy from GSH using different excitation wavelengths. Kinetic studies showed that the reaction with Cys is much faster than with Hcy, allowing them to be differentiated. The sensor was successfully applied to detect biothiols in urine samples, with good recovery values. Experiments using paper discs impregnated with Se-BODIPY were also conducted, making it possible to visualize a color change from blue to orange (for Cys) and from blue to pink (for GSH). This is a very advantageous and promising strategy that allows the detection of biothiols in the solid state being a practical and simple method.

Keywords: Seleno-BODIPY, fluorescent sensor, biothiols, bioimaging

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From the beginning of my studies in 1981 to the last expedition accomplished in January 2024, I was fascinated by bioluminescence in the marine realm. My research career started in Prof. Baguet's animal physiology laboratory at the Catholic University of Louvain, investigating isolated luminous organs of bony fishes for my master's and my Ph.D. thesis. After a post-doc stay at the University of Montreal in Canada (Prof. M. Anctil Laboratory), where I learned immunolabelling and neuronal release of tracers in midshipman fish, I launched a research program to study the possible conservation of bioluminescence control mechanisms through the evolution. Luminous Ophiuroidea (Echinodermata) represented the first step. Later came various bony and cartilaginous fishes, followed by many other taxa representatives. Multidisciplinary approaches, exploring physiology, morphology, ethology, biochemistry, and molecular biology, allowed me to integrate the control of bioluminescence into the morphological structures, biochemical compounds, and functionality of the light produced by various marine organisms. Among the various luminous species from other phyla studied, one cites (i) pelagic worms from the genus Tomopteris; (ii) the krill, Meganictiphanes norvegica; (iii) the jellyfish Periphylla periphylla from Norwegian fjords; (iv) octocorals from the Mediterranean and deep-sea; (v) abyssal arthropod; (vi) deep-sea echinoderm's representatives of Crinoidea, Holothuroidea and Asteroidea. Key results will be presented, followed by an open discussion. I strongly believe that science thrives on collaboration rather than competition. It's crucial to learn effective communication with experts who can help you achieve a bright future. Always look at the bright side of life. Always look at the light side of life. It is hard to list all the national and international collaborations that made this journey possible for one lucky marine biologist. Huge thanks to all the heads and members of the numerous laboratories and marine stations I visited in Australia, Canada, France, Italy, Japan, New Zealand, Norway, Sweden, Taiwan, the UK, USA. An exceptional thanks to the chief scientists and skillful crews of RV Marion Dufresne (Dr. Y Cherel, CNRS - Kerguelen plateau), RV Southern Explorer (Dr. A. Williams, CSIRO - Perth Canyon), and RV Investigator (Dr. T. O' Hara, Victoria Museum - East coasts of Australia) that provided access to deep-sea and abyssal fauna. Fundings from

numerous foundations represented great support to me, I am deeply embedded for this to the FNRS (Fonds National de la Recherche Scientifique) Belgium. JM is a research associate at FNRS.

Keywords: Marine biodiversity , physiology, morphology, ecology, ethology, biochemistry

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Christmas lights at the bottom of the fjord

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Bioluminescence, defined as the production of visible light by a living organism, is a fascinating phenomenon that has attracted the curiosity of scientists since antiquity. Resulting from a biochemical reaction involving a substrate (a luciferin) oxidized by a specific enzyme (the luciferase), bioluminescence sustains various ecological functions such as defense against predation, attraction of prey, and intra/interspecific communication.Light production in benthic anthozoan has been known for a long time, and particular attention was paid to the sea pansy genus, *Renilla*. The knowledge of *the Renilla* luminous system led to the extensive use of its luciferase, the so-called *RLuc*, as a tool for biotechnologies. Nevertheless, information on other sea pens remains scarce, notably concerning light emission control. Through morphological, transcriptomic, pharmacological, and biochemical analyses, we worked on two anthozoan sea pens, *Pennatula phosphorea* and *Funiculina quadrangularis*, living in sympatry within Swedish fjords, to shed light on their bioluminescence physiology. We highlighted (*i*) the conservation of the luciferase and coelenterazine requirement in the bioluminescence system among anthozoans, (*ii*) the expression site of the luciferase, (*iii*) the involvement of calcium and coelenterazine-binding protein in the light emission process, (*iv*) a catecholaminergic control of the light production. Besides, through the maintenance in captivity of *P. phosphorea* with coelenterazine-free food for a year, we demonstrated the ability of this sea pen to synthesize the coelenterazine substrate to maintain its luminous status. The two investigated species produce light in different wavelengths (*i.e.* green at 510 nm for *P. phosphorea* and blue at 485 nm for *F. quadrangularis*). Transcriptomic and morphological analyses pinpointed the use of a green fluorescent protein for *P. phosphorea*. A comparative analysis was performed with another Pennatuloidea, *Anthoptilum murrayi*. Although these new data unveiled the

luminescence physiology and evolutive conservation of light production in sea pens, questions remain on the ecological function of the light emitted by these species.

Keywords: Sea pen, Coelenterazine, Luciferase, Coelenterazine binding protein, GFP, Catecholamines

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Fluorescent filters of photophores in dragonfishes Stomiidae (Teleostei: Stomiiformes)

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The meso- and bathypelagic zones (200 – 4000 m depth) harbor the highest biodiversity of bioluminescent organisms on the Earth. The main light sources in these depths are downwelling sunlight and bioluminescence, both characterized by dim, narrow blue-green spectra. Stomiidae (Stomiiformes) is the most diverse family of bioluminescent deep-sea fishes. Stomiids bear serial body photophores that produce blue-green light for counterillumination, and sub-ocular photophores that emit red light for illumination and intra-specific communication. Red fluorescing pigments are present in both photophore types.Fluorescent proteins were extracted from the body photophores of *Stomias affinis* and sub-orbital photophore of *Malacosteus australis*. Proteins were purified by ion exchange and gel filtration chromatography. Red fluorescent fractions were run on SDS-PAGE electrophoresis gel, and respective bands were excised for nLC-MS mass spectrometry. Peptide sequences obtained from nLC-MS were tracked on transcriptomes of respective photophore types and genera. Chromophores were also analyzed using HPLC. Spectral properties of light transmission and fluorescence of the proteins were obtained by spectrophotometry.Two potential novel red fluorescent proteins were found for each photophore type of Stomiidae. The preliminary results suggest the two proteins diverge in peptide sequences, chromophores, physicochemical and spectral characteristics. Body photophores of Stomiidae evolved a lilac protein for spectral cutoff on counterillumination. Sub-orbital photophores arose exclusively in Malacosteinae using a red fluorescent protein to emit red light for illumination. Stomiids evolved two fluorescent proteins in distinct photophore mechanisms for particular ecological purposes, reflecting the benefits and complexity of bioluminescence in the evolution of these deep-sea fishes.

Keywords: Dragonfish, Evolution, Fluorescence, Bioluminescence

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Involvement of spine sensory receptors and pigmented sheath in the bioluminescence of the brittle star *Amphiura filiformis*

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Out of the 7,000 extant species of echinoderms, over 150 bioluminescent species have been identified to date. Among the five echinoderm classes, one class, the ophiuroids (brittle stars) dominate with 50% of the known bioluminescent species. The species *Amphiura filiformis*, commonly found buried in the muddy sediments of European seas, has been the subject of extensive study for over 30 years. Only two arms are extending outside the sediments when feeding on plankton and particulate organic matter. When mechanically stimulated, *A. filiformis* emits blue light at the arm spine level via a *Renilla*-like luciferase. However, our understanding of the luminescence triggering mechanism is limited to the nervous cholinergic control, while the biochemical and mechanical factors controlling its bioluminescence remain incompletely explored. The multidisciplinary approach of this study, which combines molecular biology and functional morphology, unveils a multi-level bioluminescence control. ***In silico*** **analyses** conducted on the recent reference chromosome-scale genome revealed the presence of at least 9 genes encoding *Renilla* luciferase-like proteins. Results from ***in situ*** **hybridization** suggest the involvement of several of these genes in bioluminescence, as indicated by their expression in the brittle star spines. From a cellular perspective, it is known that the light-producing cells are located at the base of the spine. Conversely, light emission is only visible at the tip of the spine, a duality that has remained rather enigmatic until now. Through **histological** and **ultrastructural** analysis, a light-guiding role is proposed for a pigmented sheath, potentially facilitating light transmission along the spine. **Electron microscopy** also revealed that different morphotypes of ciliated projections, known as *stäbchens*, are observed on the spine surface of *A. filiformis*, closely associated with the photocyte processes. In addition, **luminometric tests** show a luminescent response to conditioned water with chopped arms that mimic injured congeners. Given that *stäbchens* are generally considered as mechanoreceptors or

chemoreceptors, these structures could therefore be involved in the light response of this luminous species to predator contact and/or conspecific chemical alarms signals. This study enhances our morpho-functional understanding of bioluminescence in *A. filiformis*, and also provides new insights into accessory structures, such as ciliated receptors or pigment cells, which may be linked to bioluminescence control in luminous ophiuroids.

Keywords: Luciferases, Ultrastructure, Stäbchen, Chemical communication

Bioluminescence of marine-firefly, Ostracods – from biology to biotechnology

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The marine firefly "*Cypridina hilgendorfii Müller*" was discovered by F. Hilgendorf in around 1874 of Japan coast and introduced by W. Müller in ZOOLOGISCHE JAHRBÜCHER in 1891. The luminous Ostracod Cypridina, "Umihotaru called in Japanese", is a typical luciferin-luciferase reaction without any cofactors. Before the discover of the green fluorescent protein (GFP) by O. Shimomura et al., he achieved to isolate and crystallize the Cypridina luciferin. N. Kishi et al. determined the chemical structure of this luciferin as a second success example of determined its chemical structure and Shimomura proposed the chemical reaction mechanism on the luciferin-luciferase. (S)-Cypridina luciferin has an imidazopyrazinone compound having three functional groups at the C2, C6, and C8 positions, which probably derives biogenetically from three amino acids: L-arginine, L-isoleucine, and L-tryptophan (or tryptamine). Cypridina luciferase is both glycoprotein and secretory protein. In the proposal mechanism of luciferin-luciferase reaction, when the luciferin bound to luciferase, the C7 of imidazopyrazinone is negatively charged and reacts easily with oxygen in C2 position to forming a dioxetaone. The excited state of oxyluciferin falls to its ground state, resulted in producing a blue light (lmax = 460 nm). During this reaction, the quantum yield was measured about 0.3 at 4 C, which is higher than coelenterazine-type bioluminescence system based on similar imidazopyrazinone compound. Two genes of Cypridina luciferases were cloned by F. I. Tsuji and our group. Cypridina luciferase has a higher molecular weight and have up to 17 potential disulfide bonds between the 34 cysteine residues in its 553-555 amino acids, resulting in stable protein with higher thermal stability. After transfection of these genes, the luciferase protein can express and secret to the out of cell in the mammalian, plant, and yeast cell but not express in E.coli. Until now, our group crystalized the recombinant Cypridina luciferase and determined its three-dimensional structure. The chemical synthesis procedure of Cypridina luciferin had already established as a commercial purpose by C. Wu. On the other hand, the application of Cypridina system was available in the biotechnology field for the in vitro cell functional analysis, ex vivo and in vivo imaging for tumor tissue etc. For instance, dual reporter assay using two secreted

Cypridina and Gaussia luciferases can evaluate two gene expressions in the medium of living cell using Cypridina luciferin

Keywords: Bioluminescence, Marine firefly, luciferin, luciferin

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How long can *Amphiura filiformis* (Ophiuroidea, Echinodermata) emit light?Insights into the trophic acquisition of bioluminescence through a long-term seasonal study

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Bioluminescence is the capability to emit visible light thanks to a biochemical reaction. About 80% of the known luminous species live in the marine environment. Among luminous substrates, coelenterazine is the most widespread luciferin described in at least eight phyla. The broad phylogenetic distribution of this light-emitting molecule led to the hypothesis of its dietary acquisition, demonstrated in one jellyfish, one lophogastrid shrimp, and one brittle star species. The European brittle star *A. filiformis* is a model species within Ophiuroidea, the dominant class of luminous Echinoderms. The latter emits a blue light via a *Renilla*-like luciferase dependent on a dietary acquisition of the coelenterazine. Nevertheless, questions remain concerning this coelenterazine trophic acquisition process: (*i*) Do seasonal variations of luminescence capabilities exist? (*ii*) How long can brittle star luminous capabilities persist after a single boost of coelenterazine? (*iii*) does the luciferase expression change in photogenic tissues after the exogenous supply of coelenterazine? A multidisciplinary analysis with luminometric measurements, luciferase immunolabelling, and histological visualization was undertaken to answer these questions.Our results highlighted (*i*) no seasonal variation in *A. filiformis* luminous capabilities involving a continuous supply from prey containing coelenterazine, (*ii*) the coelenterazine availability in the brittle star diet is the only limiting factor for the bioluminescent reaction, (*iii*) a green autofluorescence signal attributed to coelenterazine over the luciferin acquisition, (*iv*) the luciferase is expressed throughout the brittle star life. Moreover, the ultrastructure description supports the hypothesis of a pigmented sheath transmitting light to the tip of the spine. All these insights improve our knowledge of the bioluminescence phenomenon of this suspensive feeder brittle star.

Keywords: Ophiuroid, Luminescence, Dietary acquisition, Coelenterazine, Luciferase

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Light projection mechanism and ecological advantages of reflector system in lanternfish photophores

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Fishes inhabiting the mesopelagic zone (200 - 1000 m depth) often bioluminesce for camouflage purposes - counterillumination. While migrating to the surface at night to feed on zooplankton, ventral light emissions from bioluminescent organs - photophores - match the narrow blue-green light penetrate the ocean waters downward. Luminescence of lanternfishes (Myctophidae) is produced by an oxidative reaction of coelenterazine in bioluminescent cells - photocytes. While other fishes tune counterillumination light to the ambient by pigmented filters, the photophores of lanternfishes are structurally unique, holding a blue-green inner reflector.Collection of myctophid *Diaphus watasei* took place in fishing ports of Kochi and Mie Prefectures, Japan. Reflection spectra of fresh photophores was obtained by spectrometry. Further analyses included light microscopy, *X*-ray diffraction and Fourier-transform infrared spectroscopy, to study the photophore histological structure, luciferase purification, and iridophore's chemical nature and morphology.Inner reflector is composed by a monolayer of packed hexagon-shaped iridophores. This unique hexagonal interlock project all the light on a precise direction while achieving low energetic costs from photon losses by minimizing cell gaps. Shaped as a parabolic mirror with photocytes at its focus, this tissue reflects all the light at an accurate vertical angle. By achieving structural colour, the reflector also modulates the spectra of light produced by the photocytes to longer wavelengths. Comparing to photophores of other deep-sea fishes, the lanternfish reflector provides a significant ecological advantage, ensuring not only a precise angle match to the deep-sea light but also adapting the camouflage spectra during vertical migrations.

Keywords: Lanternfish, Counterillumination, Photophore, Reflector

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Luminescence of the Enantiomer of (*S*)-Cypridina Luciferin with *Cypridina* Luciferase

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Luminous ostracods of the family Cypridinidae produce light through the oxidation reaction of Cypridina luciferin (CypL) catalyzed by *Cypridina* luciferase (CypLase). CypL is an imidazopyrazinone compound having one chiral carbon atom, and the absolute configuration of natural CypL was determined to be *S* by analysis using D- and L-amino acid oxidases and Cypridina hydroluciferin that was obtained by hydrogenation of natural CypL. Additionally, previous studies reported that the reaction of (*S*)-CypL with CypLase produced light. However, the luminescence of optically pure (*R*)-CypL, which is the enantiomer of (*S*)-CypL, with CypLase has not been investigated, and the ability of CypLase to recognize the chirality of CypL for light emission remains unclear. In this study, to confirm whether (*R*)-CypL functions as a luminous substrate for CypLase, we examined the luminescence of (*R*)-CypL, which was successfully obtained by chiral high-performance liquid chromatography (HPLC) separation of the enantiomeric mixture, with a recombinant CypLase. Our luminescence measurements demonstrated that the reaction of (*R*)-CypL with CypLase produced light, indicating that (*R*)-CypL must be considered as the luminous substrate for CypLase, as in the case of (*S*)-CypL, rather than a competitive inhibitor for CypLase. Additionally, we found that the maximum luminescence intensity from the reaction of (*R*)-CypL with CypLase was approximately tenfold lower than that of (*S*)-CypL with CypLase, but unexpectedly our kinetic analysis of CypLase suggested a higher affinity of (*R*)-CypL for CypLase than (*S*)-CypL. Furthermore, the chiral HPLC analysis of the reaction mixture of racemic CypL with CypLase showed that (*R*)-CypL was consumed more slowly than (*S*)-CypL. These results indicate that the turnover rate of CypLase for (*R*)-CypL was lower than that for (*S*)-CypL, which caused the less efficient luminescence of (*R*)-CypL with CypLase. Our findings will contribute to understanding the ability of CypLase to recognize the chirality of CypL for light emission and provide a new insight into the engineering of CypLase to produce light efficiently.

Keywords: Cypridina luciferin, Cypridina luciferase, enantiomer, luminous ostracod

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New genomic insights illuminate the bioluminescence of the European brittle star Amphiura filiformis

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The bioluminescence of brittle stars has long captivated scientists, and it's not over yet! Previous research suggested that the luciferase enzyme of the brittle star *Amphiura filiformis* is homologous to the one of the sea pansy *Renilla* (Cnidaria). Surprisingly, these enzymes also share high sequence identity and structural similarity with haloalkane dehalogenases which are mostly microbial enzymes that cleave carbon-halogen bonds in diverse halogenated hydrocarbons. This suggests that ancestral non-luciferase enzymes were convergently co-opted into luciferases in cnidarians and echinoderms. Using chromosome-scale genome, extensive transcriptome analyses, immunodetections and *in situ* hybridisations, we identified multiple luciferase genes in the brittle star and studied their expression during development and arm regeneration. Our investigation revealed nine luciferase-like gene copies, with seven organised in two clusters of tandem duplicates and two existing as isolated copies. In echinoderms, the presence of multiple *Renilla*-type luciferase-like gene copies stands out as a notable example of lineage-specific evolution through tandem duplications followed by asymmetric divergence. Our analyses indicate that luciferase-like genes have undergone duplication events across all echinoderm lineages except for sea stars. These luciferase-like genes possibly encode diverse functions across bioluminescent and non-bioluminescent species. Further investigation revealed the presence of luciferase mRNAs and proteins in the light-emitting spines and central nervous system of adult brittle stars. The expression of luciferase peaked during the

differentiation of spines during the regeneration process. This research provides valuable insights into the dynamic evolutionary processes that shape the functional repertoire of echinoderm genomes and drive the evolution of echinoderm bioluminescence.

Keywords: Bioluminescence, Genome, Luciferase, Echinoderm

MECHANISMS OF CHEMILUMINESCENCE AND BIOLUMINESCENCE PROCESSES

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Carbolines as Naturally Occurring Activators for Peroxyoxalate Chemiluminescence

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b-Carbolines (*i.e.*,9H-pyridine[3,4-b]indole) compose a class of naturally occurring alkaloids, characterized by the presence of a pyridine ring fused to an indole moiety, with significant biological activity. In this study, fourteen compounds were synthesized, varying the benzaldehyde derivative which was attached to the carboline skeleton. The compounds were identified, and its purity confirmed by ^{1}H- and ^{13}C-NMR, as well as melting points. The molar extinction coefficients show to be in the range of p-p* transitions and the fluorescence quantum yields range from 0.01 to 0.3, indicating that the substituents in the 1-position have a significant impact on the photophysical properties of these compounds. Furthermore, the fluorescence quantum yields indicate that these b-carbolines have potential utility as activators in peroxyoxalate chemiluminescence (CL). The synthetized carboline derivatives have been tested as activators in peroxyoxalate CL, using initially bis(2,4,6-trichlorophenyl) oxalate (TCPO) as reagent and imidazole as base and nucleophilic catalyst in organic solvents. The results indicate that these compounds act as activator in this CL transformation, although their efficiency showed to be considerably lower than commonly utilized polycondensed aromatic hydrocarbons. Some of the derivatives studied showed different kinetic behavior from its expected role as only CL activator, indicating that the carbolines could have multiple functions in the transformation, as activator but also potential base catalyst.

Keywords: peroxyoxalate, b-carbolines, alkaloids, natural products, activators.

Derivatives of 1,2,4,5-tetraphenylimidazole applied in organic light-emitting systems.

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Radziszewski was the first to describe a organic chemiluminescent system in 1877, in which he observed an yellow emission from the reaction between 1,2,4-triphenylimidazole, oxygen and a strong base. In this work, two series of 1,2,4,5-tetraphenylimidazole (TEPI) compounds were synthesized with different substituents on the 1-phenyl ring, which differed only by the absence (series a) or presence (series b) of an o-OH on the 2-phenyl ring. It was observed that the Excited State Intramolecular Proton Transfer (ESIPT) assigns significant differences in the chemiluminesent characteristics of series b when compared to series a. Electron-donor substituents, in general, had higher ΦFL values. The chemiluminescent assays showed that TEPI derivatives can be used as activators in the peroxyoxalate reaction, probably through the mechanism known as Chemically Initiated Electron Exchange Luminescence (CIEEL). Derivatives from series a exhibited lower values of ΦS∞ and ΦCL∞, and higher kCAT/kD when compared to series b. Compared to other systems, series a derivatives had their chemiluminescent parameters analogous to inefficient activators. For series b, these values were equivalent to lophines and classical activators such as anthracene and 2,5-diphenyloxazole. Linear Hammett correlations using the parameters ΦS∞ and kCAT/kD revealed that there is a possibility of an inverted CIEEL mechanism occurring during chemiexcitation, however, the determination of the electrochemical properties of these compounds is necessary to sustain this hypothesis.

Keywords: ESIPT, chemiluminescence, CIEEL, lophine, activator

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General chemiexcitation mechanism in cyclic peroxide decomposition: singlet excitation efficiency

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Chemiluminescence (CL) and bioluminescence (BL) transformations are intimately linked to the chemistry of peroxides, specifically four-membered peroxidic rings, whose decomposition involves a symmetry-forbidden concerted [2+2] retro-cycloaddition, leading to the formation of two carbonyl fragments, in a highly exothermic reaction where the chemical energy can be transformed in electronical excitation energy. Studies on the stability and the chemiexcitation capacity of synthesized cyclic peroxides have led to the formulation of general chemiexcitation mechanisms which can be used to rationalize electronically excited state formation also in complex chemiluminescence and moreover bioluminescence transformations. In this contribution, we give a general introduction to these chemiexcitation mechanisms, outlining the main experimental observations which led to their formulation, and refer to recent experimental and theoretical results. (i) The unimolecular decomposition of 1,2-dioxetanes and 1,2-dioxetanones has been intensively studied und is believed to occur by a concerted biradial-like mechanisms, leading to the preferential formation of non-emissive triplet-excited species, with singlet quantum yields of lower than 0.1 %. Therefore, this system is not an adequate model for efficient CL and BL transformations, where singlet-excited states have to be formed in high yields. Several recent theoretical approaches have been performed with the objective to clarify this mechanism and to rationalize experimentally determined chemiexcitation quantum yields. (ii) The catalyzed decomposition of 1,2-dioxetanones and similar peroxides occurs with preferential formation of singlet-excited products, although with relatively low efficiency, involving the chemically initiated electron exchange luminescence (CIEEL) mechanism and recent experimental and theoretical studies indicate the importance of sterical hinderance on charge-transfer complex formation between an activator and the peroxide as reason for its low efficiency. (iii) The induced decomposition of 1,2-dioxetanes, which contain an electron rich phenolate group, proceeds with very high singlet-excitation quantum yields, in a process that has been shown to occur in an entirely intramolecular fashion. (iv) The peroxyoxalate reaction is one of the most efficient CL systems known with singlet-excitation quantum yields of up to

100% in favorable conditions, even so it proceeds by the, frequently low-efficient, intermolecular CIEEL mechanism. 1,2-Dioxetanedione appears to be the high-energy intermediate formed in this transformation, whose favorable interaction with the activator might be the key for its high efficiency. In summary, unimolecular peroxide decomposition leads mainly to non-emissive triplet-excited carbonyl compounds, whereas preferential formation of singlet-excited products is observed in catalyzed peroxide decomposition, although with low yields, except for the peroxyoxalate system which is highly efficient. Finally, intramolecularly induced decomposition of proper 1,2-dioxetanes leads also to extremely high singlet-excitation yields.

Keywords: chemiexcitation mechanisms, cyclic peroxides, electron transfer, CIEEL, singlet excitation

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Oxy-Chemiluminescence: New Facets, Mechanistic Insights and Kinetic intricacies

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The experimental material considered herein refers to the recent advances in the elucidation of oxidation processes followed by the excited-state generation with the subsequent light emission (oxy-chemiluminescence) and consists of the two parts. The first part is devoted to the new facets of chemiluminescence in the luminol oxidation (generation of different light emitters in joint chemiluminescence of luminol and lophine, autooxidation of luminol in DMSO: effects of alkalis, quenching by nitroblue tetrazolium and elimination of quenching by hydrogen peroxide, as well as the salient features of the luminol chemiluminescence in the presence of hemin without added H_2O_2). The second part is dedicated to the chemiluminescence processes, which may be considered as chemical models of oxidative interactions leading to a weak light emission emerged from living cells and to exploring the possibilities of using them as tools for evaluating the activity of oxygen-metabolism modulators, most prominently, natural bioantioxidants, in particular, of biomedical value. Methodologically, the major attention is paid to analyzing the shapes of the time profiles of the light emission derived from model chemiluminescence systems, in particular, in the presence of lipid samples of vegetable and animal origin rich in bioantioxidants.

Keywords: oxy-chemiluminescence, luminol, lophine, hydrocarbons, free radicals, lipids, bioantioxidants

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Peroxyoxalate reaction catalyzed in aqueous medium by cationic micelles

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The peroxyoxalate reaction, discovered in 1963 by Chandross, has been extensively investigated mechanistically since then and utilized in a great variety of analytical application. Mechanistic studies were mainly performed in anhydrous media, where the chemiexcitation efficiency is very high, however, analytical and bioanalytical application mostly necessitate aqueous media, where the efficiency drops drastically. Therefore, we studied the utilization of the cationic surfactants cetyltrimethyl-ammonium chloride (CTAC) and bromide (CTAB) and 1-cetyl-3-methylimidazolium chloride (C16MeImCl) in aqueous medium for the peroxyoxalate reaction. In previous studies conducted by our group, the reaction system could be defined, comprising bis(2-(methoxycarbonylphenyl)oxalate (2-MCPO), fluoresceine as chemiluminescence activator and 5.0 mmol L^{-1} of phosphate buffer at pH 6.0. The critical micelle concentration (CMC) of the surfactants was measured by conductimetry in water and phosphate buffer (5.0 mmol L-1); the CMC of C16MeImCl decreased from 8.6 10^{-4} mol L^{-1} to 2.3 10^{-4} mol L^{-1}, of CTAB from 9.0 10^{-4} mol L^{-1} to 4.6 10^{-4} mol L^{-1} and CTAC from 9.5 mol L^{-1} to 0.55 mol L^{-1}, changing from water to phosphate buffer. Subsequently the effect of the surfactant concentration on the peroxyoxalate emission kinetics was studied in a range from 0.05 to 50 times the CMC. In all cases, the k_{obs} values show a considerable increase, followed by a gradual decrease, with increasing surfactant concentrations, although different profiles were observed with chloride and bromide as counterions. With chloride surfactants, the k_{obs} decreased from 4 × CMC to higher concentration, while for CTAB, the decrease in k_{obs} occurred only from 7 × CMC onwards. Additionally, for chloride surfactants, the chemiluminescence quantum yields (F_{CL}) reached their peak values at similar analytical concentrations but different multiples of CMC. Consequently, the impact of chlorine and bromine on the peroxyoxalate reaction in the absence of surfactant, aimed at avoiding micelle stabilization effects by anions and alterations in the reaction microenvironment, was investigated by varying the NaCl and NaBr concentrations in the reaction medium. Increasing chloride concentration led to a decrease in k_{obs} values, while the F_{CL} stay constant from 0 to 200 mmol L^{-1}, followed by a gradual decrease at higher concentrations. In contrast, for bromine, the k_{obs} increased from 0 to 5 mmol

L^{-1} and then remained virtually constant, while F_{CL} significantly decreased, indicating a quenching effect of this anion on peroxyoxalate chemiluminescence. It can be expected that around the micelle, the concentration of counterions is higher than in bulk solution; therefore, these effects could be observed at lower concentrations of bromine (due to high local concentrations), justifying the drastic decrease of F_{CL} in the variation of CTAB concentration. The higher quantity of this surfactant needed to decrease the k_{obs} could be attributed to the enhancement of k_{obs} by bromine in water.

Keywords: chemiluminescence, peroxyoxalate, reaction mechanism, cationic surfactant

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Solid State Chemiluminescence and Bioluminescence - Current State and Future Directions

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The phenomena of chemiluminescence and bioluminescence, although well-characterized in liquid phases, have long remained elusive in solid-state matrices, such as macroscopic crystals.[1] Our fundamental work in 2019[2] unveiled that chemiluminescence in centimeter-sized crystals of organic peroxides, including hydroperoxides, endoperoxides, aroyl peroxides, and dioxetanes, can be thermally induced, demonstrating the generality of this process across these classes. In a subsequent study in 2020[3], we also showed that the bioluminescence reaction of cypridina luciferin and luciferase could be mechanically induced in solid media, thus bridging the gap between liquid and solid-state chemiluminescence and bioluminescence.While follow-up studies by other research groups have greatly enhanced our understanding of these phenomena, significant challenges remain, particularly in fully elucidating the underlying mechanisms and improving the quantum yields of solid-state chemiluminescence. Moreover, the initiation of solid-state chemiluminescence has thus far been restricted to thermal or mechanical activation, potentially limiting its applications. Key questions regarding the enhancement of quantum yield and the identification of alternative activation methods are yet to be answered.To date, the practical applications of these phenomena have not been fully realized. However, their potential, especially in the realm of solar energy storage, is promising. The primary challenge for these applications is the low quantum yield of the solid-state chemiluminescence reaction, which significantly limits the efficiency of energy release. Moreover, the potential for using these phenomena in analytical tests, such as the quantification of dibenzoyl peroxide, a key polymerization initiator, suggests broader applicability as a sensor for various analytes.Future research in solid-state chemiluminescence and bioluminescence should also focus on overcoming current limitations by exploring alternative activation methods. A promising direction could involve the synthesis of peroxide-containing molecules with protective groups, which, upon reaction with a cleaving agent, could initiate the chemiluminescence reaction, similar to mechanisms observed in solution-phase reactions.This keynote presentation will offer a comprehensive overview of the

current state of solid-state chemiluminescence and bioluminescence, emphasizing the significant challenges and proposing future research directions. It aims to catalyze collaborative efforts within the scientific community to advance our fundamental understanding and explore practical applications of these phenomena, thereby fostering innovation in both academic and applied research domains.[1] M. Vacher, I. Fdez. Galván, S. Schramm, B.-W. Ding, R. Berraud-Pache, P. Naumov, N. Ferré, Y.-J. Liu, I. Navizet, D. Roca-Sanjuán, W. J. Baader, R. Lindh, *Chemical Reviews* **2018**, *118*, 6927-6974. [2] S. Schramm, D. P. Karothu, N. M. Lui, P. Commins, E. Ahmed, L. Catalano, L. Li, J. Weston, T. Moriwaki, K. M. Solntsev, P. Naumov, *Nature Communications* **2019**, *10*, 997. [3] S. Schramm, M. B. Al-Handawi, D. P. Karothu, A. Kurlevskaya, P. Commins, Y. Mitani, C. Wu, Y. Ohmiya, P. Naumov, *Angewandte Chemie International Edition* **2020**, *59*, 16485-16489.

Keywords: Solid State Chemiluminescence, Solid State Bioluminescence, Dioxetanes, Hydroperoxides, Endoperoxides

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The phenoxy group effect in the chemiluminescence efficiency of 1,2- dioxetanes derived from tetraphenylimidazoles

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In this work, we present a new phenoxy-triggered 1,2-dioxetane based on hydroxylated TEPI derivatives, utilizing methodologies our research group has explored with hydroperoxides and silylperoxides derived from triphenylimidazoles. The selected TEPI 1,2-dioxetanes vary in the position of the silyl-protected hydroxy group, featuring ortho, meta, and para substitutions. We studied their deprotection and chemiluminescence (CL) kinetics and proposed a possible mechanistic rationalization for the effect of the phenoxy position on chemiexcitation efficiency. Despite their low stability, which complicates purification, we successfully used the 1,2-dioxetanes in kinetic chemiluminescence assays. For these peroxides, our hypothesis is that an intramolecular electron transfer from the sp^2 nitrogen atom of the imidazolyl system to the O–O bond of the peroxidic ring occurs, influenced by the charge density of the phenolate group, during the intramolecularly catalyzed decomposition of these 1,2-dioxetanes. It appears that the meta-oriented derivative exhibits higher chemiexcitation efficiencies due to the so-called 'meta effect,' previously observed with other phenoxy-triggered 1,2-dioxetanes. The decomposition of the ortho and para-substituted derivatives may proceed through a more accessible pathway, leading to products in the ground state. Future computational studies exploring the influence of electronic properties and the position of substituents on CL will be invaluable for rationalizing the intramolecular CIEEL panorama. This could significantly enhance our understanding of other light-emitting systems and compounds.

Keywords: Phenoxy-triggered 1,2-dioxetanes, Hydroxylated TEPI derivatives, Chemiluminescence kinetics, Intramolecular electron transfe

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Contribution of NAD(P)H:FMN-oxidoreductase activity into viscous medium effects on kinetics of coupled enzyme system from luminous bacteria

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At present, there is a state fact that the interior of the real cellular pattern is quite different from the classical one, which is based on buffer solutions. The impact of crowding agents on enzymatic activities is one of the hot topics for the plenty of research devoted to shedding light on mechanisms of the cellular organization of the metabolic pathways. Numerous articles have been published and new knowledge about enzyme behaviour in the presence of different crowding agents and cosolvents has been received. Nevertheless, there is an issue that requires attention - whether the crowded and/or viscous medium affects, in the same way, the kinetics of a particular enzyme functioning alone and as part of a conjugation chain (metabolic pathway). To shed the light on this issue, the coupled enzyme system based on NAD(P)H:FMN-oxidoreductase and luciferase from luminous bacteria (Red + Luc) seems the unique research tool. Firstly, the activities as single enzymes as the coupled one are easy to monitor without sophisticated equipment. Secondly, the Luc activity in the presence of cosolvents has been studied by different authors. But there is little known about how the Red activity changes in the presence of cosolvents. This work is aimed to investigate the kinetic features of Red in the presence of glycerol and sucrose. The obtained data demonstrate that the Red activity decreases in the viscous medium. In the presence of glycerol, the Red activity was reduced in a diffusion-controlled manner, whereas the effect of sucrose solutions was weaker. In addition, the effect of the cosolvents on K_m (FMN) of Red was estimated. It has been shown that the presence of 20% sucrose leads to a 0.7-fold lower K_m(FMN) value compared to one in the buffer. In contrast, in the medium with 20% glycerol 1.9-fold higher K_m (FMN) has been obtained compared to one in the buffer. This could be caused by different relative solvent accessibility values of glycerol and sucrose to Red's active centre. If we compare the Red activities obtained in the presence of the cosolvents with previously published data for Luc and Red + Luc activities, there could be stated that the influence of the cosolvents on the activity of the coupled enzyme system is close to additive manner. Thus, the residual bioluminescence intensity of the Red + Luc enzyme system in the presence of the glycerol and sucrose is close to a sum of

individual effects of the cosolvents on the kinetic features of both Luc and Red. The investigation of the cosolvents effects on the kinetics of a single enzyme is relevant for figuring out the cellular enzyme's behaviour of multienzyme systems within luminous bacteria.

Keywords: NADH:FMN-oxidoreductase, bacterial luciferase, bioluminescence, viscosity, enzyme kinetics, in vivo simulated media

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Dual mode chemiluminescence property of an anthracene endoperoxide in the crystalline state

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Chemiluminescence (CL) in the crystalline state is an attractive research subject because it is applicable to construct the solid-state reaction theories including kinetics and to design functional materials having the abilities to respond to external stimuli such as light, heat, vapor, etc. The first report on the solid-state CL is about the thermolytic CL reaction of rubrene endoperoxide found in 1926. While the mechanism of the solid-state CL of rubrene has not been clarified yet, this finding encourages us to develop the chemistry of the solid-state CL of an aromatic endoperoxide. In fact, we have clarified the relationships between the CL properties and crystal structure of 9,10-diphenylanthracene endoperoxide (DPA-EP). The thermolytic reaction of DPA-EP generates DPA and singlet oxygen ($^1O_2$) and $^1O_2$ can show phosphorescence with the maximum at ca. 1275 nm. When a crystal sample of DPA-EP was heated to 200 ºC, 1275 nm-emission was observed to show that the thermolytic reaction and crystal melting proceeded simultaneously. The result indicates that the crystal lattice decreases the freedom of molecular motion for the reaction by intermolecular interactions. Based on the previous finding, we investigated here the thermolytic reaction of 9-phenyl-10-phenylethynylanthracene endoperoxide (PPEA-EP) as a more reactive endoperoxide compared to DPA-EP. Then, we found that heating of a PPEA-EP crystal sample at 120 ºC showed a dual-mode emission property with maintaining the solid state. One is 1275 nm-emission originated from $^1O_2$ and the other is 510 nm-emission originated from PPEA excimer. In this presentation, we will discuss the mechanism of this characteristic CL emissions based on crystal structure, reactivity, and an energy relationship.

Keywords: Chemiluminescence, Crystalline-state, Anthracene endoperoxide, T-T annihilation

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Linear free-energy relationships in the context of studying chemiluminescence mechanisms

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Linear free energy relationships (LFER) have long been used as tools for the determination of reaction mechanisms in physical organic chemistry, particularly to characterize the transition state of key steps within a given transformation. In this context, chemiluminescence (CL) reactions have benefited from LFER such as the Hammett (ρ), Yukawa-Tsuno (ρ, r), and Brønsted (β_{lg}) plots to gain valuable insights regarding the identity of *in situ* generated intermediates. For example, it has been observed that the formation of the 1,2-dioxetanone acting as the high-energy intermediate (HEI) of a CL system analog to the firefly luciferin substrate occurs on a fully concerted step (ρ = +1.62, r = 0.22, β_{lg} = –0.39 $_{\text{in ACN}}$, Mello et al., *J. Org. Chem.* **2024**, *89*, 345). The generation of the cyclic peroxidic dimer of CO_2 (namely, 1,2-dioxetanedione) as the HEI of the peroxyoxalate transformation (PO-CL) has also been confirmed by LFER (ρ = +2.2, β_{lg} = –1.1 $_{\text{in water}}$, Silva et al., *J. Org. Chem.* **2021**, *86*, 11434). Indeed, the PO-CL system has been investigated under the scope of Hammett plots on various occasions (Alves et al., *Photochem. Photobiol. Sci.* **2015**, *14*, 320; Maruyama et al., **2013**, *252*, 222; Koike et al., *Chem. Commun.* **2003**, 794; Silva et al., *Luminescence* **2002**, *17*, 362). Important aspects of the complex reaction sequence involved in the CL oxidation of lophine were also unveiled by Hammett plots (White and Harding, *Photochem. Photobiol.* **1965**, *4*, 1129; Philbrook and Maxwell, *Tetrahedron Lett.* **1964**, *5*, 1111), particularly to sustain the hypothesis that a 1,2-dioxetane is involved as HEI (ρ = +1.5, Boaro et al., *J. Org. Chem.* **2021**, *86*, 6633). The occurrence of an intramolecular electron transfer in the thermal CL decomposition of acridinium-substituted 1,2-dioxetanes was also proposed based on substituent effects (ρ = +1.3, Ciscato et al., *J. Org. Chem.* **2010**, *75*, 6574). This presentation will focus on these and other specific examples of CL transformations, giving a comprehensive view of how the use of LFER led to a better understanding of CL mechanisms while also suggesting possible pathways of "enlightening" with these tools.

Keywords: Bioluminescence, Chemiluminescence, Hammett, Brønsted

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Peroxyoxalate mechanism in near-neutral aqueous media: concomitance of specific acid and basic catalysis in water

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Since its discovery by Chandross in 1963, the peroxyoxalate reaction has been widely studied using kinetic and mechanistic approaches and frequently utilized for analytical purpose. Most mechanism studies have been performed in anhydrous organic solvents; only recently partially aqueous media are more frequently utilized. Given the greater applicability of the aqueous medium for analytical purposes, in addition to better environmental compatibility, an aqueous medium was designed with an expected high light intensity emission for possible analytical applications of the reaction. The mechanistic studies under these reaction conditions were carried out by kinetics of the peroxyoxalate reaction in aqueous medium using phosphate buffer as the catalyst and fluorescein as the activator. Three oxalate esters of different reactivity, TCPO (bis(2,4,6-trichlorophenyl) oxalate), 2-MCPO and 3-MCPO (bis(2/3-methoxycarbonylphenyl) oxalate), were studied at pH values 6.0, 7.0, and 8.0, by variation of the hydrogen peroxide and phosphate buffer concentrations. The aqueous environment provides a large local polarity and multiple hydrogen bond possibilities, which influences the reactivity of the oxalate ester. Therefore, the reaction occurs much faster, but with emission intensities similar to that observed in anhydrous aprotic solvents. The observed rate constants (k_{obs}) show linear correlations with the hydrogen peroxide concentrations, indicating a bimolecular rate-limiting step with the participation of the peroxide and the oxalic ester concentration. Additionally, k_{obs} values show to be independent of the phosphate buffer concentration, indicating the occurrence of specific acid or base catalysis. Furthermore, the reaction constants increase with increasing pH values, pointing out that specific base catalysis is more efficient in these conditions. From the linear correlation of k_{obs} with the $[H_2O_2]$ the hydrolysis and perhydrolysis rate constants, k_{hyd} and k_{per} can be obtained ($k_{obs} = k_{hyd} + k_{per}[H_2O_2]$). Interestingly, esters with poor phenolic leaving groups (2/3-MCPO) shows higher perhydrolysis rate constant than TCPO possessing a much better leaving group, as attested by the pK_a values of the corresponding phenols (pK_a values for phenolic leaving groups: 2,4,6-trichlorophenol: 6.1; 2-methoxycarbonylphenol: 9.53; 3-

methoxycarbonylphenol: 9.05). The aqueous peroxyoxalate system is less efficient than in organic solvent, but with similar emission intensities. The reaction appears to involve fast proton transfer by water and the limit step contains one oxalic ester and one H_2O_2 molecule.

Keywords: chemiluminescence, peroxyoxalate, reaction mechanism, specific acid and basic catalysis

Red Tide Algae Use a GPCR Mechanism to Modulate Bioluminescence

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Dinoflagellates are single-celled algae that form red tides and act as coral symbionts. Many species of dinoflagellates are bioluminescent, using a tightly regulated mechanism to produce flashes of light in response to copepod predation. However, the mechanisms for regulating the process are not completely understood. Transcriptome mining for *Lingulodinium polyedra* revealed candidates for multiple GPCRs and downstream effectors, including previously undescribed Gγ and IPTR candidates integral to canonical GPCR-led calcium signaling pathways. By targeting receptor candidates using transient knockdowns and CRISPR:Cas9 knockouts, we identified a GPCR candidate which induces bioluminescence—Bioluminescence-Inducing Receptor 1 (BIR1). Initial measurements using PRESTO-Tango and TRUPATH assays show taurine-conjugated lipids from copepods modulate BIR1 signaling. BIR1 may be targeted by drugs to reduce bioluminescence and promote predator-based red tide management. The stable BIR1-knockout cultures being developed in this project can also be used as the basis for an inexpensive GPCR screening platform: stimulation of introduced GPCRs of interest modified to interact with the endogenous G Protein associated with bioluminescence.

Keywords: Red Tide, Cell Signaling, G Protein-Coupled Receptors, Evolutionary Biology

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Triplet acetone generation by peroxidase-like activity of myoglobin: a comparative study with HRP

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In the early 1970s, Giuseppe Cilento (IQUSP), Emil White (Johns Hopkins University), and Angelo Lamola (AT&T Bell Laboratories) postulated that typically photochemical reactions could occur *in vivo* in the absence of light. This paradoxical hypothesis named "photochemistry in the dark" was chemically anchored by the synthesis and study of 1,2-dioxetanes and 1,2-dioxetanones, whose thermolysis generates excited carbonyl species in the triplet excited state, which has relatively long lifetimes and emit ultra-weak chemiluminescence. The oxidation of isobutanal (IBAL) catalyzed by horseradish peroxidase (HRP) is a model study of an enzymatic reaction that generates triplet acetone via a high-energy intermediate derived from a hypothetical 1,2-dioxetane. The generation of triplet carbonyls through dioxetane intermediates by ferrylmyoglobin (ferrylMb) has been reported for acetoacetate and methylacetoacetate substrates, yielding, respectively, methylglyoxal and biacetyl in the triplet excited state. Here, we aim to investigate the role of ferrylMb as a peroxidase, generating triplet species, through a comparative study with the already known activity of HRP. The HRP/H_2O_2/IBAL and Mb/H_2O_2/IBAL systems were characterized through chemiluminescence studies by varying the concentration of components and pH. Oxygen consumption experiments were conducted to associate the proposed O_2-dependent mechanism with the observed chemiluminescence. The HRP system reveals a zero-order kinetics on O_2 and a kinetic constant dependent on IBAL concentration similarly to the ultra-weak light emission. The Mb reaction shows roughly a first-order kinetics on O_2, as already reported for other peroxidase/substrate systems. Both systems were challenged with sorbic acid, a well-known triplet species quencher, and L-Tyr, which can act as a quencher. Applying the classic Stern-Volmer treatment, the kinetic quenching constants found for sorbic acid from HRP and Mb systems were, respectively, 8.02 x 10^8 $M^{-1}s^{-1}$ and 1.56 x 10^9 $M^{-1}s^{-1}$, considering τ = 1.2 μs for triplet acetone lifetime in aqueous solution. Both data are consistent with a collisional quenching process (diffusional coefficient in water ~ 5 x 10^9 $M^{-1}s^{-1}$). The two times difference between the values can be attributed to structural differences

between the two proteins, such as water-exposure active sites. Importantly, a quadratic function was observed for the L-Tyr Stern-Volmer plots, a typical behavior of concomitant dynamic and static processes. Thus, the quenching mechanism may be granted to the formation of L-Tyr-IBAL complex into the active site of enzyme, not observed for sorbic acid. Altogether, these data suggest that myoglobin seems to behave as a peroxidase on IBAL oxidation similarly to HRP, which can be harnessed to elucidate potential involvement of myoglobin and excited triplet species in carbonyl stress-related biological processes.

Keywords: Photochemistry in the dark, Triplet acetone, Myoglobin, HRP, Chemiluminescence, Quenching.

Using the natural fluorescence dye curcumin as a sustainable activator in peroxyoxalate chemiluminescence

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Curcumin (CurcH) is a natural fluorescent dye, found in the rhizomes of turmeric, that has a bright yellow color, and the compound has attracted attention in recent years for exhibiting antibacterial, anti-inflammatory, hypoglycemic and antioxidant properties. Its photochemical properties and the fact that it is biocompatible give rise to a wide range of potential analytical applications, such as in fluorescence microscopy, the detection of hydrogen peroxide production sites in cells through chemiluminescence or its utilization as an activator (ACT) for the peroxyoxalate system. However, its low solubility in water reduces considerably its applicability in biological medium. The simplest way to use curcumin in analysis, is to dissolve it in organic solvents such as 1,2-dimethoxyethane (DME), ethyl acetate (EtOAc) or acetone (AC), except that the biocompatibility of the system is reduced due to the cytotoxicity of these solvents. To mitigate this problem, the use of binary water / organic solvents mixtures is an applicable and more sustainable approach, maintaining the curcumin soluble and lowering the toxicity of the system. The binary system also increases the efficiency of the peroxyoxalate system since faster reactions and lower emission intensities are observed for this reaction in aqueous medium. In this communication, we report our initial experimental results of a kinetic study of the peroxyoxalate reaction using bis(2,4,6-drichlorophenyl) oxalate (TCPO) as oxalic ester and curcumin as well as 9,10-diphenylanthracene (DPA) for comparison, as activators in different binary mixtures of water and DME as reaction medium. The kinetic studies give rise to observed rate-constants (kobs) in different experimental conditions, thereby characterizing the slow reaction steps and the molecularity of each reactant. The chemiluminescence emission (FCL) and singlet excitation (FS) quantum yields were determined from the integrated emission intensity *versus* time curves, using luminol standard. The singlet excitation quantum yields at infinite ACT concentrations (FS¥) was determined from the ACT concentration dependence, using a double-reciprocal plot. The reaction kinetics are not altered by the nature and concentration of the ACT and the FS¥ are higher for curcumin as compared to DPA in

anhydrous organic medium, although the FCL are higher for DPA due to its higher fluorescence quantum yield. These results clearly demonstrate that the natural product curcumin can be utilized as ACT in the peroxyoxalate reaction in partially aqueous media, thereby contributing to more sustainable assay conditions. Currently, the toxic oxalic ester TCPO is being substituted by less toxic oxalate derivatives containing as phenolic components vanillin and other natural phenols.

Keywords: curcumin, binary mixture, peroxyoxalate, natural dye, singlet excitation quantum yield

NEW BIOLUMINESCENT SYSTEMS

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Transcriptional and proteomic comparison of non-luminescent and bioluminescent Keroplatinae larvae (Diptera: Keroplatidae) reveals the presence flavin-dependent reductase associated with keroplatin and black bodies

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Bioluminescence in Keroplatinae larvae is observed in *Keroplatus*, *Neoceroplatus*, and *Orfelia*. The bioluminescence involves a multimeric luciferase, a luciferin called keroplatin, and a Substrate Binding Fraction (SBF), whose molecular identity and function still remains uncertain. Interestingly, non-luminescent web-constructing predatory larvae of *Neoditomyia* sp. (Keroplatinae) also contain keroplatin in their bodies, suggesting additional unknown roles for this compound in non-bioluminescent species. In order to gain better understanding of the biochemical requirements of the bioluminescent system in the Keroplatinae subfamily, we compared the transcriptional and proteomic profiles of *Neoditomyia* sp. with *Orfelia fultoni* and *Arachnocampa luminosa* larvae, and also performed biochemical assays. The transcriptional profiles of the non-luminescent *Neoditomyia* sp. and the bioluminescent *O. fultoni* larvae are quite similar, with an abundance of gene products related to web synthesis that is consistent with the similar ecology of these predators and web-constructing larvae inhabiting humid habitats. *Neoditomyia* larvae transcriptomes also exhibit an abundance of gene products associated with the pteridin derivatives pathways, Co-A-ligases, and hexamerins, which were previously associated with bioluminescence in this subfamily. Noteworthy, the SBF enriched fraction of both *Orfelia* and *Neoditomyia* sp. displayed a high content of riboflavin, and NADH-dependent reductase activity involved in reducing keroplatin (luciferin), results which are corroborated by the presence of flavin-reductases in the transcriptional and proteomic analysis. These results indicate that the enigmatic SBF, which is the main component of the black bodies, consists of protein complexes composed of hexamerins, flavin-reductases associated with keroplatin and riboflavin, in which one of the possible biological functions is to keep luciferin

and other compounds in the reduced form in bioluminescent species, as well as for other biological purposes in non-luminescent species.

Keywords: bioluminescence, hexamerin, keroplatin, reductase

Bioluminescent mechanism of *Anthoptilum murrayi* Kölliker, 1880 (Anthozoa: Octocorallia: Anthoptilidae)

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In the marine environment, most organisms living below the euphotic zone can produce light by bioluminescence[1][2]. Several of these light-emitting systems have been extensively studied, with their components isolated and even cloned. Additionally, bioluminescence systems have led to the development of various new biotechnological tools, ranging from molecular markers for metabolic studies in medicine to toxicity biosensors and indicators of water contamination, essential for environmental monitoring. However, there are still several other poorly studied bioluminescent systems in terms of their light emission, as is the case of many species of deep-water bioluminescent corals, especially *Anthoptilum murrayi*, a cosmopolitan coral of the Pennatulacea order. Popularly known as "sea pen", this coral can be found on the upper slope of the southeastern coast of Brazil, at depths of about 1,000 meters, and emits green light (Lmax 515 nm) in response to mechanical stimuli[3][4]. *A. murrayi's* mechanism of light emission has never been described; however, preliminary results obtained by our group suggest a mechanism similar to that of the shallow-water coral *Renilla reniformis*. Specimens of *A. murrayi*, collected during the DEEP-OCEAN expedition, were initially utilized in cell-free extract assays to establish the necessary conditions for in vitro light emission. When these extracts were combined with coelenterazine, they produced light. Additionally, transcriptomic analyses of the soft tissues from *A. murrayi* enabled the identification and isolation of candidate proteins involved in the organism's luminescence. Our findings demonstrated that recombinant candidate luciferases from *A. murrayi*, expressed in *E. coli* and yeast under various conditions and purification methods, produced active luciferase capable of generating strong blue luminescence with coelenterazine.References [1] O. Shimomura, Bioluminescence – Chemical Principles and Methods. *World Scientific Publishing Co.* Pte. Lt. Singapura. (2006)

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Keywords: Deep-sea coral; Anthoptilum murrayi; luciferase; coelenterazine.

NOVEL CAPABILITIES IN LUMINESCENCE RESEARCH (PHOTODETECTION, SPECTROSCOPY, IMAGING, ANALYSIS)

Eu^{3+} Complexes in Castor Oil-Based Films: A Pathway to Enhanced Solar Energy Harnessing

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Considering the growing need for alternative energy sources or even the improvement of those already developed researchers today have invested in the search for alternative materials that contribute to generating energy in a more efficient and economically viable way. Among the countless potential solutions, solar energy stands out, but it requires strategies to overcome the limitations of the solar cells in use in relation to the low conversion of certain regions of the electromagnetic spectrum, such as ultraviolet and infrared. To face this challenge, the most viable alternative is the combination of solar cells with systems capable of absorbing radiation from these segments, increasing their effectiveness and performance. In this context, coordination compounds containing Eu^{3+} ions are efficient converters of UV radiation into energy suitable for the absorption region of solar cells. However, their fragility from a structural point of view requires them to be embedded in a material that increases their photostability, thus giving rise to the so-called luminescent solar concentrators. In this case, an alternative material to support such luminescent complexes and contribute to the production of efficient solar concentrators is the castor oil as a precursor to the films, a natural compound that is easy to obtain, cheap, and non-toxic for the environment. In this study, different mass percentages, in the range from 0.25% to 3.00% of the synthesized complex $[Eu(tta)_3(PIB)]$ were embedded in castor oil derivative (SiCO) to produce luminescent films by drop casting and their stability against the incidence of radiation were investigated. FTIR, mass spectrometry, elemental analysis and UV-vis spectroscopy data indicated the successful preparation of the Eu^{3+} complex, confirming the stoichiometry. Through photoluminescence spectroscopy, it was

observed that the increase in complex concentration leads to a gradual modification of the band profile assigned to the $^5D_0 \rightarrow {}^7F_2$ transition (hypersensitive transition), which may be related to a smaller spacing between complex units in the film. In concentrations above 1.50%, the $^5D_0 \rightarrow {}^7F_2$ behavior in the films is similar to that of the powder complex, suggesting that above this concentration the bulk complex behavior prevails. Data regarding the degree of asymmetry of the systems (R_{21}) also suggest greater similarity with the powder structure. Finally, the luminescent films exhibited stabilities close to 50% after 7 hours of direct exposure to radiation from a solar simulator, values slightly below those observed for the same system, produced with the PMMA as matrix. Thus, it can be suggested that the SiCO-based system can be used with the [Eu(tta)$_3$(PIB)] complex, although it produces less stable systems than those produced with PMMA.

Keywords: Polymer, Coordination Compound, Luminescence

Exploring the properties of Luminescent Materials using fourth-generation Synchrotron Light at Sirius

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Sirius is the 4th generation synchrotron accelerator hosted by the Brazilian Synchrotron Light Laboratory from the Brazilian Center for Research in Energy and Materials (CNPEM). With capability of housing 39 beamlines, the broad energy range, from the mid-infrared up the X-rays, and its light properties such high flux and coherence have allowed cutting edge studies using this facility. Among the Sirius' experimental stations, the Coherent X-ray Nanoprobe Beamline (Carnaúba) is an X-ray nanoscopy with capabilities of 2D, 3D, hyper, and multispectral studies through different contrasts such as luminescence, X-ray fluorescence (XRF), X-ray absorption (XAS), X-ray diffraction, and coherent imaging. The Carnaúba beamline is built with all-achromatic optical elements, with beamsize limited by diffraction at the Sapoti station and it covers the energy range from 2.05 up to 15 keV [1]. Beyond the Sapoti station, which has been assembled, the Tarumã one is already available for users and operates with a variable sample environment and submicrometric beamsize, achieving resolutions of about 12 nm using ptychography. Studies carried out in luminescent materials have shown that X-ray excited optical luminescence (XEOL) is a powerful tool to explore luminescence mechanism in inorganic scintillators, identifying optical channels in natural and heterogeneous materials, and following radiation damage through the optical response. Currently, the XEOL system is available to perform energy scan studies and 2D imaging [2]. Studies based on emission and excitation can be combined, bringing important information about the dynamic of charge carries upon the ionization. Furthermore, imaging studies have been carried out by raster scanning the sample in large areas, up to mm, with intensity mapping, and in smaller areas, in micrometric scale, providing hyperspectral information. Both these studies can be combined with other ones such as XAS, XRF and Scanning Transmission X-ray Microscopy (STXM) mapping providing a full description about the origin of luminescence under X-rays irradiation. Ongoing developments highlight the use of XEOL as analytical tool combining

microreactors based on microfluidics [3], and the installation of a new spectrometer covering the optical range from 200 – 1700 nm, which will open new opportunities to study luminescent materials using the Sirius 4th generation synchrotron source. **References**[1] Tolentino, Hélio CN, et al. "The CARNAÚBA X-ray nanospectroscopy beamline at the Sirius-LNLS synchrotron light source: Developments, commissioning, and first science at the TARUMÃ station." *Journal of Electron Spectroscopy and Related Phenomena* 266 (2023): 147340.[2] Teixeira, Verônica C., et al. "X-ray excited optical luminescence at Carnaúba, the Sirius X-ray nanoprobe beamline." *Optical Materials: X* 20 (2023): 100278.[3] Neckel, Itamar T., et al. "Development of a sticker sealed microfluidic device for in situ analytical measurements using synchrotron radiation." *Scientific Reports* 11.1 (2021): 23671.

Keywords: Synchrotron Light, Sirius, Carnaúba beamline, X-ray Excited Optical Luminescence (XEOL)

Laser induced white emission - phenomenon and applications

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The interaction of focused beam of infrared laser diode with inorganic crystals, glasses, nanomaterials leads to generation of efficient broadband white emission in visible. This emission is surface related and characterized by relatively low temperature. The effect in its nature occurs due to multiphoton absorption responsible for ionization processes and in consequence to the broad band emission in visible assisted by ejection of hot electrons, photocurrent and nonradiative transitions. Laser induced white emission is characterized by the excitation threshold exponential increase of efficiency with excitation laser power and saturation plateau. The forward and backward measurements of laser induced emission have demonstrated the hysteresis behavior. Moreover it was observed that this emission is characterized by coherency opening applications for white lasers. The different examples of broadband white emission in nanocrystals, ceramics, glasses and crystals are presented. Applications of laser induced white emission for lighting, photocatalysis and generation of hydrogen are presented.

Keywords: white luminescence, broadband emission, perovskites, hot electrons

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Absolute light measurement for the investigation of bioluminescence quantum yield and standardization of bioanalysis instruments

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Fluorescence and bio/chemiluminescence are widely utilized in analytical methods within biotechnology and medical fields. Generally, luminescence signals from samples are measured as relative values. However, acquiring absolute luminescence signal values, along with spectral data, provide crucial insights into the comprehensive insights into the characteristics of light emission from luminescent materials and substances. Due to the diffuse nature of light emission from samples, the "integrating sphere spectrometer" technique proves to be suitable for measuring absolute light values, expressed in units of energy (W) or number of photons. Calibration of the instrument's absolute sensitivity can be achieved using a standard lamp with traceability to national standards. Presented here are examples of absolute luminescence measurements. Firstly, quantum yield values of bioluminescence reactions were investigated using various luciferases from distinct species of firefly and glow worm. Moreover, absolute light measurement techniques contribute to establishing reference light sources for bioanalysis applications. By utilizing a stabilized LED as a reference light source, bioimaging data were collected in absolute value, resulting in more precise data comparison. The utilization of optical reference, including a reference light source, can significantly enhance reliability of bioanalysis applications, even if not absolutely calibrated but reproducible. Hence, the incorporation of optical references is recommended for bioanalysis applications within the framework of international standardization (ISO).

Keywords: quantum yield 1, absolute measurement 2, standardization 3, luminescence measurement 4

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Employing luminescence spectroscopy of Eu(III) in the investigation of catalyzed cyanosilylation reactions

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The development of green synthetic methods for organic compounds, especially with biological activity, is relevant to academia and industry. Mechanochemistry is considered by IUPAC as one of the Top 10 emerging technologies for green synthesis of organic and inorganic compounds and materials. Heterogeneous catalysis has also a strong appeal in the green synthesis of organic compounds. Thus, our research group has interest in combining mechanochemistry and catalysis with lanthanide-based compounds. Due to its peculiar and unique luminescent properties, Eu(III) was chosen to probe the structural reorganization of the Lewis-acid catalyst during organic reactions. In this context, cyanohydrins are important intermediates for the synthesis of beta-amino-alcohols, alpha-hydroxy-acids, and alpha-hydroxy-ketones, which present biological activities and are building blocks for drugs and agrochemicals. So, cyanosilylation reactions catalyzed by resistant Lewis-acid based on trivalent lanthanide ions were investigated. Eu(III)-based MOFs, namely frameworks of Eu(III)-fumarate and Eu(III)-mandelate, presented the best catalytic activities for cyanosilylation reactions involving ketones, which are much less explored than aldehydes due to their lower reactivity. The Eu(III)-mandelate catalyst showed better performance regarding recycling, because even after eight cycles, the catalyst kept its activity. The luminescent properties of the Eu(III)-mandelate catalyst were investigated before and after the eight recycling processes. Both excitation and emission spectra showed significant differences before and after the catalysis. After the Eu(III)-mandelate acting as catalyst, the excitation spectrum changed from a well-structured 4f-4f transitions with intense $^7F_0 \rightarrow {}^7L_6$ excitation to a broader (intense band from 300 to 390 nm) and less resolved spectrum, indicating amorphization of the structure. The emission spectra presented the typical 4f-4f $^5D_0 \rightarrow {}^7F_J$ (J = 1, 2, 3 e 4) transitions of Eu(III). However, after the catalysis, emission spectrum changed significantly, for instance,

all bands became broader and that associated with the $^5D_0 \rightarrow {}^7F_0$ transition became very intense. These combined results indicate that the Eu(III)-mandelate catalyst interacted strongly with the reagents and products causing significant structural changes. Most likely, the environment around the Eu(III) sites becomes less symmetric by coordination to different species and modifications of the surfaces. This shows the feasibility of using the Eu(III) luminescent properties as a structural probe of catalysts. So, further investigation should establish the number of cycles required to loss of catalytic activity as well as the gradual changes in the catalyst structure during each cycle. These investigations should provide some insights into the reaction mechanism and the action of the catalyst. They could also aid in designing lanthanide-based catalysts with enhanced performance for mechanochemistry.

Keywords: Eu(III)-spectroscopy, lanthanide catalyst, cyanosilylation, mechanochemistry

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High-pressure luminescence studies of Fe^{3+} in $LiGaO_2$ crystalline powders

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Fe^{3+} ions in solids exhibit luminescence in the spectral regions between red and near-infrared, depending on the local environment symmetry and distances between central ions and ligands. For a very long time, Fe-dopant was rather considered as being a luminescence quencher, however relatively recently it has been shown that it may be a very efficient luminescence activator. It is most probably related to pure doping with Fe in a 3+ valence state since Fe^{2+} ions act as the emission quenchers. The basic optical properties of this dopant are well described by the crystal field theory for d^5 electronic configuration. According to this theory, all optical transitions at ambient conditions occur between the $^6A_1$ ground state and higher energy excited states with a different spin, thus being strongly spin-forbidden, having very small transition probability and long decay times of luminescence. Usually, the optical transitions, especially between the ground and the first excited level are also strongly coupled with the lattice, thus both absorption and luminescence spectra are broad, often without 0-phonon lines, even at very low temperatures. An externally applied pressure may strongly influence the spectral position of luminescence as well as the luminescence decay kinetics of the ions with a d^5 electronic structure. In this report, we present the optical properties of $LiGaO_2$ doped with Fe^{3+}. The 0.25% iron (Fe^{3+}) doped $LiGaO_2$ phosphor, synthesized by a high-temperature solid-state reaction method, turned out to be a β polymorph of the $LiGaO_2$ with an orthorhombic crystallographic structure. The phosphor exhibits a photoluminescence band around 746 nm related to the $^4T_1 \rightarrow {}^6A_1$ transition with a 28% quantum efficiency at ambient conditions. The luminescence of this material shifts towards longer wavelengths with pressure increase, which agrees very well with the Tanabe-Sugano crystal field theory. Evidence of pressure-induced phase transitions

are observed in the luminescence spectra of $LiGaO_2$:Fe. At higher pressures, the luminescence is quenched due to reversible amorphization of the powder.Additional luminescence 0-ph line is observed at 695 nm wavelength, which is suspected to be related to Fe^{3+} ions in Li sites. To confirm this hypothesis several additional experiments were performed, including electron paramagnetic resonance and a ^{57}Fe Mossbauer spectroscopy study. The results of these experiments will be discussed.

Keywords: Diamond Anvil Cell, Transition metal dopants, Near Infrared luminescence

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Light conversion by electrochemiluminescence at semiconductor surfaces

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Electrochemiluminescence (ECL) is the electrochemical generation of light. It involves an interfacial charge transfer that produces the excited state of a luminophore at an electrode . ECL is a powerful technique that is widely employed for immunoassays and clinical diagnosis. On the other hand, photoelectrochemistry at illuminated semiconductors is a field of research that deals with the charge transfer of photogenerated charge carriers at an electrode surface. The combination of ECL with photoelectrochemistry at illuminated semiconductors is referred to as photoinduced ECL (PECL) and is a growing field of research.[1] PECL results in the conversion of incident photons , that are absorbed by the semiconductor photoelectrode to emitted ECL photons, produced by the ECL reaction. Although demonstrated in the seventies, PECL remained unexplored until the last five years, as a result of the considerable progress achieved in semiconductor photoelectrodes and ECL systems.[1] Nowadays, a large variety of PECL systems can be designed by combining photoelectrode materials with ECL luminophores, making it a versatile tool for light conversion.[2] In this talk, we will present the recent developments in PECL and we will show that, by engineering the photoelectrode material and carefully considering the reactivity involved for ECL , PECL enables the ultimate concept of all-optical ECL (AO-ECL), i.e., ECL generation at an illuminated monolithic device immersed into the electrolyte solution.[3] Due to the robustness of recently manufactured PECL systems, several applications can already be envisioned for microscopy, elucidation of mechanisms solar conversion mechanisms, bioanalysis, and near-infrared imaging.[4]

References:1. *Chem Sci* 2022, 13, 2528–2550. 2. **a**) *J Am Chem Soc* 2019, 141 (33), 13013–13016. **b**) *Angew Chem Int Ed* 2020, 59 (35), 15157–15160. **c**) *Angew Chem Int Ed* 2022, 61 (20), e2022018.3. **a**) *J Am Chem Soc* 2023, 145 (31), 17420–17426. **b**) *J Phys Chem Lett* 2024, 15 (1), 148–155. **c**) *Small* 2024, *in press*, 2308023.4. **a**) *Chem Commun* 2023, 59 (82), 12262–12265. **b**) *Chem. Sci.* 2024**,** 15, 2055-2061

Keywords: Electrochemiluminescence, Semiconductors, Silicon

New persistent luminescent glass composites: viscous sintering synthesis and X-ray nanoscopy characterization

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Translucent persistent luminescent glass matrix composites (PeL-GMCs) were successfully prepared using viscous sintering. The synthesis consisted by mixing commercial persistent luminescent microparticles (PeL-MPs) of $SrAl_2O4:Eu^{2+},Dy^{3+}$, $CaAl_2O_4:Eu^{2+},Nd^{3+}$, or $SrMgSi_2O_7:Eu^{2+},Dy^{3+}$ with soda-lime-silicate glass beads, followed by heat treatment in air or vacuum atmospheres at temperatures ranging between the glass transition and the liquidus temperature (in the higher-viscosity range).Thermoluminescence analysis and persistent luminescence decay times confirmed that the energy storage properties of the PeL-GMCs are similar to the Pel-Mps. Microstructural characterizations using optical and electron microscopy, revealed the pore distribution and particle morphology within the glass matrix composites (GMCs). Additionally, X-ray dispersion spectroscopy (EDX) showed the distribution of chemical elements within a polished cross-section of the GMCs, indicating no observed phase formation at the interface between PeL-MPs and the glass matrix. Despite the presence of porosity in the final materials, the PeL-GMCs exhibited translucency and prolonged persistent luminescence, demonstrating excellent compatibility between the PeL-MPs and the glass host.

Keywords: persistent luminescence, energy storage, glasses, Nanoscopy

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Optical and Electrical Insights into Eu3+ doped films as Luminescent Solar Concentrators

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Given the growing global demand for energy, researchers have explored new ways to develop more efficient and cost-effective energy generation systems. Solar energy stands out as one of the most promising sources, having been widely explored over the decades. However, a major challenge in generating electricity from solar radiation is the low conversion rate of certain parts of the electromagnetic spectrum, such as ultraviolet and infrared regions. To overcome this, an alternative is the incorporation of compounds that convert UV and IR into radiation within the absorption range of solar cells, that is, the so-called solar concentrators. In this context, systems containing Eu3+ complexes meet these requirements, by converting UV into visible radiation, and are then applicable as luminescent solar concentrators.Therefore, in this study, Eu3+ complexes, more specifically [Eu(tta)3(phen derivative)], were incorporated into PMMA or PVP polymeric substrates to produce solar concentrators. The 1,10-phenanthroline derivatives (PIB, PIB_4CH3, PIB_4F, PIN_2OH e AIP) were strategically synthesized to contain an extended aromatic chain, facilitating greater absorption of electromagnetic radiation.The complexes were characterized via FTIR, where stretches between 400 cm-1 and 600 cm-1, attributed to the Eu-O and Eu-N bonds, were observed. Mass spectrometry and elemental analysis also suggest the formation of the complexes, and the optical profiles were fully investigated via photoluminescence spectroscopy (PLS). In addition, the luminescent polymeric films were also studied via PLS and evaluated for photostability against incident radiation using a solar simulator as an exposure source.The results showed that the films maintained up to 50% of photostability after 7 hours of continuous light exposure, with particular emphasis on the [Eu(tta)3(PIB)] complex, which achieved retention rates exceeding 60%. Notably, the [Eu(tta)3(PIB)] complex embedded in PMMA and PVP demonstrated optical efficiency (□opt) of 0.52% and Power Conversion Efficiency (PCE) of 3.6.10-4 %, surpassing previous findings

in the literature. These results demonstrate the potential application of these complexes in scenarios that involve their use as luminescent solar concentrators.

Keywords: Solar Radiation Conversion, Power Conversion Efficiency, Optical Efficiency, Photoluminescence Spectroscopy

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Pseudoluciferase activity of the SARS-CoV-2 spike protein for *Cypridina* luciferin

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The SARS-CoV-2 virus infects human cells using a spike (S) protein, an antigen that decorates the surface of the virus particles. In this study, we have revealed a novel aspect of the SARS-CoV-2 S protein's bioluminescent enzyme (luciferase)-like ability to catalyze the oxidative luminescent reaction of *Cypridina* luciferin, which is a substrate of the marine luminous sea firefly (*Vargula hilgendorfii*). Moreover, we have successfully demonstrated that the pseudo-luciferase activity of the S protein itself offers a new method to detect the SARS-CoV2 S protein. From fireflies to lantern fish, most of the animals produce light emission through an enzymatic reaction between the substrate (luciferin) and the enzyme (luciferase). Although a luciferin typically emits light only in the presence of the corresponding luciferase, imidazopyrazinone-type (IPT) luciferins, which are widely present in luminous marine organisms, can emit light when encountering other proteins including serum albumins that aren't considered enzymes. Then, we first investigated 36 different IPT luciferins' abilities to react with a single unit of the SARS-CoV-2 S protein. As a result, only *Cypridina* luciferin emitted light. An adequate amount of light could also be detected with the spike protein in its natural state, as three units folded together. Additional experiments indicated that the *Cypridina* luciferin was selective because it was recognized from only the interfaces between the units of the S protein and did not glow when exposed to six proteins that occur in human saliva. We defined this specific luminescence reaction by non-luciferase biomolecules as "biomolecule-catalyzing chemiluminescence (BCL)". Finally, we found that the luciferin could detect the amount of the S protein in human saliva with the same accuracy as an ELISA (Enzyme-linked Immunosorbent Assay). The BCL-based assay system delivered results in one minute — significantly faster than the current rapid point-of-care tests. Our developed approach could serve as the basis for a simple "mix and read" test in which *Cypridina* luciferin is added to untreated saliva from someone suspected of having COVID-19. This finding opens the door to develop a novel platform to detect virus antigens simply and rapidly without antibodies and

genetic manipulation. Furthermore, we have succeeded in identifying the functional group in *Cypridina* luciferin that selectively recognizes enzymes or enables efficient luminescence reactions in S-protein-catalyzed luminescence systems. The function of each functional group in *Cypridina* luciferin has not been clarified in the natural *Cypridina* luciferase system. Therefore, this finding represents a significant contribution to the elucidation of the unknown reaction mechanism in bioluminescence (BL) and to the extension of BL applications in molecular biology and diagnostic measurement studies.

Keywords: Luciferin, Luciferase, Cypridina luciferin, SARS-CoV-2, Spike protein, Assays

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Upconversion 3D printing production of multi-colour, rigid/flexible, and dielectric/metallic plated samples

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Photopolymer 3D printing methods face a constraint: the need for sequential layer deposition, preventing multi-material fabrication. Our study introduces a novel approach enabling multi-material stereolithography [1], transcending this layer-by-layer limitation. This advancement hinges on selectively crosslinking voxels within the stereolithography (SLA) resin vat at any depth and position. The technique uses the invisibility windows and upconversion for targeted volumetric crosslinking. A developed photopolymer resin incorporates a visible light photoinitiator (fluorinated diphenyl titanocene) with broad absorption, fine-matched with an optical absorber (naphthalimide class dye, peak absorption at 445 nm) and upconversion emissions from lanthanide-doped. To harness not only UV but also the more pronounced blue light (425-500 nm) emitted by Tm3+-doped phosphor, we incorporated a visible light initiator that boasts broad absorption up to 500 nm, while providing high initiating activity, storage stability, and low toxicity. Consequently, this allowed for the use of a lower concentration (5 mg mL-1) of UC phosphor compared to previous studies, leveraging the 425-500 nm emissions effectively for photopolymer cross-linking.Employing NIR light for upconversion phosphor excitation facilitates remarkable penetration depths of up to 5.8 cm. This has enabled for the first time the application of UC as a cost-efficient pathway for multi-colour and multi-material in-volume stereolithography. To enhance resolution and mitigate over-curing effects, we introduced a naphthalimide class dye, tailored for dissolution in acrylic resins. A minor adaptation of a desktop FDM printer [2] and a 980 nm laser diode enabled in-volume 3D printing of photopolymer containing Tm3+-doped UC phosphor at a power density of 14 W cm−2, significantly lower than the used by femtosecond lasers for TPP. Moreover, a modified resin enabling copper plating was utilized to print a track within a cavity of a different material, resulting in a conductive path with low sheet resistance[3]. Demonstrations include volumetric SLA printing of intertwined multi-colour samples, versatile rigid/flexible (acrylate/elastomer) samples, and dielectric/metallic plated samples.This breakthrough unlocks diverse avenues in stereolithography, enabling the creation of samples with varied materials, 3D printing within

cavities using different materials, crafting 3D circuitry, repairing broken objects, and more.[1] Adilet Zhakeyev, Mansour Abdulrhman, et al, “Upconversion 3D printing enables single-immersion multi-material stereolithography”, Applied Materials Today, 32, 2023, 101854.[2] Adilet Zhakeyev, Rohith Devanathan, Jose Marques-Hueso, “Modification of a desktop FFF printer via NIR laser addition for upconversion 3D printing”, HardwareX, 18, 2024, e00520[3] Adilet Zhakeyev, Fenella Walker, et al, “Upconversion 3D printing enhancement via silver sensitization to enable selective metallization”, Optical Materials, 142, 2023, 114044

Keywords: Keywords: upconversion, multi-material stereolithography, 3D printing

OPTICAL SPECTROSCOPY OF INORGANIC PHOSPHORS

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Broadband anti-Stokes white emission of rare earth–manganese perovskites nanocrystals induced by laser irradiation

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Anti-Stokes laser-induced white emission (LIWE), characterised by broadband spectra in the visible region and a non-linear dependency of emission intensity on the excitation power, has been observed in several optically active materials, including YAG, organometallic compounds, or organic dye solutions. This process has been interpreted in terms of different models like multiphoton ionisation, and intervalence charge transfer, among others. The quantum efficiency of LIWE can reach 16% in inorganic phosphors, fostering interest in research about the mechanisms and for the development of more efficient materials, especially regarding solar energy conversion technologies in which perovskites yield the highest power conversion efficiency combined with commercialisation viability. In this work, rare-earth perovskites manganite ($REMnO_3$) were studied for its structural and photophysical properties. $REMnO_3$ formed a single-phase compound in an orthorhombic structure to (Nd, Eu)MnO_3 and hexagonal to (Y, Er, Yb)MO_3. The samples were synthesised by self-combustion method using a mixture of the $RE(NO_3)_3$, $Mn(NO_3)_3$, and urea (ratio 1:2.5), subjected to a furnace at 650 °C for 5 minutes followed by the calcination at 900 °C for 6hours. In XRD can be identified reflection planes to the orthorhombic $EuMnO_3$ phase (JCPDS Card No. 96-153-1804), and no raw material or impurities were determined. The absorbance analysis does not show the typical narrow peaks to 4f-transitions, possibly, due to the presence of the Mn^{2+} in the matrix. The spectra consist of two absorption bands centred around 337 nm. The origin of these bands could be associated with the overlap of the charge transfer between the trivalent lanthanide ion ($RE^{3+}\rightarrow O^{2-}$) and $Mn^{2+}\rightarrow O^{2-}$. LIWE was analysed under λ_{exc}=980 nm in function of power density (P_D), pressure and sample-compaction (power *x* pellet). In studied cases, a broadband emission from 400 nm to 650 nm and from 1175 to 2200 nm is observed. It was observed the blue shift to the emission of 13 nm, 22 nm and 29 nm to powder, pellet and pellet at low pressure, respectively. The supralinear dependence between the intensity of the emission and the excitation power() cannot describe the number of photons involved in the up-conversion

emission and indicate the P_D threshold to promote the LIWE (2168 W cm^{-2} to powder, 4508 W cm^{-2} pellet and 2947 W cm^{-2} pellet at low pressure). We discuss the influence of sample compaction, pressure, the mechanism that induces this anti-Stokes process, as well as the generation of current under photoexcitation.

Keywords: Up-conversion, Multiphoton-emission, Avalanche-process, Blackbody-radiation

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Cooperative Processes in Lanthanide Luminescence

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In the field of lanthanide luminescence initially the spectroscopic properties of individual lanthanides were explored and also applied, e.g. in lamp phosphors as $Y_2O_3:Eu^{3+}$ or x-ray phosphors as $Gd_2O_2S:Pr^{3+}$ where the performance relied on a single type of lanthanide ion. Presently it is recognized that cooperation between lanthanides enables new applications and is also interesting for fundamental studies to elucidate the nature and strength of interactions between lanthanides. In this presentation we focus on the role two types of interactions: (1) Cooperative effects and (2) Cross-relaxation in lanthanide-doped luminescent materials.Cooperative absorption, emission and energy transfer were pioneered in the 1970's with a prominent role for Yb^{3+}. After a historical and personal introduction to cooperative effects in lanthanide spectroscopy, the focus is on cooperative energy transfer from a single lanthanide to two or even three neighboring lanthanide ions. Evidence for cooperative energy transfer processes is challenging but can be obtained by modelling luminescence decay curves using the discrete shell model. In addition, correlated photon counting can serve as evidence for the presence (or not!) of cooperative energy transfer and quantum cutting.Cross-relaxation is partial energy transfer between neighboring lanthanide ions of the same or different type. It is often undesired as it can cause effective concentration quenching, e.g. in Pr^{3+}-doped phosphors. It can however also be beneficial and cross-relaxation is at the heart of photon avalanching which recently experiences a revival in photon avalanching nanocrystals. Here we use cross-relaxation between neighboring Ho^{3+} ions to probe ion diffusion in $NaYF_4$ core-shell nanocrystals and show that it serves as a sensitive method to probe the sharpness of core-shell interfaces. Analysis of luminescence decay curves for $NaYF_4$:12%Ho^{3+} core/$NaYF_4$ shell nanocrystals gives quantitative insight in diffusion of Ho^{3+} ions into the undoped shell upon heating. Finally, it will be demonstrated how temperature dependent competition between cross-relaxation and multi-phonon relaxation can be used in accurate temperature sensing.The presentation will provide insight in the important role of interactions between luminescent lanthanide ions in present and future applications and shows how the cooperative effects and

interactions between lanthanides can be quantified through different time-resolved spectroscopic experiments combined with theoretical modelling.

Keywords: lanthanides, cooperative, energy transfer, cross-relaxation, sensing, modelling

Down-shifting and Up-Conversion Luminescence in Erbium(III) Complexes via Metal and Ligand Centered Excitation

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Since some of the scarce molecular-based Er-centered emitters reported in the literature are based on $[ErN_3O_6]$ and $[ErN_9]$ coordination geometry, we explored the optical properties of two Er^{III} complexes, containing a hexaazamacrocyclic ligand with two- (**1**) or three-carbon (**2**) aliphatic lateral spacers, and three auxiliary isothiocyanate ligands. Luminescent properties were evaluated using ligand- and metal-centered excitation. Bluish-green and green emissions of the Er^{III} ion were detected upon ligand-centered excitation, demonstrating that these macrocycles act as antenna to sensitize the erbium(III) luminescence. Energy transfer mechanisms and temperature-dependent luminescence were analyzed. Besides the excitation in the ligands (Vis), the erbium-centered excitation at 980 nm (NIR) allowed the detection, in both cases, of bluish-green, green, and red up-converted emissions, and also the downshifted NIR emission. The possible mechanisms of these transitions are described and analyzed. Therefore, Vis-to-Vis (via ligand excitation), NIR-to-Vis and NIR-to-NIR emitters (upon 980 nm excitation) were achieved with these molecular systems.

Keywords: Luminescence, antenna, downshifting and up-conversion emission

Evaluation of the incommensurate to commensurate phase transition in $Ca_2MgSi_2O_7$ by Mn^{2+} luminescence spectroscopy.

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The host matrix, $Ca_2MgSi_2O_7$, belongs to the melilite group, being tetragonal and with space group P-42-$_1$m. Its standard structure presents three different sites: a tetrahedral Si^{4+} site, a tetrahedral Mg^{2+} site, and an octacoordinated Ca^{2+} site. However, there are studies on its incommensurately modulated structure, which is stable at temperatures lower than 85ºC. In these situations, Si^{4+} tetrahedra rotate at a non-commensurate periodicity, leading to distortions in the Mg^{2+} tetrahedra and the formation of non-equivalent Ca^{2+} sites with coordination numbers equal to 6 and 7. The dopant, Mn^{2+}, has an adequate ionic radius to substitute for the Ca^{2+} and Mg^{2+} sites. The activator presents spin-forbidden d-d transitions, with the $^4T_1 \rightarrow {}^6A_1$ transition being dominant when subjected to weak crystalline field strength. In addition, the energy of the $^4T_1$ level decreases as the crystalline field strength increases, leading to emission with longer wavelengths. The compounds were synthesized through a solid-state reaction with the precursors $CaCO_3$, MgO, $MnCO_3$, and SiO_2. The mixture was heated at 1350ºC for 8 hours. Mixing and heating twice under the same conditions improved the formation of the phase of interest, reducing the proportion of spurious phases. For materials doped with 2.5% at. Mn^{2+}, the emission spectra present two bands originating from the dopant, which are believed to be from the dopant replacing the site of square antiprismatic geometry of Ca^{2+} for the lower energy emission (~ 690 nm) and the tetrahedral site of Mg^{2+} for the higher energy (~590 nm). The broad emission at approximately 480 nm must be due to a defect in the matrix, being observed in the compound synthesized without dopant. Emission spectra obtained every 5ºC at varying temperatures from 30ºC to 100ºC showed that the ratio between the band at 480 nm and that at 590 nm grows linearly from 50ºC to 80ºC, from 80ºC up to 100ºC this ratio grows at an even

greater rate. The ratio was measured by the integrated area of these bands. These results show a new way of evaluating the transition from the incommensurable to the commensurable phase.

Keywords: Ca2MgSi2O7, Manganese (II), Photoluminescence, Incommensurate phase.

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$MgAl_2O_4:Eu^{3+}$(2 or 4 %) and $MgAl_2O_4:Eu^{3+}$(2 %)Li^+(2 %) red-emitters for PC-LEDs:Eu^{3+} as a spectroscopic probe in monitoring the influence of co-doping on the site occupation by the doping ion

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Nowadays, the intense use of screens has stimulated the search for devices that require lower energy consumption. LEDs are considered the cutting-edge technology in solid-state lighting, meeting this requirement. Among the production methods for white LEDs (WLEDs), the one currently commercially used is the hybrid LED type, although it suffers from low color rendering index (CRI) and high correlated color temperature (CCT) due to the lack of red-emitting component. This study reports the photoluminescence properties of Eu^{3+}-based $MgAl_2O_4$ co-doped or not with Li^+ at 2%, red-emitting phosphor, synthesized by an adapted Pechini route at 1000 °C, at air atmosphere. $MgAl_2O_4$ doped Eu^{3+} at 4% was used to study the Eu^{3+} occupation sites, in comparation to another samples, i.e., $MgAl_2O_4:Eu^{3+}$(2%) and $MgAl_2O_4:Eu^{3+}$(2%)Li^+(2%). The XRD data confirmed that all samples have the spinel-type $MgAl_2O_4$ structure and are therefore single-phase. XPS analysis for Eu^{3+}-doped sample indicated the absence of surface contamination. Excitation spectra of samples monitoring the $^5D_0 \rightarrow {}^7F_2$ transition at 612 nm displayed the $O^{2-} \rightarrow Eu^{3+}$ charge transfer band (CTB) as the most intense, while the narrow band assigned to $^7F_0 \rightarrow {}^5L_6$ at 393 nm exhibited the highest relative intensity among the *f-f* transitions. Emission spectra under CTB excitation at low temperature (12 K) revealed the splitting of the $^5D_0 \rightarrow {}^7F_0$ transition into two components, implying the insertion of Eu^{3+} in at least two non-equivalent low-symmetric sites lacking an inversion center for all samples. The two $^5D_0 \rightarrow {}^7F_0$ components observed in the $MgAl_2O_4:Eu^{3+}$(2 %) and $MgAl_2O_4:Eu^{3+}$(2 %)Li^+(2 %) emission spectra were located at 576 nm and 579 nm, being this last one more relatively intense. However, increasing Eu^{3+}concentration, i.e., sample $MgAl_2O_4:Eu^{3+}$(4%), an increase of the one at 576 nm was observed. When the excitation was fixed at 298 nm, the difference between these two components of the $^5D_0 \rightarrow {}^7F_0$ transition

became more evident and indicated the preference for occupation of this site with higher Eu^{3+} concentration. Finally, these samples were embedded in PMMA polymeric matrix, to produce luminescent films, aiming for their application in PC-LEDs with UV excitation. Although the absolute quantum yield of the films did not exhibit a significant increase with Li^{+} co-doping, staying around 16 % when the excitation was fixed in 260 nm, the 1931 Chromaticity Diagram (CIE) of all of them revealed color purity greater than 90% in the red spectral region. In this way, these results guarantee that the red-emitting phosphors were successfully synthesized, making it possible to use the Eu^{3+} probe properties to evaluate its occupancy sites. Furthermore, by incorporating the powders into a PMMA polymer matrix, it is evident that they constitute promising candidates for the development of a prototype of PC-WLED type architecture.

Keywords: solid state lighting, europium(III), aluminates, co-doping

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Structural and Spectroscopic Studies of Rare Earth-doped Polyphosphate Coacervates

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The Coacervation process refers to the aggregation of colloidal particles in solution. In this case, the droplets of dense polymeric phase formed during liquid-liquid phase separation also called coacervates are extended by colloidal particles. An example of a material that can be formed by this process is polyphosphate coacervates, which have glassy characteristics. In this work, polyphosphate coacervates doped with paramagnetic Ln^{3+} ions (Ln = Dy, Ho and Tb) were prepared with the aim of obtaining materials in the form of films that present magneto-optical properties to be explored. The coacervation process was induced by adding a solvent with a high dielectric constant, such as ethanol, to a solution of Ln-polyphosphate. The materials obtained were structurally characterized via FTIR, XRD and Raman spectroscopy. Undoped coacervates generally have amorphous structures. XRD analyzes showed that after the addition of Ln^{3+} ions, the formation of ortho and pyrophosphate crystalline phases occurred. From Raman scattering, we identified that the precursor presents two main specific vibration modes at 743 cm^{-1} and 1009 cm^{-1}, attributed to the symmetrical stretches in P-O-P (bridges) and P-O (terminal), respectively. For samples containing Ln^{3+}, it was observed that the $\upsilon_s(P\text{-}O_t)$ band shifted from 1009 to 1017 cm^{-1}. The spectroscopic properties of Ln^{3+} ions were evaluated via photoluminescence spectroscopy. In the emission spectra of samples containing Dy^{3+} and Ho^{3+} ions, it was possible to observe, in a more pronounced way, an emission band centered at 576 nm and 669 nm, referring to the transitions $^7F_{9/2} \rightarrow {}^6H_{13/2}$ and $^5F_5 \rightarrow {}^5I_8$, respectively. The samples doped with Tb^{3+} ions showed atypically intense emission in the region close to 491, 546 and 686 nm, due to the transitions $^5D_4 \rightarrow {}^7F_6$, $^7F_5$, $^7F_4$. In sequence, these materials will be evaluated for their magneto-optical properties via Faraday rotation angle experiment.

Keywords: Coacervate, Lanthanide Spectroscopic

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Temperature characterisation and quantum yields of upconverting Yb^{3+},Er^{3+}- doped $NaYF_4$ phosphors

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Photoluminescent materials have garnered significant interest for their potential in remote temperature sensing, particularly in scenarios where conventional thermometers prove inadequate, such as in biological and medical applications. One popular approach involves employing ratiometric thermometry, which utilizes the luminescence intensity ratio (LIR) between two thermally linked transitions of a lanthanide ion to measure temperature. However, aberrations in the optical collection system can alter the LIR between different setups, hindering the establishment of a standard for cross-laboratory comparison.In this study, we investigate the thermometric properties of upconverting (UC) lanthanide-doped NaYF4 phosphors in the range of micron-sized powders. Additionally, we determine their absolute photoluminescence quantum yields (PLQY) at various temperatures using a novel setup featuring a modified integrating sphere with a temperature-controlled sample holder. This setup enables the correction of optical aberrations, facilitating the derivation of a more robust LIR for the examined processes. The thermometric parameter (LIR) is then obtained at different temperatures via the integrated intensity ratios of $(^2H_{9/2} \rightarrow {}^4I_{13/2})/(^4S_{3/2} \rightarrow {}^4I_{15/2})$ transitions (526 nm/543 nm) for the Yb^{3+},Er^{3+} co-doped samples. Next, a low-cost setup for the microscopy inspection of samples has been employed for temperature mapping. Finally, the viability and metabolic activity of U-87 MG-GFP cells (cell line isolated from malignant gliomas) is assessed against their contact with the phosphors.

Keywords: Upconversion, thermometry, PLQY, NaYF4

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Core-shell persistent phosphors: surface functionalization with europium β-diketonate complexes

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With the ever-increasing development and optimization of optical properties in rare-earth-doped persistent phosphors, several bottom-up engineering methods have been widely studied for the fabrication of multifunctional luminescent materials with a wide range of applications. In this work, tris-Eu^{3+} β-diketonate hydrate complexes (*e.g.* tta: thenoyltrifluoroacetonate, or dbm: dibenzoylmethanate) were prepared by coprecipitation and later coordinated with ancillary ligand 4-picoline-N-oxide. The prepared complexes were then functionalized on $SrAl_2O_4:Eu^{2+},Dy^{3+}$ persistent phosphors by microwave-assisted silanization using (3-Aminopropyl)trimethoxysilane as a precursor for both single and double-shell structures. Powder X-ray diffraction (PXRD) analysis revealed the presence of the characteristic $SrAl_2O_4$ stuffed tridymite structure alongside $SrCO_3$ by-product due to annealing under a reducing carbon monoxide atmosphere. Additionally, surface silanization resulted in an amorphous SiO_2 network, as seen by PXRD and electron microscopy and energy-dispersive X-ray spectroscopy results, the latter also probing dopant distribution as well as the effectiveness of the silanization method. Luminescence spectroscopy revealed that single-shell materials exhibit a different emission profile for both tta and dbm complexes, with predominant Eu^{2+} and Eu^{3+} emission, respectively. On the other hand, double-shell phosphors show intense red luminescence derived mainly from the complexes during excitation. Long-lasting persistent luminescence was also observed in functionalized materials, where the single-shell phosphor functionalized with the europium tta complex displayed the highest persistence decay time. Furthermore, vacuum-ultraviolet emission spectra recorded under direct $SrAl_2O_4$ band-gap excitation corroborate with UV-Vis data, with predominant Eu^{2+} green emission. Finally, site-selective luminescence in functionalized materials was carried out at the Brazilian synchrotron (Sirius) combining X-ray fluorescence, X-ray absorption near edge structure, and X-ray excited optical luminescence spectroscopy experiments. Results showed that the ratio between Eu^{2+} and Eu^{3+} emission is intrinsically different for the edge and the bulk of the studied particles with possible energy-

transfer (ET) in the interface of the $SrAl_2O_4:Eu^{2+},Dy^{3+}$ phosphor, and the europium complexes embedded into the silica shells on distinct regions for a single particle. Such results revealed the influence of shell thickness and distance in ET processes, outlining an important framework for the development of multifunctional persistent phosphors utilizing rare-earth complexes as luminescent sensitizers.References:[1] Y. Li, M. Gecevicius, J. Qiu, et al. *Chem. Soc. Rev*. 45 (2016) 2090-2136.[2] L.H.C. Francisco, R.P. Moreira, M.C.F.C. Felinto, et al. *J. Alloys Compd*. 882 (2021) 160608.

Keywords: Persistent phosphors, Functionalization, β-diketonate

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Exploring downshift and upconversion optical responses to detail internal structure of vanadate nanocrystals

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Rare earth vanadates are classic luminescent systems offering a unique combination of properties for emerging applications combining thermal or chemical sensing and enzyme-like catalysis. Whilst appropriate control of composition, crystallinity, size, and morphology is critical for the proposed applications, vanadate nanoparticles often exhibit complex internal microstructures arising from non-classical nucleation/growth processes in liquid-phase. Furthermore, nanostructural character imposes additional restrictions on luminescence quantum yields due to surface and dielectric effects, thus increasing the number of aspects to be considered in the design of this class of materials. Rational control of the internal microstructure of colloidal oxide nanoparticles is still a matter of investigation, and development of processing techniques for the improvement of target properties requires a full picture of the internal chemical environment. Detailed information on poly- vs. nanocrystallinity, porosity, defect density, and microstrain involve a combination of multiple characterisation tools, but our recent observations regarding Eu^{3+} spectroscopic properties reveal interesting insights on the microstructure of $REVO_4$ nanoparticles. In summary, analysis of B_2 and E $^5D_0 \rightarrow {}^7F_2$ Stark components in terms of relative intensities, bandwidth, and unfolding provides direct correlation on long-range crystallinity, defect density, distortions on coordination polyhedra, and desymmetrisation in the tetragonal $I4_1/amd$ structure. We evaluated the emission spectra of bulk/single-crystalline, nano/single-crystalline, nano/polycrystalline, and nano/polycrystalline/high-entropy $REVO_4$ solids [RE=Y, Ce, and (Y,La,Gd,Yb,Lu)] doped with Eu^{3+} with different degrees of defect density. In addition to UV-excited downshift Eu^{3+} emissions, some of the particles also showed unconventional Eu^{3+} upconversion luminescence. Our results confirm the use of luminescence spectra as an additional tool to describe the internal structure of complex nanoparticles, thus enabling further advance in the rational design of $REVO_4$ colloidal particles for thermometry and catalysis applications.References: *J. Phys. Chem. C* **2024**, *128*, 1, 667–670. *Cryst. Growth Des.* **2023**, *23*, 8, 5389–5396. *Chem. Commun.* **2023**,*59*,11393-11396. *Nanoscale* **2021**,*13*, 4931-4945.

Keywords: Vanadates; Nanoparticles; Colloids; Europium

Optical properties of inorganic oxide perovskites doped with neodymium(III) ions under highly concentrated infrared excitation

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Inorganic perovskites are a huge family of materials characterized by a unique crystal structure. The first literature reports about these materials appeared in the 19th century. The composition of the perovskite determines to which group a given compound can be classified. Among them, we can distinguish layered, three-dimensional, or double perovskites. Each of the mentioned groups may contain only inorganic ions or organic ligands substituted in the position of the cation A and/or the anion X, creating the so-called hybrid perovskites. Inorganic oxide perovskites with an ABO_3 structure attract great attention in the scientific community from the point of view of basic and implementation research. The structure of three-dimensional (ABO_3) perovskites is quite flexible, which allows the A and B positions to be replaced with other ions of different sizes. As a consequence, bonds of different lengths are formed, leading to structural deformations. Therefore, the obtained materials can crystallize in various crystallographic systems, while their structural stability is maintained thanks to oxygen vacancies, which additionally determine their physicochemical properties. Here we present the optical properties of $LaAlO_3$ perovskite doped with different concentrations of neodymium(III) under excitation with a focused infrared beam. The result was a broadband white emission covering the entire visible range with characteristic dips closely related to the presence of Nd^{3+} ions. It is interesting to note that the dopant concentration has a strong influence on the shape of the recorded emission bands, Surprisingly, the full substitution of Al^{3+} ions with Nd^{3+} ions does not cause concentration quenching for the luminescence generated in this way.

Keywords: inorganic oxide perovskites, anti-Stokes white emission, broadband luminescence, infrared excitation

ORIGINS AND EVOLUTION OF BIOLUMINESCENCE

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First de novo genome assemblies of bioluminescent fungi and CAC genes study

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Fungi genomes are rarely sequenced, and bioluminescence in fungi has never been studied in context of the whole genome. This work showcases the first de novo assemblies and annotation of three bioluminescent fungi species: Neonothopanus gardneri, the current model for fungi bioluminescence studies, Mycena lucentipes and Gerronema viridilucens. Having the genome sequences of the Caffeic Acid Cycle of different species enables biotechnological studies and aplications of fungi bioluminescence, and is important to better understand its evolution.Sequencing was performed by Illumina sequencers generating high coverage paired end reads of 151bp. Adapter trimming and quality control were performed with TrimGalore. Abyss was used for genome assembly. Genome decontamination was performed by employing DIAMOND and kraken2 to identify contaminated contigs in the contigs and bowtie2 was used for read mapping. For annotation a repeat library was constructed de novo using RepeatModeler and repeat masking was carried out using RepeatMasker. Gene prediction on the masked genome was achieved using by GeneMark-ES, and functional annotation performed by EggNOG.

Keywords: genome assembly, caffeic acid cycle, genetics

PHOTOVOLTAIC AND PHOTOCATALYSIS MATERIALS

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Photoinduced oxygen evolution reaction using carbon quantum dots synthesized from lignocellulosic biomass

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Fluorescent carbon nanomaterials have recently emerged as a competitor to conventional metal semiconductors for photocatalysis. The conversion of lignocellulosic biomass into value-added carbon nanomaterials has advantages compared to the metal ones due to the low toxicity, low cost, environmental friendliness, and simple synthetic routes; moreover, there are several applications regarding drug delivery, bioimaging, biosensors, and for photoelectrocatalytic processes such as oxygen and hydrogen evolution. In this study, we synthesized carbon quantum dots (Qdots) from sugarcane biomass through pyrolysis and acid treatment. The carbon dots were applied for the photoelectrocatalytic oxygen evolution reaction. Raman spectra of pyrolyzed biomass showed a D band related to carbon atoms breathing mode due to structure defects; a G band related to stretching of C-C bonds, common of sp^2 carbon; and an I_D/I_G= 1.00, suggesting high defect intensity (thermal treatment with the formation of oxygenated functional groups). The formation of functional groups was evidenced by Fourier-transform infrared spectroscopy. With fluorescence spectroscopy, we determined the maximum emission at 526 nm. This result is due to the Stokes shift, and it is easier to comprehend with the Jablonski diagram. Four lasers were used (wavelength excitation of 365, 405, 532, and 650 nm). Except for the 650 nm laser, the emission light of Qdots is seen to be at longer wavelengths i.e. lower energy. This result is explained by the Stokes shift, and it is better understood with the Jablonski diagram. The bandgap was determined through the Tauc plot method using UV-Vis data (4.79 eV). Also, the UV-Vis spectra show two bands at 265 and 360 nm, which are related to pi → pi* transitions within the carbon structure (sp^2 network) and n → pi* transition of C=O groups at the basal plane and the edge, respectively. The size of Qdots is 1.06 nm measured by dynamic light scattering. For the photoelectrochemical experiments, the working electrode was prepared with layer-by-layer (LbL) deposition, as follows: fifteen bilayers of Qdots were deposited at indium tin oxide (ITO)-covered glass electrode, immersing alternately in poly (allylamine hydrochloride) (PAH) and Qdots suspension. Cyclic voltammetry (CV) and

linear voltammetry (LV) were done at pH = 1.0 (+0.2 V to +1.2 V). Voltametric analyses were done in the dark and with laser irradiation (365 and 405 nm). The current density increased from 0.4 µA cm^{-2} to 0.67 and 1,18 µA cm^{-2} with 405 and 365 nm laser irradiation, respectively – at potential 1.2 V vs Ag/AgCl(KCl_{sat}). In this system, Qdots could be performing light absorption and separation of electron-hole pairs, a fundamental process for photocatalytic charge transfer for water oxidation.

Keywords: photoelectrocatalysis, carbon quantum dots, lignocellulosic biomass, oxygen evolution reaction

QUANTUM DOTS, NANOCRYSTALS, AND NANO-STRUCTURED LUMINESCENT MATERIALS

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Thermal stability of $[Eu(tta)_3(H_2O)_2]$ complex incorporated in sustainable urethanesil film: Spectroscopic and theoretical studies

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Despite recent efforts to develop luminescent rare earth β-diketonate complexes, the attainment of thermal stability continues to pose a formidable challenge. The present study addresses this issue by embedding a Eu^{3+}-complex into a sustainable organic-inorganic hybrid to harness thermal stability. We report thermal-stabilized tris(thenoyltrifluoroacetonate) europium(III) complex, $[Eu(tta)_3(H_2O)_2]$, incorporated into a urethanesil castor oil-based hybrid (SiCO) material. Spectroscopic analysis reveals that heating $[Eu(tta)_3(H_2O)_2]$ in powder form to 60 °C results in irreversible quenching of its photoluminescence (PL) emission. On the other hand, the PL emission of $[Eu(tta)_3(H_2O)_2]$ complex does not change after annealing the SiCO-$[Eu(tta)_3(H_2O)_2]$ film up to 180 °C. Furthermore, $[Eu(tta)_3(H_2O)_2]$ coordination compound incorporated into the hybrid material proved to be thermally stable, maintaining its luminescent properties even after undergoing at least five successive heating-cooling cycles ranging from 29 to 70 °C. By theoretical calculations on intramolecular energy transfer (IET), it was found that temperature changes in SiCO-$[Eu(tta)_3(H_2O)_2]$ film dramatically affects IET dynamics. The increase in the temperature led to a reduction of tta→Eu^{3+} ET rates along the main pathway, T_1:tta→$^5D_J/^5L_6$:Eu^{3+}, while an increase in S_1+T_1:tta←$^5D_J/^5L_6$:Eu^{3+} backward IET was verified. This is a pioneering material, that represents a significant advance in the field of Materials Science. This innovative optical material not only shed light on the critical aspects of thermal stability in luminescent hybrid materials but also opens avenues for diverse applications in photonics, where such stability is of paramount importance.

Keywords: Europium (III), β-diketonate complex, castor oil, photoluminescence, intramolecular energy transfer, photonics.

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Cysteamine-copper supported on bacterial cellulose: a novel approach to simultaneous degradation of antibiotics in the Fenton processes

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Pharmaceutical residues are increasingly found in sewage wastewater and surface waters, and even at low concentrations, they can negatively affect water quality. Copper-cysteamine (Cu-Cys) supported on bacterial cellulose are a new type of catalyst with high potential for the removal of pharmaceutical residues from wastewater. This luminescent and photosensitizing material may be capable of producing reactive oxygen species after interaction with H_2O_2. Furthermore, they can be stimulated by UV light, microwaves, X-rays, and ultrasound to increase the generation of reactive species in the degradation system. Furthermore, Cu-Cys can be synthesized using an easy, fast, and economical synthesis method, providing an excellent cost/benefit ratio.To facilitate recovery of the nanoparticles and avoid possible copper leaching, the Cu-Cys were immobilized in bacterial cellulose, which has a high surface area, chemical stability, and the ability to disperse metal particles over its surface.This work reported a strong catalytic performance of Cu-Cys coupled to bacterial cellulose applied in the Fenton process for the simultaneous removal of two antibiotics, sulfamethazine and sulfadiazine, in purified water. The synthesized material presented phase purity and an XRD diffractogram similar to that reported in the literature. SEM images showed that the Cu-Cys were well distributed in the cellulose fibers, which contributed to the material stability during degradation experiments. Photo-Fenton experiments under UV-LED irradiation in the 365 nm region showed that after 40 min of reaction at natural pH of the solution (pH 8.1), both antibiotics were below detection limit with negligible leaching of copper to the solution, indicating that reaction occurred on material surface. The good stability and catalytic efficiency of Cu-Cys supported on bacterial cellulose make this material a potential candidate for heterogeneous Fenton processes employed for the effective degradation of emerging contaminants.

Keywords: Pharmaceutical degradation, luminescent catalysts, copper-cysteamine

Ordered Macroporous Chiral Metal-Organic Framework Film-Based Fluorescent Sensors

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Chiral film-based fluorescent sensors are promising candidates for chiral discrimination of enantiomers because of their miniaturization and low power consumption. However, their practical application is limited by the contradiction between enantioselectivity and the adsorption capability of chiral films. The construction of hierarchically porous structures in crystalline microporous materials is considered to be an effective way to improve mass transfer and accessibility of the active sites, and this provides a solution to resolve the contradiction. By use of a dielectric barrier discharge reactor, we developed a facile strategy for the fabrication of crystalline chiral metal-organic framework (CMOF)-based films with inherent microporosity and template-induced, homogeneously distributed, and macroporous structures. This method was successfully applied to obtaining various CMOF-based thin films with interconnected macro-microporous structures. The as-synthesized films preserve chiral nature, high crystallinity, high specific surface area, and strong fluorescence emission. When L-histidine (*L*-His) moieties were introduced into the MOF backbone, ordered macroporous *L*-His-ZIF-8 film was produced to form a fluorescent sensor for various chiral alcohols. Compared to the purely microporous *L*-His-ZIF-8 film, the resultant hierarchical porous film exhibited a higher enantioselectivity and better detectability.

Keywords: Chirality; Metal-organic framework; Fluorescence; Dielectric barrier discharge

Cellulose-based translucent films with XEOL and up conversion

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The up-conversion phenomenon occurs when two or more lower-energy photons are added, and one single higher-energy photon is emitted. This phenomenon finds applications in various fields, including bioimaging and solar energy conversion, given its unique non-linear optics. In this work up converting nanoparticles were added to a cellulose ether in order to make mailable and translucent up converting composites and expand on the ever-growing applications of up converting materials.The up-converting material is yttrium fluoride nanoparticles doped with ytterbium and erbium synthesized using a solvothermal method. These nanoparticles were then incorporated into hydroxypropyl methylcellulose (HPMC) films through a drop-casting process and in some cases, gold nanoparticles (AuNps) were also added to enhance the up-conversion emission. X-ray fluorescence nano mapping, conducted at the Carnaúba beamline of the Sirius Synchrotron facility, revealed an intriguing interaction between the upconverting nanoparticles (UCNps) and the AuNps, as well as a unexpected X-ray excited optical emission (XEOL).Furthermore, our photoluminescence study demonstrated an intensified up-conversion phenomenon in the presence of gold nanoparticles.

Keywords: films, nanoparticles, up-conversion, x-ray

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Cyanido iridium and rhenium complexes for next-generation materials demonstrating diverse luminescent functionalities

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There is a great scientific effort devoted to the design of new families of materials exhibiting a diversity of luminescent phenomena, including strong sensitized visible-to-NIR emission, pure or adjustable white-light emission (WLE), up-conversion luminescence (UCL), or circularly polarized luminescence (CPL), as well as the sensitivity of all these optical effects to external chemical and physical stimuli. Among various groups of inorganic, organic, or hybrid organic-inorganic materials considered tools for the generation of luminescent functionalities, the solids incorporating heavy metal ions, such as ruthenium(II), platinum(II), iridium(III), or rhenium(I or V), were found particularly attractive, especially in the contexts of high quantum yields of photoluminescence, related to their charge-transfer-type emissive electronic transitions, and processability to efficient electroluminescent devices (e.g., L. He, et al. *Adv. Funct. Mater*. **2020**, *30*, 1907169; Y. Zhang, C. Yang, et al. *Adv. Mater.* **2023**, *35*, 2303066).In this regard, recently we started a research program aimed at the design, synthesis, and characterization of a specific type of heavy transition metal complexes that combines the organic ligands inducing efficient luminescence with inorganic cyanido ligands which can generate the non-trivial ionic, supramolecular, or coordination systems responsible for tuning the optical effects by external stimuli (e.g., S. Chorazy, et al. *J. Mater. Chem. C* **2022**, *10*, 12054). As proofs-of-concept, we will present and discuss unique tetracyanido-nitrido-rhenate(V) complexes of the formula of $[Re^{V}(CN)_4(\text{nitrido})(\text{organic ligand})]^{2-}$, and the related solid luminophores demonstrating photoluminescence switchable by temperature and solvent vapors, as well as correlated with order-disorder phase transitions providing the simultaneous thermal switching of both electrical and optical properties of a material (S. Chorazy et al. *Angew. Chem. Int. Ed*. **2023**, *62*, e202308284). As a second example, we will present and discuss intrinsically chiral dicyanidoiridate(III) complexes of the formula of $[Ir^{III}(CN)_2(\text{pin-ppy-L})_2]^{-}$ (pin-ppy-L = ligand

bearing a chiral pinene-based derivative of 2-phenylpyridine), and the related solid luminophores exhibiting luminescent thermometric effects co-existing with non-linear optical activity (S. Chorazy et al. *Inorg. Chem. Front*. **2024**, *11*, 1366).

Keywords: photoluminescence, rhenium luminophores, iridium luminophores, optical sensing, multifunctionality

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Diphospine-dioxide-containing Yb(III)/Er(III) molecular nanomagnets in europium(III)-dicyanidometallate(I) luminescent matrices

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Molecule-based multifunctional magneto-luminescent materials, in particular those based on f-element complexes, promise a revolution in the fields of data storage, spintronics, quantum computing, and other cutting-edge areas.[1-3] The main approach to achieve such materials is the design of specific organic ligands, including (di)phosphine (di)oxides,[4] which can provide efficient luminescence as well as substantial magnetic anisotropy for the selected lanthanide ions as well as other possible physical functionalities, e.g., chirality, photoswitching phenomena, etc. Another distinct approach employs supporting metalloligands linked to 4f metal complexes, including octa-, hexa- or dicyanidometallates, which were presented to provide such properties as tunable luminescence, magnetic ordering effects, ferroelectricity, or permanent porosity.[5-7] Herein, we present the family of novel molecular materials, including the coordination polymer (CP) formed by 4f metal complexes bearing $dppmO_2$ (bis(diphenylphosphino)methane dioxide) ligands, which are further linked by dicyanidometallate(I) ions, $[Ag^{I}(CN)_2]^-$. They exhibit strong red temperature-dependent photoluminescence in the solid state for the Eu(III)-based derivative and slow magnetic relaxation effects below 10 K for Yb(III)- and Er(III)-based analogs. Therefore, by diluting Yb(III) or Er(III) centers in the Eu(III)-based coordination matrix, the presented material provides a stable platform for combining luminescent and magnetic properties with prospects for further ligand functionalization towards, e.g., chiral derivatives.**References**[1] D. N. Woodruff; *et al. Chem. Rev.;* **2013**; 113; 5110-5148.[2] S. T. Liddle; *et al. Chem. Soc. Rev.;* **2015**; 44; 6655-6669.[3] R. Jankowski; *et al. Chem. Commun.;* **2023**; **59;** 5961-5986.[4] Y.-Z. Pan; *et al. Inorg. Chem. Front.;* **2020**; 7; 2335-2342.[5] J. A. Hill; *et al. J. Am. Chem. Soc.;* **2016**; 138; 5886-5896.[6] S. Chorazy; *et al. Chem. Soc. Rev.;* **2020**; 49; 5945-6001.[7] J. J. Zakrzewski; *et al. Inorg. Chem. Front.*; **2021**, 8, 452-483.

Keywords: luminescent thermometry, molecular material, multifunctionality, magnetism, lanthanides

Low-temperature investigations of luminescent transparent garnet ceramics doped with rare earth ions

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The current development of laser materials technology can be determined, in a broad sense, by the goal of increasing their power and efficiency. For common applications, the economic aspect is also important. Both of these criteria are addressed by new high optical quality ceramic laser materials doped with rare earth ions. The properties of transparent yttrium aluminum garnet ceramics doped with Nd^{3+} and Sm^{3+}, which theoretically meet all the criteria for laser and cladding materials, respectively, were investigated. The phase formation, microstructure evolution, thermal properties, refractive index and spectroscopic properties of $Y_3Al_5O_{12}$ (YAG) ceramics with different concentrations of Nd^{3+} (0.5-4 at.%) and Sm^{3+} (1-10 at.%) were determined. In result, absorption, excitation, Raman spectra and thermoluminescence curves were measured and correlated with microstructural properties. Low-temperature experiments were also carried out to validate the possibility of using both materials also under cryogenic laser operating conditions. In the case of heavily doped YAG, not only the refractive index of these materials and the conductivity, but especially the concentration of defects can change, leading to non-radiative processes. Based on the results, it was possible to determine the appropriate dopant concentrations for optimal performance of a future ceramic laser operating in the low-temperature regime.

Keywords: garnet structure, low temperature, lanthanides, laser ceramics, parasitic suppressor

STRUCTURE, FUNCTION OF LUCIFERASES AND PHOTOPROTEINS

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An intrinsic N-terminus alfa-helix motif is required for the function of Ca^{2+}-regulated photoproteins in bioluminescent ctenophores

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Ca^{2+}-regulated photoproteins (CaPhs), to which the prosthetic group coelenterazine binds in the protein's internal cavity, undergo conformational changes uppon Ca^{2+} addition, causing emission of light. Recently, we reported a novel class of CaPhs - velamins - isolated from the bioluminescent ctenophore *Velamen parallelum.* In contrast to all other CaPhs, that produce light within the blue range (λ_{max} 465-495 nm), velamins are capable of emitting green light (λ_{max} 500-508 nm).CaPhs from hydromedusae (aequorin, mitrocomin, clytin, and obelin) and ctenophores (mnemiopsin, berovin, bolinopsin, and bathocyrovin) have been extensively investigated lately. Despite sharing some common structural features, including calcium-binding loops and substrate, ctenophore and hydromedusae photoproteins have low primary sequence identity and differ on certain intrinsic properties. For example, photoinactivation is present in ctenophores while hydromedusae photoproteins have a higher sensitivity towards calcium. Phylogenetic analysis of *V. parallelum* CaPhs revealed three functionally diverse clusters of photoproteins: whilst α-velamin isoforms exhibited the highest light emission activity, β- and γ-velamins were found to be more thermostable at higher temperatures. By comparing velamin sequences to other CaPhs, we found a strictly conserved ESYRYLRS motif located at the N-terminus of all ctenophore CaPhs and which is absent in hydromedusan counterparts. Here, we demonstrate that the deletion of the N-terminus alfa-helix motif in α-velamin isoform ablates its function, revealing its relevance for the bioluminescence of ctenophores. Further in silico modelling studies may provide new insights on the role of these residues in CaPhs, specially regarding the binding of coelenterazine and calcium ions. These findings reveal a robust phylogenetic marker to support the two different CaPhs classes from hydromedusae and ctenophores, as well as they contribute to our understanding of the ecology and evolution of bioluminescence in marine organisms.

Keywords: Bioluminescence, coelenterazine, Ctenophora, Hydromedusae, evolution.

Atomistic views and proposed mechanism of NanoLuc luciferase action

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The widely used NanoLuc luciferase was engineered over ten years ago but the oxidative mechanism by which it generates blue photons remained unclear [1]. Here we decipher NanoLuc luciferase action through crystallographic, spectroscopic, and computational experiments. We show that imidazopyrazinone luciferins bind to an intra-barrel catalytic site but also to an allosteric site shaped on the enzyme surface [2]. Structurally, binding to the allosteric site prevents simultaneous binding to the catalytic site, and *vice versa*, through concerted conformational changes. We demonstrate that restructuration of the allosteric site by mutagenesis can boost the luminescent reaction in the remote active site. Mechanistically, an intra-barrel arginine coordinates the imidazopyrazinone component of luciferin, which reacts with O_2 via a radical charge-transfer mechanism, and then it also protonates the resulting excited amide product to form a light-emitting neutral species. Concomitantly, an aspartate, supported by two tyrosines, fine-tunes the blue color emitter to secure a high emission intensity. Thus, we reveal that NanoLuc, despite its structural dissimilarity, employs an analogous catalytic principle to generate blue photons, as we recently revealed for coelenterazine-powered *Renilla*-type luciferases [3]. **References** [1] Hall M.P., Unch J., Binkowski B.F., Valley M.P., Butler B.L., Wood M.G., Otto P., Zimmerman K., Vidugirus G., Machleidt T., Robers M.B., Benink H.A., Eggers C.T., Slater M.R., Meisenheimer P.L., Klaubert D.H., Fan F., Encell L.P.,

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Keywords: Bioluminescence; Oplophorus gracilirostris; luciferase; coelenterazine; catalysis; allostery; azacoelenterazine

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Deciphering *Renilla*-type bioluminescence through an engineered ancestor

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The rational engineering of luciferase enzymes towards ultrasensitive bioassays is often possible only when the underlying catalytic mechanism is thoroughly known. Thus, atomic-level knowledge of a Michaelis enzyme-substrate complex, revealing molecular details of luciferin recognition and catalytic chemistry, is crucial for understanding and then rationally improving bioluminescent reactions. However, many known luciferase enzymes sample huge protein conformational space, often preventing complete structural characterization by X-ray crystallography. Moreover, using a cognate luciferin is problematic since its conversion into an oxyluciferin in the presence of the luciferase will prevent the capture of the enzyme-luciferin conformation in an activated state. Here, we outline how to deal with such obstacles, focusing on the recent discovery of a *Renilla*-type bioluminescence mechanism facilitated by a combination of engineered ancestral enzyme and the availability of a non-oxidizable luciferin analogue. The automated ancestral sequence reconstructions using FireProt^{ASR} provided an evolvable thermostable enzyme suited for structural studies [1], and a stable luciferin analogue azacoelenterazine provided a structurally cognate chemical incapable of catalyzed oxidation [2]. We suggest that an analogous strategy can be applied to various luciferases with unknown catalytic mechanisms and poor crystallizability [3].**References** [1] A. Schenkmayerova, G. P. Pinto, M. Toul, M. Marek, L. Hernychova, J. Planas-Iglesias, V. Daniel Liskova, D. Pluskal, M. Vasina, S. Emond, M. Dorr, R. Chaloupkova, D. Bednar, Z. Prokop, F. Hollfelder, U. Bornscheuer, J. Damborsky (2021) Nature Communications 12 3616.[2] A. Schenkmayerova, M. Toul, D. Pluskal, R. Baatallah, G. Gagnot, G.P. Pinto, V.T. Santana, M. Stuchla, P. Neugebauer, P. Chaiyen, J. Damborsky, D. Bednar, Y.L. Janin, Z. Prokop, M. Marek (2023)

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Keywords: Bioluminescence; Renilla reniformis; sea pansy; luciferase; coelenterazine; catalysis; ancestors; azacoelenterazine

From green to Far Red: mechanisms of bioluminescence color tuning in beetle luciferases, and beyond

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Beetle luciferases are responsible for catalyzing the oxidation of luciferin producing bioluminescence colors ranging from green to red, with unique properties. Fireflies emit yellow-green light, click beetles green to orange light depending on the lanterns, and railroad worms from green to red depending on the lantern. Furthermore, firefly luciferases can modulate bioluminescence colors from green to red depending on the pH, presence of heavy metals and temperature. Despite decades of structural/functional studies, mainly with firefly luciferases, how luciferases determine and modulate BL colors, remain an elusive issue that physicists, chemists, biochemists and molecular biologists have tried to solve. Our group has cloned the largest variety of beetle luciferases, including pH-sensitive and pH-insensitive which naturally producing green-blue, green, yellow-green, yellow, orange and red from distinct families. Through comparative studies, site-directed mutagenesis, modelling and biophysical methods like circular dichroism, our results indicate that green-yellow light emission could be obtained through: (1) a single rigid and hydrophobic active site conformation or (2) by pH-modulated rigidification in firefly luciferases during the emitting step. On the other hand, red light emission is obtained through a lousier active site conformation, especially a larger oxyluciferin binding site pocket, during the emissive step. Altogether the results indicate that oxyluciferin phenolate binding pocket rigidity modulate excited state proton transfer and electrostatic interactions, decreasing or increasing energy levels of excited and ground states, thereof modulating bioluminescence colors. The results also opened the possibility to develop Far Red emitting combinations by combining luciferase engineering and luciferin analogs, and color tuning luciferases por pH and toxic metal biosensing (**Financial support:** FAPESP 2022/04800-0; CNPq 401.050/2021-1)

Keywords: Far Red, pH-sensitivity, oxyluciferin, excited states

New Insights into Color Emission of Beetle Luciferases

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Bioluminescence is the emission of light from a biological process, and it can be found in various organisms, including bacteria, fireflies, and beetles. Luciferase is an enzyme that catalyzes a two-stage chemical reaction to oxidize luciferin in the presence of Mg^{2+} and ATP to produce oxyluciferin and release energy in the form of visible light. Previously, we determined the crystal structures of two beetle luciferases with red and blue-shifted green light emission[1]. The blue-shifted green-emitting luciferase from the firefly *Amydetes vivianii* (GB_{Av}) and the naturally red-emitting luciferase from the glow-worm *Phrixothrix hirtus* (RE_{Ph}) that was found as tetramers or octamers in solution as well as in the crystal lattice[1]. To understand the protein dynamics during the emission of light, multiple mutations were introduced in the dimer and tetramer interfaces. The loop$^{346–361}$ present at the bottom of the active site was found to be important in the blue- and red-emitting luciferases, where the green emission of GB_{Av} was shifted from 539 nm to 580 nm, and the red emission of RE_{Ph} was shifted from 623 nm to 603 nm. To better understand the conformational dynamic associated with the different color emission for the wild-type WT and mutant enzymes of GB_{Av} and RE_{Ph}, hydrogen-deuterium exchange with mass spectrometry (HDX-MS) measurements were used to study the protein dynamics at different conformational states induced by the binding of the product, oxyluciferin. High dynamics and deuterium exchange rates have been associated with the apo-state compared to the oxyluciferin bound-state. In addition, a comparative analysis is conducted on the WT enzyme and the mutants that red-shifted the green emission of GB_{Av} or blue-shifted the red emission of RE_{Ph}. The HDX-MS data reveal high dynamics on the loop$^{346–361}$ for the GB_{Av}, while less dynamic variation was observed in the RE_{Ph}. Also, the rate of deuterium labeling increased for the GB_{Av} mutants with red-shifted emission compared to the WT RE_{Ph}. In contrast, the WT GB_{Av} was more stable at half of the rate of dynamics compared to the WT RE_{Ph}.

Keywords: Firefly; luciferases; dynamics; HDX-MS; color emission.

Beetle luciferases with naturally red- and blue-shifted emission

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The different colors of light emitted by bioluminescent beetles that use an identical substrate and chemiexcitation reaction sequence to generate light remain a challenging and controversial mechanistic conundrum. The crystal structures of two beetle luciferases with red- and blue-shifted light relative to the green yellow light of the common firefly species provide direct insight into the molecular origin of the bioluminescence color. The structure of a blue-shifted green-emitting luciferase from the firefly *Amydetes vivianii* is monomeric with a structural fold similar to the previously reported firefly luciferases. The only known naturally red-emitting luciferase from the glow-worm *Phrixothrix hirtus* exists as tetramers and octamers. Structural and computational analyses reveal varying aperture between the two domains enclosing the active site. Mutagenesis analysis identified two conserved loops that contribute to the color of the emitted light. These results are expected to advance comparative computational studies into the conformational landscape of the luciferase reaction sequence

Keywords: Luciferases, red emission, blue emission and bioluminescence

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Prospecting *Cratomorphus distinctus* firefly luciferase as a sensor of heavy metals and pH: comparison with other color tuning luciferases

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Luciferases are the enzymes which catalyze the oxidation reactions of luciferins responsible for bioluminescence in different organisms. Beetle luciferases have been widely used for detection of ATP, enzymatic assays, microbiological contamination, as reporter genes for bioimaging and biosensors. More recently their pH-sensitivity has been harnessed for ratiometric indication of intracellular pH and heavy metals. Our research group has cloned the largest variety of beetle luciferases, some of them already having bioanalytical applications. However, among our luciferase gene bank, there are still several luciferases with potential analytical applicability that require characterization. The luciferase from the Atlantic rain forest *Cratomorphus distinctus* firefly (CrtLuc) was already cloned (VIVIANI et al., 2004), however, its spectral and kinetic properties were not characterized in detail. In this work we characterized the kinetic and spectral properties of *C. distinctus* luciferase, explored its suitability as a luminescent sensor for pH and heavy metals and compared with other firefly luciferases cloned by our group (*Macrolampis* sp, *Amydetes vivianii*, *Aspisoma lineatum* and *Bicellonycha lividipennis*). This luciferase was expressed in *E. coli* BL21-DE3 and purified by Nickel affinity chromatography. The kinetic parameters (specific activity, k_{cat}, K_M for substrates and optimum pH) were determined through bioluminescence intensities measurements using an AB-2200 luminometer (ATTO) and their bioluminescence spectra and sensitivity to pH and metals were measured using an AB-1850 spectroluminometer (ATTO). The specific activity was high when compared to other firefly luciferases ($5.5.10^{11}$ *cps*.mg^{-1}), with k_{cat} = 7.0. 10^{-5} cps. The optimum pH was ~8.2, $K_M(LH_2)$ = 16 µM and K_M(ATP)=24 µM. The low K_M and high k_{cat} values indicate that this luciferase has high catalytic efficiency (k_{cat}/K_M =4.4 $c.s^{-1}\mu M^{-1}$ for LH_2 and 2.9 $c.s^{-1}\mu M^{-1}$ for ATP). The bioluminescence spectrum of this luciferase has an emission peak at 564 nm at pH 8.0, and 611 nm at pH 6.0, showing that this luciferase is highly sensitive to pH. Noteworthy, mercury was the only metal which affected the bioluminescence spectrum, causing a shift of 50 nm at the concentration of 2 mM, demonstrating an unusual sensitivity of this luciferase to this

metal when compared to other firefly luciferases. Thus, these results indicate that *C. distinctus* luciferase has potential applicability as a sensor color tuning luciferase for mercury detection, and as also as an indicator of intracellular pH.

Keywords: Luciferase, mercury, pH-sensivity

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Role of H310 in pH and metal sensitivity of firefly luciferases and identification of novel metal binding sites

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Firefly luciferases are pH-sensitive: their bioluminescence spectra changes from yellow-green to red in the presence of heavy metals, acidic pH or at higher temperatures. These enzymes are being prospected as color tuning and ratiometric biosensors of intracellular pH and toxic metals. The luciferase of *Amydetes vivianii* firefly is highly efficient, thermostable and has a spectral selectivity for cadmium and mercury, making it a very promising bioanalytical reagent. The residues involved in the pH-sensing and metal binding are H310, E311, R337 and E354, which form two salt bridges, one closer to the phenolate group of oxyluciferin (E311/R337) and another more external (H310/E354). However, considering that some pH-sensitive luciferases display substitution at position 310, the specific role of H310 in pH and metal sensing is still under debate. Thus, the aim of this work was to understand the specific role of the H310 residue in the pH- and metals sensitivities using *Amydetes vivianii* firefly luciferase and to obtain better suited mutants for biosensing purposes. Site-directed mutagenesis using Phusion TM High-Fidelity DNA Polymerase (Thermo Fisher) was performed, the luciferase mutants were expressed in *E. coli* BL-21, the mutant enzymes were purified by affinity chromatography using Ni-NTA-Agarose resin and their kinetics, bioluminescence spectra and pH- and metal sensitivities were characterized. The *ab initio* modeling was performed using the I-TASSER program. MIB2 modeling server was used to screen the bivalent ion site interactions with the luciferase models. Nine mutants of H310 (C, D, E, F, G, Q, T, R and Y) were obtained. There was no significant change of the spectrum of all these mutants at pH 8.0. However, the negatively charged mutants (H310D e H310E) increased the spectral shift at pH 6.0, as well as the sensitivity to metals. Only H310F led to a significant decrease in sensitivity to pH and metals. The results indicate that the presence of negatively charged and basic side-chains at

position 310 are important for pH-sensitivity and metals coordination, but not essential, indicating that the remaining side-chains of E311 and E354 may still play a role in pH-sensitivity and coordinate some metals. Furthermore, the effect of metals on bioluminescence activity and modelling studies highlighted the existence of additional metal binding sites with high affinity for Zn2+, Ni2+ and Hg2+, which are unaffected by the substitutions of H310.

Keywords: pH-sensitivity, cadmium, mercury

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The diversification of bioluminescence color eliciting luciferases of Mastinocerinae railroadworms (Coleoptera: Phengodidae) lanterns

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Railroadworms luciferases from Matsinocerinae subfamily emit the widest range of bioluminescence colors among beetles from different lanterns, ranging from green to red. They have been used as model enzymes to investigate the relationship between structure and bioluminescence colors. However, until date only 4 active luciferases from the larval stage of railroadworms have been cloned and investigated: the red emitting luciferase from *Phrixotrix hirtus* head lanterns (PhRE); the green emitting luciferases from the lateral lanterns of *Phrixotrix spp* (PvGR), the yellow-green emitting luciferase from the dorsal lanterns of *Phengodes* sp (Ph) and *Euryopa clarindae* luciferase. Previous studies using PCR isolated sequences suggested that the luciferases from the head and lateral lanterns are paralogous, and that the head lanterns luciferases evolved by gene duplication from green emitting lateral lanterns luciferases. Here, by transcriptional analysis identified and cloned novel railroadworm luciferases from *Brasilocerus sp*, *Phrixotrix hirtus* and *Mastinomorphus* larvae, and compared them with the green and red light emitting luciferases from both cephalic and lateral lanterns. Larvae of *Brasilocerus* display a single luciferase isozyme emitting yellow-green light in both the cephalic and lateral lanterns, whereas *Phrixotrix* spp and *Mastinomorphus* have two isozymes. The luciferases from lateral the lanterns display slower luminescence reaction kinetics with higher values of K_M for luciferin, whereas orange emitting luciferase display faster kinetics and lower K_M approaching those of the red emitting cephalic lanterns luciferase. The results indicate that, in contrast with *Phrixotrix* spp, some basal genera of Mastinocerinae

railroadworms display a single isozyme in both the lateral and cephalic lanterns, and that the red light emitting luciferase of *Phrixotrix* is an apomorphic character that may have evolved quite recently in the cephalic lanterns of *Phrixotrix* lineage.

Keywords: Luciferase, Phengodidae

TERRESTRIAL BIOLUMINESCENCE

The Diversity and displays of Bioluminescent Beetles from the Southern Amazon forest

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Bioluminescent beetles are found mainly in of the Elateroidea superfamily, within Lampyridae, Phengodidae and Elateridae. Besides their scientific interest, they constitute potential novel important nocturnal bioindicators, and have provided bioanalytical reagents for biotechnological, biomedical and environmental analysis. The Neotropical region, especially Brazil with its variety of tropical biomes including Atlantic Forest, Cerrado, Pantanal and Amazon forest, accounts with the largest diversity in the world. However, surveys of BL beetles were done just for some parts of the Southeastern Atlantic rain forest, and more recently of Central Cerrado ecosystem. Considering the richness and fast decline of Amazonian forest, especially its borderline with Cerrado, biodiversity surveys are urgently needed to promote biodiversity studies, bioprospection and to aid conservation programs. In 2009 we begun to make expeditions to Amazon region and its borderline with Cerrado (Savannas), along the major Southern tributaries of Amazon river: Araguaia´s river (Tocantins state); Tapajós (Mato Grosso and Pará state) and Madeira-Guaporé (Rondonia and Amazon states). We registered above 110 species of bioluminescent beetles (Lampyridae: ~77 spp; Elateridae: ~30 spp, and Phengodidae: 8 spp), the largest ever reported, and new interesting species and displays of bioluminescence, including luminous termite mounds inside forest (*Pyrearinus fragilis* and *P.termitilluminas*), luminous clayish caves (*P.pumilus*), orange emitting click beetles and synchronous fireflies.

Keywords: Fireflies, railroadworms, click beetles, Phengodidae, Lampyridae, Elateridae

History, mechanism, biochemistry and applications of fungal bioluminescence

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Fungal bioluminescence, observed in over 125 species within the Agaricales order, arises from the oxidation of luciferin derived from caffeic acid catalyzed by luciferase enzymes. This intricate process intertwines the Krebs cycle and the Shikimic Acid pathway, enabling the organisms to emit light spontaneously. Genetic manipulation of luciferase has led to the creation of bioluminescent reporters and organisms capable of sustaining their glow, marking significant strides in biotechnology. Fungi, as sessile organisms, may employ bioluminescence for communication, particularly with spore-dispersing organisms, as indicated by the emission of light from the mycelium. However, luminescence is observed only in specific mushrooms, often from distinct parts like the pileus and stipe, presenting challenges for human observation due to variations in bioluminescent intensity across fungal cell organization. Transcriptional regulation of bioluminescence genes influences the intensity and duration of light emission, adding further complexity to the phenomenon. From historical insights to contemporary biotechnological applications, this work encompasses the breadth of fungal bioluminescence, elucidating the mechanistic underpinnings of biological glow. Exploring the biochemical and chemical processes driving fungal light emission contributes to a deeper understanding of chemiexcitation's role in biological phenomena. This presentation will emphasize the ecological significance of fungal bioluminescence, highlighting its potential applications in biotechnology, and captivates researchers and enthusiasts alike with nature's luminescent wonders. [1] Stevani C. V., Zamuner C. K., Bastos E. L., de Nóbrega B. B., Soares D. M. M., Oliveira A. G., Bechara E. J. H., Shakhova E. S., Sarkisyan K. S., Yampolsky I. V., Kaskova Z. M. (2024) The living light from fungi. J. Photochem. Photobiol. C: Reviews 58: 100654.

Keywords: basidiomycete, bioluminescence, Caffeic Acid Cycle, self-sustained luminescence

Lignin impact on *Neonothopanus gardneri's bioluminescence*

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Although understanding of the metabolic pathway responsible for light emission in basidiomycete fungi, the Caffeic Acid Cycle (CAC), and the ecological function for mushrooms has advanced, the biochemical function of bioluminescence for mycelium has not yet been fully elucidated. A plausible explanation for the ecological function of bioluminescence would be to attract spore-dispersing arthropods to bright mushrooms compared to non-bright ones. This explanation, however, cannot be applied to mycelium, which does not produce spores.In marine systems dependent on celenterazine, a hypothesis formulated in the 1990s suggests that bioluminescence could be a way to mitigate reactive oxygen species (ROS) produced by oxidative stress and respiration itself. In the case of ligninolytic basidiomycete fungi, it is known that the degradation of plant lignin involves a series of ROS: hydrogen peroxide, superoxide radical anion, hydroxyl radical, and other organic peroxides. The aim of this study is to assess whether the presence of lignin in the culture medium alters the ligninolytic activity of the bioluminescent fungus Neonothopanus gardneri mycelium and if this influences light emission. For this purpose, the mycelium was cultivated in a sugar cane molasses-based medium with different concentrations of commercial lignin.The results suggest a possible relationship between ligninolytic enzymes activity and the intensity of bioluminescence in Neonothopanus gardneri. For a more comprehensive understanding, the results of enzymatic activity can be complemented by evaluating the differential expression of genes involved in lignin degradation and light emission. This will provide a clearer insight into the impact of lignin on the CAC, contributing to a deeper understanding of the functions of bioluminescence in mycelium.

Keywords: Fungal bioluminescence; Reactive oxygen species; Ligninotlytic enzymes

Potential Second Enzymatic Pathway for Oxyluciferin Consumption in Bioluminescent Mushrooms

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Currently, only two metabolic pathways are known for bioluminescent mechanisms: one involving the lipid synthesis pathway in bacteria and the other involving the metabolization of caffeic acid by fungi. Within the fungal bioluminescence pathway, four enzymes play crucial roles: hispidin synthase (HispS), the polyketide synthases that catalysis the several carbon addition reaction on caffeic acid substrate to produce hispidin; hispidin-3-hydroxylase (H3H), enzyme that catalyzes the mono-oxygenation of hispidin at C3 of α-pyrone ring, producing the fungal luciferin (3-hydroxyhispidin); luciferase (Luz) that catalyze the oxidation of luciferin by insertion of the molecular oxygen to produce the high-energy intermediate (HEI) endoperoxide. After the decomposition of the HEI and the decay to ground state of excited oxyluciferin, the last enzyme is caffeylpyruvate hydrolase (CPH), that catalyzes the hydrolytic cleavage of oxyluciferin. Our laboratory has investigated CPH and confirmed its catalytic activity in recycling the system, producing caffeic acid and pyruvic acid from oxiluciferin. While studying extracts of total proteins from *Neonothopanus gardneri* mycelium, we identified CPH's catalytic activity. However, when conducting similar tests with bioluminescent mushrooms from the Atlantic forest, *Gerronema viridilucens* and *Mycena lucentipes*, we observed that oxyluciferin consumption resulted in another compound with a red-shifted absorbance spectrum by possible enzymatic reaction. Therefore, this study aims to present preliminary results on a potential second route of oxyluciferin consumption in addition to the known route for recycling bioluminescent systems, which may suggest a new role for this molecule.

Keywords: CPH, recycling system, fungal bioluminescence, new molecule

THEORETICAL MODELING AND COMPUTATIONAL METHODS FOR LUMINESCENCE PHENOMENA

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New Materials for Continuous Bright White Light Emission by Up-Conversion Excitation at Near-Infrared

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This presentation shall describe the preparation and characterization of new composite materials for continuous bright white light emission by excitation at near-infrared (NIR) via up-conversion guided by a theoretical model. This model was developed by the researchers at Recife, Brazil and Aveiro, Portugal is based on the power-balance equation, and it is capable of several predictions and quantitative relationships. It explains the brightness of the continuous white light emission as well as its dependence on the absorption cross-section and the conductivity of sample and of its environment. Based on these predictions, we developed a composite material of silica xerogel and lanthanide oxide nanoparticles. The silica xerogel was prepared by ageing and drying of a gel formed by mixing TEOS, resorcinol, and formaldehyde at pH 6, followed by 2h calcination at 1000 °C. The nanocomposite was prepared by embedding the silica xerogel into an aqueous solution of the lanthanide nitrate salt, followed by drying at 50 °C, thermal treatment at 300 °C for 30 min and at 800 °C for 4h. The lanthanide oxides used were PrO_2 and Tb_2O_3. Because the xerogel has a very low thermal conductivity, the brightness of the continuous white light emissions was higher than those of the pure nanopowder oxides, after considering the relative concentrations. These results were expected by the model, because in the case of the xerogel nanocomposite, the particles are heated radially and the emission occurs in 3-dimensions, whereas powdered samples emit mostly through the interface with air. This is corroborated by observing the formation of spherical particles (0.08-0.10 cm in diameter) at the spot of the laser. The relationship between the brightness of the emissions and the absorption cross-sections was also established by the integrated emission intensity and the absorbance of the sample at the laser wavelength excitation (980 nm). For PrO_2, this absorption was ascribed to the ligand-to-metal charge transfer (LMCT) states. Quantum chemical calculations were performed on a model of a $[Pr\text{-}O]^{2+}$ moiety embedded into point charges mimicking the nanoparticle (10 nm diameter). It was shown that as the $[Pr\text{-}O]^{2+}$ pair moves from the center to the surface of the nanoparticle, the wavelength associated with the LMCT state changes from visible to NIR, which explains the intense absorption at 980 nm. So, sunlight

might be a possible excitation source for generating continuous bright white light emission, which may improve solar cells.

Keywords: upconversion, white light, nanocomposite, power-balance

The light emitted by bioluminescent systems: what theoretical methods for modeling the emitted color?

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The emission of light in fireflies and other bioluminescent species stems from the electronic relaxation of oxyluciferin, an organic compound formed through the oxidation of the D-luciferin substrate within an enzyme known as luciferase. Bioluminescent systems find application in areas such as cancer cell detection. A key challenge in modeling such systems lies in accurately reproducing the absorption, fluorescence, and emission spectra observed either within the protein or in a solvent. These models offer valuable insights for better understanding experimental results and for the future design of novel bioluminescent systems.This overview will present the methodologies and modeling tools employed to investigate the spectroscopic properties of bioluminescent systems. Quantum mechanics, molecular dynamics, and hybrid (QM/MM) methods are essential for this endeavor. Accurate reproduction of experimental emission and absorption spectra is achieved when considering the system's dynamics. Modeling also provides information on transition nature and sheds light on the influence of the protein environment. The presentation will highlight challenges and future prospects in modeling bioluminescent systems, supplemented with relevant examples.

Keywords: Modeling, QM/MM, bioluminescence, emission spectra, Molecular dynamics,

Bioprospecting involved with bioluminescence enzyme of *Orfelia fultoni* from inverse virtual screening

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Bioluminescence, the process of emitting visible cold light by living organisms, is catalyzed by an enzyme generically called luciferase, acting together with a substrate known as luciferin. This biological phenomenon, which illuminates both marine abysses and terrestrial habitats, has captured scientific and public interest due to its features and its potential biotechnological applications. Despite its wide occurrence in nature, many aspects of bioluminescent systems remain unknown, particularly in certain families such as Keroplatidae (Diptera), in which the luciferase enzyme has not yet been identified. Within this family, the subfamily Keropatinae arouses special interest, presenting two recently discovered substrates that contribute to the bioluminescent process: riboflavin and 3-hydroxykynurenic acid (3-HOKA).The investigation of these biochemical components unveils fresh perspectives for grasping the variety of bioluminescence in the world. In an effort to shed light on the processes that underpin bioluminescence within the Keropatinae subfamily, we conducted a bioprospecting study employing the technique of inverse virtual screening (IVS).This method allowed the modeling of proteins expressed in the transcript of *Orfelia fultoni*, a member of this subfamily, followed by molecular docking with riboflavin and 3-HOKA. Through this approach, we identified 2,868 structures with strong interactions, culminating in the selection of 11 candidate proteins that may be intricately involved in the bioluminescent process of this species. Among the identified proteins, *NADPH-Cytochrome P450 Reductase* stands out for its reducing function and its strong binding energy with riboflavin, suggesting a crucial role in riboflavin reduction, which could sustain the light emission of these organisms, as observed in nature, for extended periods. Furthermore, the discovery of *hexamerin*-like enzymes and the exploration of their spatial configurations led us to identify two potential monomers. These monomers are candidates to form a trimeric structure that interacts efficiently with both riboflavin and 3-hydroxykynurenic acid, offering new perspectives on the molecular architecture of bioluminescence in *O. fultoni*. Therefore, we propose potential mechanisms involving these proteins in the generation of bioluminescent light in *O. fultoni*, emphasizing the importance of future in vitro investigations

to deepen our understanding of these biological processes. Despite the limitations associated with virtual screening, this study represents a significant advancement in understanding bioluminescence in Diptera, contributing to both evolutionary biology and the development of biotechnological applications.

Keywords: Bioprospecting, Inverse Virtual Screening, NADPH-Cytochrome P450 Reductase, Orfelia fultoni

Modeling of optical properties of impurity ions in solids

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The transition metal and rare earth ions with the unfilled 3d and 4f electron shells, respectively, are widely used in optical applications as active emitting ions in laser crystals and phosphors etc. The optical properties of such materials depend on interplay of electronic and structural properties of host compounds with electronic properties of impurities. In the present work an overview of spectroscopic properties of the 3d and 4f ions in a free state and in crystals will be given. Applications of several different approaches (e.g. crystal field theory, DFT-based computational techniques, configurational coordinate model etc) to various inorganic crystalline materials doped with these ions will be shown, with special emphasis on how to identify location of the impurity ions energy levels in the host band gap, calculate the splitting of the impurity ion's energy levels etc. Examples of relations between the structure of crystalline solids and emission properties of impurities will be discussed.

Keywords: First-principles calculations, Transition metal and rare earth ions, Electronic and optical properties

Shifting focus to brighter prospects: Unveiling vibronic coupling in the intersystem crossing dynamics of Eu^{3+} complexes

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The widespread application of photonic materials has spurred chemists to enhance their photophysical properties. In this sense, trivalent lanthanide ions (Ln^{3+}) coordinated with organic ligands feature unique luminescence due to $4f \leftrightarrow 4f$ transitions. Owing to their parity-forbidden nature, the primary sensitization mechanism hinges upon ligand-to-Ln^{3+} energy transfer (ET) from the singlet (S_1) and/or triplet (T_1) ligand's excited states, the latter being the most important for most of Ln^{3+}. Thus, efficient ET requires the T_1 state population, mediated by intersystem crossing (ISC) induced by the presence of Ln^{3+}. However, ISC predominantly occurs within the ligand counterpart and is intrinsically linked to the overlapping vibrational levels of the two excited states, a factor often overlooked in existing literature. Hence, this study aims to introduce a model for elucidating the vibronic coupling effect while rationalizing ISC rates in three Eu^{3+} complexes: $[Eu(tta)_3(H_2O)_2]$ (**1**), $[Eu(tta)_4]^-$ (**2**) and $[Eu(PyrCF_3)_3(phen)]$ (**3**). *tta* = 2-thenoyltrifluoroacetate, *phen* = 1,10-phenantroline, and *PyrCF₃* = (1-(1-methyl-1H-4-pyrazolyl)-4,4,4-trifluorobutane-1,3-dionate). The adopted strategy entails considering vibronic coupling in ISC through the path-integral (PI) approach. Subsequently, the nature of normal vibrations was identified by decomposing them into local vibrations. This methodology yielded ISC rates of 8.4×10^7, 1.3×10^8, and 4.2×10^{10} s^{-1} for complexes **1**, **2**, and **3**, respectively. Standard models such as the Marcus-Levich (ML) approach fail to explain the two-orders of magnitude difference between **1** and **3**. These values closely align with experimental measurements (2.6×10^7, 4.4×10^8, and 4.2×10^{10} s^{-1}, for **1**, **2**, and **3**, respectively) rather than ML predictions, which underestimated the rates by almost one order of magnitude. This outcome highlights the primary importance of vibronic coupling in ISC. In this context, for complexes **1** and **2**, the coupling stems from high-energy vibrations (above 3000 cm^{-1}), whereas for complex **3**, vibrations in the low-to-intermediate energy range (750 – 1400 cm^{-1}) dominate. This elegant

result implies that vibronic coupling could induce higher ISC rates and augment the T_1 population. However, the energies of these vibrations are crucial for emission dynamics, as high frequencies are associated with multiphonon relaxation, which diminishes the emission quantum yield. Localizing these vibrations within the molecule reveals that O−H and C−H fragments are primarily responsible for vibronic coupling in complexes **1** and **2**, respectively. Conversely, for complex **3**, the most important vibrations were delocalized across several molecular fragments, reducing the probability of multiphonon quenching. Thus, confining vibronic coupling to low-energy vibrations while dispersing them throughout the molecule enhances the ISC and mitigates the Eu^{3+} $^5D_0$ quenching. Combining both outcomes opens a pathway to reach faster ISC and tune the ET by tailoring the ligand scaffold of novel complexes.

Keywords: Lanthanides, Excited-State dynamics, Luminescence of complexes

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The importance of magnetic spectroscopy to understanding electronic structure of rare-earth ions in crystals and nanoparticles.

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The development of photonic technologies using rare-earth doped materials requires accurate modelling of electronic states. Many potential materials for quantum-information applications have low-symmetry sites, where measurements of electronic energy levels alone do not give enough information to obtain crystal-field fits. However, we have shown that measurements of magnetic splitting along several magnetic field directions provides the necessary information to obtain unique solutions. [1,2]. Nanocrystals doped with rare-earth (lanthanide) ions also have considerable potential for photonic technologies, from quantum computing to biomedical applications, including imaging, nano-thermometry, and photodynamic therapy. There has been recent interest in using magnetic fields to modulate energy transfer between lanthanide ions in nanocrystals to enhance these applications [4]. Making use of such magnetic field effects requires a better understanding of the magnetic splitting of rare-earth ions in nanocrystals. Though the particles are randomly oriented, we have recently shown that useful information may be obtained by Zeeman spectroscopy of rare-earth-doped nanoparticles [5] and this data provides a more accurate analysis of the electronic structure of the rare-earth ions in the nanoparticles than zero-field data. In this paper, we will discuss how magnetic splitting measurements can be used to provide the geometrical information essential to accurate crystal-field modelling in both bulk crystals and nanocrystals. We will discuss some outstanding issues and the potential for future improvements. References[1] S. P. Horvath, J. V. Rakonjac, Y.-H. Chen, J. J. Longdell, P. Goldner, J.-P. R. Wells, M. F. Reid, Phys. Rev. Lett. 123, 057401 (2019).[2] N. L. Jobbitt, J.-P. R. Wells, M. F. Reid, S. P. Horvath, P. Goldner, A. Ferrier, Phys. Rev. B 104, 155121 (2021)[3] Y. Alizadeh, J.-P. R. Wells, M. F. Reid, A. Ferrier, P. Goldner, J. Phys. Condensed Matter 35, 305502 (2023)[4] Y. Luo, Z. Chen, S. Wen, Q. Han, L. Fu, L. Yan, D. Jin, J.-C. G.Bünzli, G. Bao, Coordination Chemistry Reviews 469, 214653 (2022). [5] J. L. B. Martin, J.-P.R Wells, M.F. Reid, 15, 100181 Opt Mater. X. (2022).

Keywords: rare-earth, lanthanide, spectroscopy, magnetic, Zeeman