



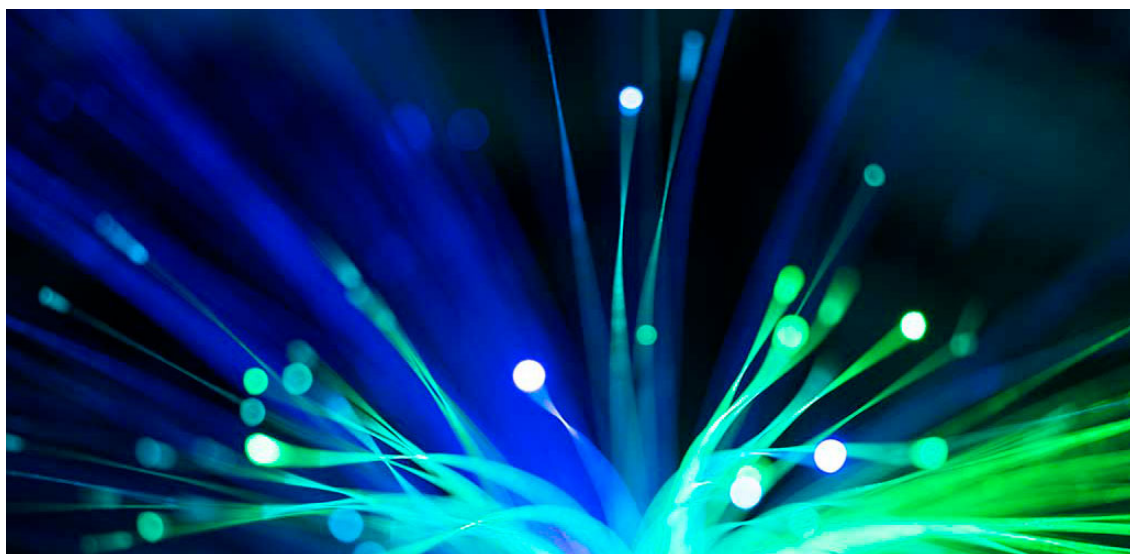
Supramolecular LUminescent Chemosensors for Environmental Security (LUCES)

COST ACTION CA22131

April 18-19, 2024

1st LUCES GLOBAL ACTION MEETING

Abano Terme (Padova) – IT



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INTRODUCTION

Dear LUCES members,

I am very happy to welcome all of you to the 1st Global Action Meeting (GAM) of our COST Action CA22131 - Supramolecular Luminescent Chemosensors for Environmental Security (LUCES).

As some of you know, arriving to this point was a long, sometimes disappointing, process that required a lot of effort, but we made it! Fortunately, along the way we have welcomed new colleagues, with scientific expertise very relevant to achieve our main goals.

I hope we can be all committed to this engaging project devoted to developing sensors, based on chemical inputs (mainly optical) for the detection of contaminants. Strengthening efforts and working together will make us a reference community worldwide on this topic.

I am so proud to have exceptional people directly supporting this project, in the Steering Committee and in the Core Group, working group co-leaders and also super relevant people ensuring the administrative and financial management, and others that can appear as invisible, but also supporting important tasks such as website maintenance.

I'm sure that all together, with the Management Committee members and all of you involved in the different Working Groups (extremely relevant for the running of the project) will make this Action a success.

I hope you all to enjoy this first GAM and take advantage of the opportunity to discover the scientific expertise that we have in our group and that will help us improve science and, in particular, applied research.

Laura Rodríguez
Action Chair

PROGRAM – 18 April 2024

09:00-09:30	Opening & Welcome words	
	<i>Chair: João Carlos Lima</i>	
09:30-10:30	Plenary Amilra P. de Silva (Queen's U. - UK): <i>From Supramolecular Chemistry to Medical Diagnostics and Information Processing</i>	p. 7
10:30-11:00	Coffee break	
	<i>Chair: Antonella Dalla Cort</i>	
11:00-11:20	C1 Luciano Boesel (EMPA - CH): <i>Nanostructured Luminescent and Colorimetric Sensors for pH, Ammonia, and Volatile Amines</i>	p. 8
11:20-11:40	C2 Wim Dehaen (KU Leuven - BE): <i>New boron chelated pyrrole-derived dyes : potential for fluorescent sensors ?</i>	p. 9
11:40-12:00	C3 M. Concepción Gimeno (U. Zaragoza - ES): <i>Exploring Luminescence in Group 11 Metal Complexes</i>	p. 10
	<i>Chair: Kari Rissanen</i>	
12:00-12:30	Flashes: Paula Bosch (P5), Estefania Delgado-Pinar (P8), Elizabeta Dimitrieska Stojkovikj (P9), Sabrina Knospe (P18), Nele Konrad (P19), George Mousdis (P21), Ignazio Roppolo (P27), Nikola Sakac (P28) & Mustafa Tabakci (P31)	
12:30-13:30	Lunch break	
13:30-15:00	Poster session	p. 28
	<i>Chair: Stefan Kubik</i>	
15:00-15:20	C4 Enrico Dalcanale (U. Parma - IT): <i>Ultra-sensitive Proteomics with Cavitands</i>	p. 11
15:20-15:40	C5 Ariadna Lazaro (Karlsruhe Institute of Technology - DE): <i>Novel on/off Hydrogel Functionalized with Cyclometallated Ir(III) Complexes for in Vitro Cell Imaging in 3D Platforms</i>	p. 12
15:40-16:00	C6 Gilles Bruylants (U. libre de Bruxelles - BE): <i>Colorimetric Sensing: a Golden Age of Silver</i>	p. 13
16:00-16:20	C7 Ivo Grabchev (Sofia U. - BG): <i>Metal Complexes of Modified Dendrimers with 1,8-Naphthalimide Luminophores and Their Sensor and Microbiological Activity</i>	p. 14
16:20-16:50	Coffee break	
	<i>Chair: Antonio Frontera</i>	
16:50-17:10	C8 Georgios Vougioukalakis (U. Athens - EL): <i>Synthesis of Tailor-Designed Photoactive Molecules for Possible LUCES-related Applications</i>	p. 15
17:10-17:30	C9 Andrea Pinto (Glasgow U. /Barcelona - ES): <i>Supramolecular Gold(I) Assemblies as Singlet Oxygen Sensitizers</i>	p. 16
17:30-17:50	C10 Demeter Tzeli (U. Athens - EL): <i>Accurate Computational Studies of Photophysical Processes of Chemosensors</i>	p. 17
17:50-18:10	C11 Riccardo Marin (U. A. Madrid - ES): <i>Pushing the Limits of Luminescence Nanosensing: From Material Optimization to Machine Learning</i>	p. 18
19:30	Dinner	

PROGRAM – 19 April 2024

Chair: Sophia Hayes

09:00-09:20	C12 Ivo Piantanida (Ruđer Bošković Institute - HR): <i>Trarylborane: Novel Type of Dye for Sensing Biomacromolecules</i>	p. 19
09:20-09:40	C13 Josef Hamacek (U. Orléans – FR): <i>Tetrahedral Lanthanide Cages as Sensors for Anion?</i>	p. 20
09:40-10:00	C14 Luca Sanfilippo (Systea S.p.A. - IT): <i>Luminescence Based Measurement Technologies Available for LUCES Project Applications</i>	p. 21
10:00-10:20	C15 Roberto Penasa (U. Padova - IT): <i>Chiroptical Enhancement of Chiral Dicarboxylic Acids from Confinement in a Stereodynamic Supramolecular Cage</i>	p. 22
10:20-10:40	C16 Romain Carpentier (U. libre de Bruxelles - BE): <i>Development of Supramolecular Calixarene-based Systems for the Slective Binding of Primary Ammoniums in aQueous Environment</i>	p. 23

10:40-11:10 Coffee break

Chair: Anife Ahmedova

11:10-11:30	C17 Aaron Torres Huerta (U. libre de Bruxelles - BE): <i>Liposomes as Nanoreactors for the Controlled Assembly of Metal-Organic Structures for Sensing Applications</i>	p. 24
11:30-11:50	C18 Ales Ruzicka (Charles University - CZ): <i>Oligocyclophosphazenes Substituted by Amines: Quest for Universal Sensors</i>	p. 25
11:50-12:10	C19 Riina Aav (Tallin U. of Technology - EE): <i>Homomeric and Chimeric Hemicucurbiturils</i>	p. 26
12:10-12:30	C20 Vladimir Sindelar (Masaryk U. - CZ): <i>Bambusurils: Macrocycles with High Anion Affinity</i>	p. 27

12:30-13:30 Lunch break

13:30-14:00 **WG4 meeting**

14:00-15:30 **Open discussion with industrial partners**

15:30-16:30 **WG1&2, WG3 parallel meetings**

16:30-17:00 Coffee break

17:00-17:50 **WG leaders reporting & Conclusions**

18:00-19:30 **MC meeting**

19:30 Dinner

ABSTRACTS

Plenary

From Supramolecular Chemistry to Medical Diagnostics and Information Processing

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One of the main principles underlying fluorescent sensors is based on photoinduced electron transfer (PET), according to which a switching 'on' of fluorescence in response to chemical¹ and biochemical^{2,3} analytes can be designed. Since its generalization in Colombo, Sri Lanka, it has now grown to involve >1200 laboratories around the world. Some of these sensor systems are serving in critical care units in hospitals and in ambulances, performing blood diagnostics (Figure 1). These form the basis of a half-billion-dollar industry⁴. Other sensors visualize intracellular players. Yet others map species distributions in nanometric spaces near membranes⁵. These spaces are too small for the tiniest silicon-based wireless devices to enter. Our introduction of molecular logic gates^{6,7} from Belfast, Northern Ireland, allows us to build more complex sensors and micro-object identification systems⁸. More complex logic operations⁹⁻¹¹ and even human-scale computations, e.g. edge detection of objects¹² and outline drawing (Figure 2)¹³, are now achieved by molecular systems. >1700 laboratories have contributed to this field so far. A short video is available at www.youtube.com/watch?v=sLGnZDP5Ecg.



Figure 1. Blood electrolyte analyser

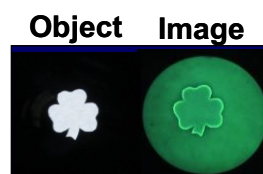


Figure 2. Molecular outline drawing

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Nanostructured luminescent and colorimetric sensors for pH, ammonia, and volatile amines

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The expertise of my group lies in the development of fluorescent sensing chemistry for the detection of analytes in liquid and gaseous environments; the use of ductile polymer optical fibers as substrates for physical, chemical, and biosensors; and the incorporation of chromophores (DASAs) into polymers (membranes, coatings, nanoparticles) to achieve sensors with potential in the environmental monitoring (VOCs, NH₃, ions, etc.). In this abstract, I will briefly cover three of our recent works in topics within the field of the COST Action LUCES.

i) We are working on a method to increase the response of fluorescent sensors by using nanoparticles. We developed a method for promoting the interaction of clay-fluorophores through dye conjugation with a biopolymer before the deposition on clay and defined the physical and chemical mechanisms that take place upon dye-clay interaction [1]. We observed, e.g., an up to 60-fold fluorescence enhancement [1,2]. Such an approach could also be potentially used in environmental sensors to detect contaminants.

ii) We have developed a unique polymer co-network platform suitable for the incorporation of a range of luminescent molecules. These are amphiphilic polymer co-networks (APCNs) with defined domain sizes in the nanoscale (5-20 nm) [3]. We prepared materials with fluorescent dyes and nanoparticles [4,5], pH- or light-responsive units [3]. These molecules are especially interesting for biomedical applications, as their pH response matches the changes occurring in pH during wound healing. We also investigated how the small size, opposite phylcities, and high surface area of the nano-domains could be used to steer the optical properties of fluorescent dyes. We incorporated hydrophilic and hydrophobic dyes in the corresponding domains and used the high interfacial area and close domain-domain distances to induce high energy transfer between dyes that are otherwise immiscible. FRET efficiencies of up to 75 % were observed, with a total energy transfer efficiency of about 99 %. [4,5]

iii) Moreover, my group has been investigating for years the development, properties, and applications of DASA-polymer conjugates.[6,7] We investigated the behavior of DASAs in such matrices and how the matrix properties influence the performance of DASAs. One potential application is as sensors with potential in environmental monitoring. We took advantage of the spontaneous reaction between furan adducts (FAs) and secondary amines and of the increased surface area of electrospun membranes to detect amines at very low concentrations. With an adequate choice of FA type, mesh morphology, and polymer physical properties, we could design sensors with a limit of detection of only 10 ppb for diethylamine. They could be used to detect volatile amines arising from food spoilage or ammonia from bacterial diseases. [8]

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New boron chelated pyrrole-derived dyes : potential for fluorescent sensors ?

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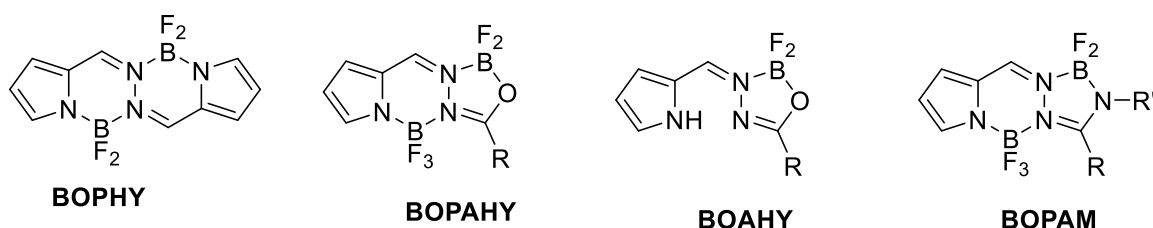
BODIPY is a well-known boron chelated dipyrromethane-derived fluorescent molecule. Many applications in sensing have been described [1] and the synthetic versatility is great due to the many possibilities for postfunctionalisation [2].

In the last years, we have described a number of alternative boron (bis)chelated structures that share some of the characteristics of the BODIPY dyes, such as the bischelated BOPHY, which are readily prepared from simple pyrrole-2-aldehyde building blocks [3]

More recently, we described BOPAHY and BOAHY chromophores available from the same aldehydes after bischelation or monochelation with difluoroboron. Some sensing behavior of BOAHY derivatives towards hypochlorite and applications in bioimaging of mitochondria were described [4].

The latest addition to the boron chelated pyrrole derivatives to be reported from our group was the BOPAM stem. Again, a straightforward one pot method allows to prepare BOPAM derivatives which can be postfunctionalized or modified to become NIR-dyes. [5]

These new dyes have a great but as yet unexplored potential to be used in fluorescent sensing, we will show the synthetic possibilities and look forward to any discussion about collaborations in the framework of this COST action.



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Exploring Luminescence in Group 11 Metal Complexes

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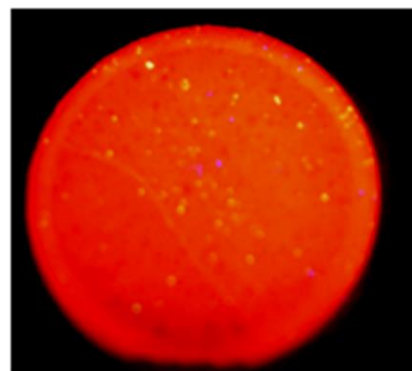
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In recent years, research into light-emitting materials has witnessed significant growth, emerging as a pivotal domain within transition metal chemistry. This surge in interest stems from the diverse applications of luminescent compounds in sensors, OLEDs, photocatalysis, medicine, and various other fields. Among these compounds, luminescent metal complexes stand out for their unique optical properties and remarkable sensitivity to environmental changes.

These complexes exhibit dynamic alterations in luminescence properties—such as intensity, wavelength, and lifetime—in response to shifts in pH, temperature, metal ions, gases, solvents, and biological molecules. Such changes act as discernible signals, rendering these complexes highly promising for sensor development across diverse applications.

The design of effective luminescent sensors hinges upon the meticulous selection of metal ions, ligands, and structural motifs that exhibit selective and responsive behavior towards target analytes or environmental factors. By fine-tuning the properties of metal complexes, researchers can engineer tailored responses to specific stimuli.

Our focus lies particularly on the synthesis of luminescent metal complexes featuring group 11 metals. The versatility inherent in altering the metal, oxidation state, and the myriad ligands with diverse donor centers capable of coordinating to metals across various oxidation states allows for precise tuning of emission energy. This tuning spans the entire visible spectrum, facilitating the customization of properties for application in sensing technologies.



ULTRA-SENSITIVE PROTEOMICS WITH CAVITANDS

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Chemical sensing represents one of the key enabling technologies which will deeply impact our society, because of its foremost relevance in point-of-care diagnostics,¹ environmental monitoring,² industrial quality control and security. The major hurdle to overcome for the full exploitation of chemical sensing is the lack of selectivity in the currently available technologies, which leads to an unacceptable frequency of false positive and false negative responses.³ The exploitation of molecular receptors as sensing materials is particularly attractive to address the selectivity issue. The progress made in designing synthetic receptors enables the modulation of the sensor selectivity towards different classes of compounds by mastering the weak interactions occurring between the sensing material and the analytes.⁴ In this presentation the following case will be discussed:

N-methylated amino acid sensing in histones: Based on our results in the specific detection of N-methylated amino acids in water,⁵ sarcosine (biomarker of aggressive forms of prostate cancer) in urine,⁶ designer drugs⁷ and DNA G-quadruplexes⁸ we studied tetraphosphonate cavitands as selective ligands for the detection of lysine methylation in histones.⁹ Histones have positively charged amino-terminal tails that are exposed on the outside of nucleosomes. These tails are subject to several post-translational covalent modifications, including methylation. Histone post-translational modifications (PTMs), as lysine methylation, are important for many cellular processes including transcription and DNA repair. The ability to reliably detect PTMs is crucial to understand epigenetic processes and the functions of histone PTMs in human diseases. The identification of PTMs across the proteome is currently performed via mass spectrometry (MS). MS requires an enrichment step generally performed using antibodies, but these have several limitations including high costs and batch-to-batch variability. A cost-effective, fast and efficient tool overcoming the current limitation is presented. It consists in ferromagnetic nanoparticles (FeNPs) functionalized with molecular receptors able to selectively enrich, after proteolytic digestion, peptides containing mono-methylated lysines for subsequent epigenetic MS analyses. The developed tool outperforms antibodies, in terms of number of recognized peptides and sensitivity.

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Novel on/off switch hydrogel functionalized with cyclometallated Ir(III) complexes for in vitro cell imaging in 3D platforms

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Three-dimensional (3D) cell culture has shown to better mimic cells natural environment and to allow cell proliferation in a more realistic manner, compared to two-dimensional substrates in which cells are cultured on traditional flat substrates and adapt to this synthetic 2D environment, often becoming flattened and showing a non-natural behaviour. Therefore, the direct visualization of living cells growing onto 3D platforms in real-time promises to be a powerful tool to reveal information for biomedical investigation. However, cell staining often requires tedious sample preparation and can induce alterations of the natural cell cycle. Thus, the incorporation of a luminescent probe for cells visualization within 3D hydrogels, which combines the advantages of emission detection and hydrogel for 3D in vitro cell proliferation, is highly desirable for opening new paths for in vitro imaging techniques.¹

Amongst the most studied emitters, cyclometallated Ir(III) complexes are very appealing as bio-imaging reagents for cellular visualization.² Besides their outstanding photophysical properties, they exhibit the possibility to easily tune the excited state energy over the whole visible electromagnetic spectrum, from the ultraviolet to the near infrared region by ligand modification.³ In addition, the complexes emit from a triplet excited state displaying a very long excited state lifetime, in the microsecond range. These characteristic results in increased sensitivity and possibility of implementation of time-gated techniques with elimination of short-lived fluorescence background (~ns), rendering cyclometallated Iridium(III) complexes optimal candidates as luminescent bio-probes.⁴

Herein, we introduce a novel hydrogel for in vitro cell study, with covalently incorporated cyclometallated Ir(III)-luminescent probes. An Iridium(III) complex was designed with a “off/on” emission response versus different environments. In particular, this turning on and off of the emission relies on the interaction of an Ir(III) complex, covalently anchored to the hydrogel, with the cells plasma membranes or with its position in the water phase. Such a change in the environment, from aqueous solution to lipid layer, causes the turn on of the emission of the iridium complex.

The mechanism for the off/on switching from water to the lipophilic environment of the cell's plasma membranes is studied in detail, demonstrating that this novel luminescent probe-incorporated scaffold is a very interesting 3D platform for in vitro real-time investigation of cells.

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Colorimetric Sensing: a Golden Age for Silver

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In the search for more effective colorimetric reporters than traditional gold nanoparticles, silver nanomaterials (AgNMs) are of particular interest due to their superior plasmonic properties.¹ Silver nanostructures could therefore lead to more sensitive sensing devices than their gold counterparts. However, their use has not been widely reported due to their poor chemical and colloidal stability in complex media or over time. Indeed, AgNMs are very sensitive to oxidation and their conjugation with biomolecules is difficult to achieve without significant particle loss or degradation. Their dispersion in biological media also remains a challenge.

We have recently reported a new nanoparticle functionalization strategy that exploits the remarkable properties of calix[4]arene-tetradiazonium salts.² It has been shown that thin layers of these molecular platforms can be strongly and irreversibly grafted to the NP surface via the reduction of their diazonium groups, leading to the formation of multiple covalent bonds (Fig 1, Top). Furthermore, it has been shown that the composition of mixed layers on NMs can be controlled,³ thus allowing to control the coupling density of different biomolecules on their surface.⁴ This strategy could be extended to the synthesis of silver - as silver nanoplates (Fig 1, Bottom) - and alloyed gold-silver nanostructures⁵ which show high colloidal and chemical stability despite the thinness of the organic layer. These Ag nanostructures could be functionalized with targeting ligands and used to detect biomarkers of interest (the Mdm2 oncoprotein, anti-SARS-CoV-2 antibodies, Troponin) using lateral flow or turbidimetric assays with improved LoDs compared to traditional gold nanoparticles.⁶ We believe that this strategy could pave the way for the development of many other biosensing systems based on AgNPs coated with a calixarene layer as robust and efficient colorimetric reporters.

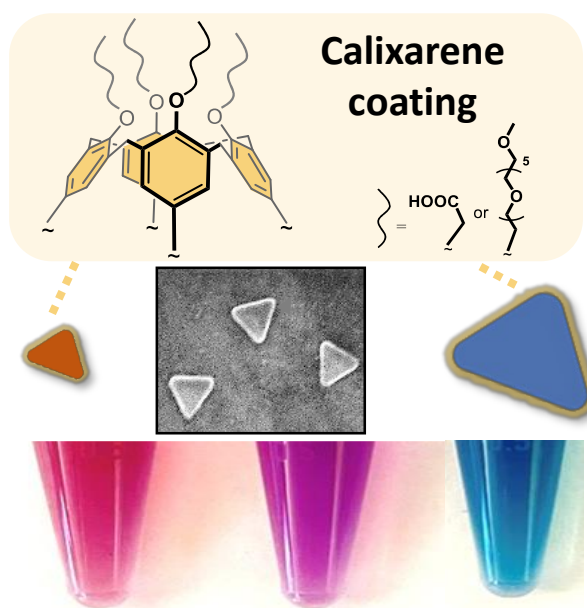


Fig 1. Top: Schematic representation of the calixarene coating of the nanostructures. Bottom: pictures of calixarene coated silver nanoplates of different sizes.

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Metal complexes of modified dendrimers with 1,8-naphthalimide luminophores and their sensor and microbiological activity

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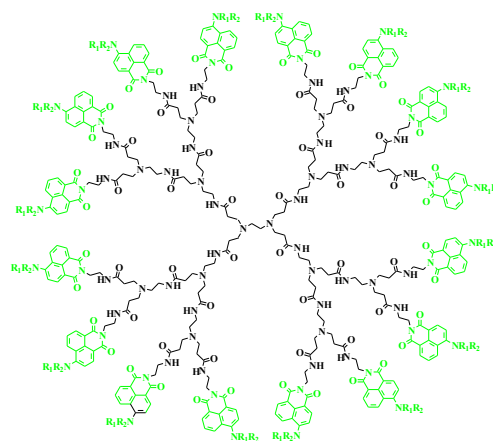
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Dendrimers are a particular class of synthetic polymer having a highly branched, three-dimensional structure and low polydispersity. They exhibit specific functionality due to their high number of functional groups in the dendrimer core or periphery. Low toxicity and structural advantages allow them to play an essential role in the new advanced scientific fields such as nanotechnology, pharmaceutical, and medicinal chemistry. Polyamidoamine (PAMAM) and polypropylene amine (PPA) dendrimers are the most investigated dendrimer structures due to their commercial availability and good possibility for structural modifications. Dendrimers containing chromophore fragments have been developed for their vanguard applications in different scientific fields such as medicine, biology, sensors, and optoelectronics.

Very promising organic fluorophores are 1,8-naphthalimide derivatives, emitting fluorescence with different colours and intensities depending on their molecule polarization. On the other hand, 1,8-naphthalimides are valuable compounds with diverse pharmacological and biological activity. Dendrimer modification with biologically active 1,8-naphthalimides opens possibilities for their diverse biomedical and sensing applications. Our laboratory has investigated PAMAM and PPA dendrimers modified in the periphery with 1,8-naphthalimide units.



Those modified fluorescent dendrimers have shown the potential of effective sensors for metal ions and protons detection. It has been found that the sensor activity depends strongly on the chemical structure of the substituents at the C-4 position of the naphthalene nucleus. Metal complexes with biologically vital metal ions such as Cu(II) and Zn(II) have been synthesized, and the microbiological and anticancer activity of the metallodendrimers have been described. The introduction of metal ions into such dendrimer systems has emerged as a promising research area since, in this case, the properties of the dendrimer matrix complement those of the metal complex.

This work describes the evolution of PAMAM and PPA dendrimers subjected to modification with 1,8-naphthalimides. Their photophysical characteristics, sensor ability, and microbiological activity have also been discussed.

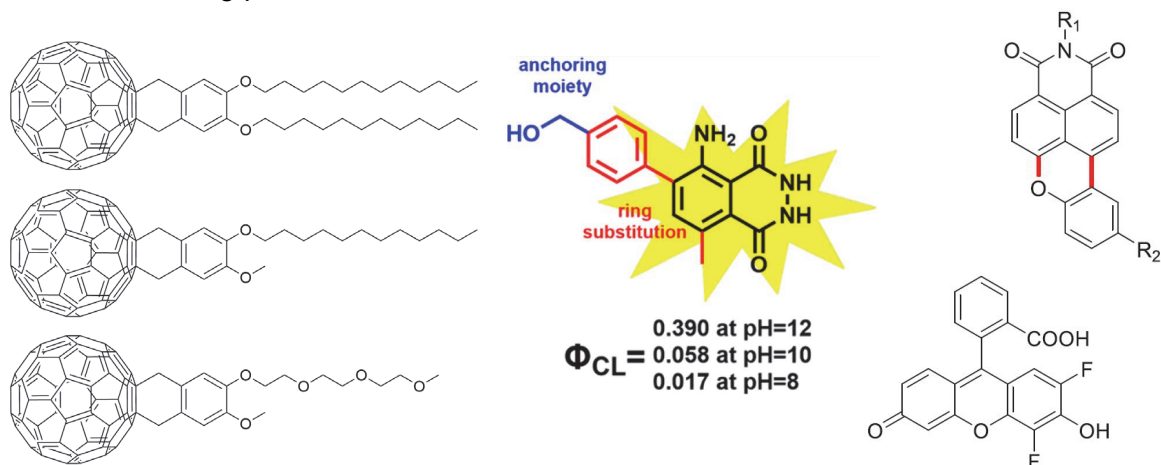
Acknowledgements: The authors acknowledge Grant КП-06-H49/2, Scientific Research Fund, Ministry of Education and Science of Bulgaria.

Synthesis of Tailor-Designed Photoactive Molecules for Possible LUCES-Related Applications

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After a brief introduction to our research group and wider research interests, some recently developed photoactive molecules of potential interest to the LUCES consortium will be presented, towards establishing possible collaborations.



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Supramolecular gold(I) assemblies as singlet oxygen sensitizers

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Population of the triplet state in chromophores is an important aspect that plays a key role in many numerous applications such as photodynamic therapy, bioimaging, photocatalysis, light-emitting diodes (OLEDs) and oxygen sensing among others. In particular, singlet oxygen production stays at the forefront of research due to its reactivity as a synthetic reagent, as an intermediate in oxygenation reactions of polymers or as a reactive oxygen species (ROS) for biological purposes. Molecules acting as photosensitizers must have a populated triplet excited state higher in energy but close to the lower excited state of the oxygen, 1O_2 . Thus, molecules with populated triplet excited states are of great relevance in this field and this can be managed by the presence of heavy atoms. Metal complexes containing heavy atoms, such as gold(I) complexes, are scarcely explored in this field and deserve their investigation.[1]

On the other hand, supramolecular chemistry and thus, intermolecular contacts, are of great importance in these studies. This is particularly relevant in gold(I) complexes due to the possibility of establishing $Au \cdots Au$ contacts that may increase the intermolecular contacts and that also play a key role in the population of the triplet state and photophysical properties.[2,3]

In this way, we have explored the photophysical properties of a series of gold(I) complexes and its capability to produce singlet oxygen in different media (e.g. solution, thin films and microspheres). [4]

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Accurate Computational Studies of photophysical processes of Chemosensors

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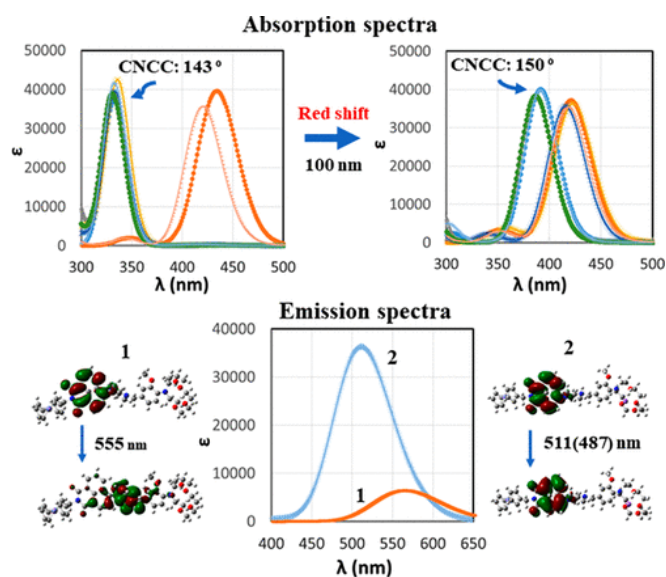
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The development of stand-alone luminescence-based chemosensors which exemplify selectivity, sensitivity, and applicability is hot research area¹. Up to now supramolecular luminescent sensors have solved significant problems in a variety of research areas, for instance in food and agricultural safety,² in biological imaging,³ medical diagnostics,⁴ national security,⁵ and environment⁶.

Theoretically, the accurate calculation of the electronic structure, absorption, and fluorescence spectra of luminescence-based chemosensors candidate and the prediction of the most promising ones is not a routine task.

In this presentation, the photophysical properties of chemosensors of Ca²⁺, Na⁺, Hg²⁺, Zn²⁺, and Sn²⁺ will be discussed and analyzed. Some of these sensors also can serve as molecular logic gates.⁷⁻⁹ Additionally, key factors for the accurate prediction of the absorption and fluorescence spectra of chemosensors will be analyzed.⁸⁻¹⁰ Finally, structural characteristics of molecules that can make them ideal molecules as sensors will be discussed.⁹⁻¹⁰



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Pushing the limits of luminescence nanosensing: From material optimization to machine learning

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In *nanoBIG*, we develop solutions based on luminescent nanomaterials for imaging and sensing purposes to push the boundaries of nanotechnology applied to the biomedical field. It is specifically in the field of nanothermometry where we have put most of our efforts over the past years^{1,2} – albeit currently we are also exploring the use of luminescent nanoparticles to sense mechanical pressure.³ Our workhorses are lanthanide-doped nanoparticles⁴ and semiconductor nanocrystals,⁵ whose optical properties we tailor for maximum performance in terms of brightness, biocompatibility, and response to physical cues of interest. This is what we refer to as *upstream action*, whereby we design luminescent nanosensors leveraging our longstanding experience in the use of nanoparticles in *in vivo* animal models.⁶ As of late, we have realized the need to introduce a complementary *downstream action*, which entails the use of advanced algorithms to analyze the calibration datasets – i.e., the sets of emission spectra or luminescence decay curves collected while varying the parameter of interest. Via this approach, we were able to overcome longstanding issues that affect luminescence nanosensing, like reduced readout precision in situations of low signal level and simultaneous sensitivity towards multiple parameters.^{7,8}

In this talk, I will provide a bird-eye view of the recent advancements we were able to achieve in the field of luminescence nanosensing through *upstream* and *downstream* actions. Examples of control of the nanosensor composition, architecture, and surface chemistry will be presented both in the case of lanthanide-doped nanoparticles and semiconductor nanocrystals. On the other hand, I will showcase some of our most recent successes in the implementation of machine learning algorithms to push the boundaries of luminescence nanosensing. Future directions of the research in this complex and rewarding field will be discussed.

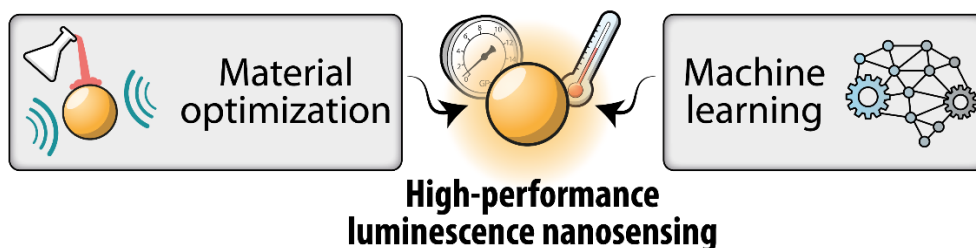


Figure. Representation of the *upstream* and *downstream* actions of material optimization and advanced data analysis to improve the performance of luminescence nanosensing.

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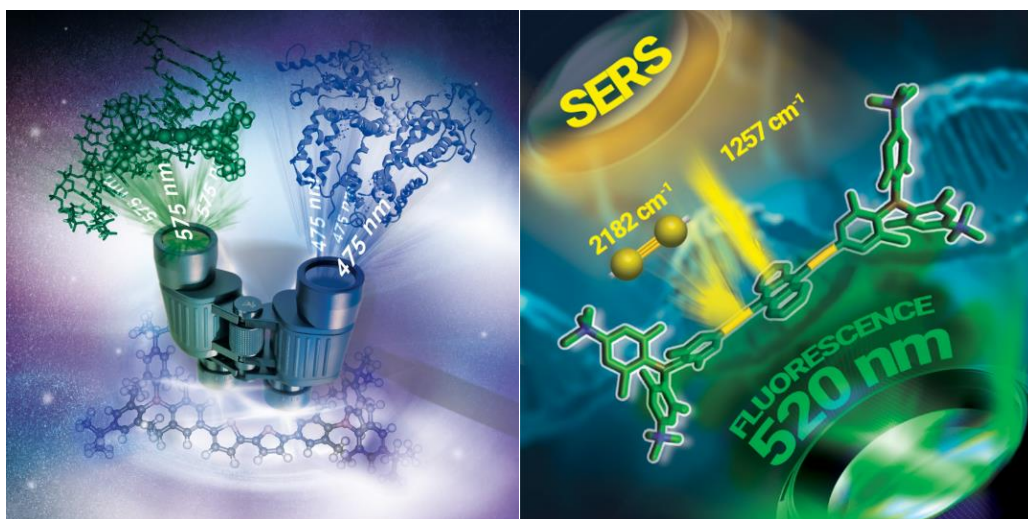
TRIARYLBORANE: NOVEL TYPE OF DYE FOR SENSING BIOMACROMOLECULES

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Low molecular weight fluorescent probes are frequently used tools in most molecular biology or biochemistry experiments today.¹ Due to problems related to covalent attachment of dye to biomolecule, non-covalently binding molecular probes that readily recognize and distinguish between different types of biomolecules are of huge interest.² However, the small size of a molecule presents a significant challenge in the design of selective probes, particularly in well-explored fluorophore families. Thus, development of a novel structural motif represents a valuable contribution. Here we report the development of a novel family of dyes based on the triarylborane system, which showed remarkable features in the interaction with biomacromolecules (Scheme 1., DNA, RNA, proteins).



Scheme 1. Some applications of triarylborane dyes: LEFT: fluorescent response differing between DNA and protein,³ or RIGHT: dual sensing of DNA or protein by fluorescence and SERS.⁴

Namely systematic structural variation (mostly linkers between two triarylborane units) revealed high tunability of a system in respect to emission response and Raman (SERS) response, also promising photo-bioactivity and intriguing DNA, RNA or enzyme-staining properties.

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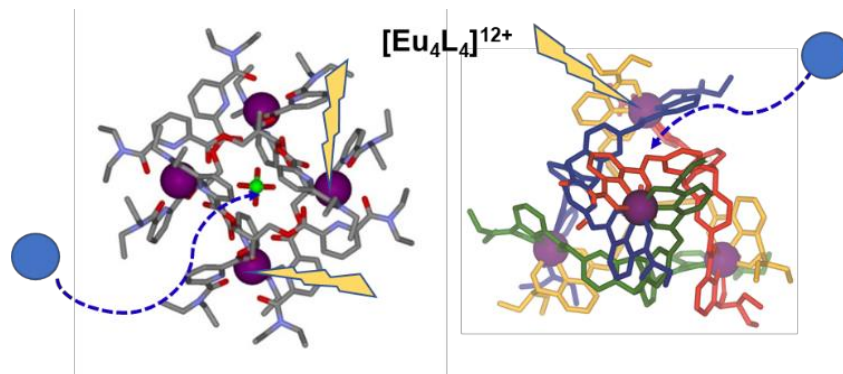
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Tetrahedral Lanthanide Cages as Sensors for Anions?

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A successful building of supramolecular receptors for sensing purposes requires a good stereochemical and thermodynamic control of the self-assembly process between ligands and metal ions. Simultaneously, this scaffold should provide (i) well-defined recognition sites for analytes, and (ii) a readable signal reporting on the quantity of bound analyte, which is globally a complex task. In this contribution, we present a sensing strategy exploiting the use of tetranuclear tetrahedral assemblies containing lanthanide cations Ln(III). Interestingly, these complexes form cationic cages,^{1,2} which may accommodate neutral and negatively charged guests. Moreover, the specificity of recognition can be tuned with the cage size, i.e., by changing the linker length in ligands. How can we detect binding events? It can be quantitatively determined with NMR, for instance, but also by measuring Ln(III) luminescence modulated by the interactions of the edifices with guests. Several tetranuclear Ln(III) cages were previously characterized due to a combination of structural and physico-chemical techniques. The self-assembly of our tripodal ligands with Ln(III) is “templated” with perchlorate anions inside cage.³ The exchange kinetics with several anions of interest will be thus shown and discussed. Promising applications of these “cage” sensors will be presented.



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**Luminescence based measurement technologies
available for LUCES project applications**

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The safeguard of the environmental quality and hygiene of water bodies involves the integration of chemical and biological monitoring tools. A new line of discrete analyzers for fully automated toxicity measurements based on luminescent bacteria was developed by Systea in the last decade for on-line, laboratory and in situ application. The Easychem® TOX Early Warning is a random-access on-line analyzer managed via dedicated software, with a refrigerated reagent plate and a luminometer integrated on a 80-position thermostated cuvette rotor and an automated washing station. Two analytical procedures, based on lyophilized bacteria, were designed and tested to comply with ISO 11348-3¹, using *Allivibrio fischeri*, and GB/T 15441-1995², using a proprietary *Photobacterium phosphoreum* strain. Long term unattended use is allowed by the fact that toxicity can be measured on-line by using automatically or manually incubated *A. fischeri* which is able to preserve a measurable bioluminescence signal and an unaltered sensitivity to reference compounds for more than two weeks. Instead, unprecedented analytical throughput allowing for 15 measurements per hour (one sample every 4 minutes), each including blank and sample runs, is achieved using the fast-reacting *Photobacterium phosphoreum*. Both instrument models allowed for low-cost through-put for toxicological assays and offered the possibility to run at any time quality control cycles in association with sample analysis, avoiding false positives and false negatives. Analytical results were highly repeatable and reproducible, as percentage deviations of blank and sample replicates were mostly calculated to be lower than 3 %³. Automated luminescent toxicity analysis was demonstrated to be truly applicable for offline and online measurements. The Easychem® TOX Lab is a robotic system based on the same automation concepts but adapted for benchtop analysis by introducing 64 refrigerated positions for sample analysis fully replicating the regulated manual standard assay. Additionally, Micromac SmarTox is a portable device for rapid field detection.

The use of ATP to rapidly detect live microorganisms and indicate locations of microbial proliferation can prevent both infrastructural, ecological and health damage depending on the scope of use. Because the ATP test is so rapid, providing almost instant results, it is ideal for prevention purposes. It is useful in the following areas: evaluation of the ecological quality of sea water, determination of microalgae and plankton in sea water, desalination and sterilization systems for sea water, ballast water treatment systems in ships, microbiological analysis of drinking water, wastewater purification, including hospital wastewater, and quality control of purified water. In addition, it has recently been demonstrated that the variation of the ATP content of a given inoculum in the presence of toxic substances might be used as an alternative/supplementary acute toxicity test to the analysis of bacterial luminescence. The ATP method is particularly suitable for this type of analysis precisely because ATP, being a measure of living biomass, is an excellent indicator of toxicity. Recent studies conducted on sewage sludge and water purification techniques have confirmed this potential. In summary, Systea started this year a new research project funded by Lazio regional Government which aims to develop a new line of online, laboratory and portable analyzers capable of determining the total microbial load through measurement of ATP and acute toxicity through reduction of ATP activity.

Our scope is to verify within the LUCES project the possibilities of automation of new innovative methods for water analysis, to satisfy the current market demand of control of emergent pollutants under the frame of EC regulation.

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Chiroptical Enhancement of Chiral Dicarboxylic Acids from Confinement in a Stereodynamic Supramolecular Cage

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The fundamental implications that chirality has in science and technology require continuous efforts for the development of fast, economic and reliable quantitative methods for enantiopurity assessment. [1] Among the different analytical approaches, chiroptical techniques in combination with supramolecular methodologies have shown promising results in terms of both costs and time analysis. [2,3] Within this work, a tris(2-pyridylmethyl)amines (TPMA) – based supramolecular cage is able to amplify the Circular Dichroism (CD) signal of a series of chiral dicarboxylic acids also in the presence of a complex mixture (Figure 1). [4] This feature has been used to quantify tartaric acid in wines and to discriminate different matrixes using Principal Component Analysis (PCA) of the raw CD data. Finally, a TD-DFT computational investigation have been carried out to clarify the origin of the dichroic signal of the cage induced by the chiral guests.

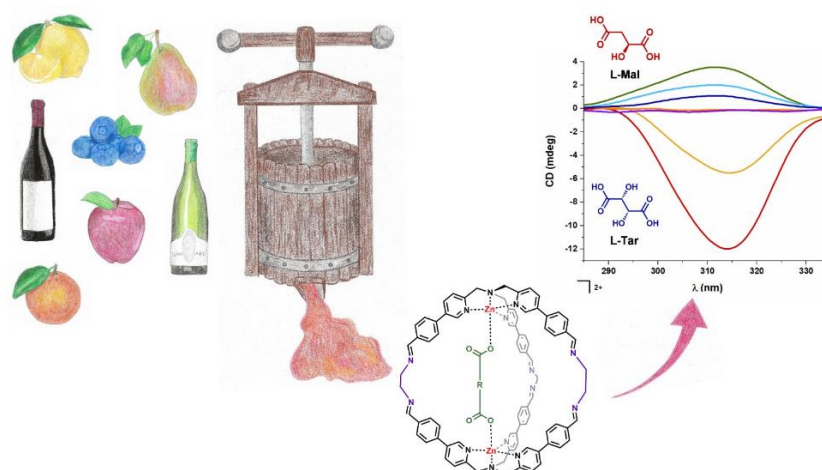


Figure 1. Chiroptical output of the chiral dicarboxylic acids confined within the TPMA-based supramolecular cage.

Acknowledgements

Dedicated to Prof. Ottorino De Lucchi in occasion of his 70th birthday. Department of Chemical Sciences. University of Padova is acknowledged for funding (P-DiSC#10 BIRD2020-UNIPD) and for computational resources (LICC).

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Development of supramolecular calixarenes-based systems for the selective binding of primary ammoniums in an aqueous environment

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There is a strong interest in the selective detection of ammonium ions in aqueous environments as several are known pollutants (i.e. aromatic amines) or biomarkers (i.e. spermidine).^{1,2} The recognition and complexation of charged species in aqueous media is however particularly challenging due to the competitive nature of water.³

An appealing strategy for the design of ammonium ion receptors consists in using calixarene-based systems, which provide ethereal oxygen atoms and a π -electron-rich pocket that can participate in the binding of the guest through H-bonds, cation- π and CH- π interactions while ensuring size and shape cavity-based selectivity.⁴ Homooxacalix[3]arenes and calix[5]arenes have been widely studied in organic solvents for their selective binding of primary ammoniums.^{5,6} They can furthermore easily be functionalized on their upper and lower rims with hydro-solubilizing groups.

We present here our recent work on the selective complexation of primary ammonium ions in an aqueous environment by homooxacalix[3]arene **1** and calix[5]arene **2**. Both receptors can be directly solubilized in water, following the deprotonation of their carboxylic acid groups but exhibit different complexation properties as only receptor **2** binds primary ammoniums. However, when incorporated in DPC micelles, binding of primary ammoniums is observed with both systems.

Through extensive ¹H NMR (DOSY, PRE) and molecular modeling studies, we have been able to unravel the role of the microenvironment on the recognition properties.

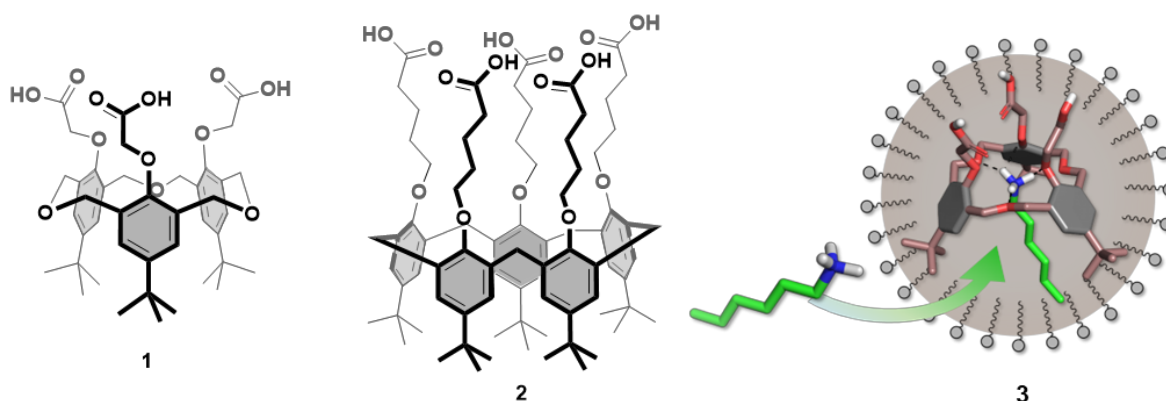


Figure 1. Homooxacalix[3]arene **1**, calix[5]arene **2** and schematic representation of the recognition of primary ammonium in micelles.

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Liposomes as Nanoreactor for the Controlled Assembly of Metal-Organic structures for Sensing Applications

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MOFs are extended networks of metal ions or clusters connected with organic linkers. MOFs are used in many applications, such as gas storage, catalysis, bioimaging, optics, sensing, etc.¹ Lanthanides-based MOFs are particularly attractive materials due to their optical properties, which include pure colour emission, narrow bandwidth signal, and various lifetimes.² However, current challenges rely on the fabrication of nano-MOFs (NMOFs) with monodisperse particle sizes in aqueous solutions, which is crucial for bioimaging and sensing applications.³

To address these issues, we have developed an innovative approach that involves the pre-encapsulation of metal ions inside liposomes and the controlled transport of carboxylate anions through the phospholipid membrane using an anion carrier.

Our current results showed the successful formation of Tb-BDC@Liposome materials, where the formation kinetics of the NMOFs was modulated by varying the transporter concentration. These materials have been characterized by luminescence spectroscopy (Figure 1b), corroborating the coordination between the Ln³⁺ and the organic linker. In addition, DLS measurement showed that composites have a narrow particle size distribution and long-term colloidal stability. Finally, Tb-BDC@Liposome materials were tested for their ability to sense various inorganic salts, organic anions and nitroaromatic compounds.

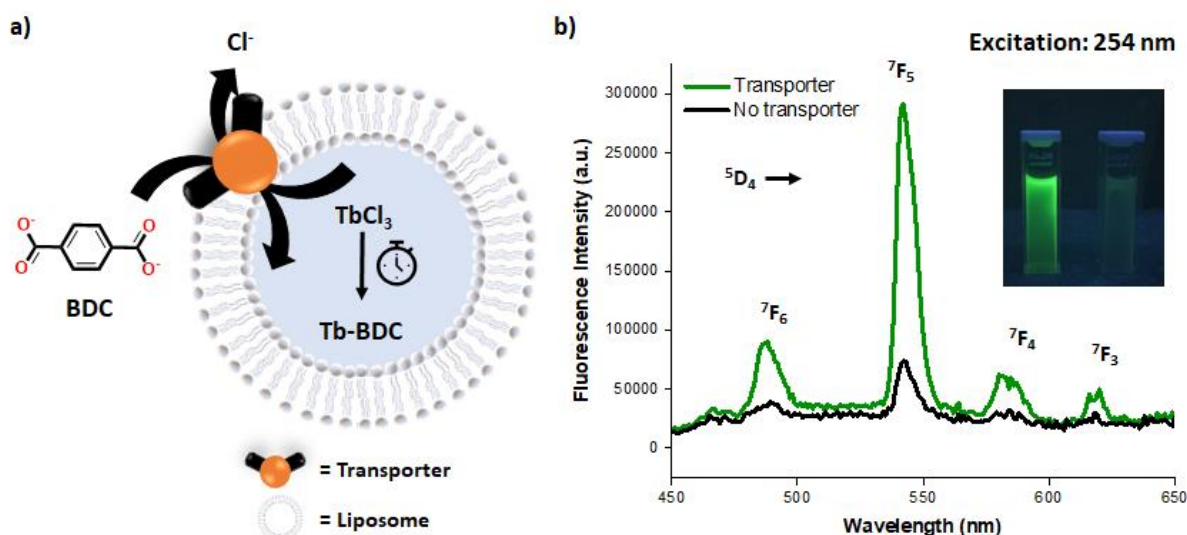


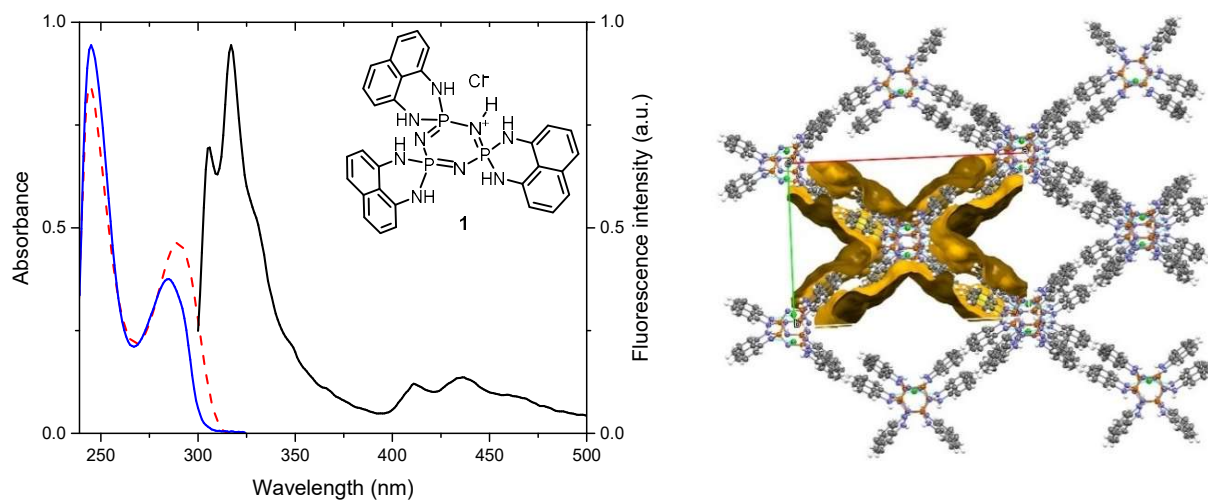
Figure 1: a) Schematic representation for the assembly of Terbium-BDC inside liposomes using a molecular transporter. b) Emission spectra ($\lambda_{\text{ex}} = 254 \text{ nm}$) of Tb-BDC@Liposome solution.

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Oligocyclophosphazenes Substituted by Amines; Quest for Universal Sensors

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Phosphazene derivatives have found applications in various fields due to their interesting properties from flame retardants to medicine or optoelectronics. Phosphazenes substituted by one or more amino functions are geometrically rigid and have the possibility of interaction with protonating agents or metal ions. We have already succeeded in partially verifying this assumption by preparing and studying the structure of tris[(1,8-diamino)naphthyl]cyclotri-phosphazene hydrochloride (Fig. 1 - right). The hydrogen atom in this compound quaternizes the imine nitrogen of the ring and forms tubular structures. An interesting feature is that the phosphazene columns interact only through hydrogen bonds and thus create a porous material with solvent cavities of approximately 12 x 16 Å occupying 52% of the crystal volume. In our opinion, this type of substance is suitable for the adsorption of gases and small molecules as well as HOF, COF and MOF materials. In addition, these materials exhibit interesting fluorescence (Fig. 1 - left) properties, and as such could be used as multi-stimuli responsive sensors.



Homomeric and Chimeric Hemicucurbiturils

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We have demonstrated approaches for the synthesis of chiral homomeric cyclohexanohemicucurbit[n]urils ($n = 6, 8, 12$) in solution or via mechanochemical agitation in the solid state.¹⁻⁴ The supramolecular properties of hemicucurbiturils (HCs) are appealing, as they can bind both anions and organic compounds^{5,6}. Additionally, functionalization of HCs can be easily achieved either through the incorporation of biotin monomers⁷ or by derivatizing already formed macrocycles.⁸ We have utilized chiral hemicucurbituril complexes with Zn-porphyrins to prepare an enantioselective electronic nose sensor⁹ and are currently exploring the properties of chiral materials derived from HCs. This presentation will focus on the binding of organic guests and the spectroscopic properties of chiral hemicucurbiturils synthesized in our laboratory.

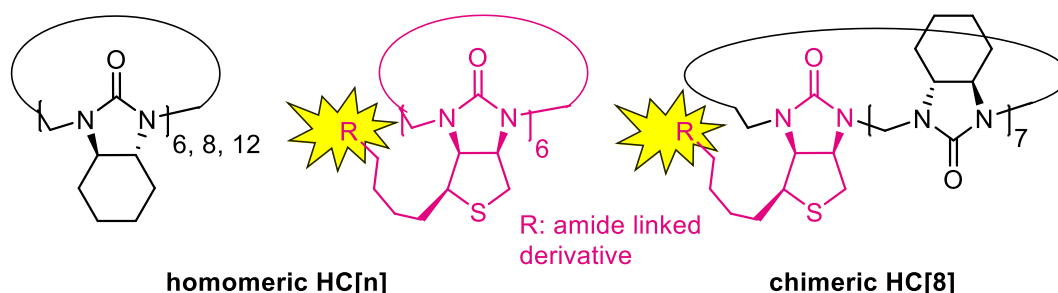


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Bambusurils: macrocycles with high anion affinity

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Bambusuril macrocycles are characterized by an electron-deficient cavity, which is formed by six glycoluril units connected by six methylene bridges (Figure 1).¹ Bambusurils can form very stable complexes with inorganic anions of different sizes starting from small F^- and ending with large SbF_6^- not only in organic solvents but also in water.^{2,3} In this presentation, we want to briefly introduce the supramolecular properties of bambusurils. We will present approaches leading to modification of the bambusuril structure in order to modulate their binding affinity and selectivity. We will mention development of enantiomerically pure bambusurils and show their discrimination for chiral organic carboxylates. We will also summarize examples of bambusuril-based systems for sensing and extraction of anions including toxic perchlorate. The main purpose of this presentation is to attract the attention of possible collaborators to develop optical sensing devices based on bambusurils for the detection of inorganic anions in aqueous media.

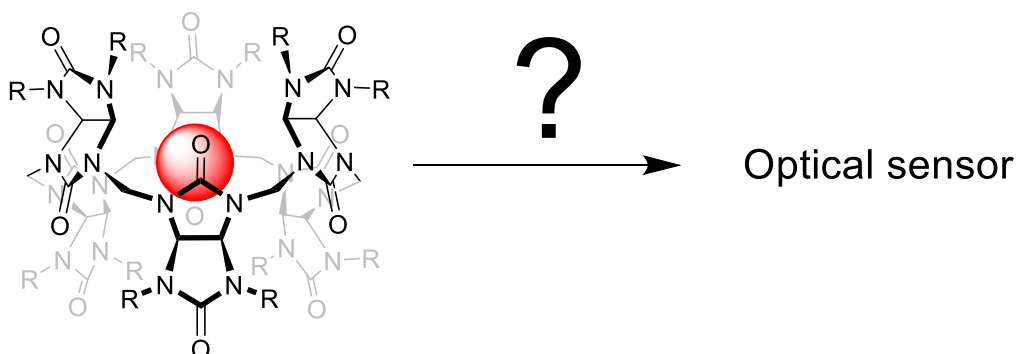


Figure 1. General structure of bambusurils with an anion bound inside their cavity.

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Fluorescent metal complexes and metallosupramolecules with application in cancer therapy or imaging

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In this poster will be presented three recent topics that the group from Faculty of Chemistry and Pharmacy of Sofia University in Bulgaria is working on, in collaboration with the relevant experts, as showcases for the areas of our expertise and instrumental availability.

The biomedical use of metallosupramolecular systems has been our topic of interest for some years as they are becoming increasingly popular for cancer chemotherapy [1]. Jointly with synthetic chemists from Tokyo-Tech, we have discovered that their M₂L₄ capsules (with M= Pd(II) or Pt(II)) exert very high cytotoxicity against human cancer cells (HL-60, SKW-3, HT-29, and T-24) [2]. The trends in the anticancer activity of the capsules and their host-guest complexes correlate very well with their stability in presence of glutathione, which was estimated by NMR-based kinetic experiments. The disassembly-triggered fluorescence was used for imaging the treated cancer cells along with ICP-MS estimation of the Pt uptake. Our results suggested the glutathione-triggered disassembly of the capsular structures as a potential activation pathway for the observed cytotoxicity [3].

We further used the studied host-guest phenomenon to design new pyrene containing guest molecules with intrinsic anticancer activity. Mono- and di-substituted pyrene-butyrate complexes of Pt(IV) showed anticancer activity in the nanomolar concentration range that we attempted to correlate with the structural and reactivity characteristics of the complexes [4]. Similarly, complexes' reactivity in presence of biological reductors was followed by ¹H- and ¹⁹⁵Pt NMR and the Pt uptake was estimated by ICP-MS measurements of treated cancer cells.

Based on our earlier survey on Copper chelators to be implemented as radiopharmaceuticals for theranostic purposes [5] we ended up with the synthesis of the sarcophagine bicyclic chelator, which recently was introduced in the design of fluorescent sensors [6]. Despite the poor sensing potential of the particular sarcophagine-linked fluorescent system, this excellent bicyclic chelator for various metal ions is available for synthetic modifications with numerous potential areas of application.

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Tailoring thermally activated delayed fluorescence (TADF) emitters towards efficient electrochemiluminescence in aqueous media.

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A family of thermally activated delayed fluorescence luminophores has been synthesized and characterized. Their electrochemical and photophysical properties were investigated as was their application in ECL. We have shown that ECL performance is mainly related to the electrochemical reversibility of the redox processes rather than to their photophysical properties in terms of photoluminescence quantum yield and excited-state lifetimes. Some compounds showed extremely high efficiencies in ECL, surpassing the Ru(bpy)₃ standard with a record value of 28x when using benzoyl peroxide co-reactant (reductive-oxidation mechanism) and 38x under co-reactant-free conditions, we have also shown that the latest efficiency strongly depends not only on the applied potential in term of absolute number, but also on the order of the applied potentials. Furthermore, the imidazole group present in the structure can be conveniently alkylated allowing the insertion of (bio)conjugable groups, such as carboxylic acids, thus making them suitable for practical applications. Increasing the acceptor strength anodically shifts the reduction potential allowing ECL in the presence of TPA as coreactant (oxidative reduction mechanism) reaching an efficiency almost double respect the standard Ru(bpy)₃. By inserting sulfonate groups in the scaffold, it is possible to obtain water soluble emitters enabling ECL in aqueous media.

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A methodology to assess contaminants released from waste collection centers

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The different categories of waste delivered to waste collection centers are collected into containers according to the material type, waiting for the subsequent recovery or disposal steps. One of the main critical issues relating to the storage phase, concerns the potential release of contaminants from the containers in which they are stored. In fact, the storage method for non-hazardous waste does not require watertight containers that, when placed outdoor, are subject to various atmospheric phenomena, including rain (Fig. 1). Rainwater could potentially produce leachate from the deposited waste that will consequently accumulate in various receptor bodies (i.e. surface waters, sewage systems, soils), specific for each eco-center. These runoffs, before being discharged into the eco-center's receiving body, are conveyed via drains towards an oil separator for the removal of sludge, oil and fat, and then they are disposed as wastewater according to Directive 2008/98/EC. However, these measures allowed to manage only specific classes of substances potentially released from the stored waste, while others could be discharged into the environment. In this context, this work aims at identifying the most critical types of waste by investigating hazardous substances potentially released by them (e.g., metals, surfactants), to improve the sustainable management of the investigated eco-centers, and the quality of the water leaving the plants. Emerging pollutants will also be considered.

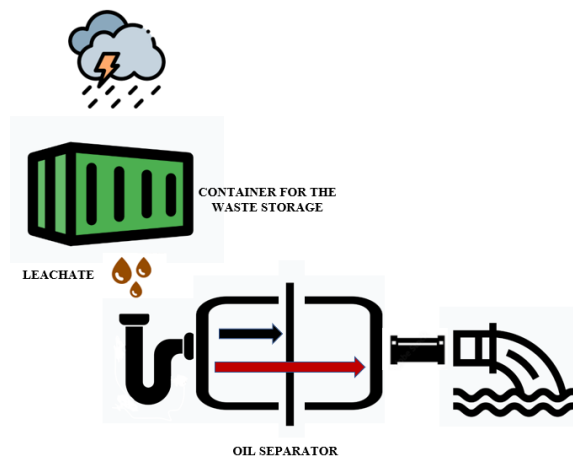


Figure 1 Schematic representation of the pollutant leaching process

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Directive 2008/98/EC European Parliament and of the Council (2008) Directive 2008/98/EC

V-catalytic aerobic C-C bond cleavage of 1,2-diols: photoactivated process and preliminary mechanistic studies

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The predicted shortage of fossil resources leads to the search for a “greener” and renewable alternative to produce high-value chemicals. The valorisation of waste biomass, in particular lignin, is proposed as a valid solution for replacing current non-renewable sources. However, the complex and irregular structure of this biopolymer poses a challenge for obtaining target aromatic organic molecules. In recent years, a series of catalytic methods of lignin degradation have been developed, but always without reaching high levels of selectivity. Among these, some of the most relevant are photocatalysis and the use of complexes with transition metals.¹ Licini’s research group has recently developed a new vanadium-based aerobic catalytic system for the oxidative cleavage of 1,2-diols (simple lignin models) working in organic² and micellar systems,³ yielding the corresponding carbonyl derivatives with high Tons (up to 81,000) and Tofs (up to 4100 h⁻¹).

In this communication we report preliminary results obtained in the photo-induced aerobic C-C-bond cleavage of 1,2-diols using a vanadium aminotriphenolate complex as catalyst (Figure 1). The influence of different reaction parameters (ligands, temperature, solvent, wavelength, substrate) on the reaction course will be described as well as preliminary results on the photoactivated oxidative mechanism of the reaction, supported by experimental and computational studies.

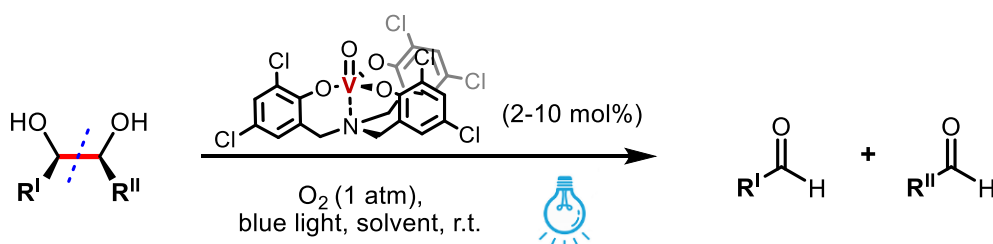


Figure 1. Photoinduced C-C bond oxidative cleavage of 1,2-diols catalyzed by V(V) aminotriphenolates

Acknowledgements

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A Facile, Green and Versatile Microwave-Assisted Strategy for Surface Functionalization with Environmentally-Sensitive Probes

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In this work, microwave-assisted functionalization reactions are presented as facile, green, rapid and versatile strategy to functionalize polymeric surfaces with different environmentally-sensitive probes. The method is presented as to show the possible variations in terms of: type of materials, type of probes and type of device shape/architectures.

The approach involves the inclusion of different reactive functional groups in the material as the substrate for further modification steps. Acrylic polymer surfaces are obtained by photopolymerization reaction with tunable functional groups, depending on the composition of the formulation. Post-polymerization functionalization reaction with a variety of organic molecules is conducted in a two-step procedure, exploiting the presence of these remaining functional groups on the surface. Other already preexistent polymeric surfaces can be also functionalized slightly modifying the first step of the procedure.

Microwave-assisted reactions, are classified as green technologies because they minimize energy consumption and reaction times, they avoid the use of solvents (or they use ecofriendly solvents, such as water or ethanol) and they eliminate purification steps. As a consequence of all of this, secondary product formation is minimized, so yields are considerably increased.

In this work, a description of the general approach for functionalization of different polymeric surfaces is detailed, as well as the characterization techniques employed. Examples for the preparation of a microfluidic device bearing two different fluorescent probes, functional coatings and prefilters for air-conditioning equipments are described in detail (Figure 1).

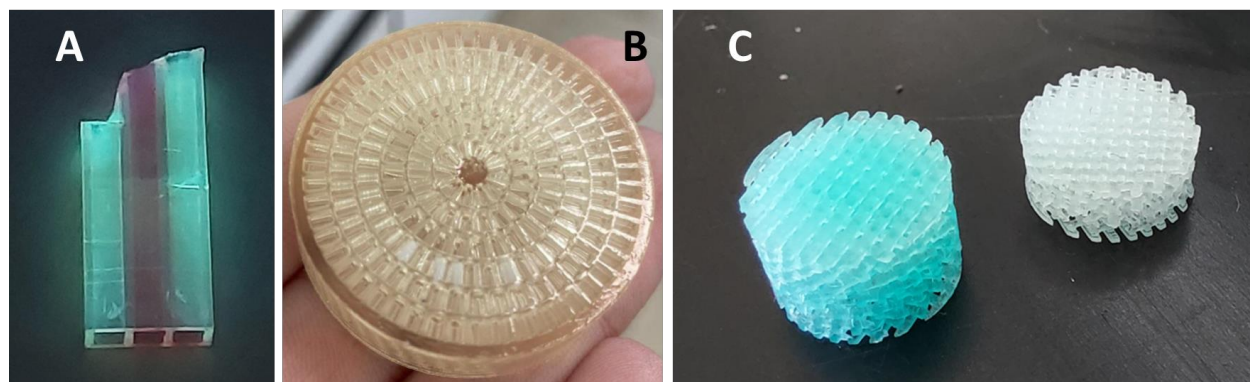
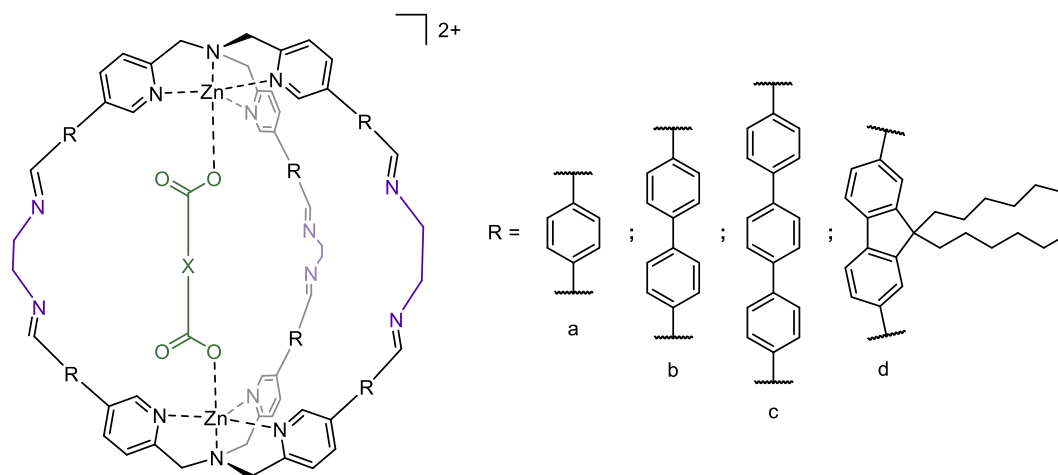


Figure 1.- Examples of (A) fluorescent microfluidic devices, (B) concentric arches filters, and (C) grid geometry filters

New molecular cages for chiroptical sensing

F. Carnio¹, F. Begato¹, G. Licini¹, C. Zonta¹¹Dipartimento di Scienze Chimiche, Università di Padovafrancesco.carnio@phd.unipd.itFigure 1. **TPMA**-based molecular cages with different R substituent.

Metal complexes of tris(2-pyridylmethyl)amine (**TPMA**) ligands have gained interest in sensing applications due to the seminal contributions of Canary^{1,2} and Anslyn.³ Recently, these complexes have been exploited by our research group as building blocks for the synthesis of novel molecular cages.⁴ These architectures are obtained through imine bond formation from the self-assembly of a modified **TPMA**-based metal complex bearing three aldehyde groups and diamine linkers.^{4,5}

The present work illustrates the synthesis of new **TPMA**-complexes and the corresponding novel molecular cages (Figure 1). Furthermore, the synthesis of new chiral hydrolytically stable cages, exploiting a method recently published by our research group,⁶ is described. The goal of this project is to obtain new chiroptical properties like, for example, an amplification of circular dichroism (CD) and circularly polarized luminescence (CPL) signals. In order to achieve these aims, chiral cages could be employed together with fluorophore guest molecule appropriately functionalised. Otherwise, the fluorophore could be embedded in the chiral cage structure as in the case of the 9,9-dihexylfluorene unit.

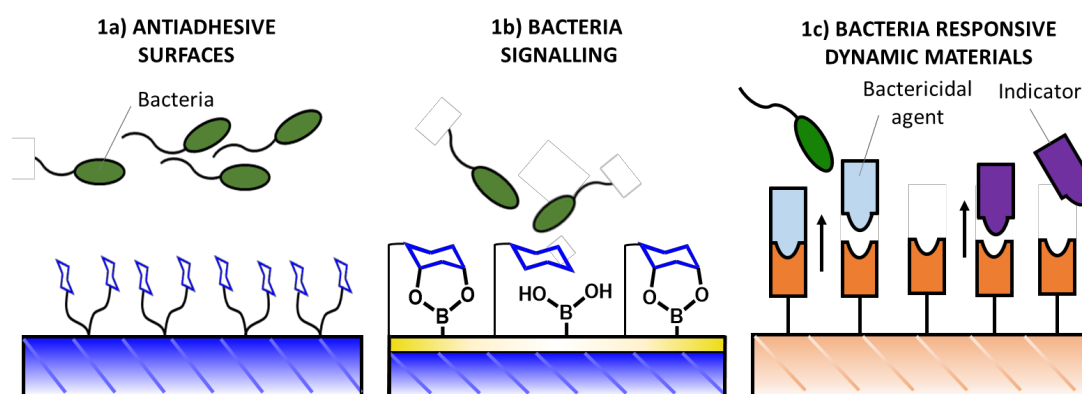
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Functionalised antimicrobial materials: towards antimicrobial surfaces

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With antibiotic resistant bacteria responsible for a rising number of fatalities, new avenues to limit the spread of infection must be developed¹. The infection inducing pathogen *Pseudomonas aeruginosa* (PA) causes a significant proportion of hospital acquired respiratory tract infections, which can be fatal for individuals with chronic lung conditions such as cystic fibrosis and chronic obstructive pulmonary disease^{2,3}. To address the concern of antibiotic resistant pathogens, the Byrne group is developing multivalent glycoconjugates which can target characteristic carbohydrate-binding proteins secreted by bacteria (lectins). Modifying galactosides (e.g. multivalency, variation of linker length; altering rigidity/flexibility, incorporating adjacent aromatic groups⁴) has been shown to increase lectin affinity; such modifications are being probed by the Byrne group. Glyco-functionalised hydrogel surfaces have been prepared (Fig. 1a) revealing modest anti-adherent activity against PA. Further, the competitive interplay between glyco-structures, lectins, and a fluorescent boronic acid probe⁵, has been examined for the development of PA sensing materials/films. The materials' physical properties are currently being optimised for use as medical device coatings (e.g. urinary catheters, endotracheal tubes) which can signal for bacterial contamination (Fig. 1b).



Independent research avenues through Queen's University Belfast include the use of boronic acid dynamic covalent bonding interactions for bacteria responsive disassembly of materials/coatings, leading to a fluorescent output (Fig. 1c). This approach aims to deliver therapeutic agents in response to contamination on a material surface, or simply to allow for the early identification of opportunistic infections, sparing the administration of antibiotics.

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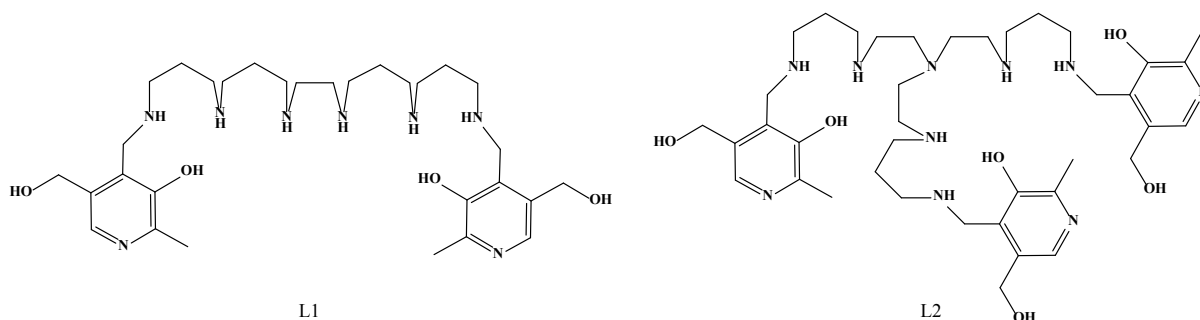
Pyridoxal-polyamine scaffolds for the detection of analytes of environmental interest

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One of the biggest problems facing chemistry arises from the everyday increasing pollution of the environment. Pollutants range from toxic or radioactive metal ions and anions to chemical products like herbicides, pesticides or drugs. Supramolecular complexes offer a new and efficient way for the monitoring and removal of many pollutant substances [1]. Polyamines have been chosen as recognition units since it is possible to modulate their binding affinities by changing the pH and pyridoxal moiety as fluorophore because its lack of toxicity (acts as a coenzyme of different enzymes) and their solubility in 100 % aqueous solution.



Here, the synthesis, acid base behaviour and heavy metal (Hg^{2+} , Cd^{2+} , Pb^{2+} and UO_2^{2+}) coordination chemistry of two polyamine containing pyridoxal as the sensing unit have been studied by potentiometric and NMR. Furthermore, the variation of their photophysical properties has been fully analysed.

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An overview for research expertise of Faculty of veterinary medicine-Skopje related to environmental contamination

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The complexity of environmental research requires a multidisciplinary approach which assumes involvement of diverse scientific disciplines and professional backgrounds. The research groups from the Faculty of veterinary medicine – Skopje, related to environmental contaminants, comprise researchers with background in analytical chemistry, environmental engineering and veterinary science. Quality of analytical results acquired from the research activities are valorized by methodology accreditation according to ISO 17025. The research is dedicated on several topics, and on this occasion summarized overview on peer-reviewed results will be presented.

Radiological examination of soil. The research was focused on measuring primordial and fission radionuclides in cultivated and uncultivated agricultural soils by gamma-spectrometry, following their vertical distribution [1]. Besides activity concentrations of ²²⁶Ra, ²³²Th, ⁴⁰K and ¹³⁷Cs in soils, absorbed doses by the population following the pathway of out-door exposure were estimated, and radionuclide's transfer to food commodities was predicted [2, 3].

Environment protection by applying environmentally friendly livestock production. Quantification of gas emissions, soil and waste water contamination from livestock housings are in the focus of this research topic [4]. Specific gas sensors are utilized to measure the emissions of carbon dioxide and ammonia in the livestock housings and the local environment. The severity of chemical contamination in soil and wastewater are analyzed with UV-Vis spectrophotometry. This research in our faculty is in its infancy, and strives on developing methodology procedures intended for research on environmental contaminants emerging in water and soil.

Bioindicators for environmental contamination. By measurement of contaminants levels in bioindicator samples, such as wild game tissues and honey, the environmental contamination was assessed. Wild game tissues from hunting areas in North Macedonia were exploited as bioindicators for Pb, Cd, As and Hg contamination of the environment, utilizing atomic absorption and ICP-MS techniques [5, 6]. Current research strives on expansion the scope to other chemical elements as bioindicators and their deployment in the environment. Testing of honey samples for pesticide residues with UHPLC-MS/MS unveiled not only presence of residual pesticides from bee hives treatment, but also encompassed those from contaminated environment [7].

The environmental contamination research in FVMS is carried out with analytical techniques suitable to detect analytes at ppb and sub-ppb level. However, most of them require preliminary sample pretreatment, therefore, are not feasible for rapid on-site contaminants testing. Nonetheless, as reference methods, they may be valuable external assessment tool for developed luminescent chemosensoric device(s) under the LUCES COST Action.

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Improving the photocatalytic activity in visible light of g-C₃N₄ doped with holmium

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In the presented study, g-C₃N₄ (CN) is a promising candidate to amplify the impact of visible light in as new photocatalysis, g-C₃N₄ (CN). Recent efforts to enhance the photocatalytic performance of CN have focused on utilizing rare earth metals as dopants, leveraging their distinctive electron configurations. In this current investigation, pure and varying concentrations of Ho-doped g-C₃N₄ (HoCN) photocatalysts were successfully synthesized via the one-pot method employing urea as a precursor. The morphological, structural, optical, and vibrational characteristics of the synthesized photocatalysts were analyzed through SEM, EDX, XRD, TGA, XPS, FTIR, PL, Raman, DRS, and BET techniques. Furthermore, theoretical computations utilizing density functional theory (DFT) were conducted to elucidate the alterations in the structural and electronic properties of g-C₃N₄ upon holmium doping. The photocatalytic efficiency of the pure and doped g-C₃N₄ photocatalysts was evaluated by monitoring the degradation of methylene blue under visible light. The findings demonstrate that holmium doping has enhanced the photocatalytic performance of CN samples. Particularly noteworthy is the observed enhancement in the photocatalytic activity of the 0.2 mmol doped CN sample, exhibiting twice the efficiency compared to the pure counterpart

TRIPHENYL POLYAMINE SYSTEMS FOR THE MOLECULAR RECOGNITION AND TARGETING OF MONOMERIC AND MULTIMERIC G-QUADRUPLEX STRUCTURES

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Appropriately designed supramolecular receptors can be highly interesting for selectively recognising given substrates and for facilitating their transport through synthetic and natural barriers.^[1] These systems can be applied in drug discovery and delivery, pollution remediation, catalysis and in many other areas.

Among the novel drug targets, epigenetic alterations, including histone modification, nucleosome remodelling and other non-coding mediated structures^[2] have attracted the attention in the last decades because of the development of drug resistance. One of the most attractive non-coding structures in anticancer drug development are G-quadruplexes (G4s). DNA and RNA. G4s are non-canonical nucleic acid structures formed in guanine-rich sequences, in which four guanine bases held together by Hoogsteen hydrogen bonds form a G-quartet, and then two or more G-quartets stack to form the G-quadruplex structure retaining sodium or potassium ions in a central core channel.^[3] Strikingly, a large number of putative G-quadruplex forming sequences have been identified in the genomes of human, microorganisms and viruses, and evidences suggest their pivotal role in key biological processes. In particular, telomeres are regions enriched with putative G4-forming DNA sequences and have been associated to ageing and cancer. Telomere sequences comprise hundreds of TTAGGG repeats which form a superstructure constituted by multiple G4s, termed as multimeric G4s (multG4s). Therefore, multG4 structures are currently tested as a therapeutic target to block telomere elongation in cancer cells.

Herein, we present a family of linear, macrocyclic and cryptand polyamine ligands containing triphenylamine moieties able to interact with G4s and multG4s.^[4] Several biophysical assays (FRET melting, fluorescence spectroscopy and gel electrophoresis) have been used to characterise the interaction towards monomeric G4s and multG4s. Furthermore, we evaluated the encapsulation ability of our ligands for anionic species such as cell-staining agents and drugs by potentiometry and NMR.

Within the series, cryptand-like ligands arise as potent and selective G-quadruplex binders of multimeric G4 structures as well as capable of encapsulate molecules.

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Metallic electrochemical sensors and sensors modified with nano-carbon materials used in stripping voltammetry for the determination of trace amounts of metal ions in environmental waters

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One of the most sensitive methods used in environmental analytical chemistry is stripping voltammetry. Measurements can be carried out by anodic stripping voltammetry, adsorption stripping voltammetry or cathodic stripping voltammetry, depending on how the analyte to be determined is accumulated on the electrochemical sensor and the subsequent recording of the analytical signal. For many years, mercury electrodes have been the main choice for voltammetric analysis of metal ions. Recently, safety and environmental protection considerations have limited their use and encouraged the search for alternative materials that are more environmentally friendly. Our scientific work deals with analytical issues, with special respect to the trace and speciation analysis using various electrochemical sensors in voltammetric methods. Electrochemical sensors convert the information associated with electrochemical reactions (the reaction between an electrode and analyte) into an applicable qualitative or quantitative signal related to the current intensity. To date, we have developed dozens of voltammetric procedures for determining trace concentrations of selected ions using the following electrochemical sensors:

- renewable mercury film silver based electrode (Hg(Ag)FE). This electrode is designed in such a way that the thin liquid layer can easily be regenerated before each measurement cycle. A small amount of the silver amalgam, tightly sealed inside the electrode corpus makes the electrode safe to use both in the laboratory and in onsite conditions [1];
- bismuth solid microelectrode [2-3];
- bismuth film, lead film, copper film generated on different base surfaces such as glassy carbon electrode (GCE), multi-walled carbon nanotubes/spherical glassy carbon electrode (MWCNTs/SGCE) and multi-walled carbon nanotube modified screen-printed carbon electrode (MWCNTs/SPCE).

MWCNTs/SGCE was developed in our laboratory using a mixture of multiwall carbon nanotubes, glassy carbon spherical powder, and epoxy resin. The MWCNTs/SGCE has already been successfully used as a competitive substrate to the glassy carbon electrode to create bismuth or lead films applied in determination of Cd(II) Ti(IV) and Ga(III) [4-6].

Screen printed electrodes are more and more popular in recent years. They are easily and cheaply produced in large quantities and much more convenient to use under environmental conditions since one small strip contains the three electrodes necessary for voltammetric measurements. The range of screen-printed electrodes produced is very wide with different modification. In our works MWCNTs/SPCE, which was further modified by applying a copper film, was used for the determination Cd(II) and Pb(II) [7,8].

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Voltammetric sensing of chloride based on redox active complex: terpyridine-Co(II)-dipyrromethene functionalized anion receptor deposited on gold electrode

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Abstract

Redox-active complex containing Co(II) with terpyridine (TPY) and dipyrromethene functionalized anion receptor (DPM-AR)^{1,2} was created on the gold electrode surface. This host-guest supramolecular system based on a redox-active layer was used for voltammetric detection of chloride anions in aqueous solutions. The sensing mechanism was based on the changes in the redox-activity of the complex observed upon binding of the anion to the receptor. The electron transfer coefficient (α) and electron transfer rate constant (k_0) for the modified gold electrodes were calculated based on Cyclic Voltammetry experiments results. On the other hand, sensing abilities were examined using Square-Wave Voltammetry. More importantly, the anion receptor was selective to chloride, thereby resulting in the highest change of Co(II) current intensity and allowing to distinguish chloride, sulfate and bromide. The proposed system displayed the highest sensitivity to Cl⁻ with a limit of detection of 0.50 fM. The order of selectivity was: Cl⁻ > SO₄²⁻ > Br⁻, which was confirmed by the binding constants (K) and reaction coupling efficiencies (RCE).

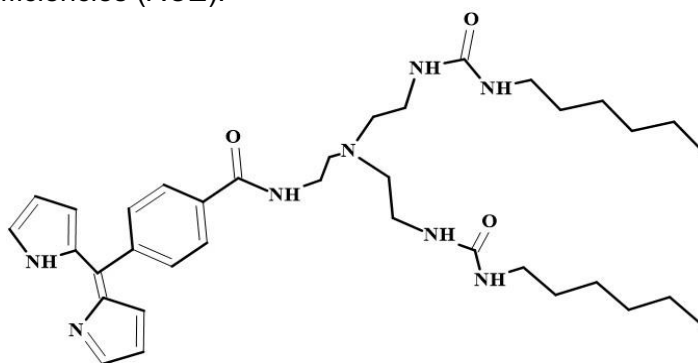


Fig. 1. Structure of anion receptor (DPM-AR).

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Keywords: voltammetric sensor, anion recognition, host-guest interaction, terpyridine- Co(II)-dipyrromethene complex, chloride sensing

Polymer materials for real-time potentiometric sensing of inflammation and infection

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We describe new polymeric materials for use in an electrochemical multisensor, which will provide a potentiometric response upon contact with selected analytes, such as pH changes, presence of reactive oxygen species, free iron ions, etc., selectively detecting and distinguishing multiple biomarkers of bacterial and sterile pathologies in real time. The sensor electrodes also include a non-biofouling layer to minimize interferences. The target application of the new materials is the integrated potentiometric biosensor for early indication of the presence and the type of inflammation. They are to be used in devices for in vitro sensing of inflammation-related analytes in body fluids, such as synovial liquid, directly on-site in the operating room during the surgery. Alternatively, electrodes in such a sensor might be miniaturized and integrated into an implant with a wireless data transfer device with an external readout to allow in situ sensing without the necessity of invasive intervention. Our general “big picture” concept of the prosthetic joint infections detection is based on several (finally miniaturized) sensors and the presented partial sensors enable implementation of it into such a multisensor with a shared reference electrode. More detailed information can be found in the cited references¹⁻⁴.

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Pillararenes – Cage Molecules with a Potential for CO₂ Capture

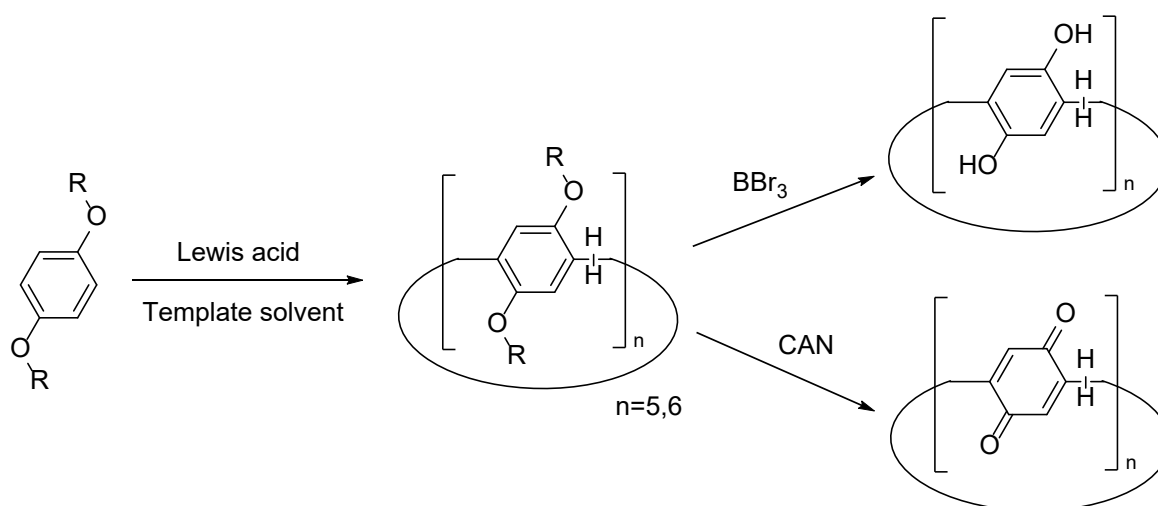
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Pillararenes are cage like molecules formed by self-assembly from 1,4-dialkoxybenzene and paraformaldehyde in a Lewis acid catalysed process.^{1,2} A template solvent helps control the process towards the desired ring sizes. The R-group strongly affect the self-assembly and only a few substituents allow the formation of pillararenes, favouring ring sizes of either 5 (P[5]A) or 6 (P[6]A) monomers. Deprotection of methoxy groups with BBr₃ releases the hydroxy groups and allow modifications of the rim of the pillararene providing a possibility to tune the physical properties. Similarly, deprotection with ceric ammonium nitrate (CAN) form pillarquinones that can be further modified.



In a project targeted towards CO₂ capture, we are exploring the absorption properties of pillararenes³ towards CO₂ and other gas mixtures. Aided by computational studies we will make modified pillararenes to enhance the host-guest complexation abilities and uptake of guest molecules and hopefully verify the potential of these materials to capture CO₂ through absorption and adsorption methods under realistic conditions.

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Electrochemical Detection of Gallic Acid using m-GCE with Zn/Ga-substituted Cobalt Ferrite Nanoparticles

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In this investigation, nanoparticles of cobalt ferrite and zinc/gallium-substituted cobalt ferrite (CoFe_2O_4 , CFO; $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$, CFO_Zn; $\text{CoFe}_{1.5}\text{Ga}_{0.5}\text{O}_4$, CFO_Ga) were synthesized using solvothermal method, with dihydrocaffeic acid (DHCA) as a surfactant, to examine their applicability for electrochemical detection of gallic acid. Additional modification of surface chemistry of nanoparticles was performed by annealing at 450 °C in air. X-ray diffraction revealed that structure of all samples corresponds to the cubic spinel phase, while transmission electron microscopy has shown non-agglomerated and spherical nanoparticles with an average size of 5 ± 1 nm. The presence of DHCA on the nanoparticles' surface was confirmed by Fourier Transform Infrared Spectroscopy. It was concluded that DHCA binds through both carboxyl and catechol groups to the surface of nanoparticles. However, annealing of nanoparticles caused structural transformation of DHCA, which is confirmed by changes in thermal desorption profile of CO and CO₂ in temperature-programmed desorption method. To examine electrochemical detection of gallic acid, modified glassy carbon electrodes (m-GCE) were fabricated using CFO, CFO_Zn, and CFO_Ga nanoparticles. All of the annealed samples exhibited good reversibility for $[\text{Fe}(\text{CN})_6]^{3-/4-}$ system. Optimal electron transfer efficiency was achieved for sample-to-Vulkan® mass ratio of 85:15, respectively. m-GCE with CFO_Zn demonstrated the highest sensitivity to gallic acid (in Britton-Robinson buffer at pH=2). These results show the importance of selective functionalization and surface modification of nanoparticles for enhancing electrochemical sensing properties.

Metallated Amino Acid Bioconjugates: Supramolecular Chemistry and Catalysis

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Conjugates of transition metal complexes and amino acids or peptides attract significant attention in recent years. In particular, the unique combination of properties of metal complexes and biologically relevant amino acids can result in the development of new selective catalysts as well as new tools for medicinal chemistry.

In this communication, examples of recent advances in bioinorganic chemistry and stereochemistry, with applications in homogeneous catalysis and medicinal inorganic chemistry will be presented. Particular emphasis will be laid on inorganic stereochemistry of hexacoordinated metal complexes with tridentate ligands.¹ Potential biological applications will be highlighted by electron transfer in biologically active late transition metal complexes and turn-on fluorescence of ruthenium pyrene complexes in response to bovine serum albumin (Figure 1).² In addition, a novel approach to metal complexes for *in cellulo* catalytic applications will be discussed.³

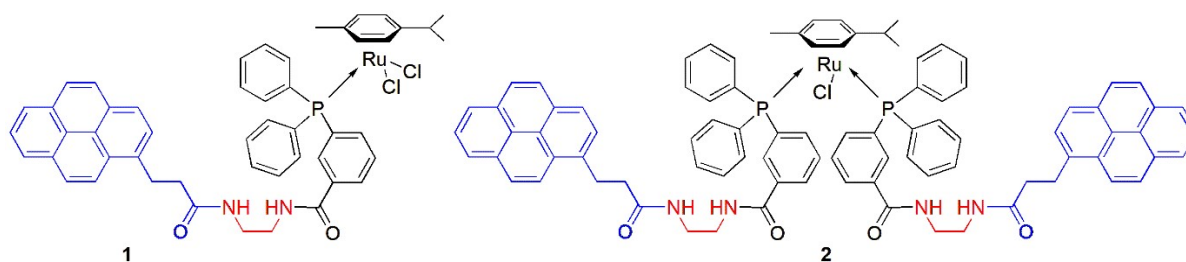


Figure 1. Ruthenium pyrene complexes, **1** (mono complex) and **2** (bis complex).

Acknowledgement: Support by the European Regional Development Fund (KK.01.1.1.04.0013) and the Croatian Science Foundation (IP-2022-10-8456) is gratefully acknowledged.

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Cyclodextrin-induced Aggregation of Surface-modified Gold Nanoparticles

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Our group recently described mixed monolayer-protected gold nanoparticles that can be used for the optical sensing of sulfate, phosphate and nucleotides.^[1,2] The analyte-induced crosslinking of the nanoparticles led to a color change of the solution that could be easily followed with the naked eye. In addition, the solution remained homogeneous, allowing complex formation to be followed by UV/Vis spectroscopy. Previous work has shown that the aggregation of nanoparticles can be influenced, among other factors, by varying the receptor content on the nanoparticle surface. To gain a better understanding of this relationship, the cyclodextrin-induced aggregation of gold nanoparticles containing adamantyl residues is now investigated.

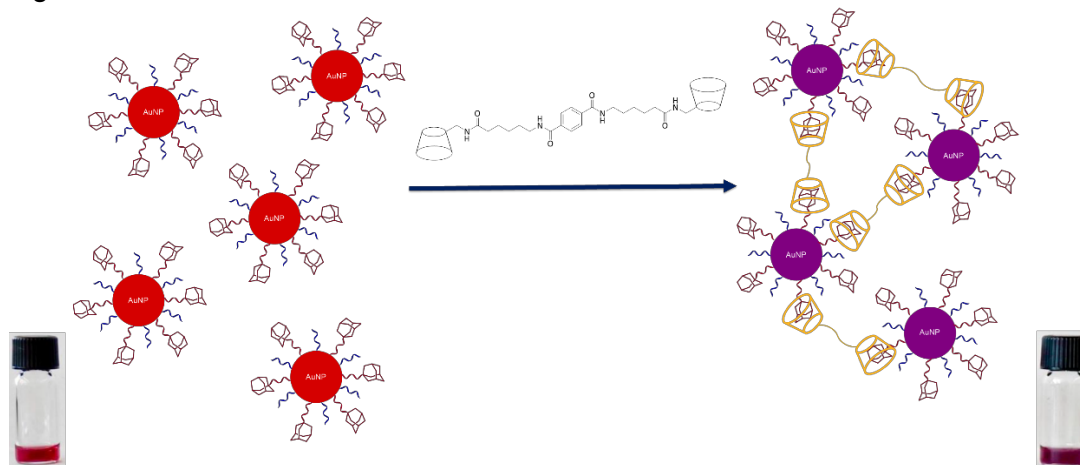


Figure 1. Schematic representation of the functionalized gold nanoparticles (right) and bis(cyclodextrin)-induced nanoparticle cross-linking (left).

The investigations showed that the aggregation behavior can be influenced by the structures of the ligand and the bis(cyclodextrin), as well as by the ligand ratio on the nanoparticle surface. But what happens when different nanoparticles are mixed? Is it possible to precipitate only one species while the other remains in solution? For example, is it possible to mix silver and gold nanoparticles and precipitate only one, which could lead to self-sorting nanoparticles?

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Chiral material composed of hexakis(Zn-tetraphenylporphyrin)-D-biotin-L-sulfoxide[6]uril and silica nanohelices

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D-biotin-L-sulfoxide[6]uril (BU) is a chiral cucurbituril-type macrocycle¹. Its amide coupling with a corresponding tetraphenylporphyrin derivative affords a novel bulky and chiral hexakis(Zn-tetraphenylporphyrin)-D-biotin-L-sulfoxide[6]uril ((ZnTPP)₆BU), in which six achiral porphyrin moieties are linked to the chiral macrocycle via flexible side chains. Metalloporphyrins possess unique spectral and coordination properties which make them excellent chemosensors². Therefore, combination of the chiral structure of BU reinforced by the specific features of porphyrins enables extraordinary binding and chiroptical properties to (ZnTPP)₆BU. The conformational flexibility of (ZnTPP)₆BU side chains allow assembling of “super-structures”, in which the host-guest interactions are led by the porphyrin units. It has been shown that BU derivative coupled with only one porphyrin unit³ can bind silica nano helices⁴ with organic core (*i.e.* hybrid helices). Moreover, enantiodiscrimination towards hybrid helices by such macrocycle was observed.

In this work, we show complexes between silica nano helices without organic core (*i.e.* inorganic helices) and six porphyrins containing (ZnTPP)₆BU. Such complexes exhibit attractive chiroptical and binding properties, including promising circularly polarized luminescence (CPL) signal.

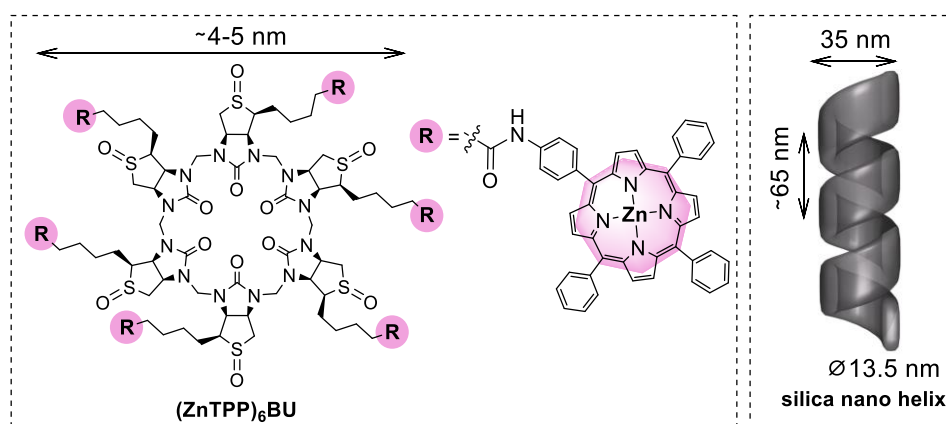


Figure. Structure of (ZnTPP)₆BU and schematic representation of silica nano helix.

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Modified Photochemistry in the Strong Coupling Regime

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Light-matter interaction is a fascinating topic with a wide range of practical applications. Familiar phenomena, such as fluorescence and photochemical reactions, typically happen in the weak in the coupling regime where the light-matter interaction can be treated perturbatively. However, when the light mode is tightly confined in a nano-cavity, the quantum properties of light become relevant and the light-matter coupling can be significantly increased. When the coupling strength surpasses all decay processes, the strong coupling regime is reached. Here, the light field and the molecular degrees of freedom can hybridize – in a similar way as atomic orbitals hybridize to form molecular orbitals – and the molecular properties are heavily modified. The first experimental realisation of this effect was demonstrated on a ring opening reaction of Spiropyran [1]. The photochemical reaction rates were significantly modified within an optical cavity. Since then this effect has been demonstrated for many other reactions, such as the triplet-triplet annihilation [2]. However, this fascinating effect is not fully understood yet and still subject of many ongoing experimental and theoretical investigations.

In this contribution I will present excerpts from our theoretical work on photochemical reactions in the strong coupling regime. Over the last few years my group has studied the photochemistry under the influence of strong light matter coupling and its possibilities. A few examples of photochemical processes that we have studied are, chemoluminescence [3], non-radiative decay in BODIPY [4], and the photoinduced hydrogen abstraction of pyrrole [5]. I will give a brief introduction into the topic and present some of the above named examples.

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Luminescent Au polymer stabilized nanoparticles.

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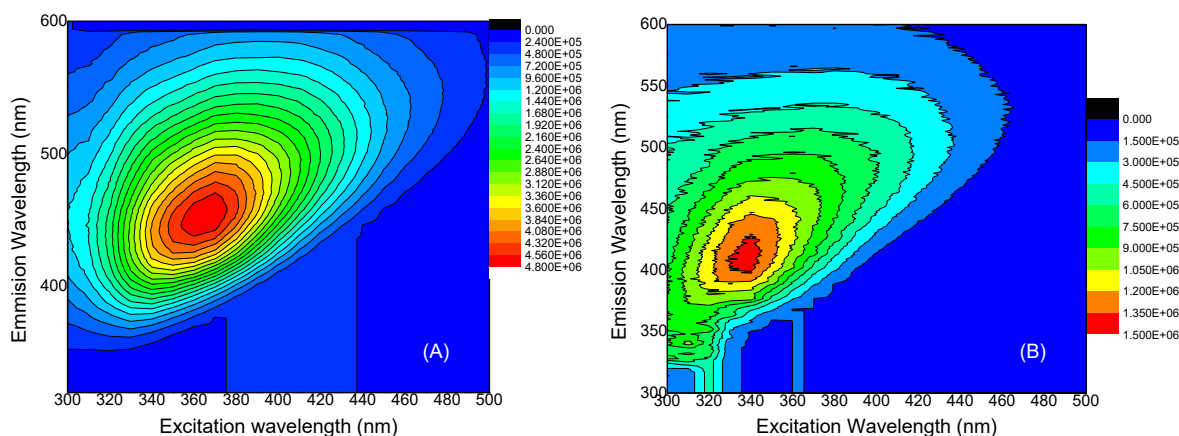
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Metal nanoparticles (NPs) with sizes of a few nm can form colloidal solutions that show characteristically strong luminescence. The peak position and intensity of their luminescence depend on the size and environment of the nanoparticles. Gold nanoparticle (AuNP)- based sensors have the potential to detect toxins, heavy metals, and inorganic and organic pollutants in water rapidly with high sensitivity, and they are expected to play an increasingly important role in environmental monitoring¹. The main problem with these nanoparticles is their stability, as they tend to aggregate and precipitate. To avoid precipitation, auxiliary stabilizers such as surfactants, functionalized polymers, inorganic solids, or organic ligands were used.

Block copolymers with amphiphilic character may lead, via self-organization, to well-defined structures such as polymer micelles. The properties of such micelles can be tuned by the nature and molecular architecture of the blocks. The block polymers in these micelles can have a dual role as templates for solubilizing and stabilizing nanoparticles and for their interaction with the environment.

Metal nanoparticles of Au and Cu of some nm radius were prepared and stabilized by block polymers². These colloidal solutions showed strong and stable luminescence.

The interaction of the outer part of the stabilizing polymers with possible pollutants is expected to change the polarity of the NPs environment and change their optical properties, giving the ability to detect water pollutants. Additionally, the prepared stable colloidal solutions can be used for the tracing of water flow in various systems.



Total fluorescence spectra of Au (A) and Cu (B) nanoparticles

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Effect of grafting fluorescent esterase substrate onto mesoporous silica on the hydrolysis rate

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Responsive nanoparticles constructed to function as sensors are particularly attractive, as they enable monitoring of physical quantities (concentration of an analyte, pH, temperature, etc.) in small enclosed spaces, inaccessible to larger devices (e.g., inside a human body)¹. Nanoparticles exhibit versatility — their surface can be modified to include different functionalities on one particle, which presents an advantage over single molecular sensors or probes. Enzyme substrates can be attached to the surface of nanoparticles to track enzyme activity. To construct such sensors, a better understating of enzyme activity on the nanoparticle surface is required².

We synthesized mesoporous silica nanoparticles with parallel orientation of pore channels. The particle surface was modified with organosilanes and fluorescein was covalently grafted onto the surface. The fluorophore was rendered non-fluorescent by acetylation of the hydroxyl groups to yield fluorescein diacetate (FDA). The system was stable in aqueous medium in absence of the esterase — the nanoparticles remained white and non-fluorescent. Upon addition of the esterase, the ester bonds of the grafted FDA molecules were hydrolyzed, which converted the particles into colored and fluorescent. Two enzymes, namely porcine liver esterase (PLE) (168 kDa) and lipase from *Aspergillus niger* (LAN) (45 kDa) were incubated with free fluorescein diacetate (FDA) and with FDA grafted onto the mesoporous silica. We observed the following order of rates for free FDA hydrolysis: 1x PLE ~ 1x LAN < 5x LAN < 10x PLE < 10x LAN as depicted in Figure 1A (the number preceding the x refers to the relative concentration). In the case of grafted FDA we observed a different order of rates: 1x PLE < 10x PLE < 1x LAN < 5x LAN ~ 10x LAN as depicted in Figure 1B. The hydrolysis was slower with PLE than with LAN in the case of silica-grafted FDA, while comparable in the case of free FDA. This difference points to the effect of nearby nanoparticle surface on the enzyme ability to catalyze the hydrolysis of the grafted substrate.

Further investigations are underway to explore the effect of different pore sizes and surface organic functional groups on the enzyme activity near the particle surface, substrate transformation and ultimately fluorescent response of the systems.

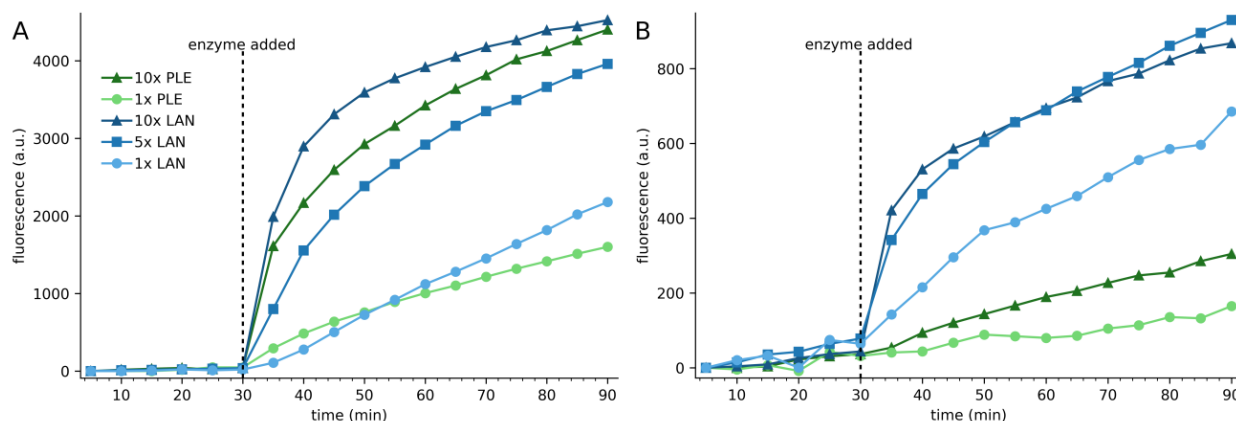


Figure 1. Fluorescence intensity over time for free FDA (A) and silica-grafted FDA (B) in the presence of different concentrations of the enzymes PLE and LAN.

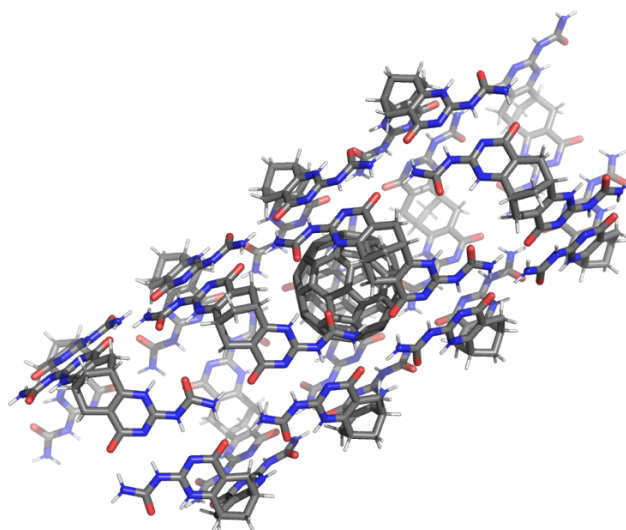
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Dynamic Tubular H-Bonded Supramolecular Systems

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The protein tertiary structures and the iconic DNA double helix demonstrate the significance of hydrogen bonding (H-bonds) for the stability, structure, and operation of the basic building blocks of biosystems. They also provide chemists with ideas for creating synthetic, non-covalent constructs. Due to its strength and directionality, the H-bond is arguably the most adaptable non-covalent interaction exploited in supramolecular chemistry. Thanks to the reversible nature of H-bonds, the utilization of rigid molecular scaffolds and tautomeric equilibrium allowed for the design and synthesis of new stimuli-responsive H-bonding monomers with a variety of self-assembly pathways and structural characteristics. Herein, several unique methods to obtain new types of dynamic supramolecular tubular aggregates and polymers assembled from very small and thus easily modifiable chiral H-bonding bicyclic building blocks will be discussed.



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Novel molecular design and synthesis toward Boron-based chemosensors

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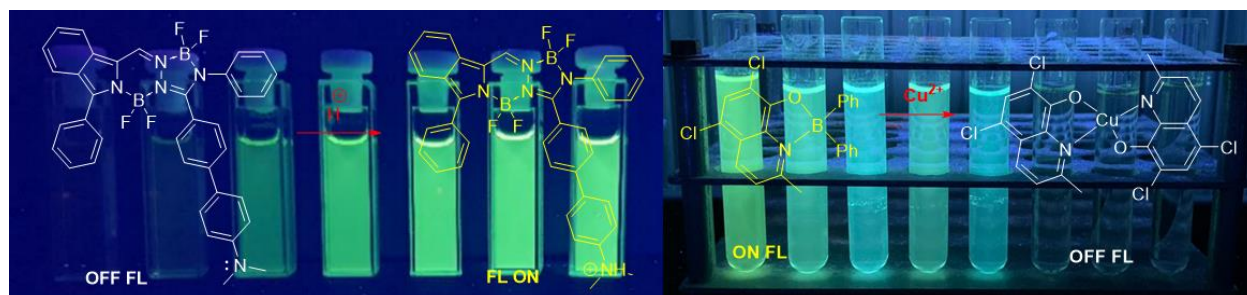
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Fluorescent chemosensors designed for the detection of ions and neutral analytes have found extensive applications across diverse fields, including biology, physiology, pharmacology, and environmental sciences. The recent proliferation of such chemosensors underscores their utility in identifying biologically and environmentally significant species. While substantial progress has been achieved in this domain, the burgeoning potential of chemosensors is particularly promising for both established and emerging biotechnologies [1].

Moreover, the comprehension of sensing mechanisms through computational studies has garnered significant attention. This approach facilitates the development and synthesis of molecular systems endowed with specific signaling units tailored for the detection of gases, ionic contaminants, and residual drugs in aqueous environments, soil, or food matrices. Recent investigations into novel Boron-based fluorophores, such as BOPAM and Boron tetracoordinate complexes of 8-quinolinolato (BTQ), have revealed compelling photophysical properties, including high fluorescence emission quantum yield, photostability, and large Stokes shift [2]. Computational studies have delved into the electronic excited states of these fluorophores, offering fresh insights into kinetic (non-)radiative decay processes.

In this study, we endeavor to design and synthesize innovative chemosensors based on boron complexes, specifically BOPAM and BTQ. The emission characteristics of BOPAM-based chemosensors were found to be augmented in the presence of protons, while those based on BTQ exhibited decreased emission in the presence of copper cations. Computational studies unveiled a novel mechanism of ON-OFF fluorescence for these chemosensors. These findings not only showcase the potential applications of these chemosensors in biological and natural environments but also contribute to the development of new molecular designs for fluorescent chemosensors.



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Combining Imine Condensation Chemistry with [3,3] Diaza-Cope Rearrangement for One-Step Formation of Hydrolytically Stable Chiral Architectures

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Dynamic covalent chemistry (DCC) has, in recent years, provided valuable tools to synthesize molecular architectures of increasing complexity.¹ Our group took also advantage of imine DCC chemistry to prepare TPMA-based supramolecular cages for molecular recognition applications.² However, the versatility of this approach has as a major drawback: the intrinsic hydrolytic lability of imines, which hampers some applications.

We present herein a synthetic strategy that combines the advantages of a thermodynamic-driven formation of a supramolecular structure using imine chemistry, together with the possibility to synthesize chiral hydrolytically stable structures through a [3,3]-sigmatropic rearrangement.³ A preliminary mechanistic analysis of this one-pot synthesis, the scope of the reaction and the supramolecular applications of the newly synthesized structures are also discussed.



Figure 1. Diaza-Cope rearrangement

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Supramolecular Single Crystal X-ray Crystallography

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An exciting research challenge in supramolecular chemistry is to design, synthesize, and characterize nano-sized architectures with applications in biology, chemistry, and materials science.[1] Predicting and designing non-covalently bound supramolecular complexes and assemblies is difficult because of the weakness of the interactions involved, thus the resulting superstructure is often a compromise between the geometrical constraints of the building blocks and the competing weak intermolecular interactions.[2]

Our research interest has been focused on the studies of weak non-covalent intermolecular, *viz.* supramolecular interactions as the driving force in self-assembly and molecular recognition, especially in the solid state by single crystal X-ray diffraction. The lecture will highlight some of our recent studies on halogen bonded systems[3], anion... π interactions[4] and metal ion coordination[5] in molecular self-assembly and molecular recognition in various systems such as rotaxanes, M_4L_6 tetrahedra, M_8L_6 cube, spheres, knots, etc..

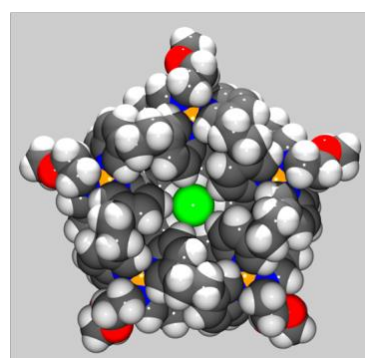


Fig. 1. The X-ray structure of the pentafoil knot.[5a]

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Light Responsive Dyes in Vat 3D printing: beyond the precision

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3D printing is predicted to revolutionize the production process, exceeding mass production and economy of scale, and thus our life. Nevertheless, it is still perceived as a hobby tool or, in the best case, as a technology for niche applications. One of the main reasons that still prevents the complete development of 3D printing is the limited number of printable materials, which restricts the available applications fields. In particular in light-based VAT 3D printing technologies, such as SLA and DLP, the few available materials limit the use of these technologies to rapid prototyping, jewelry, hobby and few others. The most common approach for modifying the materials' properties consists in playing with the monomers/oligomers or adding fillers. However, other strategies could be undertaken for widening the palette of functionalities.

Here we present how an engineered use of the dye in the printable formulation, which is commonly used for limiting light penetration and thus for improving the printing precision, could be employed for imparting new functional properties to the printed objects¹, obtaining functional devices such as sensors,^{2,3} photoluminescent⁴ or light responsive devices.^{5,6,7}

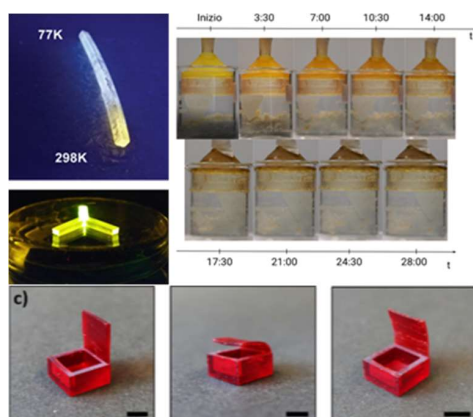


Figure 1 Examples of 3D printed structure with light-responsive fillers fabricated @PoliTO

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Surface active agents – potentiometric sensors and challenges in optical sensors detection

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Surface active agents, or surfactants, are organic compounds that reduce the surface tension of water. They consist of a hydrophilic head and a hydrophobic carbohydrate-rich tail. There are four types of surfactants: anionic, cationic, nonionic and amphoteric. Anionic surfactants make 2/3 of the global surfactant market and are used as detergents for washing and cleaning at home and industry.¹ Cationic surfactants are used as antiseptics, disinfectants, bactericides, corrosion inhibitors and cleaning agents in home products, hospitals, industry, as oilfield chemicals and in agronomy. Nonionic surfactants are used to enhance properties of other surfactants. The global surfactant market is expected to increase by 4.5% in the period from 2020 to 2025 due to high demand and standard growth.¹

Surfactants can cause skin irritation, reproductive and respiratory problems; and represent a threat to the environment. For this reasons it is important to establish reliable analytical tools in surfactant monitoring.

Classical methods of quantification include two-phase titration and methylene blue active substances (MBAS) method. Both are time consuming, use toxic organic solvents for extractions, and the reproducibility depends on the analyst experience. Instrumental methods for surfactant analysis include variety of chromatographic methods with different detectors. They require expert personnel, use toxic solvents and are expensive to operate. An alternative to mentioned methods are chemical sensors for surfactants. Potentiometric surfactant sensors are low-cost analytical devices, ion-selective electrodes which are sensitive to the surfactant concentration change in liquid samples. The mechanism is described by the Nernstian equation and is based on the ion-pair dissolved in a high lipophilic organic PVC/plasticizer sensing membrane. These sensors prove to be low-cost, simple to operate, don't use toxic solvents, they are robust, selective and sensitive, with limits of detection $\approx 10^{-8}$ M.³ Potentiometric surfactant sensors are used for surfactant analysis of commercial detergent samples, but also industrial and wastewater analysis. Challenges in development of optical chemical sensors for surfactants will be discussed.

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Thermodynamic and Kinetic Parameters Driving Assembly and Disassembly of a Supramolecular Cage

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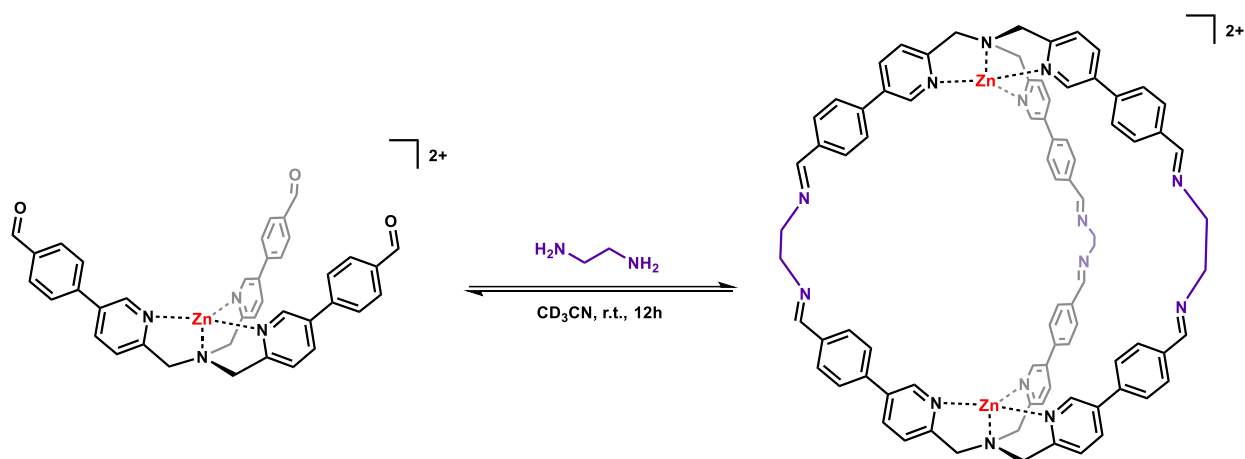


Figure 1. Synthesis of a **TPMA**-based molecular cage.

In the last few years dynamic covalent chemistry has been increasingly used for the self-assembly of supramolecular cages. This work presents the synthesis of a novel imine-based bimetallic molecular cage built from two tris(2-pyridylmethyl)amine (**TPMA**) zinc complexes bearing aldehyde groups, which are connected by ethylenediamine linkers¹ (Figure 1).

As **TPMA**-based complexes have been previously employed by the groups of Canary and Anslyn² and also by our research group³ for sensing application due to their capability to bind carboxylic moieties, the encapsulation of dicarboxylic acids of various length has been investigated. In particular, both thermodynamic properties of the formed cage and the kinetics of assembly and disassembly in presence of a guest have been explored. While the binding constants of the acids, and in a similar way the rates of assembly, show a pseudo-Gaussian profile, typical of recognition phenomena in confined spaces, the rates of disassembly have an unexpected trend varying with the length of the guest. Knowing the kinetic properties of the templated cage, it is possible to modulate both the formation and the hydrolysis processes: in particular, an unprecedented method to enhance the hydrolysis rate has been developed. The knowledge of these kinetic properties could open the possibility to time molecular functions such as delivery, structural reorganization and stimuli programmed molecular events.

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Mesoporous materials with tuned properties as a basis for development of sensors and indicators

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Mesoporous materials are defined as materials containing pores in diameter between 2 and 50 nm according to IUPAC. With well-defined, ordered porous structure, which could be additionally modified with various organic compounds through covalent bonding (surface functionalization), they present an interesting material for different applications including sensing^{1,2}. The properties of the mesoporous materials can be varied by changing the synthesis procedure: selection of synthesis pathway, the choice of the precursor, the temperature and pH of reaction mixtures, addition of swelling agents, etc.¹ as well as additional post synthetic covalent and non-covalent functionalization with different groups^{1,2}.

We synthesized mesoporous materials with different morphological, structural and textural properties characterized using nitrogen sorption, XRD analyses and transmission electron microscopy. These materials provide basis for further introduction of different functionalities on their surface and development of gas sensors, indicators and gate materials.

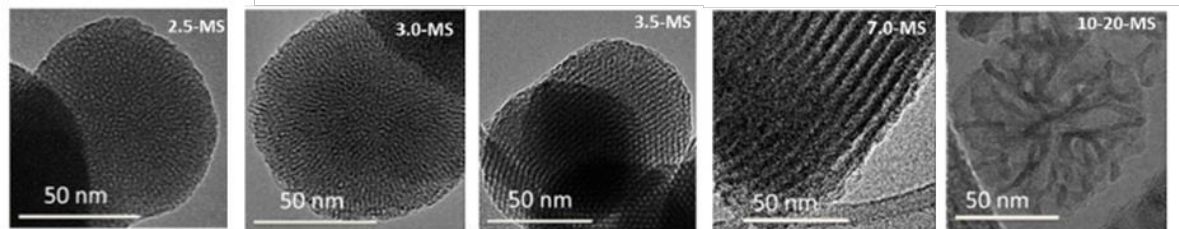


Figure 1: TEM micrographs of the silica-based mesoporous materials with different defined pore diameters¹.

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Calixarene-based fluorometric sensors for pharmaceutical substances: A fluorescent probe for metronidazole

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Antibiotics are an important group of drugs used in the treatment of diseases in humans and animals. The increase in the use of antibiotics in recent years has led to an increase in the presence of drug substances in the environmental ecosystem, especially in aquatic environments through wastewater. This poses a significant potential risk to the health of living organisms. Therefore, it is crucial to minimize the risk by controlling discharges and releases from human activities. Metronidazole (MET) is an antibiotic and antiprotozoal used in the treatment of *Entamoeba histolytica*, *Giardia lamblia*, *Gardnerella vaginalis* and *Trichomonas vaginalis*. However, inappropriate use of MET has potential risks of teratogenicity, carcinogenicity and nerve mutagenesis.¹ Therefore, high-sensitivity and specific quantitative detection of MET is crucial and its control in food and pharmaceuticals is a serious issue for human health and food safety.

Several analytical techniques for MET measurement have been reported so far. At this point, ultraviolet-visible (UV-Vis) and fluorescence (FL) spectrometry stand out as the most suitable techniques for detecting and visualizing low levels of analytes in various media. FL spectrometry is a superior technique to UV-Vis for the detection of analytes due to its sensitivity, simplicity and applicability. The organic molecule-based fluorescence sensors are seen to be in the forefront due to some of their superior features such as high inherent sensitivity, convenience, remarkable detection selectivity, operational simplicity, cost-effectiveness, fast and easy signal detection.² Different polymer or synthetic molecules can be used in these organic-based sensor systems. Among these molecules, calixarenes, a popular member of supramolecular chemistry, are macrocyclic compounds with unlimited derivatization capability, three-dimensional structure and the ability to complex with different molecules.³

Several studies have been carried out to find calixarene-based sensors selective for certain species. In these studies, interesting fluorescent receptors for both ionic and molecular specific analytes have been reported, which were specifically developed by designing calixarene derivatives bearing fluorescent organic groups.⁴ However, to the best of our knowledge, no study on the preparation of calixarene-based fluorescent materials to detect MET has been found in the literature. Therefore, this work introduces a highly selective and sensitive calix[4]arene-based fluorescent sensor with 1H-phenanthro[9,10-d]imidazolyl fluorophore for the detection of MET on various substances such as ionic or pharmaceutical species (Fig. 1).

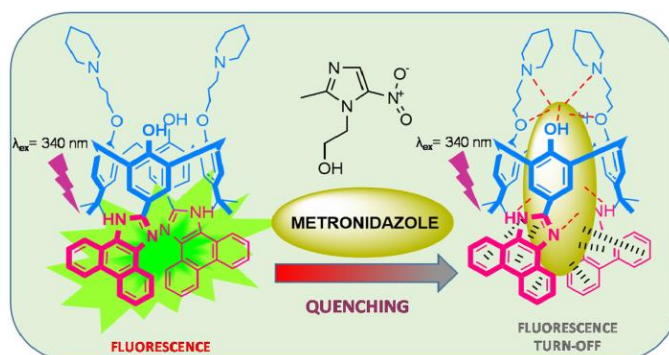


Fig. 1. Plausible interactions between calixarene-based fluorophore and MET.

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Ion-selective electrodes with solid contact based on nanocomposite materialsC. Wardak¹, K. Morawska¹, M. Grabarczyk¹

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Ion-selective electrodes (ISEs) are the largest and most popular group of electrochemical sensors. At the end of the last century, a new version of their design was introduced, which involved the removal of the internal electrolyte solution. Thanks to this, these sensors called solid contact permanent contact ion-selective electrodes (SCISEs) have become easier to handle, use and transport. Moreover, miniaturization of ISEs has become possible. For this type of electrodes, it is very important to select the appropriate material that will act as an ion-electron transducer, thus enabling the proper operation of the electrodes, by ensuring appropriate stability and reproducibility of the potential. There are many materials used in the role of a solid contact. The most popular materials include carbon based nanomaterials such as carbon nanotubes and nanofibers, conductive polymers, metal and metal oxide nanoparticles, and ionic liquids, among others. Our research group has been dealing with the topic of potentiometric sensors for many years. The latest research concerns the use of composite and hybrid materials for the development of solid contact ion-selective electrodes. We study the quality of the obtained sensors using various electrochemical techniques such as potentiometry, chronopotentiometry and electrochemical impedance spectroscopy. It has been proven that composite materials often have better mechanical, thermal, electrical, optical and chemical properties than the original components [1]. With regard to their use in the construction of ion-selective electrodes, it is particularly important to increase the capacitance and surface area of the material, which makes them more effective in the process of charge transfer between the polymer membrane and the substrate material. This allows to obtain sensors with better analytical and operational parameters. So far we successfully developed electrodes sensitive to nitrate, chloride, potassium, lead and copper ions using various nanocomposite based on carbon nanomaterials and ionic liquid [2-4], polyaniline nanofibers [5] nickel-cobalt nanoparticles [6] and copper oxide nanoparticles [7].

The poster will explain why it is so important to use a solid contact, what composite materials are and what types of this materials are known and utilized. The results of research on the impact of a composite material based on carbon nanotubes and other components on the most important parameters of selected ion-selective electrodes with solid contact, i.e. the slope of the characteristics, the limit of detection and the range of linearity, stability and reversibility of the potential. The electrodes we have developed can be analyzed in real samples such as natural water, food and pharmaceutical preparations. Examples of such applications will also be presented on the poster.

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