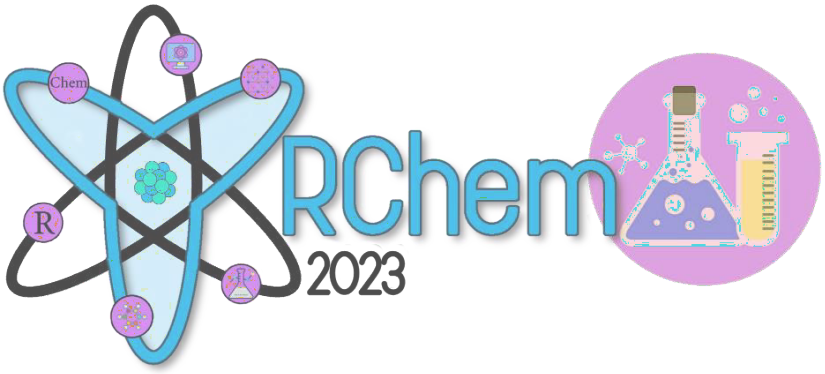
3er Workshop for Young Researchers in Chemistry



May 18th – 19th

Faculty of Chemistry

University of València

VNIVERSITAT DE VALÈNCIA Facultat de Química

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Welcome

Dear colleagues,

The organizing committee kindly welcomes you to the third edition of the Workshop for Young Researchers in Chemistry, which is being held in the Faculty of Chemistry of the University of Valencia.

The aim of this workshop is to share the research done by PhD students in the different fields of chemistry. This workshop is thought of as an excellent opportunity for every PhD student in chemistry to practice and give an oral communication in a friendly environment and, even, open new multidisciplinary collaboration lines between the different departments of the Faculty. Although the congress has been designed by and for PhD students, undergraduate or Master's students are also welcome to present their research in the format of a poster presentation.

We hope that this workshop is of interest to you, and that you enjoy your time with us.

Organizing committee

Organising committee

- Adolfo Manuel Blasco Asencio. Institut Interuniversitari d'Investigació de Reconeixement Molecular i Desenvolupament Tecnològic - IDM
- Carmen Fernández Conde. Institut de Ciència Molecular - ICMOL
- Adrián García Martínez. Institut de Ciència Molecular - ICMOL
- María Dolores Garrido Blay. Institut de Ciència dels Materials de la Universitat de València - ICMUV
- Héctor Martínez Pérez Cejuela. Departament de Química Analítica
- Manuel Pérez Escribano. Institut de Ciència Molecular - ICMOL
- Paula Rodrigo Martínez. Institut Interuniversitari d'Investigació de Reconeixement Molecular i Desenvolupament Tecnològic - IDM
- Cristina Rodríguez Carrillo. Institut Interuniversitari d'Investigació de Reconeixement Molecular i Desenvolupament Tecnològic - IDM
- Ana María Rubio Gaspar. Institut de Ciència Molecular - ICMOL
- Sheila Sánchez Artero. Institut Interuniversitari d'Investigació de Reconeixement Molecular i Desenvolupament Tecnològic - IDM
- Iván Soriano Díaz. Institut de Ciència Molecular - ICMOL

Coordination

- Prof. Dr. Begoña Milián Medina. Departament de Química Física
- Prof. Dr. Rafael Ballesteros Garrido. Departament de Química Orgànica

Workshop structure and program

18 th of May

15.00h	Registration	
15.30h	Opening	
Session 1.	Chair: Adolfo Manuel Blasco Asencio	
16.00h	L1	**José David Badia Valiente**: "Digital identity tools and strategies to boost scientific activity visibility"
16.45h	OC1	**Álvaro Seijas Da Silva**: Molecular and cationic design of Fe-based layered double hydroxide for water oxidation
17.00h	OC2	**Milorad Andelkovic**: QM/MM study of the enzymatic mechanism of human asparaginase type III
17.15h	OC3	**Pau Peiró Vila**: Adapting a global retention model for HPLC-based classification of medicinal herbs
Session 2.	Chair: Héctor Martínez Pérez-Cejuela	
17.30h	OFC1	**Sofía Casal García**: A DyIII layered MOF with field-induced slow relaxation of the magnetization
17.35h	OFC2	**Alba Roselló Carrió**: 3D printed stir-sticks modified with selective ligands for bisphenol A extraction
17.40h	OFC3	**Natalia Piqueras García**: Determination of β-lactoglobulin in foods using an aptamer-modified stir bar followed by MALDI-TOF-MS
17.45h	OFC4	**Jaume Béjar Grimalt**: DrogoFinder: an open-source graphical user interface for the identification of illicit drugs using infrared spectroscopy
17.50h	OFC5	**Borja Fructuoso Castaño**: Organocatalytic Synthesis of δ-Sultones via nucleophilic addition of coumarine derivatives and sulfonyl fluorides
17.55h	Questions	
18.00h	Coffee break	
Session 3.	Chair: Sheila Sánchez Artero	
18.30h	OC4	**Borja Peris Camarasa**: Human biomonitoring of urinary acrylamide biomarkers in the eastern Spanish adult population
18.45h	OC5	**Eva María Garrido García**: Lateral flow-type indicator displacement assay: a promising tool for γ-hydroxybutyric acid (ghb) detection in beverages
19.00h	OC6	**Jesús Cases Díaz**: Protein encapsulation through MOF mineralization mediated by Lewis-acidity for effective intracellular delivery
Session 4.	Chair: Manuel Pérez Escribano	
19.15h	OC7	**Alejandro Orellana Silla**: Broad-range spin-crossover modulation in guest-responsive 2D Hofmann-type coordination polymers
19.30h	OC8	**Inés Adam Cervera**: Incorporation of phase change materials in polymer nanoparticles: applications in coatings and textiles
19.45h	OC9	**Thibaut Le Huec**: Hybridized MOF-on-MOF heterostructures: beyond MOF individual performances

19 th of May

Session 5.	Chair: Carmen Fernández Conde	
9.00h	OC10	**Paola Ogando Rivas**: Study of physicochemical parameters in honey from the Dominican Republic
9.15h	OC11	**Alberto Montoya Ruiz**: Molecular modification of the spin-phonon coupling in the 2D magnet CrSBr
9.30h	OC12	**Luis Fernando Jiménez Hernández**: Conducting polymer/metal oxide nanoparticles: application as hybrid thermoelectric films
Session 6.	Chair: Paula Rodrigo Martínez	
9.45h	OC13	**Mariana Barros Nogueira**: Spermine and spermidine detection: a look at two novel approaches
10.00h	OC14	**Julia Requena Ramírez**: Carbon nano-onions (CNOs) as promising photothermal and photodynamic therapeutic agents
10.15h	OC15	**Carlos Tereba Mamani**: Reversed-phase liquid chromatography with micellar mobile phases of sodium dodecyl sulphate and ionic liquid
10.30h	OC16	**Matteo Andrea Lucherelli**: Two-Dimensional graphene hybrid heterostructures – a covalent approach to their synthesis and properties
10.45h	Coffee break	
Session 7.	Chair: Cristina Rodríguez Carrillo	
11.15h	L2	**Enrique J. Carrasco-Correa**: "How to survive postdoc: Options, paths and alternatives in the academic way"
12.00h	OFC6	**Carlos Rodríguez-Arias Santiago**: Organocatalytic synthesis of spiro-indoline-pyrazolones through a [4+1] cyclization reaction of bromopyrazolones and aza-ortho-quinone methides
12.05h	OFC7	**Alejandro Gil Aparicio**: Development of sorbents based on porous functional materials for the extraction and preconcentration of perfluoroalkylated acids
12.10h	OFC8	**Roser Payà Pou**: Extraction and determination of bisphenols in environmental waters using 3D printed spiral columns combined with metal organic frameworks and molecularly imprinted polymers
12.15h	OFC9	**Mathilde Meyer**: Sustainable platforms for the extraction of emerging contaminants
12.20h	Questions	
Session 8.	Chair: Adrián García Martínez	
12.25h	OC17	**Jordi Hernández Contreras**: New chemodosimeter for detecting scopolamine and ketamine in beverages: a promising tool against drug-facilitated crimes
12.40h	OC18	**Camilo Andrés Jaramillo Hernández**: The effects of scaling-up CoAl layered double hydroxides synthesis through a hydrothermal approach
12.55h	OC19	**Miguel Muñoz Bartual**: A semiautomatic method for the determination of 28 synthetic hallucinogens in oral fluids using microextraction by packed sorbent coupled to liquid chromatography-tandem mass spectrometry
13.10h	OC20	**Eduardo Andrés García**: Industrial 'breakthrough' in carbon dioxide capture
Session 9.	Chair: Iván Soriano Díaz	
13.25h	OC21	**Álvaro Castilla Mocholí**: Enantioselective addition of sodium bisulfite to β,β-disubstituted nitroalkenes
13.40h	OC22	**Pau Congost Escoin**: In situ X-ray Absorption Spectroscopy Study of Sb-based Nanomaterials Stability in biological environments
13.55h	OC23	**Víctor Navarro Esteve**: PoC quantification and profiling of urine cells by integrated cytocentrifugation and infrared spectroscopy
14.10h	Lunch beak	
15.30h	L3	Round table: "Between academy and industry"
16.30h	Closure	

Plenary lectures

José David Badia Valiente es coordinador de investigación del grupo MATS (@iqmats_uv), y formador en el @sfpieuv en el ámbito de competencias de gestión de la investigación. Nos hablará sobre la importancia de seleccionar las herramientas y estrategias de identidad digital para potenciar la visibilidad de la actividad científica.

Enrique Javier Carrasco-Correa received his Ph.D. degree from the University of Valencia (UV) in 2015. He worked as a Ph.D student in CLECEM group at the Department of Analytical Chemistry in the UV. After Ph.D., he continued at the UV as a doctor through knowledge transfer projects to industry. Next, he obtained a two-year Postdoc contract from Generalitat Valenciana, shared between the UV and the University of Balearic Islands, in the group of Dr. Manuel Miró. Currently, he is working as assistant professor at the Department of Analytical Chemistry of the UV. So far, he is principal investigator of one project, and he has published more than 40 research articles, 1 patent, 4 book chapters and participates in more than 30 national and international symposiums, some of them as organization member, where has presented more than 80 oral and poster communications. His current research interests focus on the assessment of novel hybrid materials (e.g., monoliths, micro/nanomaterials, 3D-printed devices) in sensing, separation and microextraction techniques. He participates in divulgation activities, training of novice researchers and in the organization of workshops for young researchers. He also collaborates with industry for the development of novel products and methodologies.

Herramientas y estrategias de identidad digital para potenciar la visibilidad de la actividad científica

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Trabajar en ciencia es inspirador, vibrante y genera satisfacción cuando todo sale bien… pero, ¿qué hacemos cuando sale todo bien y, además, conseguimos publicarlo? Nos quedamos con la satisfacción personal y profesional, o seguimos adelante algún plan de transferencia a nuestro entorno de los resultados de la investigación. El impacto depende tanto de la importancia de los resultados, como de su alcance y posterior usabilidad. En un mundo tan interconectado y rodeados de información, la capacidad de posicionar los resultados de la investigación es esencial. Por ello, tenemos a nuestra disposición una cantidad elevada de herramientas que nos ofrecen esa y otras funcionalidades. ¿Qué hacemos con ellas? ¿Cómo las utilizamos con eficacia y eficiencia? Más aún… ¿Cómo combinamos todo esto con nuestra labor profesional sin morir en el intento? Hablemos de herramientas de visibilidad, y de estrategias de posicionamiento digital científico.

¿Cómo sobrevivir al postdoc?
Opciones, caminos y alternativas en la vía académica

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"¿Cómo sobrevivir a la etapa postdoctoral o postdoc?" es una pregunta común que se hacen muchos investigadores en el mundo académico. El postdoc puede ser un momento desafiante para los recién doctorados, ya que requiere de un alto nivel de compromiso y dedicación para lograr el éxito. Además, es una etapa crucial para aquellos que desean seguir una carrera académica. En esta etapa, los investigadores buscan consolidar su formación, ampliar sus redes de contactos y seguir publicando trabajos de investigación de calidad. Sin embargo, sobrevivir al postdoc puede ser un desafío, ya que implica enfrentar una competencia feroz, presiones por publicar y falta de estabilidad laboral.

Para sobrevivir al postdoc y avanzar en la vía académica, es fundamental establecer metas realistas, administrar el tiempo de manera efectiva, aprender a manejar el estrés y la ansiedad, y establecer redes de apoyo con colegas y mentores. Además, es importante explorar diferentes opciones y caminos para avanzar en la carrera académica, ya sea a través de becas, programas de intercambio, colaboraciones internacionales, entre otros. Todo esto, sin olvidarse de mejorar el curriculum investigador, docente y general para mantener el nivel. En resumen, sobrevivir al postdoc y avanzar en la vía académica requiere de una combinación de habilidades, estrategias y actitudes que permitan enfrentar los desafíos y aprovechar las oportunidades que se presenten en el camino.

En esta presentación oral, se abordarán diversas estrategias para lograr la estabilidad en la carrera académica, incluyendo las oportunidades de becas, contratos y empleos que pueden ayudar a alcanzar este objetivo. Además, se ofrecerán consejos e ideas para orientar el currículum investigador hacia la carrera académica, sin dejar de lado otras alternativas como la industria o la docencia. Además, se plantearán consejos e ideas desde la experiencia para aprender a gestionar la vida postdoctoral.

Round table

Between the academia and the industry

Carmina Alfonso holds a PhD in Chemistry from the University Jaume I of Castellón, a Master in Applied and Pharmacological Chemistry from the same university and an International Master in Project Management from the EAE Business School. She obtained her PhD in the group of Professor Rosa Llusar and carried out an international stay at the Leibniz Institut für Katalyse (Rostock, Germany) under the supervision of Professor Matthias Beller. After defending her doctoral thesis in 2016, she decided to redirect her professional career as industrial formulator of hygiene products in Dydsa, a valencian company which is now Christeyns España. Nowadays, she is part of the personal care division of Zschimmer & Schwarz Spain, company where she started in 2018, and among her responsibilities are included technical assistance to cosmetic formulators, development of market strategies and creation of scientific content for social networks and different specialized media outlets.

Ana Gonzálvez obtained her PhD in Chemistry from the Faculty of Chemistry at the University of Valencia in 2011, with 12 publications in scientific journals. Her doctoral thesis was on Analytical Techniques for the determination of denomination of origin in food. Subsequently, she began her professional path in SPB (softeners and bituminous plastics) as a homologations technician. She followed her career at RNB Cosmetics Laboratories as product development and purchasing manager for 10 years. She is currently working at Germaine de Capuccini as technical director. She has taken a program on Management Development (PDD20) at IESE in Madrid, as well as specific courses in the cosmetic field. She has been part in 2 CDTI projects of the Ministry, as well as person in charge for them during 2019- 2022. She has annually collaborated with ITENE in the Master of Containers and Packaging, and at the University of Valencia with the subject Projects in Chemistry.

Alicia Monleón graduated in Chemistry in 2008 by the University of Valencia, where she also obtained her PhD in Organic Chemistry in the field of asymmetric catalysis in 2013. She then held postdoctoral researcher positions in Aarhus University and the Institute of Chemical Research of Catalonia (ICIQ), where she gained expertise in remote functionalization reactions by asymmetric organocatalysis and nickel catalysis, respectively. She has also worked in Inesfly Coorporation and the Technological Institute of Plastic (AIMPLAS), where she developed applied research projects. She currently holds an assistant professor position at the University of Valencia. Besides her background as a scientist, she worked as a People Development Officer at ICIQ in 2018, where she was responsible for career development actions. Since then, she has been training young researchers in transferable skills and guiding them in their career. Her research has been focused on the utilization of catalysis to improve reactivity and develop more sustainable processes. In particular, she has wide expertise in asymmetric metal and organocatalyzed reactions.

Patricia Gómez obtained her Chemistry degree at the University of Valencia in 2012 after defending her degree's dissertation internationally at the Univerzita Karlova v Praze in Check Republic under the supervision of Prof. Ivan Lukes. After two years, she obtained her masters in nanoscience and nanotechnology at the University of Valencia in the Instituto de Ciencia Molecular (ICMol) in the area of multifunctional materials, research that followed a PhD in nanoscience and nanotechnology in lantanide odxalate and anilate based muntifunctional molecular materials studying their magnetic properties in 2018 while univeristy teaching from 2013 to 2017. Afterwards, her professional carrer moved on to the industrial area at AL-Farben from 2017 to 2019 taking part in research projects CDTI and CIDETEC and the development of new inorganic pigments for pains as well as testing new organic and inorganic raw materials. Nowadays, she is working since 2020 at Torrecid as an I+D technitian in the development of new ink formulations over plain glass and also scaling different industrial process along the way, among other duties.

Oral contributions

OC1. Álvaro Seijas Da Silva: Molecular and cationic design of Fe-based layered double hydroxide for water oxidation.

OC2. Milorad Andelkovic: QM/MM study of the enzymatic mechanism of human asparaginase type III.

OC3. Pau Peiró Vila: Adapting a global retention model for HPLC-based classification of medicinal herbs.

OC4. Borja Peris Camarasa: Human biomonitoring of urinary acrylamide biomarkers in the eastern Spanish adult population.

OC5. Eva María Garrido García: Lateral flow-type indicator displacement assay: a promising tool for γ-hydroxybutyric acid (ghb) detection in beverages.

OC6. Jesús Cases Díaz: Protein encapsulation through MOF mineralization mediated by Lewis-acidity for effective intracellular delivery.

OC7. Alejandro Orellana Silla: Broad-range spin-crossover modulation in guest-responsive 2D Hofmann-type coordination polymers.

OC8. Inés Adam Cervera: Incorporation of phase change materials in polymer nanoparticles: applications in coatings and textiles.

OC9. Thibaut Le Huec: Hybridized MOF-on-MOF heterostructures: beyond MOF individual performances.

OC10. Paola Ogando Rivas: Study of physicochemical parameters in honey from the Dominican Republic.

OC11. Alberto Montoya Ruiz: Molecular modification of the spin-phonon coupling in the 2D magnet CrSBr.

OC12. Luis Fernando Jiménez Hernández: Conducting polymer/metal oxide nanoparticles: application as hybrid thermoelectric films.

OC13. Mariana Barros Nogueira: Spermine and spermidine detection: a look at two novel approaches.

OC14. Julia Requena Ramírez: Carbon nano-onions (CNOs) as promising photothermal and photodynamic therapeutic agents.

OC15. Carlos Tereba Mamani: Reversed-phase liquid chromatography with micellar mobile phases of sodium dodecyl sulphate and ionic liquid.

OC16. Matteo Andrea Lucherelli: Two-Dimensional graphene hybrid heterostructures – a covalent approach to their synthesis and properties.

OC17. Jordi Hernández Contreras: New chemodosimeter for detecting scopolamine and ketamine in beverages: a promising tool against drug-facilitated crimes.

OC18. Camilo Andrés Jaramillo Hernández: The effects of scaling-up CoAl layered double hydroxides synthesis through a hydrothermal approach.

OC19. Miguel Muñoz Bartual: A semiautomatic method for the determination of 28 synthetic hallucinogens in oral fluids using microextraction by packed sorbent coupled to liquid chromatography- tandem mass spectrometry.

OC20. Eduardo Andrés García: Industrial 'breakthrough' in carbon dioxide capture.

OC21. Álvaro Castilla Mocholí: Enantioselective addition of sodium bisulfite to β,β-disubstituted nitroalkenes.

OC22. Pau Congost Escoin: In situ X-ray Absorption Spectroscopy Study of Sb-based Nanomaterials Stability in biological environments.

OC23. Víctor Navarro Esteve: PoC quantification and profiling of urine cells by integrated cytocentrifugation and infrared spectroscopy.

Molecular and cationic design of Fe-based Layered Double Hydroxide for Water Oxidation

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Nowadays, in the field of electrocatalysts for the oxygen evolution reaction, Fe-based LDHs stand out as one of the best oxygen evolution reactions (OER) electrocatalysts in alkaline conditions. In the attempt to improve the electrochemical performance of Fe-LDHs-based electrodes, many approaches have been reported.[1] Beyond these, Fe-clustering and covalent functionalization have been not explored, being the last two synthetic challenges within the field of LDHs.

On one hand, to shed light on the influence of Fe-clustering on the OER performance, firstly, we have selected MgFe-based LDHs phases as model systems. By optimization of a hydrothermal method based on triethanolamine different Fe-clustering degree has been achieved, and thanks to the diamagnetic behaviour of Mg, a simple magnetic characterisation allows us to identify the Fe-clustering degree. Nevertheless, both samples behave identically in terms of OER performance when glassy carbon electrodes are used. Surprisingly, striking differences arise when the samples are tested on nickel foam. Specifically, the sample exhibiting the lower Fe-clustering behaves as a better electrocatalyst with a reduction of the overpotential values of more than 50 mV to reach 100 mA/cm2, as a consequence of a favoured surface transformation of MgFe-LDHs phases into more reactive oxyhydroxide NiFe-based ones during the electrochemical tests. [2] To extend our study to NiFe-LDH, we have successfully synthesized high-clustering nanometric NiFe-LDHs using a scalable synthesis approach. This synthetic protocol has allowed us to obtain a significantly higher concentration of approximately 100 g/L of our materials, which is almost two orders of magnitude larger than current state-of-the-art synthetic methods. Importantly, the Fe-clustering of this scale-up NiFe-LDH results in improved electrochemical performance compared to traditionally synthesized NiFe-LDH/FeOOH across various current density ranges and different electrochemical setups, including rotatory disk electrode (RDE) and Anion Exchange Membrane Water Electrolyzer (AEMWE), with testing conducted up to a current density of 3 A·cm-2. For instance, the overpotential at 2.5 A·cm-2 for the scale-up NiFe-LDHs is measured at 1.96 V, whereas the traditionally synthesized NiFe-LDH/FeOOH exhibit a higher overpotential of 2.18 V. [3]

Last but not least, the covalent functionalization of LDHs has been explored to enhance their processability and stability as an electrocatalyst, for this, we develop for the first time the covalent functionalization of Fe-LDHs beyond silane-based molecules due to the reversible character of this bond in alkaline media. By a modified hydrothermal method from Kuroda et al. [4], the covalent functionalization of NiFe-LDHs with tris(hydroxymethyl) aminomethane (Tris) was performed. The NiFe-Tris LDH were fully characterized to identify the structural differences with a bare LDH. At the same time, the stability of the covalent functionalization in basic media was proved. Interestingly, the Tris molecule anchored to LDHs increases the electrocatalytic stability in absence of binder material. Thus, after 40 hours of the OER, the overpotential increase is 37% lower in the NiFe@Tris than in the NiFe-Cl@bare. To check the origin of this overpotential decrease, ICP analysis of electrolytes pre-treated with acid after the stability test was performed. A reduction of 27% and 17% of Ni and Fe respectively is observed in the electrolyte for functionalized samples. Consequently, it is demonstrated that, regardless of the decomposition process (detachment or dissolution), the NiFe-LDH functionalized presents greater stability. [5]

References

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[3] Abellán G.; Et al. Manuscript in progress.
[4] Muramatsu, K.; Et al. Inorg. Chem. **2020**, 59, 6110−6119.
[5] Seijas-Da Silva, A; et al. Manuscript in process.

QM/MM Study of the Enzymatic Mechanism of Human Asparaginase Type III

M. Andjelkovic[1], K. Zinovjev[1], C. A. Ramos-Guzmán[1,2], J. J. Ruiz-Pernía[1], I. Tuñón[1*]

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L-asparaginases (ASNases) are a group of enzymes catalyzing asparagine (Asn) hydrolysis reaction to aspartate (Asp). They play a significant role as a powerful treatment for acute lymphoblastic leukemia (ALL) due to the fact that ALL cells are unable to produce their own Asn and therefore the hydrolysis of Asn in blood can lead to their death.[1] Due to the immunogenic response and various side effects of enzymes of bacterial origin, many experimental attempts have been made to replace enzymes of bacterial origin with mammalian enzymes, such as human asparaginase type III (hASNaseIII).[2] ,

This study investigated the mechanistic proposal of hASNaseIII through molecular dynamics simulations, QM/MM and Adaptive string method [3]. Molecular dynamic simulations revealed that the dimeric form of the enzyme plays a vital role in stabilizing the substrate in the active site, despite the active site residues stabilizing the substrate originating from a single protomer. Thermodynamic Integration calculations revealed that the deprotonated state of the N-terminal group of Thr168 is compatible with experimental conditions at a relatively modest energy cost (1.4 kcal·mol^{-1}) and then can act as the base activating the nucleophile. Our QM/MM simulations, performed at the B3LYPD3/6-31+G*/MM level of theory, indicated that the enzymatic cycle has seven steps that can be divided into two parts (Figure 1): (i) formation of the acyl-enzyme and (ii) hydrolysis of the acyl-enzyme by a water molecule. The rate-determining step was found to be the second step of the hydrolysis part of the cycle, with a calculated free energy barrier of 20.9 kcal·mol^{-1}, in good agreement with the experimentally derived value of 17.6 kcal·mol^{-1}. Comparison of the theoretically obtained tetrahedral acyl- enzyme conformation with the X-ray structure provided further verification of the proposed mechanism.

The mechanistic proposal found in this work did not only provide a theoretical basis for understanding the necessity of the cleavage process and liberation of the N-terminal to activate hASNase3, but also the lack of enzymatic activity upon mutation of Thr186 and Thr219, due to its important role in transition states stabilization. The results presented in this study hold a great significance as they can serve both as a basis for further research on the ALL treatment and as a foundation for the reaction mechanism of the whole enzymatic family, due to the high similarity between the N-terminal hydrolases.

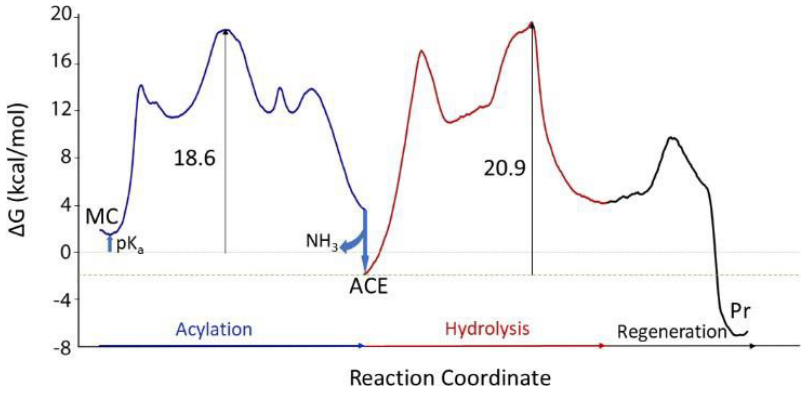

Figure 1. Free energy profile associated with the hydrolysis mechanism of Asn in the hASNaseIII.

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Adapting a global retention model for HPLC-based classification of medicinal herbs

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Medicinal plants are commonly used for both disease treatment and drug development. Chromatographic fingerprints (CFs) are used to authenticate and classify these natural materials by expressing the diversity of their chemical constituents through gradient separation. The quantity of constituents present in a sample can impact the informativeness of its CF, with more constituents providing higher discriminant quality in classification studies. However, obtaining accurate analytical methods for CFs is often challenging due to the need to model the retention behaviour of the constituents and forecast the most favourable separation conditions. This requires knowledge of the nature of all components and available standards, which are not always available for natural products. Global retention models provide a solution for optimizing separation in the absence of standards. These models separate the common effects on retention produced by the column and solvent from the specific effects associated with the chemical nature of each solute. The methodology involves fitting a limited set of representative solutes to create a "restricted global model," which is then extended to include the rest of the chromatographic peaks using an arbitrary gradient to form an "extended global model." This approach has been successfully applied and validated using extracts from various medicinal plants, including green tea, linden, mint, lemon balm, and chamomile.

The research presented in this article aims to (i) study the transferability of a global model developed two years ago to a new instrument and sample with similar nature, (ii) use the transferred model to optimize a multilinear gradient program to obtain a chromatogram with maximum visible constituents, and (iii) classify a set of commercial tea samples according to their variety using the optimized gradient. Updating the global model requires a single experiment to update the solute parameters and measure dead, extra-column, and dwell times. After determining these parameters, accurate chromatographic profiles can be predicted. As green tea contains many of the characteristic compounds found in different tea varieties, the optimal gradient is expected to have general applicability. Gradient optimization is performed by monitoring the sum of peak purities of the constituents comprising 99.95% of the total area. The gradient with maximum resolution that best balances the solute distribution is selected using Pareto optimality, considering the wide dispersion of polarities. The optimal gradient is validated by comparing the predicted chromatogram with the experimental one, with signals corrected by baseline subtraction and quantified into three datasets: direct signals, elution bands, and band ratios. Classification studies are carried out using this information to test predictive performance.

Acknowledgments

Work supported by Grant PID2019-106708GB-I00 funded by MCIN (Ministery of Science and Innovation of Spain)/AEI/10.13039/501100011033. Pau Peiró Vila thanks the Generalitat Valenciana for a pre-doctoral grant ACIF 2022.

HUMAN BIOMONITORING OF URINARY ACRYLAMIDE BIOMARKERS IN THE EASTERN SPANISH ADULT POPULATION

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Acrylamide (AA) is a chemical compound classified as "Probably carcinogenic to humans" by International Agency for Research on Cancer (IARC) [1]. It is formed in processed carbohydrate-rich foods and in tobacco smoke, so the general population mainly exposed to AA by dietary intake and inhalation. Thus, exposure to AA might represent a potential public health threat. After dietary exposure, humans eliminate about 50% of AA in 24h in the urine as mercapturic acid conjugates, primarily as N-acetyl-S-(2-carbamoylethyl)-L-cysteine (AAMA), N-acetyl-S-(2-carbamoyl-2-hydroxyethyl)-L-cysteine (GAMA3), and N-acetyl-3-[(3-amino-3-oxopropyl)sulfinyl]-L-alanine (AAMA-Sul), which can be used as short-term biomarkers of AA exposure.

A representative sample of the adult population (aged 18-65 years) living in the Valencian Region (Spain) was recruited in 2020-2021 as part of the BIOMOVAL project. The main aims of the present study were: i) to determine the urinary levels of AA metabolites, and ii) to estimate the risk associated to AA exposure in this population group.

First-morning urine samples were collected and analysed using a "dilute-and-shoot" method. The major urinary AA metabolites, AAMA, GAMA3 and AAMA-Sul, were determined by liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS (QqQ)). The limit of quantification (LoQ) was 0.25 $\mu g \cdot L^{-1}$ for all metabolites.

To evaluate the risk associated to AA exposure, the estimated daily intake (EDI) was calculated based on the obtained urinary levels and compared with the Benchmark Dose Lower Confidence Limit ($BMDL_{10}$) by calculating the margin of exposure (MOE). The forward dosimetry approach was also used, where urinary AAMA levels were compared with its Biomonitoring Equivalent (BE) [2], by the calculation of the hazard quotient (HQ) [3]. AAMA, GAMA-3 and AAMA-Sul, were detected and quantified in 100% of the analysed samples, with geometric means (GM) of 84, 11 and 26 $ng \cdot mL^{-1}$, respectively. The calculated EDIs of AA ranged between 1.33 and 2.13 $\mu g \cdot kg\text{-}bw^{-1} \cdot day^{-1}$ in the GM.

In a risk context, only a MOE lower than 125 was found in the assessed population group at the P95 distribution. By contrast, AAMA levels at GM were significantly higher than the BE, leading to HQ values between 4.6 and 8.2 in the GM. Due to the high detection frequencies of AA metabolites on the analysed urine and that urinary levels of AAMA are between 5 and 8 times higher than the corresponding BE, the risk of exposure to AA in the target population could not be discarded. Thus, AA exposure in the Eastern Spanish population should be closely monitored and continuously evaluated in a risk context.

Acknowledgments

This work was supported by the Public Health General Directorate of Valencia together with FISABIO, which financed the BIOMOVAL project, and by the ACIF/2021/337 and ACIF/2019/183 projects funded by the Valencian Government. The European Commission financed the analytical instruments used here through the European Regional Development Funds (ERDF) Operation Program of the Valencian Region (2014-2020). P. Dualde acknowledges his "Ayudas para la contratación PTA" (PTA2018-016320-I) from Ministry of Science and Innovation (Spain). The authors would like to express their gratitude to the donors, SERPRECOVA and the UJI for their cooperation in the recruitment of participants and the sample collection, and the IBSPCV BioBank (PT13/0010/0064) for their collaboration in the processing and storage of the samples.

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LATERAL FLOW-TYPE INDICATOR DISPLACEMENT ASSAY: A PROMISING TOOL FOR γ-HYDROXYBUTYRIC ACID (GHB) DETECTION IN BEVERAGES.

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γ-hydroxybutyric acid (GHB) is a natural metabolite, which is currently used as a date rape drug. Particularly, GHB is rapidly eliminated and its detection in realistic environments is only possible within 6-12 h after ingestion [1]. Owing to the increasing use of GHB for criminals purposes, a need has arisen to develop simple and *in situ* efficient assays for its identification in aqueous and alcoholic drinks [2].

Based on the above, we report herein an indicator displacement assay (*IDA*) for GHB detection that consists of a Cu^{2+} complex with a tetradentate ligand and the fluorescent dye, coumarin 343 (*IDA* probe **1**). Firstly, the tetradentate ligand was synthesized by reductive amination of a 1,2-cyclohexyl diamine with 2-quinolinecarboxaldehyde. Subsequently, this ligand was reacted with $Cu(CF_3SO_3)_2$ to obtain the corresponding copper complex, which generates the final sensing ensemble by coordinating with coumarin 343 (*IDA* probe **1**). The sensing mechanism relies on a displacement of coumarin 343 from the sensing ensemble **1** thus restoring its fluorescence, as a consequence of the higher binding constant between GHB and complex, showing a high sensitivity in MES buffer (50 mM, pH 6.0) (detection limit of 0.03 μM). Likewise, system design and optimization led to a straightforward integration into a lateral-flow assay without further treatment or conditioning of the test strips while guaranteeing fast overall assay times of 1 min (Figure 1). In this way, *IDA* probe **1** was incorporated into a coated PEG-glass fibre (**PEG-GF**) membrane to obtain a highly robust and sensitive lateral flow assay for GHB detection in spiked alcoholic drinks with a detection limit of 0.1 μM in less than 1 min coupled to smartphone readout.

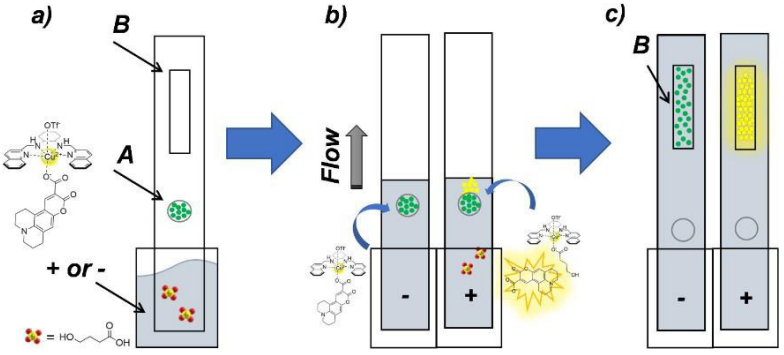

Figure 1. Design of the lateral flow assay on strip with *IDA* probe **1** integrated into a coated **PEG-GF** membrane.

Acknowledgments
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Protein encapsulation through MOF mineralization mediated by Lewis-acidity for effective intracellular delivery

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The use of solid scaffolds as supports for biomolecules has a great relevance for their widespread application in pharmaceutical and chemical processing, as these matrixes confer stability towards harmful conditions. Recently, different Metal-Organic Frameworks (MOFs) have been explored as supports, resulting excellent candidates for the immobilization of biomolecules [1] owing to their physico-chemical stability, their convenient biodegradability and the possibility of synthesis under biocompatible conditions. This last trait opens the possibility to the so called in-situ synthesis, that consists of the spontaneous assembly of protective MOF coatings onto the biomolecules. This strategy has been shown to depend on the effective interaction between the MOF precursors, mainly the metal cation, and the biomolecule surface, in some cases being hampered by its surface electrostatics.[2] Also, the scarce number of MOFs that can be synthesized under biocompatible conditions has restricted the number of supports that can be employed for the immobilization of biomolecules.

Herein, we present a general in situ biomolecule encapsulation using a biocompatible MOF, the mesoporous trimesate iron-based MIL-100(Fe) material. We demonstrate that MOFs based on cations exhibiting considerable inherent acidity are suitable for biomolecule encapsulation regardless of their isoelectric points (5<pI<11). MIL-100(Fe) scaffold retains protein activity and permits release under biocompatible conditions, allowing their use in desired biological applications.

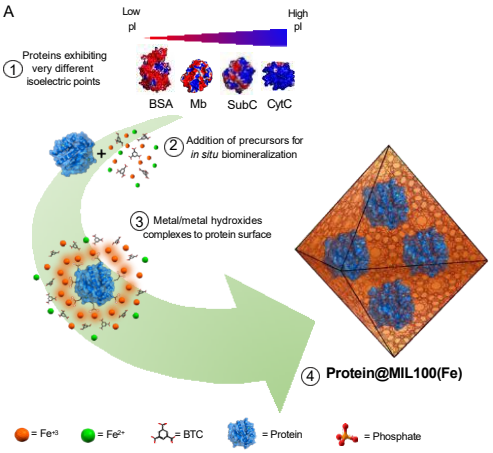

Figure 1. Mechanism of spontaneous MOF growth onto a broader variety of proteins and its intracellular release. Schematic representation of in situ protein encapsulation of a variety of proteins into MIL-100(Fe). The theoretical electrostatic surface potentials of BSA, Mb, SubC and CytC proteins calculated using PDB2PQR web service33 (PDB files: BSA: 3v03, Mb: 1azi, SubC: 1c3l, CytC: 2b4z) and visualized with PyMOL. Charge levels are represented from –12.85 mV (red) to +12.85 mV (blue).

Acknowledgments

The authors acknowledge financial support from MCIN/AEI/10.13039/501100011033 (grant PID2020-118564GA-I00 and CEX2019-000919-M), Generalitat Va-lenciana GentT Program (SEJI/2020/036) and "la Caixa" Foundation (LCF/BQ/PI19/11690022). M. G.-M. acknowl-edges the Spanish MICINN for a Ramón y Cajal Contract (RYC2019-027902-I). B. L.-T. acknowledges her current Margarita Salas postdoctoral fellowship from MIU and «Next Generation EU» program contract.

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Broad-range spin-crossover modulation in guest-responsive 2D Hofmann- type coordination polymers

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Rationalizing the role of chemical functionalization in the synergy between spin crossover (SCO) and guest adsorption properties in porous Fe^{II} coordination polymers is a central topic in the switchable materials field[1]. However, obtaining meaningful magneto-structural information requires the comparison between structural platforms whose topology remains unaltered upon chemical function exchange. Here, based on the previously reported SCO two-dimensional Hofmann-type compounds $\{Fe(NH_2Pym)_2[M(CN)_4]\}\cdot x$guest (**1(NH$_2$)^M·xguest**; NH_2Pym = 5-aminopyrimidine; M = Pd^{II}, Pt^{II}; guest = H_2O, MeOH, EtOH; x = 0-1)[2], we present the isostructural networks **1(OH)^M·xguest** resulting from the replacement of the 5-NH2Pym axial ligand with 5-OHPym (5- hydroxipyrimidine) (figure 1). The evaluation of their temperature dependent magnetic and calorimetric data reveals that whereas the unsolvated counterparts (**1(NH$_2$)^M** and **1(OH)^M**) undergo complete one step spin transitions with small variations in their SCO temperatures (T_c), the solvated species markedly differ not only in Tc but also in the shape of the spin transition curve. A relevant example is observed for **1(NH$_2$)^M·0.5MeOH** and **1(OH)^M·0.5MeOH**, which present incomplete one-step and complete three-step spin transitions, respectively. These changes are also complementary to the higher adsorption capacities of the hydroxy-functionalized compounds according to the guest uptake isotherms, powder X-ray diffraction and thermogravimetric data. The single crystal-to-single crystal transformations occurring upon the sorption-desorption of guest molecules have permitted us to determine the structural reasons explaining the variation of the SCO and adsorption properties with chemical functionalization.

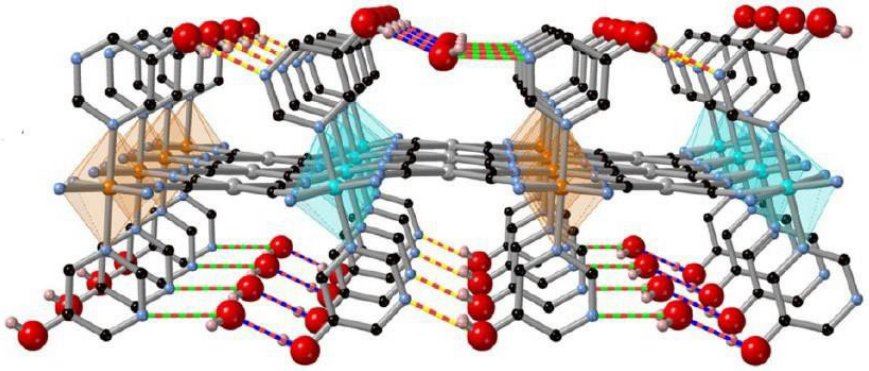

Figure 1. Single bimetallic layer of **1(OH)^{Pt}·H$_2$O**.

Acknowledgments
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Incorporation of Phase Change Materials in Polymer Nanoparticles: Applications in Coatings and Textiles

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Phase change materials (PCMs) are materials that have the ability to store thermal energy in the form of latent heat during a phase change and release it when returning to the initial phase. These properties have made PCM very attractive materials for the development of new energy storage systems in a sustainable way.[1]

In this context, this work focuses on the encapsulation of solid–liquid organic PCMs, namely the alkanes hexadecane and octadecane, by using the miniemulsion polymerization technique. Hexadecane and octadecane are attractive PCMs for many applications because of their good thermal conductivity and their high efficiency in storing significant amounts of heat at temperatures close to room temperature. Nevertheless, they also present problems, such as large volume changes during the phase transition or potential negative effects on the environment. For this reason, to control volume changes, avoid leaks, protect the surrounding medium from negative effects and guarantee the cyclability of the process, in this work hexadecane and octadecane were encapsulated in polystyrene capsules prepared by direct miniemulsion polymerization.[2,3]

In addition to the encapsulation of PCMs, this work also presents the preparation of different coatings embedding encapsulated PCM. The incorporation of PCMs in coatings improves the structural stability and allows for an easy application and processing on the desired surfaces. Furthermore, the application in the form of coatings increases the resistance to fracture of the material and avoids leakage of the PCMs to the direct environment.

Two types of coating have been prepared. First, polymer films were prepared by redispersing the PCM capsules in a polymer solution. Second, PCM capsules were deposited on textile fabrics and copper films by using the layer-by-layer (LbL) technique. The efficacy of the prepared nanocomposites for energy storage applications was evaluated by differential scanning calorimetry (DSC).

Acknowledgments
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Hybridized MOF-on-MOF heterostructures: beyond MOF individual performances

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Metal-Organic Frameworks (MOFs) also known as porous coordination polymers (PCPs) are versatile materials that have transformed the field of porous solids. Their hybrid modular nature, together with their unprecedented porosity are responsible of their multiple uses in very distinct fields including storage/separation, catalysis, water harvesting and remediation, and drug delivery.

Integration of different Metal-Organic Frameworks (MOFs) to construct hybrid MOF-on-MOF heterostructures has produced an emerging class of materials with tailored compositions and functionality.[1][2] These hybrid heterostructures have shown promising uses surpassing in some cases individual performances. However, control over the synergistic effects identified among individual MOF ingredients remains challenging.

Herein we present the synthesis of a family of highly crystalline hybridized MOF-on-MOF nanostructures obtained by strategic combination of phase-matching MOF nanocrystals. The synthesis relies on the epitaxial growth of flexible iron-based MIL-88A and MIL-88B MOF onto the (111) facet of robust zirconium-based MOF nanoparticles of UiO-66 and UiO-66-NH_2. Structure characterization reveals the retention of MIL-88´s flexibility after the epitaxial growth.

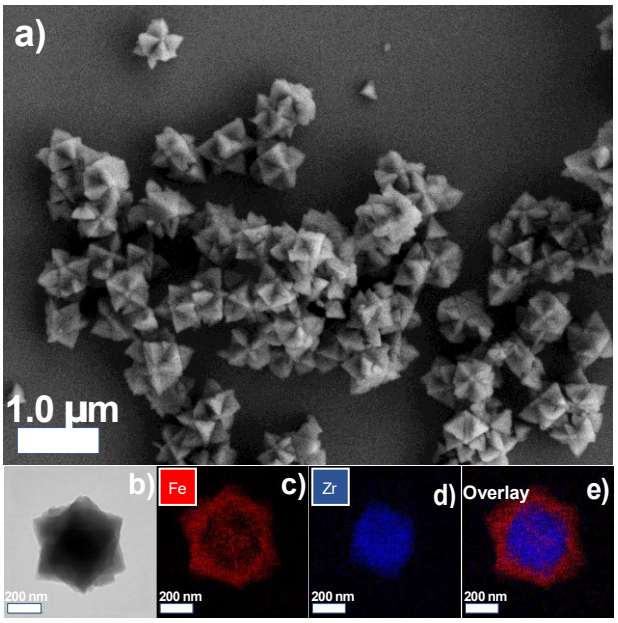

Figure 1. a) SEM image of MIL-88B-on-UiO-66-NH_2, b) HRTEM image of MIL-88B-on-UiO-66-NH_2 and c,d,e) EDS mapping of MIL-88B-on-UiO-66-NH_2.

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Study of physicochemical parameters in honey from the Dominican Republic

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Beekeeping is a subsector of agriculture in the Dominican Republic that was declared of national interest in 2006. However, the productive capacity of this sector is currently significantly lower than its potential, considering the abundant natural resources available in the country. Promoting beekeeping could not only benefit rural populations by providing an economic opportunity but also complement their conventional agricultural activities. As a first step, it is necessary to identify the characteristics of the honey currently being produced in the country and assess its compliance with commercial transaction standards to effectively leverage this opportunity. Therefore, the objective of this work has been to evaluate the characteristics of honey produced in the Dominican Republic.

To establish the quality of honey produced in the Dominican Republic, 72 samples were collected from different provinces across the country's three regions: North Region (Monseñor Nouel, Santiago, Monte Cristi, Dajabón, Santiago Rodríguez, and Puerto Plata), South Region (Peravia, Azua, San Cristóbal, Elías Piña, and Bahoruco), and East Region (Monte Plata, San Pedro de Macorís, Santo Domingo, and Hato Mayor). The honey analysis was divided into four approaches:

1) Evaluation of the physicochemical parameters, such as hydroxymethylfurfural (HMF), diastatic index, humidity, and free acidity, which are quality indicators established by international legislation.
2) Analysis of other physicochemical parameters that define honey, including conductivity, color, water activity (aw), and pH.
3) Implementation of novel techniques and methodologies, such as gold nanoparticles and porous organic polymers, to synthesize functional materials that provide additional information about the honeys.
4) Study of the influence of region and province on the different evaluated parameters by using chemometric approaches, such as linear discriminatory analysis, to classify the honeys according to their regions.

Overall, the analysis showed that the physicochemical parameters of honey from the Dominican Republic met the standards required for commercial transactions. Moreover, the use of gold nanoparticles in combination with porous organic polymers provided a simpler and faster way to extract and preconcentrate proteins from honey for subsequent analysis by liquid chromatography. The preconcentrated protein profiles revealed differences between the different regions of the Dominican Republic. Finally, the different obtained parameters were used to develop classification systems using chemometrics to classify the honeys based on their regions.

Acknowledgments

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Molecular modification of the spin-phonon coupling in the 2D magnet CrSBr

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The recent discovery of two-dimensional (2D) magnets has provided an unexplored and ideal platform to manipulate and control 2D magnetism [1]. Among them, the semiconducting CrSBr has received special attention due to its air-stability and high critical temperature (T_c = 146 K), making it a promising candidate for applications in spintronics or magnonics at the single-layer limit. [1] Furthermore, the properties of CrSBr have been proved to be sensible to be modified with different methods such as defect induction, strain engineering or atomic substitution. [2] In this talk we will explore the modification of spin-phonon coupling (SPC) of CrSBr by the deposition of the donor TTF organic molecule (with π (pz) electrons). Firstly, we calculate the (SPC) interaction in CrSBr monolayer by means of first-principles calculations to determine the influence of the magnetic state in the amplitude and direction of phonon modes. Then, we will introduce a method that overcomes the computational challenge of simulating the phonon frequencies for hybrid systems. By applying a finite displacement approach, combined with DFT calculations we obtained second derivatives of total energies as a function of displacement following the corresponding phonon eigenvector direction (u_j). [3] Finally, we prove that some modes (three of them visible by first order Raman scattering) are shifted in frequency upon TTF deposition, agreeing well the order of change observed experimentally after ambient, heating and water exposure or He^+ irradiation of CrSBr. [4]

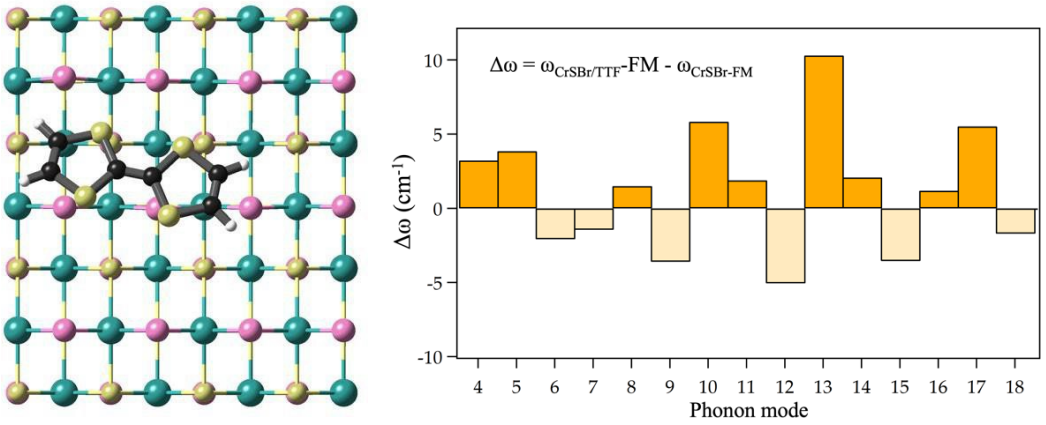

Figure 1. Figure: Graphical representation of TTF deposited upon CrSBr (left) and frequency shift of the 15 optical modes of CrSBr due to TTF deposition (right). Cyan, yellow, pink, black and white balls represent chromium, sulfur, bromine, carbon and hydrogen atoms, respectively.

Acknowledgments

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Conducting Polymer/Metal Oxide Nanoparticles: Application as Hybrid Thermoelectric Films.

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The increasing demand of sustainable energy has motivated the development of materials capable of converting heat into electricity [1]. Intrinsically conductive polymers (ICPs) have emerged as promising materials for trending applications due to their lightweight and availability, however, inorganic semiconductors still possess higher thermoelectric properties. Extensive efforts have been made to improve the electrical conductivity (σ) and Seebeck coefficient (S) of ICPs by filling them with metal oxide nanoparticles [2]. The larger thermoelectric power observed for these composites has been attributed the synergy between the inorganic semiconductors and the conductive polymer matrix. However, the simultaneous enhancement of both properties is a well-known challenge related to the limited electronic interaction between the inorganic and organic moieties in the composites prepared after conventional methods [2]. On the other hand, miniemulsion polymerization has been studied for the preparation of functional polymers nanoparticles. The addition of inorganic nanoparticles into the final polymers can be achieved either by their incorporation to the surface of growing polymer particles or through their encapsulation into the monomer droplets before polymerization [3].

In this work, we present two pathways for the incorporation of cerium(IV) oxide and magnetite nanoparticles into polyaniline and polypyrrole by means of miniemulsion polymerization. Pure polymer nanoparticles were synthesized using a non-ionic, a cationic, and an anionic surfactant. In the first strategy, surfactants were replaced by CeO_2 and Fe_3O_4 nanoparticles as Pickering stabilizers. The second strategy consisted of the addition of highly hydrophobic CeO_2 nanoparticles to the dispersed phase. The incorporation of the inorganic moiety was studied by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and thermogravimetry (TGA). Finally, the electrical conductivity, Seebeck coefficient, and thermoelectric power factor of each system was determined for thin films prepared after the final colloids.

The results show that the incorporation of metal oxides into the conducting polymer, therefore the properties of the hybrid composites, is influenced by the chemical environment to which metal oxide nanoparticles are exposed during polymerization. In the filling strategy, the encapsulated inorganic nanoparticles are protected against the acidic oxidant conditions of the aqueous phase upon polymerization, thereby resulting in a major incorporation when compared to the Pickering strategy. Significant differences were found for the power factor of both, polyaniline and polypyrrole hybrid nanoparticles, with respect to the control group. For polyaniline, a greater thermoelectric performance was observed in systems prepared by the entrapping rather than the Pickering strategy, whereas for polypyrrole there were not significant differences between both groups. Specifically, the simultaneous enhancement of σ and the S in hybrid polyaniline/CeO_2 was related to this higher incorporation and tighter electronic interactions between the polymer and the inorganic nanoparticles.

Acknowledgments
The authors acknowledge financial support by Generalitat Valenciana through a Consolidated Group Grant (AICO/2021/237) and a Santiago Grisolía Fellowship (CIGRIS/2021/061) to L.F. J.-H.

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Spermine and Spermidine detection: A look at two novel approaches

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Spermine (Spm) and spermidine (Spd) are naturally occurring biogenic polyamines that can be found in almost all eukaryotic cells and fluids. These molecules play important roles in numerous physiological processes and functions related to cell growth and development. As a result, they have captured the interest of researchers as potential biomarkers for identifying various pathological conditions. Of particular interest is their quantification in the diagnosis of diseases, with cancer being a significant area of study. This is due to the fact that Spm and Spd are found in abundance in tumor cells, tissues, and urine of cancer patients[1-3]. However, detecting these polyamines can be challenging, so the design and synthesis of new probes for their easy and cost-effective detection is an area of continuous development.

Bearing this in mind, we present two detection systems for Spm and Spd. The first system employs a Tetraphenylethylene (TPE) derivative – **Figure 1a** – to detect Spm and Spd in urine[4], which shows the aggregation-induced emission (AIE) effect. This means that their fluorescent properties become more pronounced upon aggregation, which occurs due to the inhibition of aromatic-ring rotation, thereby activating their chromophore core and inducing fluorescence emission. The second system is based on functionalized MCM-41 with a N-hydroxysuccinimide derivative and loaded with rhodamine 6G – **Figure 1b**. A covalent bond is formed between silica nanoparticles and the inner layer, and hydrogen and hydrophobic interactions occur to create an external organic layer that traps the dye inside the porous structure. In the presence of amine groups, this coverage is removed, and the pores open, releasing the dye[5].

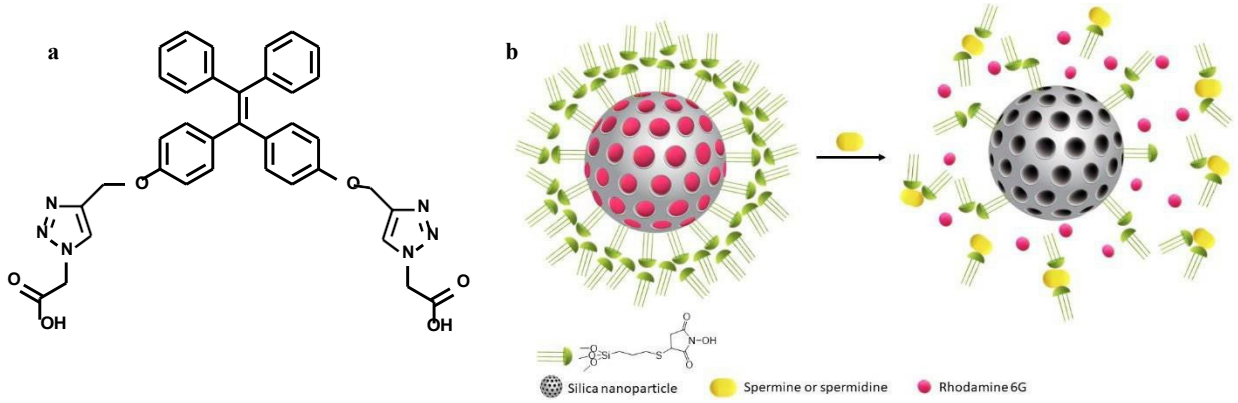

Figure 1. a) Structure of the TPE derivative. **b)** Sensing protocol for detecting Spm and Spd.

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Carbon nano-onions (CNOs) as promising photothermal and photodynamic therapeutic agents

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Carbon nano-onions (CNOs) are nanomaterials with a multi-layered fullerenes-like structure, first reported by Ijima in 1980.[1] Since their discovery, this carbon allotrope has been researched in a wide range of fields due to its outstanding physicochemical properties, such as graphitic core-shell morphology, large surface area to volume ratio, and biocompatibility, among others. These properties make CNOs excellent candidates in high-ending technological applications, such as energy conversion and storage, catalysis, and nanomedicine.[1,2] In 2005, *Ding et al.* demonstrated the biocompatibility of this nanomaterial, which was even greater than other carbon-based nanomaterials, for example, carbon nanotubes (CNTs).[3] For this reason, in recent years, studies have investigated their potential in biomedical applications, where they stand out as effective drug delivery systems, bioimaging, sensing, and theranostics agents. In this regard, a very important aspect to consider is the reactive oxygen species (ROS) generation. In most nanomaterials, the main form of cytotoxicity is ROS generation[3], which leads to oxidative stress causing cell death. In this context, ROS generation can be exploited in some biomedical approaches like photodynamic therapy (PDT), which selectively causes local cell-death through the photo-oxidation of nanomaterials.[4] On the other hand, CNOs could exhibit an efficient photothermal conversion to induce cell death through the generation of local heat. So, with this work, we would like to expand the knowledge of CNOs, paving the way for the application of this exotic carbon nanomaterial in PDT and PTT.[4]

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Reversed-phase liquid chromatography with micellar mobile phases of sodium dodecyl sulphate and ionic liquid

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In conventional reversed-phase liquid chromatography (RPLC), basic cationic compounds give rise to broad asymmetric peaks with high retention, due to the interactions between the cationic compounds and the free silanol groups in the stationary phase. RPLC where the anionic surfactant sodium dodecyl sulfate (SDS), or an ionic liquid are added to the mobile phase, has been proposed as a solution for the chromatographic analysis of basic compounds, since they are able to block the silanol effect. This improves the chromatographic conditions. With both additives, it is however necessary to increase the elution strength by adding an organic solvent, such as an alcohol or acetonitrile. In this work, the chromatographic behaviour of six basic compounds of pharmaceutical interest (the β-blockers acebutolol, atenolol, carteolol, metoprolol, oxprenolol and propranolol) has been studied, with mobile phases composed exclusively of SDS and an ionic liquid of diverse chain length (1 ethyl-, 1 butyl- or 1-hexyl-3-methylimidazolium chloride). This avoids the addition of organic solvent, which provides a type of green liquid chromatography. To know the chromatographic behaviour of this type of mobile phases, the changes in retention, profile of the chromatographic peaks and separation of mixtures of the analytes were examined. The study was performed with mobile phases at fixed concentration of surfactant and variable concentration of ionic liquid, as well as with mobile phases at fixed concentration of ionic liquid and variable concentration of surfactant.

Acknowledgments

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Two-Dimensional graphene hybrid heterostructures – a covalent approach to their synthesis and properties.

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Two-dimensional (2D) materials, of which graphene is the first and most famous member, has gained increasing attention due to their unique properties, such as high surface area, thermal, and electrical properties, tunable electronic properties, and mechanical strength.[1] Moreover, other 2D materials such as transition metal dichalcogenides, black phosphorus, or layered double hydroxide (LDH), have shown great potential due to their diverse properties capable of overcome graphene limitation, such as semiconducting behavior, high dielectric constant, and strong piezoelectricity.[2,3]

The combination of these materials could lead to new properties, such as enhanced electrochemical performance, improved mechanical strength, and tailored electronic properties. The control over hybrids morphology, type and order of assembly, oxidation and chemical composition could also permit to tailor their specific applications by adjusting the composition and morphology of the materials.[4–6] However, to date, despite large knowledge about graphene and 2D materials functionalization, most of the investigation focused on non- covalent hybrids synthesis, leaving a lack of knowledge about covalent hybrid materials, that could actually have the potential to be the most effectiveness in combing materials properties.

This talk, through the presentation of the work about 2D heterostructures developed in our laboratory (Figure 1), is intended to give to the audience a general overview about 2D material chemistry, their functionalization and characterization methods and the wide possibility offers by these. The organic chemistry approach to obtain hybrids of graphene with molybdenum disulphide, Ni-Fe layer double hydroxide and perovskite will be presented, together with the main results of these investigations.

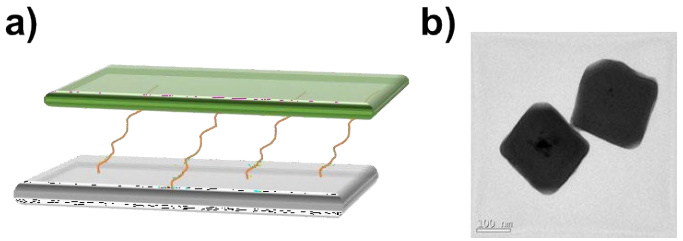

Figure 1. Example of 2D heterostructures: a) Schematic representation of covalent heterostructure; b) Graphene-Perovskite heterostructure.

Acknowledgments
M.A.L acknowledge the APOSTD/2021/255 fellowship.

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New chemodosimeter for detecting Scopolamine and Ketamine in Beverages: A promising tool against drug-facilitated crimes.

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In recent times, there has been a surge in incidents of chemical submission crimes, which involve the use of psychoactive substances to manipulate or alter the behavior of victims for criminal purposes, such as perpetrating sexual assaults [1]. Scopolamine and ketamine are frequently utilized in drug-facilitated sexual assaults because even low doses of these drugs can cause unconsciousness. Despite having valid medical applications, the potential for these drugs to be abused and employed in criminal activities underscores the need for effective regulation and control of their use [2]. The present research introduces a new chemodosimeter, depicted in Figure 1, which can identify scopolamine and ketamine using Cu(II). Remarkably, this detection can be carried out simultaneously, with naked-eye, under visible light, and even under fluorescence lamp, as demonstrated in Figure 2. This chemodosimeter is designed by incorporating a BODIPY moiety as a fluorophore and a phenanthroline in the meso-position as a ligand that can coordinate a copper ion. The outcomes of the investigation suggest that the proposed chemodosimeter is capable of detecting the existence of scopolamine and ketamine in water and beverages.

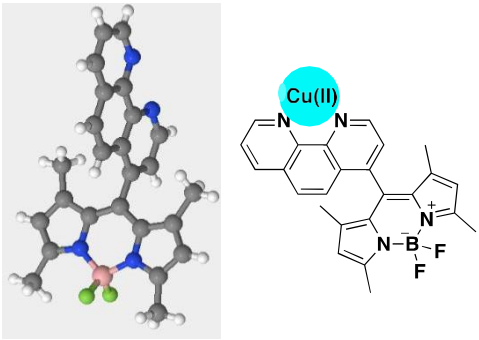

Figure 1. Chemodosimeter structure by X-Ray results

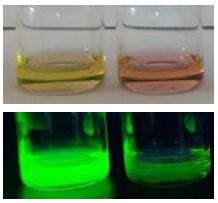

Figure 2. Color and fluorescence changes in presence of scopolamine in water (Blank/Spiked)

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The effects of scaling-up CoAl layered double hydroxides synthesis through a hydrothermal approach

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Research on layered materials is a significant field in material science and layered double hydroxides (LDHs) are particularly noteworthy due to their potential applications in photo-catalysis, energy storage and conversion systems, and environmental applications. However, using LDHs in real-life devices requires large-scale production. [1,2] In this work, we study the effects of the scaling-up processes by both mass (25-times: up to 375 mM) and volumetric (20-times: up to 2 L) approaches for the urea-based hydrothermal synthesis of CoAl-based LDH. [3] In the case of the volumetric scaled-up, a reduction of 45% (from 3.7 to 2.0 μm) is observed as the reaction volume increases. This fact is related to the modification on heating-up processes affecting the alkalinization rates and concomitantly the precipitation, even under hydrothermal recrystallization. On the other hand, similar morphological aspects on pure CoAl-LDH were observed for the mass scaled-up up to 10-fold, assigned to changes in the nucleation and growth. However, at higher concentration scenarios, the presence of simonkolleite-like Co-based LH as an impurity is observed, denoting phase competition during the precipitation: thermodynamic stability of the on-growing phases.

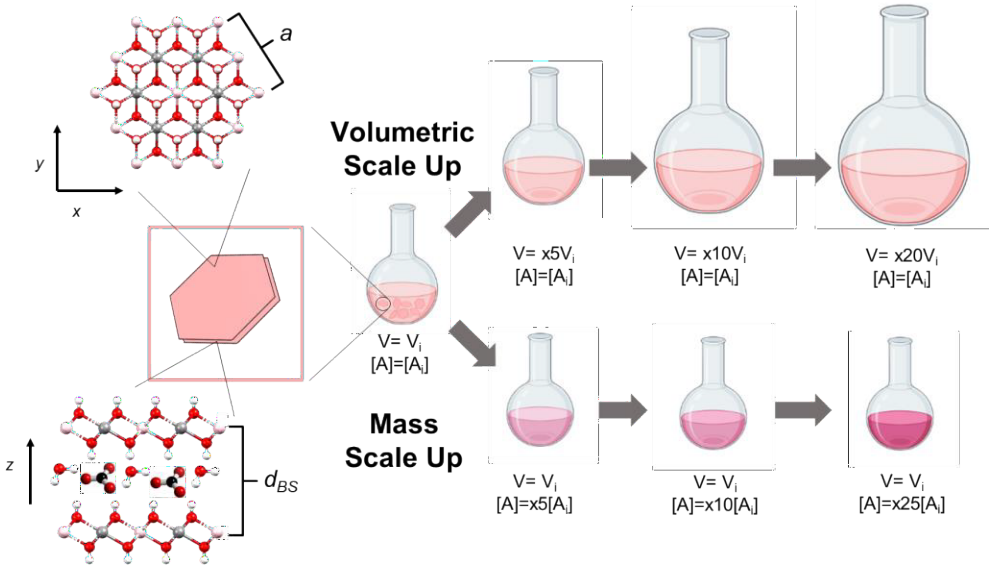

Figure 1. Schematic representation for the scaling-up process employing CoAl-based layered double hydroxides as reference material for both volumetric and mass approaches. LDH structure highlighting both crystal facets, xy (in-plane) and z (out-of-plane) views and their crystallographic parameters, basal space distance (dBS) and a parameter.

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A semiautomatic method for the determination of 28 synthetic hallucinogens in oral fluids using microextraction by packed sorbent coupled to liquid chromatography-tandem mass spectrometry

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Synthetic hallucinogens are threatening psychoactive substances that are nowadays slightly monitored despite the numerous fatal consequences highlighted by case reports. Among synthetic hallucinogens, NBOMe-type substances have gained a high notoriety in the last years. These drugs are designed to mimic the effects of conventional hallucinogens, they are generally taken sublingually via blotter paper and they are often falsely sold as lysergic acid. Since their introduction into the drug market, NBOMe derivatives have been frequently associated with intoxication and fatal incidents [1]; consequently, the abuse of these substances presents a severe risk to the consumers, being crucial the fast and right identification of the consumed hallucinogen to provide an effective intoxication treatment. A simple procedure based on microextraction by packed sorbent and liquid chromatography-tandem mass spectrometry has been developed for the simultaneous quantification of 28 synthetic hallucinogens in oral fluids (Figure 1), including lysergic acid diethylamide and substances from NBOMe, NBOH, NBF, 2C, and substituted amphetamine categories.

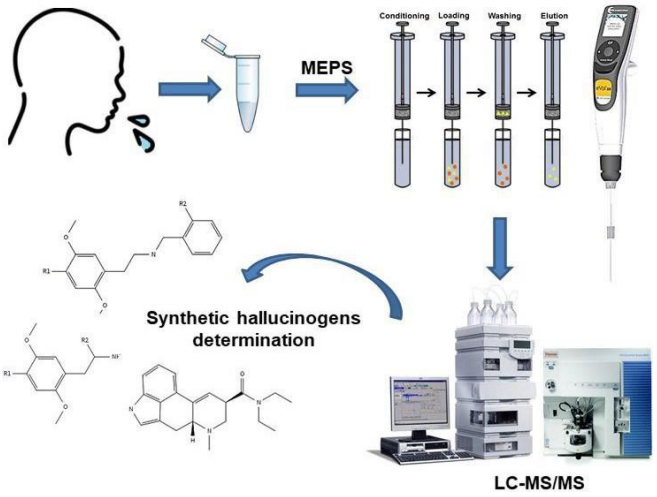

Figure 1. Graphical abstract

Extraction conditions such as type of sorbent, sample pH, number of charge/discharge cycles, and elution volume were studied. Hallucinogenic compounds were extracted from oral fluid samples using C18 MEPS, loading with 100 µL sample (adjusted to pH 7) in 3 cycles, washing with 100 µL deionized water, and eluting with 50 µL methanol in 1 cycle, giving quantitative recoveries and no significant matrix effects. Limits of detection from 0.09 to 1.22 µg L^{-1}, recoveries from 80 to 129 % performed in spiked oral fluid samples at 20, 50, and 100 µg L^{-1}, and high precision with relative standard deviations lower than 9%, were obtained. The proposed methodology demonstrated to be appropriate for the simple and sensitive determination of NBOMe derivatives and other synthetic hallucinogen substances in oral fluid samples.

Acknowledgements

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Industrial 'Breakthrough' in Carbon Dioxide Capture

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Separation processes represent around 70% energy costs in a typical chemical engineering industry.[1] Carbon dioxide (CO_2) is a common component in outline industrial and combustion streams, and its potential as greenhouse gas is worldwide recognized. This anthropogenic contribution escalates above 80% of CO_2 global emissions,[2] increasing its atmospheric concentration and exacerbating Global Warming effects.

Traditional distillation technologies have been preferentially used for its high separation efficiency; however, its energy requirements derive in elevated operational costs, decreasing the economic benefits of the whole industrial production. Adsorptive separation processes are a real advantageous alternative, due to its low energy requirements, convenient regeneration and vast material availability. The tunability of Metal-Organic Frameworks (MOFs) place them as the most promising available adsorbents. Indeed, many MOFs have been already reported efficient for CO_2/N_2 separation, usually with some limitation in the operation conditions.

Given that water vapour is also a usual (trace) component in industrial streams, MOFs performance must be maintained under humidity conditions, preserving both adsorption capacity and selectivity, and avoiding framework degradation.

In this work, we present the potential of a meta-carborane-based MOF[3] in adsorptive separation processes. Their exceptionally stable 3D-aromatic boron-rich clusters promote industrially favourable properties, such as thermal and chemical stability and high hydrophobicity. This novel MOF exhibits unaffected performance for CO_2/N_2 separation under humid atmosphere, validating the results by breakthrough experiments at different temperature, concentration and humidity operation conditions. Environmentally, carbon dioxide represents a terrific threat, here we propose an opportunity to oppose climate change evolution by an industrial revolution.

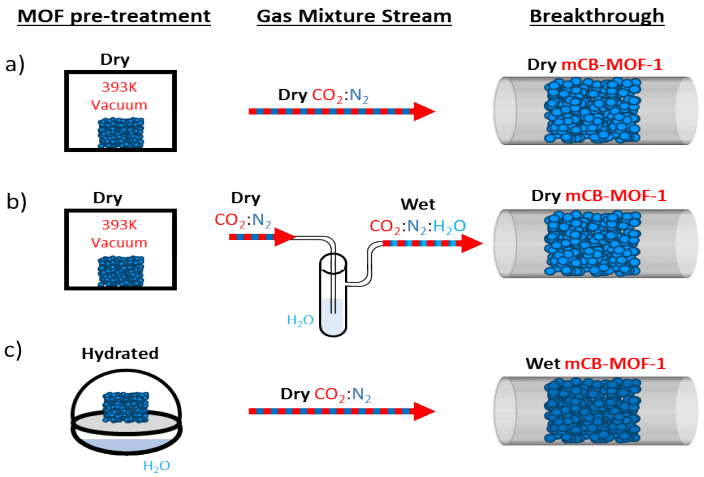

Figure 1. Schematic representation of MOF pretreatment and gas mixture composition used in the breakthrough experiments, to understand the variety of selected humidity operation conditions.

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Enantioselective Addition of Sodium Bisulfite to β,β-Disubstituted Nitroalkenes

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Organo-sulfur compounds have remarkable significance and application in natural product and pharmaceutical chemistry. Specifically, chiral sulfonic acids and its derivatives have shown a broad spectrum of biological activities, such as antibacterial, antiviral or antitumoral, among others [1].

Therefore, the development of new methodologies to readily obtain chiral sulfur-containing organic molecules in a catalytic manner has become a prevalent topic in current modern synthetic organic chemistry [2]. The first catalytic enantioselective synthesis of sulfonic acids *via* nucleophilic addition of sodium bisulfite was described by Adamo and coworkers in 2011[3]. Following this approach, our group and others have successfully synthesized chiral taurine-derivatives [4].

Pursuing this line of research, in this communication we report the development of a procedure for the catalytic enantioselective addition of sodium sulfite to β,β-disubstituted nitroalkenes (**Figure 1)**, which provide chiral sulfonic acids bearing a quaternary stereogenic center. We also present our preliminary results on the extension of this methodology to azadienes derived from aurone, which provide chiral sulfonic acids substituted with a benzofuran ring that can be precursors of tricyclic sultams.

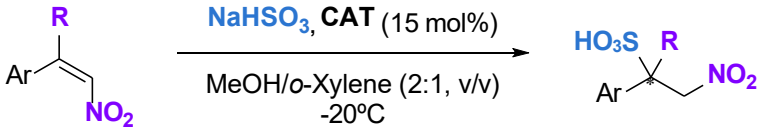

Figure 1. Enantioselective addition of sodium bisulfite to β,β-disubstituted nitroalkenes.

Acknowledgments
Grant PID2020-116944GB-100 funded by MCIN/AEI/ 10.13039/501100011033 and by the "European Union Next Generation EU/PRTR". Grant CIAICO/2021/147 funded by Conselleria d'Innovació, Universitats, Ciència i Societat Digital (If required). Grant Atracció de Talent INV21-01-13 funded by Universitat de València to A.C.

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In situ X-ray Absorption Spectroscopy Study of Sb-based Nanomaterials Stability in biological environments.

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Antimonene (AM) is a new and exciting two-dimensional allotrope of antimony with a unique buckled honeycomb structure that boasts impressive physical properties.[1, 2] These include a tunable bandgap and excellent photothermal conversion efficiency, together with ROS generation capabilities, holding great promise for the use of AM-based nanomaterials in various biomedical applications like biosensing, photothermal cancer therapy, and theragnostic.

However, most of the studied AM materials exhibit poor quality in terms of morphology homogeneity, surface oxidation and particle size distribution, and they are difficult to obtain in large amounts. Moreover, the stability of bare AM in biological conditions has not been thoroughly studied, as to date all the investigations regarding the biological performance of AM have been carried out using coated AM-based materials, hindering the understanding of the effects of the material once liberated in the biological environments.[1]

Herein, Herein we present the first report of the stability of AM nanomaterials in cell culture media, by means of synchrotron-based *in situ* X-ray absorption spectroscopy (XAS), which presents as a fundamental tool to follow the chemical evolution of nanomaterials under biological conditions and thus their biomedical performance. Moreover, we investigated the correlation of the cytotoxic effects of the AM nanomaterials with their degradation, and shed light on the toxic mechanisms they exhert. From our perspective, this will pave the way for the rational functionalization of AM, to enhance its biomedical performance in cancer treatment such as photothermal therapy or as drug delivery vehicles.[1]

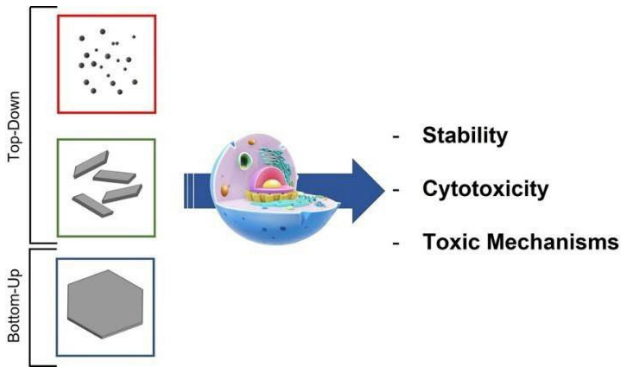

Figure 1: Schematic representation of the experiments conducted in this study. Three different Sb nanomaterials were synthetized following different methodologies and their cytotoxicity, stability and toxic mechanisms were investigated in different cell lines.

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PoC QUANTIFICATION AND PROFILING OF URINE CELLS BY INTEGRATED CYTOCENTRIFUGATION AND INFRARED SPECTROSCOPY

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The presence of cells in urine and in particular White Blood Cells (WBCs) is often associated with Urinary Tract Infections (UTIs) and other diseases. Non-invasive screening of WBCs requires the development of cost- effective Point-of-Care (PoC) diagnostic tools. Fourier transform infrared (FTIR) spectroscopy has the potential to identify and quantify cells in urine. However, urine is a complex matrix and the quantification of components such as cells by compact IR spectrophotometers can be hindered by the presence of highly concentrated biomolecules such as urea or creatinine. Here we propose coupling cytocentrifugation with FTIR spectroscopy for the isolation and quantification of cells in urine using our recently developed device, the ATR-Spin[1], which enables cytocentrifugation directly onto an Attenuated Total Reflectance (ATR) crystal or transflection substrates. Using spiked samples, FTIR integrated bands were proven to be linear (R^2=0.98) in the 8 10^3-2 10^5 cells ml-1 range, thus demonstrating the detection of cells at pathological numbers (pyuria, i.e. >10^4 WBC ml^{-1}) in ATR and transflection modes. Nonetheless, Transflection FTIR yielded better results than ATR in terms of reproducibility and clinical applicability. Finally, to mimic real samples with varying cell types, urine samples containing both monocytes and T-lymphocytes were analyzed to determine their concentration simultaneously. Partial Least Squares (PLS) regression was able to perform a multiparametric determination with cross validation errors of 3 10^4 and 5 10^4 cells ml^{-1}, for monocytes and T-lymphocytes, respectively. The results suggest that the technique has the potential to be a fast, simple, versatile, and cost-effective method for quantifying and profiling cells in urine.

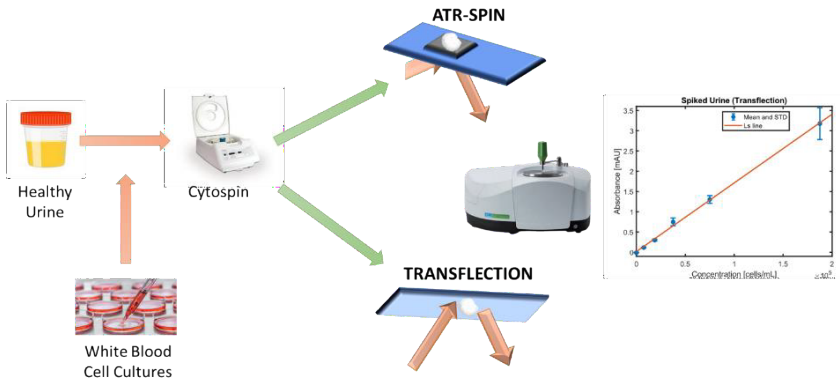

Figure 1. Conceptual Scheme of the methodologies and analysis

Acknowledgments

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V.N.E. acknowledges the financial support by the grant PRE2021-098833 from the Spanish MICIN/AEI/10.13039/501100011033 and the FSE+

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Flash Oral Contributions

OFC1. Sofía Casal García: A DyIII layered MOF with field-induced slow relaxation of the magnetization.

OFC2. Alba Roselló Carrió: 3D printed stir-sticks modified with selective ligands for bisphenol A extraction.

OFC3. Natalia Piqueras García: Determination of β-lactoglobulin in foods using an aptamer-modified stir bar followed by MALDI-TOF-MS.

OFC4. Jaume Béjar Grimalt: DrogoFinder: An open-source graphical user interface for the identification of illicit drugs using infrared spectroscopy.

OFC5. Borja Fructuoso Castaño: Organocatalytic Synthesis of δ-Sultones via nucleophilic addition of coumarine derivatives and sulfonyl fluorides.

OFC6. Carlos Rodríguez-Arias Santiago: Organocatalytic synthesis of spiro-indoline-pyrazolones through a [4+1] cyclization reaction of bromopyrazolones and aza-ortho-quinone methides.

OFC7. Alejandro Gil Aparicio: Development of sorbents based on porous functional materials for the extraction and preconcentration of perfluoroalkylated acids.

OFC8. Roser Payà Pou: Extraction and determination of bisphenols in environmental waters using 3D printed spiral columns combined with metal organic frameworks and molecularly imprinted polymers.

OFC9. Mathilde Meyer: Sustainable platforms for the extraction of emerging contaminants.

A DyIII Layered MOF with Field-Induced Slow Relaxation of the Magnetization

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This work summarizes the research project about the synthesis, characterization and study of the properties of a new two-dimensional (2D) metal-organic framework (MOF). For this purpose, we used Dy(III) as lanthanoid ion, the ligand chloranilato ($C_6O_4Cl_2^{2-}$ = dianion of the 3,6-dichloro,2,5-dihydroxy-1,4 benzoquinone) and formamide (fma) as co-ligand and solvent. In this way we have prepared $[Dy_2(C_6O_4Cl_2)_3(fma)_6]\cdot 4fma\cdot 2H_2O$, which is the first Dy^{III}-containing MOF with fma and chloranilato.[1-2]

The formation of neutral (6,3)-gon 2D networks and the nona-coordination of the lanthanoid ion are some interesting aspects of the compound obtained. In this case, the type of synthesis has a key role in the formed structure. In addition, this coordination complex has very interesting magnetic properties. It is a field induced single ion magnet (SIM) since it shows a slow relaxation of the magnetization only when a DC magnetic field is applied.

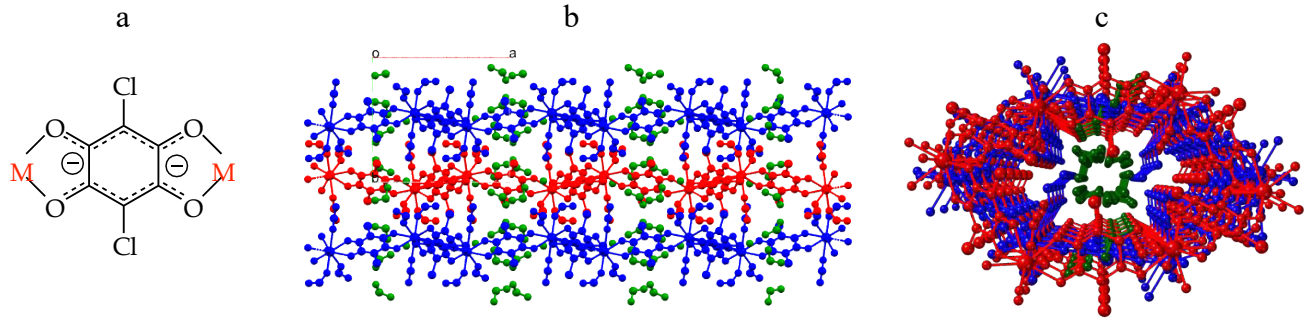

Figure 1. a) Bis-bidentate coordination of chloranilate. b) Side view of three consecutive layers showing the formamide and water molecules located in the hexagonal channels (in green). c) Perspective view of one hexagonal channel with the solvent molecules located inside (in green).

Acknowledgments

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3D printed stir-sticks modified with selective ligands for bisphenol A extraction.

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Bisphenol A (BPA) is an emerging pollutant of concern due to its prevalence in the environment and its potential effects on human health and wildlife. It is used in the production of polycarbonate resins and as a stabilizing agent in many plastics. BPA can migrate from plastics into food and the environment through various pathways. This emerging contaminant it is known to be an endocrine disruptor and can potentially alter the development of mammary glands, affect egg cells, and cause chromosomal defects in humas. Besides, this compound can alter the behavior and reproductive success of fish and affect the growth and development of aquatic organisms. For these reasons, it is important to develop accurate and reliable analytical methods to determine the trace levels of BPA in the environment and contribute to identify sources and pathways of BPA contamination to develop strategies to reduce its release and exposure.

In the last years, the use of 3D printed systems is increasing in diverse areas, including analytical chemistry due to its benefits such as: preparation of devoted systems, low-cost instrumentation and fabrication[1]. In this sense, the creation of novel designs for sample preparation in Analytical Chemistry is currently breaking barriers. Inside the different 3D printing modalities, the most interesting one in the sample preparation area is the stereolithography mode, which has interesting features such as extremely high layer resolutions, high-quality surfaces, easy surface modification, and high compatibility with organic solvents, among others. However, the surface area and the selectivity of these 3D printed devices is extremely low, and it is necessary to be combined with other functional materials to provide the specific interactions to improve their characteristics. In this sense, the use of aptamers, single-stranded nucleic acid molecules (DNA and RNA) with high affinity and specificity[2], could be an interesting alternative to overcome the 3D printed limitations.

In this work, a novel stir-stick 3D printed design surface modified with an aptamer specific for the retention of BPA was developed. Different studies to characterize the surface modification, cleaning the 3D printed structures and optimize the BPA extraction have been performed to obtain an analytical methodology for the extraction of BPA in environmental waters.

Acknowledgments

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Determination of β-lactoglobulin in foods using an aptamer-modified stir bar followed by MALDI-TOF-MS

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In this work, the development of a stir bar sorptive extraction (SBSE) with an aptamer coating devoted to the extraction, pre-concentration and determination of the allergenic milk protein β-lactoglobulin (β-LG) in foods has been carried out. For this purpose, the thiol-aptamer for β-LG was immobilized onto a vinylized polytetrafluoroethylene stir bar surface via “thiol-ene” click chemistry. Then, several SBSE parameters were investigated to optimize the loading and elution process. The enriched fractions were analyzed using matrix-assisted laser desorption/ionization mass spectrometry (MALDI-TOF-MS). The optimized method provided appropriate linearity (0.25-50 μg·mL-1) and satisfactory limit of detection (0.08 μg·mL-1 β-LG). This sorbent was used to extract the β-LG in different milk-free food samples (i.e. a 100% cocoa dark chocolate, a dairy-free white bread, and a hypoallergenic formula for infants) and in a bread containing milk. The resulting recoveries were comprised between 84 and 93%, and a good reproducibility was found with a RSD less than 2.2%.

Acknowledgments
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DrogoFinder: an open-source graphical user interface for the identification of illicit drugs using infrared spectroscopy.

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The in-situ identification of seized illicit drugs is an essential procedure in forensic analysis. However, there is a lack of fast, easy-to-use, and portable methodologies that can be directly carried out by non-expert users and with capability to identify new psychoactive substances (NPS) that are constantly appearing on the ''market''. Infrared (IR) spectroscopy, especially by means of direct attenuated total reflectance (ATR) measurements, is one of the best analytical techniques to provide a versatile solution to this challenge[1]. Nevertheless, the treatment of the spectroscopic data, which includes the quality control of spectra, the subtraction of possible excipients and the comparison with well-defined libraries can be complex and limit the application on the field analysis by non-expert users. Here it is described an open-source new graphical user-friendly interface for drug identification which has been developed under the MATLAB environment. The interface allows the identification of psychoactive substances in an intuitive way including i) automatic quality controls that warn the user possible technical problems during spectrum acquisition (e.g., water vapor, CO2), ii) the automatic subtraction of excipients and other substances present on the sample, and iii) the creation of custom and constantly updated cloud-based libraries. The developed interface was tested by experts and non-expert users comparing the results of the analysis of different seized drug samples with those obtained by dedicated software using the same spectral libraries. Although this interface has been developed in MATLAB it can also be installed as a standalone windows app.

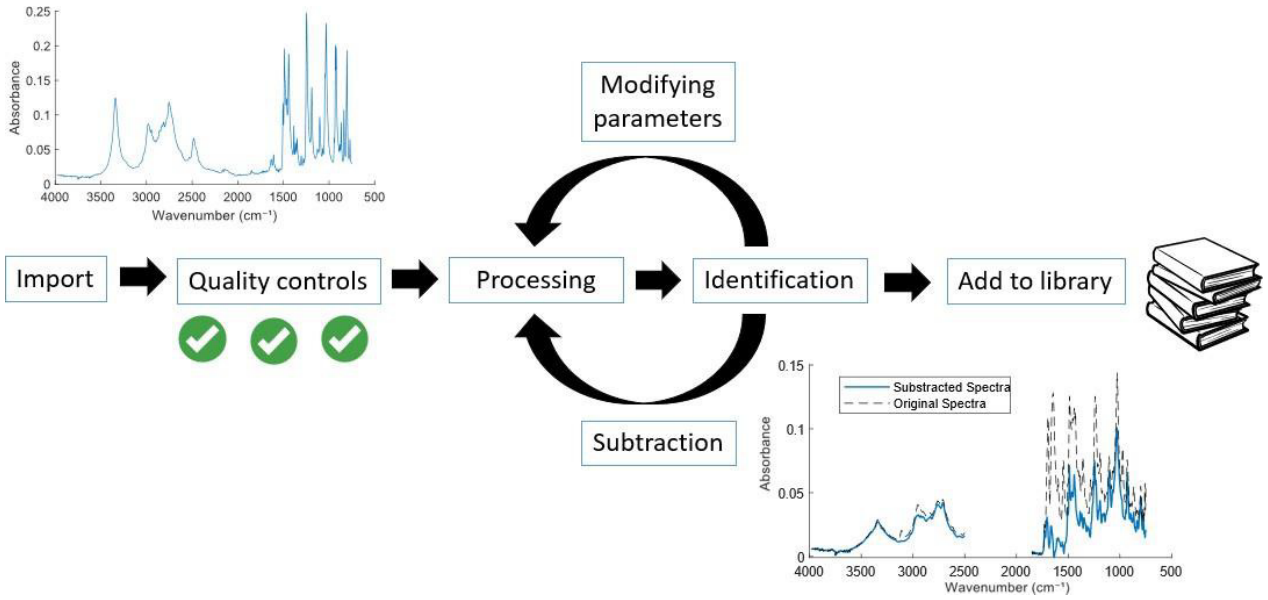

Figure 1. Workflow of the drug identification using the GUI**.**

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Organocatalytic Synthesis of δ-Sultones via nucleophilic addition of Coumarine derivatives and sulfonyl fluorides

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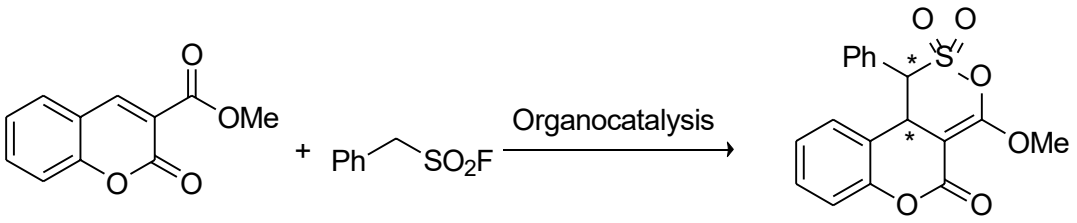
Organo-sulfur compounds are of paramount importance in organic chemistry. Thus, chiral sulfonic acids have shown remarkable significance and application in the areas of natural product and pharmaceutical chemistry. Similarly, sulfonates have become important pharmacophores in medicinal molecules with a broad spectrum of biological activities, such as antiviral, antibacterial, antitumor and so forth.[1] Among the pool of alkyl sulfonates, sultones (cyclic sulfonate) have emerged as privileged structures in drug discovery due to their diverse biological properties.

On the other hand, the alkylation of stabilized carbanions has been recognized as one of the most useful and straightforward methods for C-C bond forming. However, unlike α-alkylation of carbonyl compounds, the enantioselective α-alkylation of sulfonic acid derivatives is more challenging because of the lower acidity of the α-H to the sulfonic group that requires the use of strong bases and because the electronic and steric features of the sulfonic group makes coordination of the catalyst less effective. Examples involving the catalytic asymmetric α-functionalization of sulfonic acid derivatives are almost inexistent.[2]

In this communication, we describe the enantioselective cycloaddition of sulfonyl fluorides and 3-alkoxycarbonylcoumarins catalyzed by *N*-Heterocyclic Carbene Ligand.



Scheme 1: *Organocatalytic addition of coumarine derivatives to sulfonyl fluorides.*

Acknowledgements

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Organocatalytic Synthesis of Spiro-indoline-pyrazolones through a [4+1] Cyclization Reaction of Bromopyrazolones and Aza-ortho-Quinone Methides

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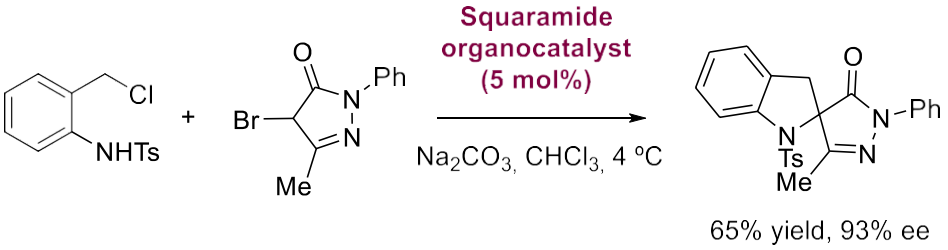
Organocatalysis[1] has been established as an effective methodology for obtaining enantiomerically enriched compounds. In this context, the synthesis of chiral nitrogen heterocycles is essential for organic synthesis.[2] Pyrazolone motif is an outstanding class of nitrogen heterocycle due to its important applications in pharmaceutical and agricultural chemistry because of its biological activity.[2] On the other hand, chiral indolines are particularly important building blocks for asymmetric synthesis of natural products or biological active compounds.[3] Thus, the development of efficient methodologies for the synthesis of chiral indolines is a pivotal topic in synthetic organic chemistry.

In addition, the combination of both pyrazolone and indoline moieties into one molecule could be expected to result in novel chiral indolines with potentially biological activity.[4] Herein, the asymmetric [4+1] annulation reaction of bromopyrazolones with aza-*ortho*-quinone methides catalyzed by a quinine-derived squaramide is presented.



Scheme 1. Organocatalytic [4+1] Annulation Reaction of Bromopyrazolones with Aza-*ortho*-Quinone Methides

Acknowledgments

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Development of sorbents based on porous functional materials for the extraction and preconcentration of perfluoroalkylated acids

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Perfluoroalkylated acid (PFAs) compounds are man-made chemicals that contain covalent bonds between carbons and fluorine, making them highly resistant to environmental degradation and biodegradation. Due to this resistance, PFASs have been used in a wide variety of products and applications[1]. However, for all this, PFASs are also harmful to human health and the environment, as some forms of PFASs have been shown to be toxic, persistent and bioaccumulative, meaning that they can accumulate in the body and the environment over long periods of time and affect human health and wildlife. Amongst long-chain PFAS, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) are the most detected in the aquatic environment, although their use has been limited by recent regulations[2]. However, the short-chain PFAs has been appeared in the last years and rapidly convert in an emerging concern in the environment. In addition, their determination at low-trace levels in waters is complicated and materials with specific interactions should be developed to overcome this problem.

Therefore, in order to develop accurate and reliable analytical methodologies to determine PFAs in environmental waters, such as seawater, novel materials based on mesoporous silica obtained from different surfactants are proposed to be used as material for the solid-phase extraction of PFAs. In addition, the prepared mesoporous silica has been modified with fluorine compounds to provide halogen bond interactions to improve the retention of PFAs[3, 4]. Finally, the determination of PFAs after extraction, preconcentration and elution has been carried out by gas chromatography coupled to an electron capture detector using benzyl bromide as derivatization reagent.

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Extraction and determination of bisphenols in environmental waters using 3D printed spiral columns combined with metal organic frameworks and molecularly imprinted polymers

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In the last years, the use of 3D printed systems is increasing in diverse areas due to its benefits such as: preparation of devoted systems, low-cost instrumentation and fabrication. Inside the different 3D printing modalities, stereolithography mode allows to print with extremely high layer resolutions and high-quality surfaces using materials that can be compatible with organic solvents, which are interesting features in Analytical Chemistry applications such as sample preparation [1]. However, these novel 3D printed devices have low surface areas and low selectivity, which is in detriment of the analysis of trace emergent contaminants, such as bisphenols (BPs). These compounds are an important concern in the environment since affect the wildlife and its mobility can produce its incorporation in the food chain. For these reasons, it is important to develop novel analytical methodologies to analyze these emerging contaminants. In the present work, a 3D printed system, including a coiled tubular channel whose surface has been modified with a metal organic framework and a molecularly imprinted polymer for the retention of BPs (A, S, C, AP and AF), has been designed and synthetized. In addition, the extraction protocol was performed by placing the device in a sequential injection analysis system to extract BPs from environmental waters prior its analysis by high-performance liquid chromatography with fluorescence and UV detection.

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Sustainable platforms for the extraction of emerging contaminants

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Since the discovery of penicillin in the 1930s, the use of antibiotics has been one of the greatest advances in clinical practice [1]. Cephalosporins are amphoteric antibiotics belonging to a class of semi-synthetic beta-lactam antibiotics widely used in human and veterinary treatment. Most antibiotics cannot be completely metabolized by humans, animals or biodegraded in natural environment. Antibiotics as contaminants has been observed in both water and soil, being classified as an environmental risk [2].

On the other hand, metal-organic frameworks (MOFs) are porous materials comprised of an ordered structure of metal ions linked together by organic ligands [3]. These materials present high specific surface area, pore volume and uniform pore size along with tunable surface chemistry, which gives them great potential in different applications [4]. Additionally, for MOFs applications in water systems, such as pollutants' removal, it is necessary to use a MOF that is stable in water medium [5]. In this sense, UiO-66, a MOF comprised by $Zr_6O_4(OH)_4$ metal clusters and 1,4-benzenedicarboxylate organic linkers, is the most commonly used in aquatic environments due to its hydrophilicity and exceptional adsorption capacity [6].

In this work, the use of UiO-66 MOF for the extraction of cephalosporins in water is proposed. For this purpose, the MOF will be anchored on plastic platforms, specifically high-density polyethylene (HDPE) coming from recycled plastic. After optimization of the experimental conditions (plastic platform derivatization, MOF anchoring conditions, loading and elution solvents, time and temperature), the MOF-functionalized platform will be applied to water samples.

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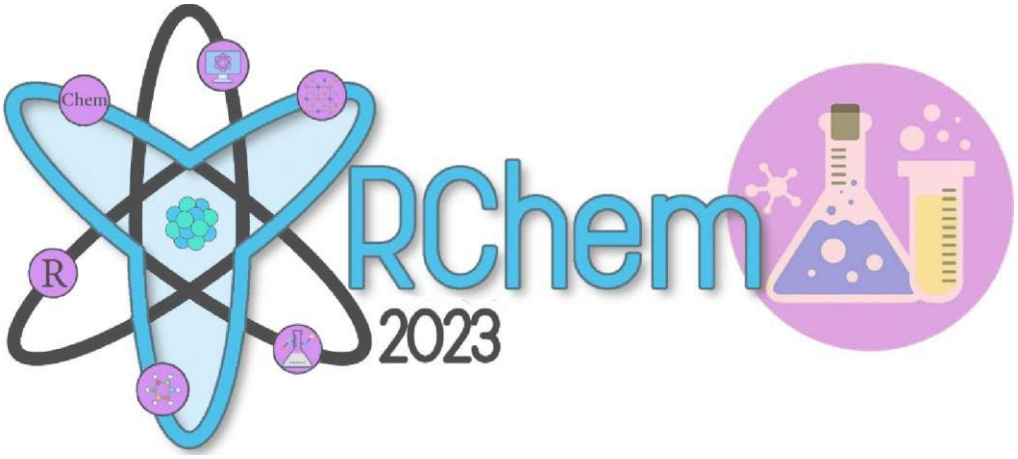

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