ACAC 2024

Athens Conference on Advances in Chemistry
November 6 – November 8, 2024

HELLENIC REPUBLIC
National and Kapodistrian
University of Athens
-------------EST. 1837-------------
Department of Chemistry

www.acac2024.gr

Analytical Chemistry

Biochemistry

Enviromental Chemistry

Food Chemistry

Industrial Chemistry

Inorganic Chemistry

Organic Chemistry

Physical Chemistry

Organized by:
Department of Chemistry,
National and Kapodistrian University of Athens

CO - ORGANIZER

FunShield4Med
SECURING FOOD

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Under the auspices of IADNS

IADNS

QR-CODE for oral & poster presentations

WELCOME NOTE

Dear friends and colleagues,

On behalf of the scientific and organizing committees, it is a great pleasure to welcome Researchers from Academia, Industry and technology providers from all over the world to the **4th Athens Conference on Advances in Chemistry (ACAC 2024)**, that will be held on **November 6th - 8th, 2024** in Athens, Greece.

ACAC 2024 is the fourth of a series of International Conferences that were initiated on the occasion of the Centennial Anniversary of the Department of Chemistry, of the National and Kapodistrian University of Athens since its establishment in 1918. The conference will be held in Aristotelis Congress Center, that is located on the University of Athens campus. All previous ACAC conferences were highly successful and attended by Academia, Researchers, postgraduate students, postdoctoral research associates and technology providers. During the Conference, several plenary and invited lectures, contributed talks, and poster presentations, will lead to fruitful discussions on the latest topics of Chemistry in a relaxed and inspiring atmosphere.

Our aim is to establish a forum for exchanging innovative ideas on the latest advances in Chemistry and initiating new collaborations among researchers in Greece and from all over the world. Chemistry has expanded into many multidisciplinary research areas involving large numbers of chemists, physicists, biologists and medicinal scientists. Many of our former students are now in academic and research positions all over the world. It is thus our great pleasure to welcome all of you in Athens.

Warm regards,

Evi Lianidou, PhD
ACAC 2024 Chair
Chairman, Dept of Chemistry,
Professor of Analytical Chemistry and Clinical Chemistry
National and Kapodistrian University of Athens,
Athens, Greece

Organizing Committee

Evi Lianidou, Professor of Analytical Chemistry and Clinical Chemistry, Chairman, Department of Chemistry, University of Athens, Greece

Margarita Chatzichristidi, Professor of Industrial Chemistry, Department of Chemistry, University of Athens, Greece

Marilena Dasenaki, Assistant Professor of Food Chemistry, Department of Chemistry, University of Athens, Greece

Eleni Efthimiadou, Associate Professor of Inorganic Chemistry, Department of Chemistry, University of Athens, Greece

Evangelia Emmanouilidou, Assistant Professor of Biochemistry, Department of Chemistry, University of Athens, Greece

Sotirios Karavoltsos, Assistant Professor of Environmental Chemistry, Department of Chemistry, University of Athens, Greece

Christos Kokkinos, Associate Professor of Analytical Chemistry, Department of Chemistry, University of Athens, Greece

Athina N. Markou, Assistant Professor of Analytical Chemistry, Department of Chemistry, University of Athens, Greece

Victoria Magrioti, Associate Professor of Organic Chemistry, Department of Chemistry, University of Athens, Greece

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Anthoula-Chrysa Papageorgiou, Assistant Professor of Physical Chemistry, Department of Chemistry, University of Athens, Greece

Nikolaos Pinotsis, Associate Professor of Biochemistry, Department of Chemistry, University of Athens, Greece

Marinos Pitsikalis, Professor Industrial Chemistry, Department of Chemistry, University of Athens, Greece

Charalampos Proestos, Professor Food Chemistry, Department of Chemistry, University of Athens, Greece

Athanasios Tsekouras, Associate Professor Physical Chemistry, Department of Chemistry, University of Athens, Greece

Nikolaos Tsoureas, Assistant Professor Inorganic Chemistry, Department of Chemistry, University of Athens, Greece

Stamatia Vassiliou, Professor Organic Chemistry, Department of Chemistry, University of Athens, Greece

Scientific Committee

Evi Lianidou, Professor of Analytical Chemistry and Clinical Chemistry, Chairman, Department of Chemistry, Department of Chemistry, University of Athens, Greece

Demetrios Anglos, Professor, Department of Chemistry, University of Crete, Greece

Evangelos Bakeas, Professor of Environmental Chemistry, Department of Chemistry, University of Athens, Greece

Costas Biliaderis, Emeritus Professor, Aristotle University of Thesaloniki, Greece

Dimitris Georgiadis, Professor of Organic Chemistry, Department of Chemistry, University of Athens, Greece

Michael John Hannon, Professor of Chemical Biology, University of Birmingham, United Kingdom

Hermis Iatrou, Professor of Industrial Chemistry, Department of Chemistry, University of Athens, Greece

Andreas Koutselos, Professor of Physical Chemistry, Department of Chemistry, University of Athens, Greece

George Leondaritis, Assistant Professor of Biochemistry, University of Ioannina, Greece

Christina-Anna Mitsopoulou, Professor of Inorganic Chemistry, Department of Chemistry, University of Athens, Greece

Mirjana Pešić, Professor, Faculty of Agriculture, University of Belgrade, Serbia

Dejan Stojković, Associate Research Professor, Institute for Biological Research "Siniša Stanković" – National Institute of the Republic of Serbia (IBISS), University of Belgrade, Serbia

Efstratios Stratikos, Associate Professor of Biochemistry, Department of Chemistry, University of Athens, Greece

CHRYSOULA TASSOU, Research Director, Institute of Technology of Agricultural Products, ELGO – DIMITRA, Greece

Vassilis Valdramidis, Associate Professor Food Chemistry, Department of Chemistry, University of Athens, Greece

Maria Vamvakaki, Professor, Department of Material Science & Engineering, University of Crete, Greece

Plenary Speakers

- **Michael Graetzel,** Professor, Director of the Laboratory of Photonics and Interfaces, School of Chemistry, Ecole Polytechnique Fédérale de Lausanne, (EPFL), Switzerland
- **Dario Omanović,** Senior Scientist, Laboratory for Physical Chemistry of Traces, Center for Marine and Environmental Research, Ruđer Bošković Institute, Croatia
- **Michal Bassani-Sternberg**, Assistant Professor, Ludwig Institute for Cancer Research, Switzerland
- **Andreas Steffen**, Professor, Department of Chemistry and Chemical Biology, Technical University of Dortmund, Germany
- **JIANBO XIAO,** Adjunct Professor, Jinan University (China), Department of Food Science and Technology, University of Vigo, Spain
- **Brianna Heazlewood,** Professor, University of Liverpool, United Kingdom
- **Thomas Carell,** Professor, Ludwig Maximilian University Munich, Germany
- **Marinos Pitsikalis,** Professor, Department of Chemistry, University of Athens, Greece

Invited Speakers

- **Nikolaos Thomaidis,** Vice-Precident of NKUA Administration Council, Professor, Department of Chemistry, University of Athens, Greece
- **Spiros A. Pergantis,** Professo, Environmental Chemical Processes Laboratory, Department of Chemistry, University of Crete, Greece
- **Nikolaos Mihalopoulos,** Research Director, Institute for Environmental Research and Sustainable Development, National Observatory of Athens, Greece
- **Simos Malamis,** Associate Professor, Department of Water Resources and Environmental Engineering, School of Civil Engineering, National Technical University of Athens, Greece
- **Niki Chondrogianni**, Research Director, Institute of Chemical Biology (ICB), National Hellenic Research Foundation (NHRF), Greece
- **George Leondaritis,** Assistant Professor, Department of Pharmacology, Faculty of Medicine, School of Health Sciences, University of Ioannina, Greece
- **Dominik Halter,** Junior Group Leader, Inorganic and Metal-Organic Chemistry, TUM (Technical University of Munich), Germany
- **Carole Duboc,** Research Director, Department of Molecular Chemistry, University of Grenoble, France
- **Dejan Stojković**, Senior Research Associate, Department of Plant Physiology, University of Belgrade, Serbia
- **Kostas Biliaderis,** Emeritus Professor, Department of Food Science and Technology, Agricultural School of the Aristotle University of Thessaloniki, Greece
- **Francesco Allegretti,** Professor**,** Privat Dozent, Technical University of Munich, Germany
- **David A. Duncan,** Associate Professor, University of Nottingham and Diamond Light Source, United Kingdom
- **Konstantinos Neohoritis,** Associate Professor, Department of Chemistry, University of Crete, Greece
- **Christos Stathakis**, Assistant Professor, Department of Chemistry, University of Crete, Greece
- **Panagiota Petrou**, Research Director, NCSR “Demokritos”, Greece
- **Stergios Pispas,** Research Director, Theoretical and Physical Chemistry Institute, NHRF, Greece

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Program

Day 1: Wednesday November 6th

8:30 – 9.00	**Registration**
9:00 – 10.00	**Welcome address - Opening Remarks**
Plenary Session 1: ANALYTICAL CHEMISTRY **Chairs: A. Oikonomou, E. Gikas**	
10:00 – 10:30 PL-1	**Michael Graetzel, Director of the Laboratory of Photonics and Interfaces, School of Chemistry, Ecole Polytechnique Fédérale de Lausanne, (EPFL), Switzerland** “Molecular Photovoltaics and the Stunning Rise of Perovskite Solar Cells”
10:30 – 10:50 IL-1	**Nikolaos Thomaidis, Vice-Precident of NKUA Administration Council, Department of Chemistry, University of Athens, Greece** “Alleviating the need of standards and Leveraging advances in High Resolution Mass Spectrometry for integrated, holistic environmental monitoring of emerging contaminants”
10:50 – 11:10 IL-2	**Spiros A. Pergantis, Environmental Chemical Processes Laboratory, Department of Chemistry, University of Crete, Greece** "A Combination of Atomic and Molecular Mass Spectrometric Techniques for the Determination of Arsenolipid Compounds in Food of Marine Origin"
11:10 – 12:00 **POSTER VIEWING, EXHIBITION AND NETWORKING COFFEE BREAK** **POSTERS P#1 – P#25**	
Plenary Session 2: ENVIRONMENTAL CHEMISTRY **Chairs: E. Bakeas, S. Karavoltsos**	
12:00 – 12:30 PL-2	**Dario Omanović, Laboratory for Physical Chemistry of Traces, Center for Marine and Environmental Research, Ruđer Bošković Institute, Croatia** "Multimethodological study of trace metal speciation in marine waters"
12:30 – 12:50 IL-3	**Nikolaos Mihalopoulos, Institute for Environmental Research and Sustainable Development, National Observatory of Athens** "Climate change in the Eastern Mediterranean: Drivers and impacts"
12:50 – 13:10 IL-4	**Simos Malamis, Department of Water Resources and Environmental Engineering, School of Civil Engineering, National Technical University of Athens** "Adopting Nature-based solutions to build water resilience”
13:10 – 14:30 **LUNCH BREAK**	
ORAL PRESENTATIONS, 14:30-15:30 **Session 1: (n=6, 10min each)** **Chairs: C. Kokkinos, E. Bakeas**	

Oral presentations: Analytical Chemistry	
14:30 – 14:40 OP-1	**Anastasios Oikonomou, Department of Chemistry, University of Athens, Greece** “Applications of paper-based devices in (bio)analytical chemistry”
14:40 – 14:50 OP-2	**Evangelos Gikas, Department of Chemistry, University of Athens, Greece** “Are MS/MS-Based Molecular Networks another solution for omics? An application to a food authenticity challenge”
14:50 – 15:00 OP-3	**Eleni Koukouviti, Department of Chemistry, University of Athens, Greece** “Lab-made conductive filament for the 3D printing of ready-to-use multiplexed electrochemical sensors”
Oral presentations: Environmental Chemistry	
15:00 – 15:10 OP-4	**Nikolaos Katsikatsos, Department of Chemistry, University of Athens, Greece** “Autonomous Vehicles as an innovative monitoring strategy in environmental studies”
15:10 – 15:20 OP-5	**Sevasti Panagiota Kotsaki, Department of Chemistry, University of Athens, Greece** “SOA tracers in a background site in the Eastern Mediterranean: exploring formation pathways”
15:30 – 15:30 OP-6	**Georgios Katsouras, EYDAP SA** “Innovative monitoring of emerging micropollutants in Psyttalia WWTP and the Saronikos Gulf Ecosystem”
15:30 – 16:30 POSTER VIEWING, EXHIBITION AND NETWORKING COFFEE BREAK POSTERS P#1- P#25	
Plenary Session 3: BIOCHEMISTRY Chairs: E. Stratikos, E. Emmanouilidou	
16:30 – 17:00 PL-3	**Michal Bassani-Sternberg, Ludwig Institute for Cancer Research, Switzerland** "Antigen discovery for development of personalized cancer immunotherapy"
17:00 – 17:20 IL-5	**Niki Chondrogianni, Institute of Chemical Biology (ICB), National Hellenic Research Foundation (NHRF), Greece** "The proteasome as a key player in the progression of aging and age-dependent diseases"
17:20 – 17:40 IL-6	**George Leondaritis, Department of Pharmacology, Faculty of Medicine, School of Health Sciences, University of Ioannina, Greece** "Lipid Signalling in Health and Disease"
17:40 – 18:00 POSTER VIEWING, EXHIBITION AND NETWORKING	
ORAL PRESENTATIONS, 18:00-19:00 Session 2: (n=6, 10min each) Chairs: E. Emmanouilidou, N. Tsoureas	

Oral presentations: Biochemistry	
18:00 – 18:10 **OP-7**	**Efstratios Stratikos, Department of Chemistry, University of Athens, Greece** "A conformation and substrate-selective small molecule inhibitor of Insulin Regulated Aminopeptidase provides insight into the intricacies of the enzyme's catalytic cycle"
18:10 – 18:20 **OP-8**	**Evangelia Emmanouilidou, Department of Chemistry, University of Athens, Greece** “Astrocyte calcium signaling can protect against neuroinflammation induced by α-synuclein oligomers”
18:20 – 18:30 **OP-9**	**Galateia Georgaki, Department of Chemistry, University of Athens, Greece** “Polymorphic positions 349 and 725 of the autoimmunity protective allotype 10 of ER aminopeptidase 1 are key in determining its unique enzymatic properties”
18:30 – 18:40 **OP-10**	**Martha Nikopaschou, Department of Chemistry, University of Athens, Greece** “ERAP1 as a regulator of the immunopeptidome, proteome and cellular homeostasis of cancer cells”
Oral presentations: Inorganic Chemistry	
18:40 – 18:50 **OP-11**	**Irene Ligielli, Department of Chemistry, University of Athens, Greece** “Trigonal Planar Chromium (II) N-Heterocyclic Carbene Complexes as Potential Mononuclear Single Molecule Magnets”
18:50 – 19:00 **OP-12**	**Ioannis Vagiakos, Department of Chemistry, University of Athens, Greece** “Taming arenes: A comparative and systematic study”
19:00-20:00 **FunShield4Med Session on Food Safety Mycotoxins & Climate change,** **EU funded project,** **(Grant agreement ID: 101079173)**	
20:30 – 22:00 **Faculty Dinner**	

Day 2: Thursday November 7th

<table>
<tr><td>9:15 – 10:00</td><td>**Sotirios Kiokias, PhD, European Research Executive Agency, Belgium**
“EU research funding opportunities (Horizon Europe)/Marie-Sklodowska Curie Program (MSCA) with focus on Staff Exchanges Action”</td></tr>
<tr><td colspan="2">Plenary Session 4: INORGANIC CHEMISTRY
Chairs: C. Mitsopoulou, P. Kyritsis</td></tr>
<tr><td>10:00 – 10:30
PL-4</td><td>**Andreas Steffen, Department of Chemistry and Chemical Biology, Technical University of Dortmund, Germany**
"Our journey towards molecular single-photon sources – Fast and bright… but still Dark "</td></tr>
<tr><td>10:30 – 10:50
IL-7</td><td>**Dominik Halter, Inorganic and Metal-Organic Chemistry, TUM (Technical University of Munich), Germany**
"Transition Metal Catalyzed Electro-Organic Synthesis with Water & Ex Situ Electrosynthesis for Unique Selectivity"</td></tr>
<tr><td>10:50 – 11:10
IL-8</td><td>**Carole Duboc, Department of Molecular Chemistry, University of Grenoble, France**
"A bio-inspired approach for electrocatalytic H_2 production"</td></tr>
<tr><td colspan="2">11:10 – 12:00
POSTER VIEWING, EXHIBITION AND NETWORKING COFFEE BREAK
POSTERS P#26 – P#63</td></tr>
<tr><td colspan="2">Plenary Session 6: FOOD CHEMISTRY
Chairs: C. Proestos, V. Valdramidis</td></tr>
<tr><td>12:00 – 12:30
PL-5</td><td>**Jianbo Xiao, Adjunct Professor at Jinan University (China), Department of Food Science and Technology, University of Vigo, Spain**
"Formation of nitrogenous flavonoid derivatives by reacting with amino acids"</td></tr>
<tr><td>12:30 – 12:50
IL-9</td><td>**Dejan Stojković, Department of Plant Physiology, University of Belgrade, Serbia**
"Mushrooms as natural resources of functional food and biologically active compounds"</td></tr>
<tr><td>12:50 – 13:10
IL-10</td><td>**Kostas Biliaderis, Department of Food Science and Technology, Agricultural School of the Aristotle University of Thessaloniki, Greece**
"Cereal grain polysaccharides as functional food ingredients: structure-property relations"</td></tr>
<tr><td colspan="2">13:10 – 14:30
LUNCH BREAK</td></tr>
<tr><td colspan="2">ORAL PRESENTATIONS, 14:30-15:30
Session 3: (n=6, 10min each)
Chairs: E. Efthimiadou, K. Methenitis</td></tr>
</table>

Oral presentations: Inorganic Chemistry

14:30 – 14:40 OP-13	**Patrina Paraskevopoulou, Department of Chemistry, University of Athens, Greece** “Polyurea-crosslinked biopolymer aerogels - novel nanostructured materials for diverse applications”
14:40 – 14:50 OP-14	**Nikolaos Tsoureas, Department of Chemistry, University of Athens, Greece** “Unexpected Reactivity of a Low Valent Titanocene with Azides”
14:50 – 15:00 OP-15	**Evangelos Papangelis, Department of Chemistry, University of Athens, Greece** “New Pyridine Dicarbene Pincer Ligands with Ring Expanded N-Heterocyclic Carbene Donors and their Transition Metal Complexes”
15:00 – 15:10 OP-16	**Evangelia Tsitsou, Department of Chemistry, University of Athens, Greece** “Evaluation of Fe:Eu nanoparticles as imaging probes of cervical cancer cells”
15:10 – 15:20 OP-17	**Charalampos Papapanagis, Department of Chemistry, University of Athens, Greece** “Exploring New Tripodal N-Heterocyclic Carbene Ligands Towards High- and Low-Valent Iron Complexes”
15:20 – 15:30 OP-18	**Stamatis Passadis, Department of Chemistry, KU Leuven, Belgium** “Revitalisation of Group IV metal-oxo clusters: Synthetic approaches, structural motifs and applications”

15:30 – 16:30
POSTER VIEWING, EXHIBITION AND NETWORKING COFFEE BREAK
POSTERS P#26 – P#63

Plenary Session 6: PHYSICAL CHEMISTRY
Chairs: D. Tzeli, G. Souliotis

16:30 – 17:00 PL-6	**Brianna Heazlewood, University of Liverpool, United Kingdom** " New methods for studying ions and radicals at low temperatures "
17:00 – 17:20 IL-11	**Francesco Allegretti, Privat Dozent, Technical University of Munich, Germany** "On-surface synthesis and post-synthetic modification of low-dimensional organometallic networks "
17:20 – 17:40 IL-12	**David A. Duncan, University of Nottingham and Diamond Light Source, United Kingdom** "Understanding the structure of two-dimensional films using X-ray standing waves"

17:40 – 18:00
POSTER VIEWING, EXHIBITION AND NETWORKING

ORAL PRESENTATIONS, 18:00-19:00
Session 4: (n=6, 10 min each)
Chairs: C. Proestos, V. Valdramidis

Oral presentations: Physical Chemistry

18:00 – 18:10 OP-19	**Dimitra Tzeli, Department of Chemistry, University of Athens, Greece** “Breaking covalent bonds in the context of the many-body expansion”

Oral presentations: Food Chemistry

18:10 – 18:20 OP-20	**Mirjana B. Pešić, University of Belgrade - Faculty of Agriculture, Serbia** “Goat milk proteins as a promising ingredient for functional food”
18:20 – 18:30 OP-21	**SHIYE LIN, Jinan University (China), Department of Food Science and Technology, University of Vigo, Spain** “The stability and degradation products of polyhydroxy flavonols in boiling water”
18:30 – 18:40 OP-22	**Wenqi Huang, Jinan University (China), Department of Food Science and Technology, University of Vigo, Spain** “Stability and degradation mechanism of (-)-epicatechin in thermal processing”
18:40 – 18:50 OP-23	**Pelagia Lekka, Department of Chemistry, University of Athens, Greece** “Metabolic Responses to Acute Wine Consumption: A Time-Dependent Nutri-Metabolomic Study of Phenolic Metabolites using High-Resolution Mass Spectrometry”
18:50 – 19:00 OP-24	**Evmorfia Athanasopoulou, Agricultural University of Athens, Department of Food Science and Human Nutrition, Greece** “ICHTHYS: Optimization of novel value chains for fish and seafood by developing an integrated sustainable approach for improved quality, safety and waste reduction”

19:00-20:00

NanoCosmos Session: Nanoencapsulation of bioactive compounds from plant by products to produce sensitive skin cosmetics,
EU funded project (Grant agreement ID: 101086323)

20:00 – 22:00, ACAC 2024 Reception (on site)

Day 3: Friday November 8th

Plenary Session 7: ORGANIC CHEMISTRY **Chairs: G. Vougioukalakis, T. Mavromoustakos**	
10:00 – 10:30 **PL-7**	**Thomas Carell, Ludwig Maximilian University Munich, Germany** " Non-Canonical Nucleosides and Click Modification of Nucleic Acids "
10:30 – 10:50 **IL-13**	**Konstantinos Neohoritis, Department of Chemistry, University of Crete, Greece** " Access to high rotational barrier atropisomers "
10:50 – 11:10 **IL-14**	**Christos Stathakis, Department of Chemistry, University of Crete, Greece** " A Special Case of Divergent Synthesis "
11:10 – 12:00 **POSTER VIEWING, EXHIBITION AND NETWORKING COFFEE BREAK** **POSTERS #64-84**	
Plenary Session 8: INDUSTRIAL CHEMISTRY **Chairs: M. Chatzichristidi, M. Pitsikalis**	
12:00 – 12:30 **PL-8**	**Marinos Pitsikalis, Department of Chemistry, University of Athens, Greece** "Inorganic Chemistry/Polymer Chemistry: A success story The case of coordination polymerization of isocyanates employing half-titanocene complexes "
12:30 – 12:50 **IL-15**	**Panagiota Petrou, NCSR “Demokritos”, Greece** "Optical immunosensors: Analytical tools with many application "
12:50 – 13:10 **IL-16**	**Stergios Pispas, Theoretical and Physical Chemistry Institute, NHRF, Greece** "Novel synthetic copolymers for creating biohybrid nanostructures"
13:10 – 14:30 **LUNCH BREAK**	
ORAL PRESENTATIONS, 14:30-15:30 **Session 5: (n=6, 10min each)** **Chairs: M. Chatzichristidi, T. Mavromoustakos**	
Oral presentations: Organic Chemistry	
14:30 – 14:40 **OP-25**	**Georgios C. Vougioukalakis, Department of Chemistry, University of Athens, Greece** “Multicomponent Reactions: Creating Complexity via Sustainable Catalytic Transformations”
14:40 – 14:50 **OP-26**	**Victoria Magrioti, Department of Chemistry, University of Athens, Greece** “Microwave-assisted and base-dependent synthesis of γ-lactones or esters using N-heterocyclic carbenes as organocatalysts”
14:50 – 15:00	**Nikitas Georgiou, Department of Chemistry, University of Athens, Greece**

OP-27	“Chalcones and 4-hydroxy-2-quinolinone-triazole hybrid derivatives a, b and c as potential anti-inflammatory agents”
Oral presentations: Industrial Chemistry	
15:00 – 15:10 **OP-28**	**Iren G. Stavrakaki, Department of Chemistry, University of Athens, Greece** “Complexation of anticancer Pt-drugs on Polymers containing poly(L-Histidine)”
15:10 – 15:20 **OP-29**	**Athanasia Fouka, Department of Chemistry, University of Athens, Greece** “Optimization of hydrothermal synthesis of copper oxide on flexible substrates”
15:20 – 15:30 **OP-30**	**Nikolaos V. Plachouras, Department of Chemistry, University of Athens, Greece** “Statistical copolymers of N–Vinyl Pyrrolidone and 2–Chloro Ethyl Vinyl Ether via Radical RAFT Polymerization as scaffolds for the synthesis of complex macromolecular architectures”
15:30 – 16:30 **POSTER VIEWING, EXHIBITION AND NETWORKING COFFEE BREAK** **POSTERS P#64 – P#84**	
16:30-17:30 **Closing Ceremony** **Best poster awards – Best oral presentation awards**	

POSTERS

Poster #	Session	Name	Abstract title
1	**Analytical Chemistry**	Aliki Ntzifa	Comprehensive liquid biopsy analysis for monitoring NSCLC patients under second-line osimertinib treatment
2		Stavroula Smilkou	Detection rate for ESR1 mutations is significantly higher in CTC-derived gDNA than in paired plasma-cfDNA samples as revealed by ddPCR
3		Stavroula Smilkou	Pyrimidine-dependent UV-mediated crosslinking magnifies minor genetic or epigenetic changes in clinical samples
4		Stavroula Smilkou	Detection rate for ESR1 mutations is significantly higher in CTC-derived gDNA than in paired plasma-cfDNA samples as revealed by ddPCR
5		Eleni Thanou	NALCN promoter methylation as a biomarker for metastatic risk in a cohort of NSCLC patients
6		Anastasia Zafeiriadou	Evaluation of PCR-enhancing approaches to reduce inhibition in wastewater samples and enhance viral load measurements
7		Alexandra Delipetrou	Combining Metabolomics and Liquid Biopsy to Identify Diagnostic and Prognostic Biomarkers in Patients with Non-Small Cell Lung Cancer
8		Nikolaos Boinis	In-Depth Investigation of Organic Micropollutant Burden in the Dnipro River Basin During Wartime Using HRMS-Based Workflows
9		Dafni Preza-Mayo-Kataki	The impact of 4D metabolomics and wide-scope screening methodologies for the investigation of Greek bee products' bioactive content
10		Anna Papoutsa	Investigation of the presence and removal of emerging contaminants at various stages of industrial wastewater treatment
11		Ioannis Chrysovalantis Vyzaniaris	Optimization and validation of a method for the determination of PFAS in soil
12		Kostas Peroulis	An Innovative Toolkit for Enhanced Water Quality Monitoring of Water Supply Network
13		Ioannis Konstantinou	Development and validation of analytical methodology for the determination of per– and poly–fluoroalkyl substances (PFAS) in fish feed samples using modified QuEChERS and LC– HRMS
14		Theodora Paramana	Destressing the Mediterranean Sea from chemical pollution: application of innovative technologies in the Thriasio Wastewater Treatment Plant
15		Anthi Panara	Development and validation of methods for the determination of a new mitochondrial antioxidant (TPP-Hydroxytyrosol) in cerebellum and liver of mice
16		Anthi Panara	Could MS/MS-based molecular networking be an alternative to multivariate analysis in omics studies? The saffron trimming case

Poster #	Session	Name	Abstract title
17		Antigoni Cheilari	1H-NMR and UHPLC-HRMS based chemical profiling of Cypriot carob syrups
18		Ioanna Barla	Time series untargeted metabolomics to investigate the impact of blood transfusion in patients with thalassemia
19	**Environmental Chemistry**	Sotiris Karavoltsos	Preliminary evaluation of trace elements content and sulfur speciation of wines produced in Greece
20		Anthi Yfanti	Total mercury in the water column of the coastal zone in the Red Sea, the Gulf of Aqaba, and the Arabian Gulf
21		Eleni Sdoukou and Ioannis Konstantinou	Waste tire char valorization by preparing Ni-Cu carbocatalyst for applications in sulfate radicals based advanced oxidation processes (SR-AOPs) : Degradation of metronidazole emerging pollutant
22	**Biochemistry**	Anastasia-Georgia Dedemadi	Screening of a marketed drug library identifies dantrolene as an activator of the antioxidative enzyme paraoxonase-1
23		Konstantina Dimoula	Aggregated α-synuclein in erythrocytes as a potential biomarker for idiopathic Parkinson’s Disease
24		Christina Machalia	The inhibition of α-synuclein aggregation using marine-derived bacterial metabolites as a novel neuroprotective approach for Parkinson’s Disease
25		Christina Paschou	Failure of major proteostatic mechanisms and lysosomal malfunction in p.A53T-αSyn PD patient iPSC-derived astrocytes
26	**Inorganic Chemistry**	Anastasia Chatzivasiloglou	Copper(II) and nickel(II) complexes with coumarin derivatives: Structure and biological evaluation
27		Christos Bintas	Development of bio-MOFs as drug delivery systems for cancer treatment
28		Alexandra Efthimiadou	GreenSynthesisofcarbon Quantum dotsforGeoenvironmentalApplications
29		Polidoros C. Ioannou, Dimitrios G. Fragkis	Synthesis of Fused-Cyclic Aryl Amino Carbene Ligand Precursors
30		Argirios Gomatos	Polyurea-crosslinked alginate aerogels with no need for supercritical drying
31		Posoula Korakianiti	Antitumoral effect and Mechanisms of action of Silver Nanoparticles on Breast Cancer cells
32		Panteleimon Kotidis	Sorption study of two amide-based MOFs towards heavy metal cations in aqueous environment.
33		Maria Kourmousi	"Bioinspired Electrocatalysts for Hydrogen Evolution Reaction"
34		Stelios Liagos	Synthesis Antimicrobial and Photocatalytic applications of TiO2@CuO nanoparticles
35		Konstantinos Methenitis	Synthesis and characterization of a Cu(II) and a Ni(II) complex with a curcumin derivative. Study of their interaction with CT-DNA and BSA
36		Panagiotis Oikonomopoulos	New Novel Metal-Organic Frameworks Based on Polynuclear Rare-Earth Metal Clusters
37		Georgia Pantela	Copper Single Atom-diimine Catalytic centers immobilized on TiO2 for water purification under-visible-light irradiation.

Poster #	Session	Name	Abstract title
38		Asimina Andreana Papadopoulou	Photocatalytic hydrogen production vi bioinspired heteroleptic Ni complexes
39		Anastasia Ravanou	Chitosan-derived carbon aerogels: effect of crosslinking strategy and pyrolysis conditions on textural and material properties
40		Ankica Šarić	The influence of the solvent on the growth of zinc oxide
41		Vasileios Tsonis	New terephthalate 3D-MOF based on Y6 cluster
42		Panagiotis Tzevelekidis	A novel $CuNaTi_3O_8$ Freudenbergite-type photocatalyst for efficient water purification under visible light irradiation
43		Markella Ioanna Vogia Rompazani	Activation of TiO2 nanoparticles with N-doped CQDs for photodegradation of Methylene Blue and reduction of H2
44		Maria Roulia	Association of the Oxazine Azo Dye C.I. Basic Blue 3 with Humates
45		Varvara Vlahopoulou	Polyurea-crosslinked alginate aerogels with antibacterial properties
46	**Food Chemistry**	Ioannis Dimitros	Application of Response Surface Methodology for the optimization of natural compounds' extraction from pomegranate seed oil using acoustic cavitation technology
47		Foteini Gerodimou	Antifungal efficacy of SiO2@Ag/CeO2 core-shell nanoparticles against A. niger.
48		Artemis Mastrotheodoraki	Multi-mycotoxin detection in dried and fresh fruits Occurrence of mycotoxins in food commodities in the Greek market
49		Pantelis Natskoulis	Investigation of the presence of zearalenone and fumonisin in cereals from the Greek market applying rapid immunological detection methods (ELISA)
50		Georgia Soultani	Effect of wood alternatives origin and size on the chemical composition and aging of tsipouro.
51		Georgia Soultani	Assessment of Ochratoxin A levels in Thessalian wines and evaluation of consumer exposure
52		Kyriaki Xanthidou & Panagiota Drillia	Non intentionally and intentionally added substances screening tests in food contact materials
53		Konstantina Avdala	Assessing the antifungal resistance of silver nanoparticles against Aspergillus niger isogenic mutants
54		Maria Metafa	Analytical Approaches to Optimizing Retsina Wine: Effect of Resin, Yeast Strain, and Oak Type on Chemical Composition and Sensory Attributes
55	**Physical Chemistry**	Constantinos Demetriou	Electronic structure of the MoLi, MoBe, and RuB molecules: Ground and Low-Lying States
56		Chrysi Giannitsa	Clustering Studies in Peripheral Collisions between Heavy Nuclei
57		Pnevmatiki Athanasia Karantoni	Computational study of the copper-catalyzed α-alkylation of aryl acetonitriles with benzyl alcohols
58		Stergios Koulouris	Probing the Production of Neutron-Rich Nuclei Towards the r- Process Path via Multinucleon Transfer Reactions

Poster #	Session	Name	Abstract title
59		Eleftherios Papamichalis	Photophysical properties of Donor-Acceptor (D-A) fluorescent sensors
60		Fylaktos Panagiotis-Dimitrios	A molecular dynamics simulation method for the reproduction of the motion of flexible macromolecules in ion mobility spectrometry
61		Aliki Soufla	Carbenes to tune 2D metal organic frameworks
62		Eleftheria Travlou	Properties of projectile-like fragments from peripheral nuclear collisions of 86Kr (25 MeV/nucleon) on 208Pb
63		Christina Eleftheria Tzeliou	The solvent and nitrogen geometry effect on the absorption spectra of a ferrocene-naphthalimide derivative
64	**Organic Chemistry**	Ektoras Apostolou	Synthesis and characterization of hybrid cadmium compounds exhibiting intense fluorescence
65		George Atsaves, Christina Kakomanoli	Generation and Study of a Novel DNA Base Lesion
66		Savvas Chalkidis	DABCO-Catalyzed Synthesis of Thiazolidine-2-thiones: System Development and Mechanistic Insights
67		Dimitrios Giannopoulos	Synthesis and functionalization of step-growth polymers prepared by the A3 multi-component coupling reaction
68		Stella Gkiola	Studies Towards the Synthesis of Natural Products Ornosol and Insularoside
69		PANAGIOU MAVROEIDI	Investigating the interactions of a new set of quaternary propargylamine derivatives with monoamine oxidase enzymes.
70		Vasiliki Skandali, Aris MIchalis	Synthesis of Carbasugar Derivatives as Potential Inhibitors of Glycogen Phosphorylase
71		Anna-Krinio Papagiorgou	β-Lactones and β-lactams: Design and synthesis of novel antimycobacterial compounds
72		Konstantinos Patiniotis	Synthesis of phosphinic pseudopeptidic inhibitors of M1 aminopeptidases using a late-stage diversification strategy
73		Efthymios Alexandros Routsi	Halogen-Bonded Complexes (XBCs) in Solution: A Spectroscopic and DFT Study
74		Efstathios Tonis	Modular Synthesis of Azines Bearing a Guanidine Core from N-Heterocyclic Carbene (NHC)-Derived Selenoureas and Diazo Reagents
75		Eleftherios Massios	Docking studies of drugs acting on Myasthenia Gravis
76	**Industrial Chemistry**	Evangelos Apostolakis	"Synthesis of Star-Shaped Poly(n-hexyl isocyanate) Homopolymers via Coordination Polymerization and Core-First Methodology Using Multi-Functional (Half-)titanocene Alkoxy Complexes "
77		Agnieszka Feliczak-Guzik	Deposition of fragrances on carriers with different physicochemical parameters
78		Alexandra Gkolosi	Cross-Linking of PVA-Based Coatings for Antifouling Applications
Poster #	**Session**	**Name**	**Abstract title**

79		Aikaterini Katara	Synthesis and characterization of statistical and block copolymers comprising of allyl– and dodecyl–isocyanate via titanocene–mediated coordination polymerization as scaffolds for complex macromolecular architectures
80		Maria-Eleni Mylona	Modification of fluoropolymer surfaces using ultraviolet irradiation
81		Ioannis Papaioannou	Development of sustainable mixed matrix alginate membrane substrates for gas separations
82		Rafailia Papandreou and Charitini Papandreou	Stereoselective synthesis of chiral cyclopentanols towards macrocyclic natural products of the Jasminun species
83		Christina Varfi	Synthesis of pH-Responsive Hybrid Copolymers and Their Conjugation with Protein to Combat Myasthenia Gravis
84		Agata Wawrzyńczak	Car-washing formulations based on biosurfactants – synthesis and characterization

ABSTRACTS

On-surface synthesis and post-synthetic modification of low-dimensional organometallic networks

Authors:

F. Allegretti[1] (*invited*), **F. Haag[1], W. Zhao[1], B. Yang[1], I. Piquero-Zulaica[1], A. P. Seitsonen[2], Y.-Q. Zhang[3], and J. V. Barth[1]**

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The rise of low-dimensional systems with extraordinary electronic and mechanical properties such as graphene, graphyne and graphdiyne has strongly spurred the scientific research on novel organic materials supported on surfaces. In this talk, the on-surface synthesis of organometallic networks (OMNs) on a model metal surface, the Ag(111) surface, is presented. By exploiting interfacial coupling reactions of suitable molecular precursors and metal adatoms picked up from the substrate, OMNs with very high order and mesoscopic regularity can be obtained, which feature a single sheet of Ag-metalated graphdiyne. The combination of mixed sp^2 - sp hybridization and metal centres with Kagome ordering leads to the prediction for the resulting single-layer OMN of an intriguing, unconventional electronic structure, which – however – may be strongly modified by the presence of the underlying support. We also show that further tailoring of the OMN chemical and geometric structure can in principle be achieved by exchanging the metal centres via transmetalation strategies. Current stand and future challenges of the presented work are discussed.

Antigen discovery for development of personalized cancer immunotherapy

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The precise identification and prioritization of antigenic peptides presented by class-I and -II human leukocyte antigens (HLA-I and -II) recognized by autologous T cells is essential for advancing cancer immunotherapies. Although several clinical neoantigen prediction pipelines are currently available, none support the direct integration of mass spectrometry immunopeptidomics data, which can reveal antigenic peptides from a variety of canonical and non-canonical sources. To address this gap, we have developed NeoDisc, a unique 'end-to-end' clinical proteo-genomic pipeline.NeoDisc is a rapid, modular computational pipeline that integrates state-of-the-art publicly available and in-house software for genomics, transcriptomics, immunopeptidomics, and in-silico tools to identify, predict, and prioritize tumor-specific and immunogenic antigens from multiple sources. In my presentation I will demonstrated the superiority of NeoDisc in prioritizing neoantigens compared to recent neoantigen prioritization pipelines and highlight its diverse features enabling personalized antigen discovery.

Cereal grain polysaccharides as functional food ingredients: structure-property relations

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Mixed linkage (1→3),(1→4) linear β-D-glucans and arabinoxylans constitute major polysaccharide components of the pericarp and endosperm cell wall matrix of cereal grains (e.g., wheat, barley, oat) which can provide a significant portion of the recommended daily dietary fiber intake. These non-digestible polysaccharides have been attracting research and industrial interest due to several health benefits linked with their consumption, in relation to risk reduction and/or better management of inflammatory conditions associated with chronic diseases; in fact, they are among the very few constituents that regulatory authorities (FDA, EFSA) have permitted the use of health claims, providing marketing opportunities for development of functional products enriched with these fibers. The nutritional benefits of cereal fibers, in terms of structure-function relations, are not fully elaborated, although solubility, extractability, viscosity and molecular structure seem to be important. The physical properties of β-D-glucans and arabinoxylans, such as solubility, propensity for chain aggregation and rheological behavior, in solution and gel state, are dependent on linkage type and substitution patterns, molecular weight and chain conformation. Despite the strong incentive to incorporate cereal fibers in food products, using isolates or concentrates, their industrial usage still remains a challenge from a processing-formulation and sensorial perspective; e.g. among other factors, compositional-processing effects and endogenous enzymic systems seem to have a strong impact on structure modification and their physical properties. Moreover, phase separation phenomena can take place in composite food matrices (e.g., dairy formulations), affecting the sensorial acceptability and shelf life of the end-product. This presentation aims to highlight some aspects on chemistry, properties and use of cereal cell wall polysaccharides, with an effort to elaborate on molecular structure - functionality relations and their impact on end-product quality attributes.

The prebiotic origin of the RNA nucleosides and translation

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Keywords: Prebiotic chemistry, purine & pyrimidine bases, wet-and-dry-cycles, Origin of the ribosome

Abstract: The widely accepted RNA world hypothesis suggests that life emerged from RNA, which was able to (self)-replicate and evolve.[1] Replication of the information in RNA requires the formation of the complementary pyrimidine-purine Watson-Crick base pairs (A:U and G:C) for which we need to find prebiotically plausible synthesis scenarios.[2,3] I am going to report about new chemistry that allows the formation of these four canonical nucleosides[4,5] plus a set of non-canonical RNA bases[6] that are found until today in the transfer-RNA of organisms on earth [7]. The synthesis is achieved under plausible prebiotic conditions. The new prebiotic access to these molecules is based on the FaPy-pathway towards the purine nucleosides,[3] and an isoxazole pathway that generates the pyrimidines.[4] The chemistry is driven exclusively by fluctuations of physicochemical parameters such as pH, temperature and concentration. Importantly, the described chemistries are compatible with each other so that all four RNA building blocks can be formed in the same geochemical environment.[4]

Next to the formation of nucleosides, the emergence of life also required amino acids and the process of translation. We were able to show that certain RNAs have the property to self-decorate with amino acids and that these amino acids can react directly attached to RNA to peptides. This so far unknown property of RNA allows to extend the RNA world theory[1] to an RNA-peptide world concept for the beginning of life.[8]

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The proteasome as a key player in the progression of ageing and age-related diseases

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Ageing is a physiological process that represents a high-risk factor for the progression of age-related diseases. Several molecular pathways deteriorate with ageing or the progression of age-associated proteinopathies, including the proteasome system. Proteasomes are constituents of the proteostasis network responsible for the proteolysis of normal and abnormal proteins. Using the replicative senescence model of human primary fibroblasts and the multicellular nematode *Caenorhabditis elegans*, we have shown that proteasome activation (either through genetic means or through natural or synthetic compounds), results in lifespan extension. More importantly, the lifespan extension is accompanied by healthspan (time period free of diseases) improvement. With regard to the progression of the Alzheimer's disease (AD) phenotype, elevated proteasome function confers lower paralysis rate in various AD nematode models accompanied by decreased Aβ deposits, thus ultimately decelerating the progression of the disease. Similar positive results were also obtained when primary murine cortical neurons were co-treated with proteasome activators and increased concentrations of various Aβ forms. More recently, we have shown that proteasome activation in the nervous system can enhance the proteasome activity in the muscle of *C. elegans*, thus revealing a cell non-autonomous communication. Mechanistically, this communication depends on Small Clear Vesicles (SCVs), with glutamate as one of the neurotransmitters required for the distal regulation. The identified distal communication may have serious implications in the design of therapeutic strategies based on tissue-specific proteasome manipulation.

A bio-inspired approach for electrocatalytic H_2 production

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Research in multi-electron reduction catalysis for small molecules has gained importance in addressing energy and environmental challenges. Metal ions commonly promote these redox processes, and our focus is on thiolate-based scaffolds inspired by the active sites of enzymes like hydrogenases. The goal is to design robust water-active catalysts utilizing thiolate ligands and noble-free metal ions for innovative catalysis in H_2 production.

In this presentation, I will outline our strategy for developing optimized catalytic systems, which combines not only rational design and understanding of mechanisms but also takes into account various aspects of the catalytic conditions, such as homogeneous or heterogeneous processes and how to supply electrons, i.e., chemically, via electro-assisted or photo-assisted processes.

Understanding the structure of two-dimensional films using X-ray standing waves

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Two dimensional materials have grown significantly in importance over the last two decades. However, the term "two dimensional" is a misnomer for almost all such materials as there is always a degree of three-dimensionality due to the interaction of the material with its supporting substrate, as indicated in Figure 1.

How two-dimensional a film is, thus, an interesting question and is one that can be neatly resolved by quantitative structural measurements. X-ray standing waves has been used to determine the structure of over 15 two dimensional graphene-like films (e.g. graphene[1,2,3], boron nitride[4], silicene[5], transition metal dichalcogenides[6,7]). This work has provided the beginnings of insight into how these 2D films interact with their growth substrates from films that basically free-standing on the growth substrate [1], to those that are effectively alloyed with it [2]. Herein, I will introduce the X-ray standing wave technique and provide several key examples into how these structural measurements address the question of just how two dimensional a two dimensional material is.

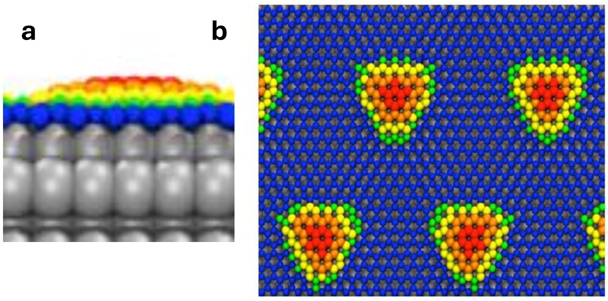

Figure 1: (a) Side and (b) plan view of graphene on Ru(0001), where the colourscale represents the variation in height of the C atoms above the surface, where blue corresponds to the lowest adsorption height and red to the highest. Reproduced from Ref. [3]

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Transition Metal Catalyzed Electro-Organic Synthesis with Water & Ex Situ Electrosynthesis for Unique Selectivity

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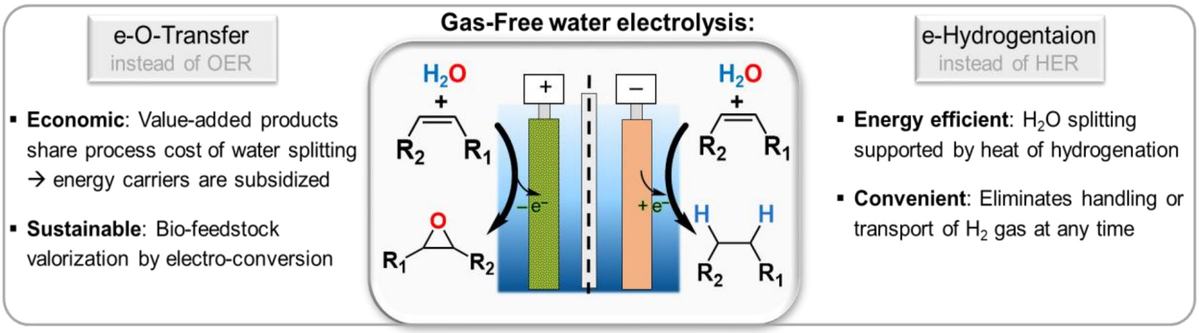


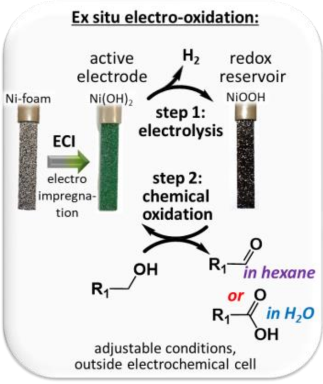
- **Economic**: Value-added products share process cost of water splitting → energy carriers are subsidized
- **Sustainable**: Bio-feedstock valorization by electro-conversion

- **Energy efficient**: H_2O splitting supported by heat of hydrogenation
- **Convenient**: Eliminates handling or transport of H_2 gas at any time

H_2 production by water electrolysis is proposed to store excess renewable electricity in chemical energy carriers. O_2 evolution is the typically paired anode reaction in standard electrolyzers, but the unsalable side product O_2 cannot support process costs.
We develop **electrocatalytic oxygen atom transfer (e-OAT)**, **to replace O_2 evolution by anodic value-added product formation** together with water electrolysis-based energy carrier production. A specific target reaction is the electro-epoxidation of alkenes with H_2O.[1]

Besides cost, H_2 gas storage is another challenge, for which liquid organic hydrogen carriers (LOHCs) emerged as a potent solution. In this context, we develop **direct electro-hydrogenation of alkenes,[2] organic carbonyls, and aromatic systems with H_2O in one step**, mediated by transition metal pincer complexes and porphyrins. Mild overpotentials (energy efficiency) and suppression of typically dominant parasitic HER (current efficiency), is achieved by structure-reactivity tuning of catalysts and the design of unique mechanisms, including H_2O activation instead of H^+ reduction.

Beyond classic *in situ* electro-synthesis (substrates added into electrolyzer), we develop ***ex situ* electrosynthesis—a new concept to separate chemical and electrochemical reaction steps in time and space for unrestricted flexibility in reaction design**.[3] Exemplarily, we use the reversible $Ni(OH)_2$ / NiOOH couple for short term storage of redox equivalents. The bulk electro-conversion of $Ni(OH)_2$ to NiOOH is performed together with energy carrier (H_2) production in an electrolyzer. The chemical oxidation of organic substrates to value-added products is then performed outside the electrolyzer under freely choosable reaction conditions (solvent, temperature, pressure), which allows orthogonal selectivity for products that are inaccessible to traditional electrosynthesis.



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Examining the reactions of ions and radicals at low temperatures

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It is challenging to study gas-phase reactions between ions and radicals at low temperatures, and with control over all of the reaction parameters. I will present our approach for generating beams of velocity- and state-selected radicals with tuneable properties using magnetic fields [1-2]. While our approach was initially developed to produce slow H-atom beams, we show that the same principles can also be applied to generate filtered beams of molecular radical species (including O_2 and OH).

Recently, we have combined one of our radical beam sources with a cryogenic ion trap, with the goal of studying ion–radical reactions under cold and controlled conditions (see Figure 1). Reactions take place within Coulomb crystals, enabling us to monitor the reaction processes with exceptional sensitivity (down to the single-ion level) [3-4]. The advantages of studying reactions within a Coulomb crystal environment will be set out, and a new imaging method that enables spatial and temporal detection of ions will be presented [5]. Finally, potential broader applications of our methods, including the exploration of new research directions and collaborative projects, will be discussed.

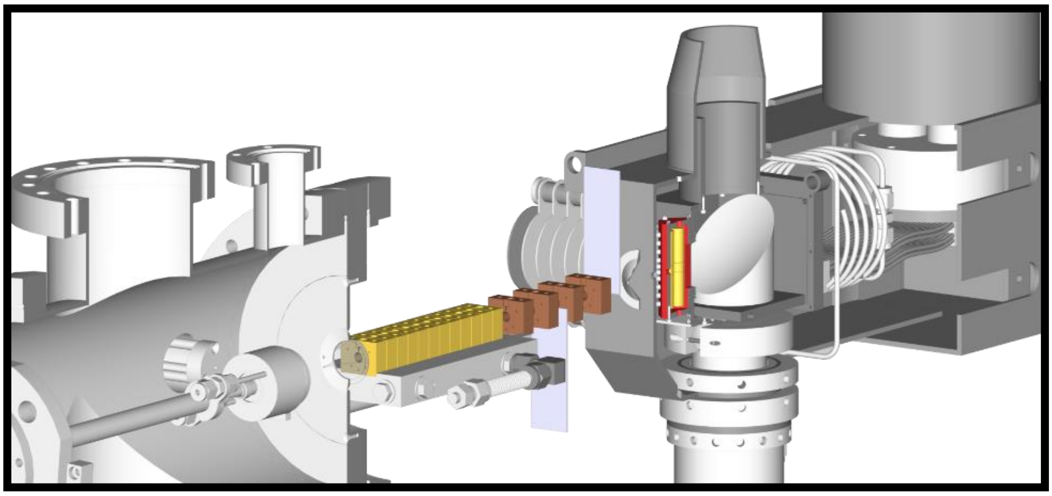

Figure 1. Schematic illustration of the combined radical beam and cryogenic ion trap apparatus.

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Lipid Signaling in Health and Disease

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Lipid signaling involves two distinct groups of lipids. Intracellular lipids that function as second messengers in prominent signal transduction pathways and extracellular lipids that function as agonists for plasma membrane receptors. We will discuss two examples: the second messenger phosphatidylinositol 3,4,5-trisphosphate (PIP3) and the bioactive lipid phosphate agonist lyso-phosphatidic acid (LPA). Deregulation of PIP3 and LPA metabolizing enzymes and/or their effector proteins impacts on almost all aspects of CNS function including, neuronal growth, differentiation, migration, axon guidance and branching, as well as synapse formation and function. Knowledge of the repertoire and the modes of function of these signaling lipids pave the way for pursuing novel pharmacological approaches for treating psychiatric and developmental CNS diseases in the future.

Drivers and Impacts of Climate Change Over Eastern Mediterranean

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Recent observations and modeling highlighted the Eastern Mediterranean (EM) as an important climate change hotspot. Over the last decades, the EM atmosphere is warming at a rate almost double the global average, while greenhouse gas emissions in the EM and Middle East regions are also growing at high rates. Seawater temperature is increasing rapidly and “marine heatwaves” have been frequently observed over the last years, thus facilitating the migration of invasive species as well as extreme events such as storms and floods. Recently, the IPCC highlighted that extreme weather events including wildfires, floods, drought frequency and severity, as well as aridity, agricultural and hydrological droughts, desertification, and sea-level rise will increase in the coming years. These events will affect infrastructures, human activities and economy in a wide range of sectors, including agriculture, forestry, health, ecosystem functioning, displacements and migration with important societal impacts.

During my talk I will provide an updated overview of the drivers affecting climate change in the region, and highlight the impacts of climate change at various societal sectors as well as the need for tools development for early warning systems.

Key words: Eastern Mediterranean, climate change, drivers, impacts, tools, early warning

Access to high rotational barrier atropisomers

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The today's drug discovery is profoundly affected by chirality; enantiomers may differ significantly in biological activity with tremendous impact. Atropisomerism is a type of axial chirality resulting from hindered rotation of a σ bond that yields non superimposable stereoisomers (coined as "atropisomers"). The phenonemenon has been widely applied in materials, asymmetric organic synthesis and of course pharmaceuticals. Most of the atropisomers have low energy barriers (*class 1,* $\Delta E_{rot} < 20$ *kcal/mol*), thus rapidly equilibrating. Nowadays, in drug discovery, it is almost prohibited to synthesize class 2 atropisomers ($\Delta E_{rot} \approx 20\text{-}30$ *kcal/mol*), whereas it is highly recommended that molecules with one or more atropisomeric axes has to be developed as class 3 *(>30 kcal/mol*). However, the synthetic access to such molecules might be extremely challenging . Herein, we would like to report for the first time, a synthetic access to high rotational barrier atropisomers via multicomponent reaction chemistry (MCRs). A novel class of atropisomers is reported through a Ugi-tetrazole multicomponent reaction (UT-4CR) using various aromatic and polyaromatic aldehydes, benzylamine, ortho-substituted phenyl isocyanides and trimethyl silyl azide to afford the corresponding products in high yields. Several single crystal structures have been obtained demonstrating the effect, combined with DFT calculations and NMR studies.

Multimethodological study of trace metal speciation in marine waters

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Most elements occur in seawater in very low concentrations, in traces. Traditionally, the focus of research interest has been on the so-called heavy metals such as Pb, Cd, Cu, Zn, Hg. While knowing the total concentrations of metals is important to determine the general status of water quality, it is even more important to determine their speciation, as the bioavailability and toxicity of metals depends largely on the chemical species in which the metals occur in natural waters. Electrochemical techniques offer both adequate sensitivity and selectivity to determine the concentrations of many trace metals and the ability to provide information on chemical speciation (interaction with natural organic matter). This presentation will focus on the most commonly used voltammetric techniques for analysis and speciation of trace metals in seawater, such as anodic stripping voltammetry and adsorptive cathodic stripping voltammetry (ASV and AdCSV). In addition, the application of the copper ion selective electrode (Cu-ISE) and passive sampling technique for the speciation of trace metals based on diffusive gradients in thin films (DGT) in estuarine waters will be presented. Challenges in their applications and solutions to overcome known obstacles will be discussed. In addition to the capabilities and application of the voltammetric methods themselves, the automation of the measurement and the mathematical treatment of raw voltammograms to improve the overall analytical procedure will also be discussed.

A Combination of Atomic and Molecular Mass Spectrometric Techniques for the Determination of Arsenolipid Compounds in Food of Marine Origin

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Arsenolipids represent a novel group of organic lipophilic arsenic compounds that have recently been shown to be present in the marine food web, including fish. However, studies on their metabolism, origin, abundance, and toxicity are still limited. Based on their chemical structure, arsenolipids (AsLps) range from arsenic-containing hydrocarbons (AsHC) and arsenic-containing fatty acids (AsFA), to the more structurally complex arsenic-containing triacyglycerides (AsTAGs). AsLps can occur at high levels in edible fish, often constituting 20% of the total arsenic content or even higher in fatty fish such as sashimi tuna[1]. As the toxicity of arsenicals depends on their chemical form, knowledge of the speciation of AsLps in marine samples is vital for health risk assessments.

So far, our knowledge concerning the abundance and identity of these compounds is limited compared to what we know about the water-soluble arsenic compounds present in marine organisms. This is partly due to analytical challenges in isolating trace amounts of AsLps from their lipid matrix and the lack of suitable analytical methods for the determination of AsLps in complex As compound mixtures found in marine fish. To overcome these difficulties a few recent studies have reported on the synthetic preparation of AsLp standards and the preliminary characterization of the AsLps present in a few reference materials[1]. However, commercially available AsLps are still not available, and reference materials require more detailed characterization for their AsLp content.

We will be presenting the development and application of a range of advanced analytical techniques for the detailed determination (structural characterization and quantitation) of AsLp species in a tuna fish certified reference material (CRM) BCR 627. More specifically, we will be demonstrating the use of gradient elution HPLC – inductively coupled plasma mass spectrometry (ICP-MS), in combination with HPLC - electrospray ionization high resolution MS with a single AsLp standard in order to determine AsLps in the widely used BCR 627. We will be presenting data to confirm the presence of several already reported AsLp species in BCR 627, and also identify unknown AsLp species. This combination of techniques and materials may prove vital in assisting with the broader determination of AsLps in seafoods and facilitate a new era in their study.

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Optical immunosensors: Analytical tools with many applications

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Optical transducers are widely used as biosensing tools due to their high detection sensitivity, immunity to parasitic electronic noise, multi-analyte capabilities and, in many cases, ability for label-free detection. Most label-free optical biosensors rely either on refractrometric or reflectrometric detection principles. In the first category fall all sensors based on surface plasmon resonance and interferometry, including Mach-Zehnder and Young interferometers, while the second category includes mainly sensors based on reflectance spectroscopy. Aiming to develop optical biosensors that could offer high analytical sensitivity but also ease-of-use at the point-of-need, in the last 15 years, we have focused our research efforts to the development of silicon-based Mach-Zehnder interferometers (MZIs) as well as to a system based on white light reflectance spectroscopy [1, 2]. The integrated MZIs consist of silicon nitride waveguides fabricated on a silicon chip along with broadband light-emitting diodes and photodetectors. The implementation of a broadband light source resulted to a new detection approach that benefiting from the information gained by processing the whole transmission spectrum provided high detection sensitivity. Over the years, several chip layouts have been realized seeking the most suitable for implementation to portable devices that could perform at the point-of-need. Thus, chip formats that included along with the MZIs, light sources, spectral analysers and photodiodes were fabricated leading to the ultimate level of integration. On the other hand, chips with only the MZIs and external light source and spectrometer have been exploited as "dipstick" sensors in order to abolish the need for microfluidics and pumps. Regarding the biosensors based on white light reflectance spectroscopy (WLRS), in addition to optimization of their analytical performance, the main targets were to minimize the size of the whole system and built-up an instrument that could automatically perform all the assay steps and process the data for presentation to the user. Both systems have been applied to the immunochemical detection or either single or multiple analytes related to food and environmental safety in different matrices as well as of disease biomarkers in biological fluids.

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Novel synthetic copolymers for creating biohybrid nanostructures

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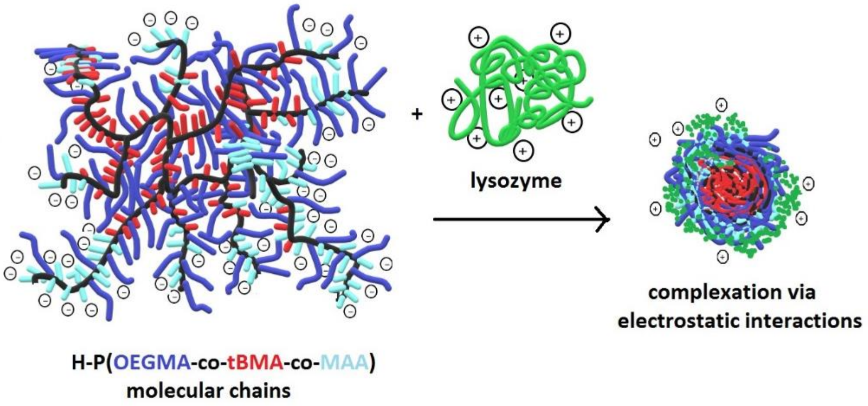
The need for functional nanomaterials with advanced properties is increasing in modern society. Polymeric nanomaterials can contribute to several applications especially in the biomedical field. RAFT polymerization provides several types of intriguing polymer architectures, including branched synthetic macromolecules with diverse chemical functionalities and physicochemical properties. Designed chemical functionalities in conjunction with non-linear macromolecular topologies allow for finetuning interactions of synthetic polymers with biological species (protein, peptides, nucleic acids) and nanostructuration following biomimetic self-assembly schemes, through non-covalent interactions.

In this presentation the synthesis of amphiphilic, hyperbranched, charged copolymers through RAFT polymerization and post-polymerization modification schemes is presented. Furthermore, the electrostatic self-assembly of hyperbranched copolymers with proteins and peptides towards the creation of biohybrid nanostructures is discussed. Their structure and properties in aqueous media are elucidated using a gamut of advanced physicochemical techniques, including light scattering techniques and cryo-electron microscopy. Such nanoscopic structures are designed as functional nanocarriers/nanoconstructs for protein delivery, enzyme immobilization and for antimicrobial protocols related schemes.



Scheme 1: Schematic depicting the complexation of H-P(OEGMA-co-tBMA-co-MAA) hyperbranched copolymer with lysozyme.

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Inorganic Chemistry/Polymer Chemistry: A success story

The case of coordination polymerization of isocyanates employing half-titanocene complexes

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Abstract

Transition metal complexes have been proven to promote the coordination polymerization of numerous monomers acting either as catalysts or initiators. Recent advances in both Inorganic and Polymer Chemistry have allowed the synthesis of macromolecular structures with controlled molecular characteristics, stereochemistry and complex architectures. In this specific study coordination polymerization techniques were employed using the half-titanocene complex $[(\eta^5\text{-}C_5H_5)((S)\text{-}2\text{-}Bu\text{-}O)TiCl_2]$ as initiator for the synthesis of statistical and block copolymers of *n*-hexyl isocyanate, HIC, with 2-chloroethyl isocyanate, ClEtIC, 2–phenylethyl isocyanate, PEIC, and 3-(triethoxysilyl)propyl isocyanate, TESPI. In addition, statistical and block copolymers of n-dodecyl isocyanate and allyl isocyanate were also synthesized via the same polymerization methodology. The copolymers were characterized by NMR and IR spectroscopy, Size Exclusion Chromatography, SEC, and circular dichroism, while their thermal properties were investigated through Differential Scanning Calorimetry, DSC, and Thermogravimetric Analysis, TGA. In the case of the statistical copolymers the monomer reactivity ratios were calculated employing various graphical methods, as well as the COPOINT program, in the frame of the terminal copolymerization model. Structural parameters, such as the dyad monomer sequences and the mean sequence lengths were investigated as well. The kinetics of thermal degradation of the statistical copolymers was studied, and the activation energies of thermal decomposition were examined through the Kissinger, Ozawa-Flynn-Wall, OFW and Kissinger-Akahira-Sunose, KAS approaches. The block copolymers were synthesized by sequential addition of monomers. SEC, IR and NMR measurements confirmed the synthesis of well-defined products. The copolymers containing allyl isocyanate units were employed as scaffolds to conduct thiol-ene click reactions leading to functionalized polymers or more complex macromolecular architectures.

A Special Case of Divergent Synthesis

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Divergent synthesis has emerged as a powerful tool to promote rapid access to a plethora of natural and unnatural compounds with discrete structural features. As a common practice, starting material(s) are advanced to a *key common intermediate* from where several distinct products are produced in a short and efficient manner, typically in less than five steps. In this work, we present a special case of this tactic, in which natural products from the chiral pool serve as the common intermediate. The so called "natural product to divergency" logic has already been presented before with impressive results, leading to valuable for drug discovery purposes libraries of natural-product-like compounds.[1] Here, we demonstrate the potential of (–)-caryophyllene oxide as a starting point for divergency and convert it to a number of natural and unnatural compounds, some of them being synthesized for the first time.[2] All our targets are reached within 5 steps or less and were selected on the basis of their unique structural features within the family of compounds they belong.

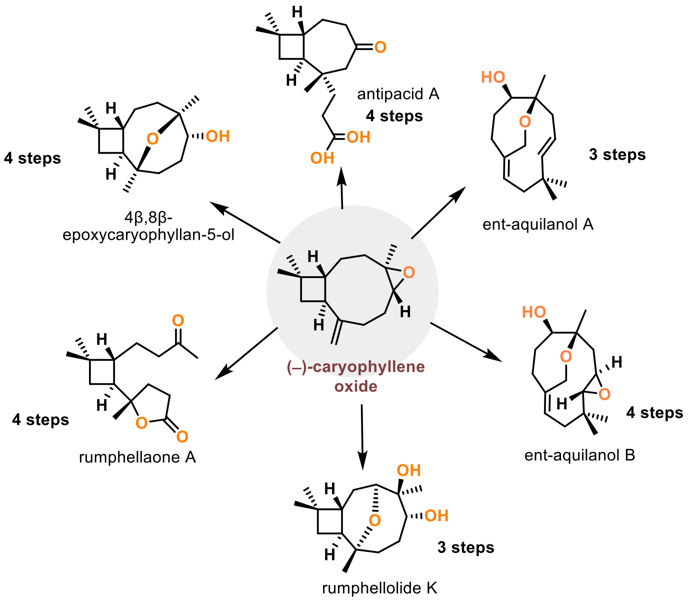

Figure 1: Conversion of(–)-caryophyllene oxide to several natural products

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Our Journey to Molecular Single Photon Sources –

Fast and Bright… but still Dark!

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Abstract:

Emitter materials that can exploit triplet excitons in the near-IR are of interest due to their potential application in quantum information networks, device technologies and encryption schemes. One of the biggest challenges for the design of suitable metal complexes for these purposes is the enhanced non-radiative decay of low energy states due to the energy gap law. In this presentation we will show our efforts to improve the relative radiative (k_r) and non-radiative (k_{nr}) rate constants of Cu^I and Zn^{II} based TADF emitters for high quantum yields ϕ for emission beyond 600 nm in order to provide molecular single photon sources. Part of the strategy is the invention of paracyclophane based carbene ligands as π-chromophore ligands, giving k_r up to $2 \cdot 10^6$ s^{-1} and $\phi = 0.8$ for deep red to near-IR emission from copper(I) complexes. Bearing in mind that many IT relevant applications require circularly polarized emission (CPL), we have also investigated design criteria to maximize the dissymmetry in the excited states up to g_{lum} = +/- 0.023 for application in CP-OLEDS.

Mushrooms as natural resources for functional foods and biologically active compounds

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From ancient times, food has served not only for nourishment but as a source of essential nutrients. However, modern dietary habits often prioritize taste over nutritional value, contributing to diet-related issues ranging from nutrient deficiencies to chronic conditions like coronary heart disease, hypertension, atherosclerosis, and type 2 diabetes. Growing awareness of the link between diet and health is driving demand for foods that offer benefits beyond basic nutrition, forming the foundation of the functional foods concept. Mushrooms, with their unique taste, nutritional and low-calorie profile, as well as presence of numerous health-beneficial compounds are in the spotlight as ideal candidates for functional foods. Thus, fruiting bodies of mushrooms are a mixture of dietary fiber, proteins, and a variety of vitamins (B1, B2, B12, C, D, E), along with minerals (iron, copper, manganese, zinc) and beneficial bioactive compounds like terpenes, fatty, phenolic and organic acids, tocopherols etc. These compounds are not only nutritionally valuable but also support metabolic pathways and show bioactive properties beneficial to human health. Recent research commended mushrooms for their antimicrobial, antitumor, anti-inflammatory, hepatoprotective, neuroprotective, cardioprotective, and immunostimulatory effects. These beneficial properties, along with their culinary appeal, versatility, and functional properties positioned them at the front line of modern food industry, with numerous mushroom-based foods and beverages being developed. This high exploitation of mushroom biomass is enabled by the fact that mushrooms may be cultivated on various substrates (including various types of waste) as well as in reactors in controlled conditions. This could allow mushroom use as source of vegan proteins, nutraceuticals, and food flavoring agents on a larger scale or in populations with limited access to mushrooms. Furthermore, this could increase circular economy initiatives in the near future.

Keywords: mushrooms; food; health-beneficial; biological activity

Alleviating the need of standards and Leveraging advances in High Resolution Mass Spectrometry for integrated, holistic environmental monitoring of emerging contaminants

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Thousands of chemicals are released daily into the environment, posing potential risks to ecosystems and human health. Recent advancements in high-resolution mass spectrometry (HRMS) and software development have facilitated comprehensive contaminant monitoring in complex matrices. To investigate environmental samples, methodologies such as LC-ESI (RPLC and HILIC) and GC-APCI-HRMS, along with advanced workflows (target, suspect, and non-target screening) and chemometric tools, have been developed to detect known contaminants and identify unknowns. For target screening, extensive datasets of over 2,400 organic pollutants—including various compound classes and transformation products—have been developed, while the integration of ion mobility-derived CCS values and TIMS technology into LC-QTOFMS has improved sensitivity and detection accuracy. New algorithms for suspect screening enable the chemical curation of regulatory databases, yielding a comprehensive suspect list with in-silico predictions of properties (e.g., RT, RTI, fragments, toxicity). Machine learning models now optimize the selection of LC-HRMS or GC-HRMS methods, increasing identification confidence, and novel semi-quantification techniques improve concentration estimations for newly identified chemicals. These methodologies have been applied in environmental studies globally, including research on the Danube River, Black Sea, and biomonitoring in apex predators, making significant strides in the field of chemical management.

Nitrogenous flavonoid derivatives production by reacting with amino acids

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A class of nitrogenous derivatives of flavonoids was detected using *in vitro* cell culture medium and *in vivo* mice produced without enzymatic catalysis have been consistently overlooked in literature. In this study, 39 flavonoids were incubated in Dulbecco's modified eagle's medium (DMEM) at 37℃ for 2 h to explore the reaction mechanism behind nitrogenous derivatives from flavonoids. Baicalein, scutellarein, DMY, GC, EGC, and EGCG were found to produce corresponding nitrogenous derivatives in both DMEM and mixed amino acid solution. The nitrogen source of these 6 flavonoid nitrogenous derivatives was revealed to be amino acid. The reaction site with amines in these flavonoid nitrogenous derivatives was identified as OH of the pyrogallol moiety in flavonoids *via* LC-MS/MS and NMR. This pyrogallol group was a key motif being first oxidized into quinone, further, to react with Strecker degradation of amino acids to yield N-flavonoids and corresponding aldehydes. Reaction optimization revealed that a slightly alkaline environment accelerates flavonoid nitrogenous derivatives formation by promoting the formation of flavonoid quinone. These results provide the first mechanistic evidence for the *in vitro* generation of flavonoid nitrogenous derivatives yet to be tested using *in vivo* assay.

Keyword: Nitrogenous flavonoids; baicalein; dihydromyricetin; catechin; pyrogallol; amino acids

Acknowledgement

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Applications of paper-based devices in (bio)analytical chemistry

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The birth of the modern field of paper-based analytical devices (PADs) is attributed to the pioneering work by the Whitesides' group which demonstrated that it was possible to perform complex manipulation of liquids within hydrophilic paper channels delimited by hydrophobic barriers [1]. The key features of paper and nitrocellulose as platforms of analytical devices are: flexibility; low thickness and lightness; absorbency; high surface-to-volume ratio; hydrophilicity and capillary action; chemical and biological inertness; disposability and biodegradability; low cost and wide availability; compatibility with various detection modes. Combined with low-cost and portable instrumentation, PADs are well suited to on-site assays and point-of-care testing and relevant applications have been developed in various fields such as clinical diagnostics, environmental monitoring and food quality control [2-4].

In this work, we describe different types of paper-based and nitrocellulose-based devices and selected applications to (bio)chemical analysis using various detection modes (optical and electrochemical) and fabrication methodologies (such as pen-plotting, screen-printing and thermal printing). Representative applications will be demonstrated including: the determination of trace heavy metals in several matrices; the enzymatic assay of glucose in food; the multiplexed estimation of antioxidant activity of wines; the assay of carcinoembryonic antigen in serum; the quantification of thiocyanate in saliva, and; the detection of ochratoxin A in foodstuffs.

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Astrocyte calcium signaling can protect against neuroinflammation induced by α-synuclein oligomers

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It is now realized that Parkinson´s Disease (PD) pathology extends beyond the substantia nigra affecting both central and peripheral nervous systems and exhibits a variety of non-motor symptoms often preceding motor features. Neuroinflammation induced by activated microglia and astrocytes is thought to underlie these manifestations. Aggregated α-synuclein has been strongly associated with neuroinflammation; however, we still lack critical information about the structural identity of the α-synuclein conformers that activate microglia and/or astrocytes and the molecular pathways involved. To address this important gap, we have used primary microglia and quiescent astrocytes, post-mortem brain tissue from PD patients and A53T α-synuclein transgenic mice that recapitulate, in the absence of cell death, key features of PD-related inflammatory responses, i.e. increased levels of pro-inflammatory cytokines and complement proteins. We found that these mice exhibit significant elevations in endogenous antibodies indicating an active immune reaction that positively correlated with the levels of SDS-resistant oligomeric but not monomeric α-synuclein. Detailed 3D reconstruction analysis of individual cells revealed altered microglia and astrocyte number and retraction of astrocyte processes. Using RNAseq and secretomic analyses combined with cell type-specific immunofluorescence intensity, we mapped the signaling pathways that are stimulated in microglia and astrocytes in the presence of α-synuclein oligomers. Our results indicate that astrocyte activation promotes the upregulation of T-type Ca^{2+} channels on astrocytes that mediate the secretion of IGFBPL1, an IGF-1 binding protein of neuroprotective potential. Our work supports a causative link between neuron-produced α-synuclein oligomers and sustained neuroinflammation *in vivo* and proposes that the induction of astrocytic calcium signaling can act as a cell type-specific compensatory mechanism against α-synuclein-induced neuroinflammation by promoting IGF-1 signaling.

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Optimization of hydrothermal synthesis of copper oxide on flexible substrates

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Flexible sensors are a key advancement in wearable tech, adapting to various surfaces and used in medical devices and smart fabrics.[1] They are often cheaper and easier to manufacture, with copper oxide nanostructures improving electrical properties due to their reactivity and conductivity.[2] Copper(II) oxide is an excellent p type semiconductor and has in general good electrical, catalytic and antimicrobial properties.Copper oxides are ideal for flexible circuits and sensors, offering gas sensitivity, stability, and low-cost synthesis. These lightweight sensors are perfect for health monitoring, industrial safety, and environmental applications. Research into integrating copper oxide nanostructures into flexible substrates is crucial for improving sensor performance and durability.[3]

In the present study, the development of nanostructures of copper(II) oxide (CuO) was studied on top of Kapton substrate, suitable for future use in flexible sensors, with the combination of the sol-gel method and the hydrothermal synthesis.

Initially the synthesis of the oxide under different conditions was studied on silicon and gold substrates to find the ideal conditions for the development on Kapton with Cu electrodes. Next the development on the desired substrate was carried out. The conditions during the sol-gel stage were studied, while keeping the conditions for the hydrothermal synthesis the same. Specifically, the following were studied: the concentration of the sol-gel solution, the coating method of the substrate, the number of coatings, as well as the time and temperature of the heating stage after the coating. Lastly, the samples which had Kapton as substrate were characterized with different methods.

It was concluded that the development of copper(II) oxide on top of Kapton substrates was feasible, low cost and easy to apply. The formation of nanostructures of the oxide was also confirmed through Scanning Electron Microscopy (SEM), which was one of the goals of this study.

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Polymorphic positions 349 and 725 of the autoimmunity protective allotype 10 of ER aminopeptidase 1 are key in determining its unique enzymatic properties

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ER aminopeptidase 1 (ERAP1) is a polymorphic intracellular aminopeptidase with key roles in antigen presentation and adaptive immune responses. ERAP1 allotype 10 is highly protective towards developing some forms of autoimmunity and displays unusual functional properties, including very low activity versus some substrates [1]. To understand the molecular mechanisms that underlie the biology of allotype 10 we studied its enzymatic and biophysical properties focusing on its unique polymorphisms V349M and Q725R. Compared to ancestral allotype 1, allotype 10 is much less effective in trimming small substrates but presents allosteric kinetics that ameliorate activity differences at high substrate concentrations. Furthermore, it is inhibited by a transition-state analogue via a non-competitive mechanism and is much less responsive to an allosteric small-molecule modulator. It also presents opposite enthalpy, entropy and heat capacity of activation compared to allotype 1 and its catalytic rate is highly dependent on viscosity. Polymorphisms V349M and Q725R significantly contribute to the lower enzymatic activity of allotype 10 for small substrates, especially at high substrate concentrations, influence the cooperation between the regulatory and active sites and regulate viscosity dependence, likely by limiting product release. Overall, our results suggest that allotype 10 is not just an inactive variant of ERAP1 but rather carries distinct enzymatic properties that largely stem from changes at positions 349 and 725. These changes affect kinetic and thermodynamic parameters that likely control rate-limiting steps in the catalytic cycle, resulting in an enzyme optimized for sparing small substrates and contributing to the homeostasis of antigenic epitopes in the ER.

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Chalcones and 4-hydroxy-2-quinolinone-triazole hybrid derivatives a, b and c as potential anti-inflammatory agents

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4-Hydroxy-2-quinolinones are heterocyclic compounds with various biological activities, including anti-inflammatory and antifungal effects. Their adaptable structure allows for modifications to enhance bioactivity. This study involved the synthesis of a hybrid molecule with an N-benzyl-triazole group added to the 4-hydroxyquinolinone framework to evaluate its impact on lipoxygenase inhibition. The compound 1,3-diphenylprop-2-en-1-one, commonly referred to as "chalcone" (a term introduced by Kostanecki and Tambor), is also known as benzalacetophenone or benzylidene acetophenone. Specifically, chalcone derivatives b and c were explored as potential drug candidates. Their structures were analyzed using 2D NMR spectroscopy and Density Functional Theory (DFT), while docking and molecular dynamics simulations assessed their binding affinity to the LOX-5 enzyme. *In silico* studies and DFT calculations indicated favorable binding, and in vitro experiments confirmed promising results against lipoxygenase

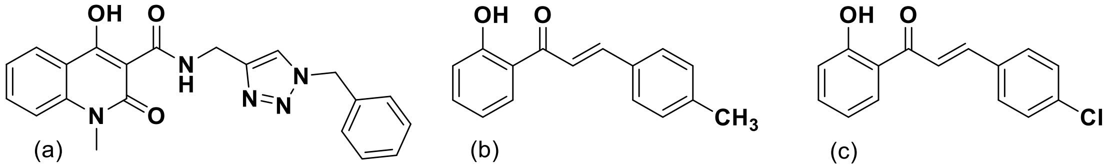

Figure 1: Structures of a 4-hydroxy-2-quinolinone-triazole (a) and chalcone hybrid derivatives (b,c).

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MS/MS-Based Molecular Networking: A new tool for omics-based food authenticity

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The mass spectrometric study of metabolites, the so-called (mass spectrometry based) metabolomics, is of paramount importance for the comprehensive understanding of the biochemistry of living organisms. As metabolomics tackles the regulation of small molecular weight substances, it has also found vast acceptance to other scientific fields such as food chemistry and adulteration. In this notion a myriad of approaches have been and still are being developed, most of them based on the multivariate analysis of molecular ions and the confirmatory power of MSMS fragmentation to statistically highlight the most influential molecules and annotate their structure with adequate statistical power respectively. Nevertheless, the MSMS spectra, despite their significance, have remained neglected in the developed workflows. Recently the MSMS based molecular networks have started to exemplify their usefulness in statistical treatment through newly developed variants of the graph theory and started to become an indispensable tool especially in the case of natural products annotation. In the current presentation the opportunities of molecular networks are explored under the prism of being an alternative approach to the classical metabolomics workflows, in terms of statistical tratment. Thus, GNPS derived data have been treated for discovering unique MSMS signals that could potentially be used as markers of authenticity, concerning the trimming of the plant Crocus Sativus, used for highlighting the proof of concept. Although these are only preliminary results it seems that this is a viable approach that could arm the metabolomics arsenal with novel approaches.

Stability and degradation mechanism of (-)-epicatechin in thermal processing

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The processing method is an important factor to greatly affect the stability and profile of dietary flavonols, which are highly dependent on their chemical structures [1]. Thermal processing (e.g. baking, roasting, pasteurization, steaming) are common cooking methods for dietary sources of (-)-epicatechin (EC), in addition to heat exploited during extraction. In the meantime, chemical reactions such as oxidation can place leading to EC degradation [2,3]. Nevertheless, the exact reaction mechanisms of EC degradation during thermal processing have yet to be revealed. In this study, bathing in boiling aqueous solution (100 °C) was used for simulating high temperature of boiling EC-rich food in water followed by profiling degradation products using UPLC-ESI-TSQ-MS/MS analysis. UPLC-MS is the optimum analytical tool for monitoring biotransformation or chemical reaction products in dietary sources considering its high separation potential, sensitivity, in addition to the strong structural elucidation power of the TSQ mass spectrometer [4,5]. The results revealed for ca. 65.2% loss of EC was detected in the first 10 min, and over 99.5% of EC was degraded within 30 min. A total of 22 degradation products were identified based on retention time, full and tandem MS data are first time to be comprehensively reported. Isomerization, oxidation, hydroxylation, dimerization, and ring cleavage were the main chemical reactions that occurred for EC in boiling aqueous solution.

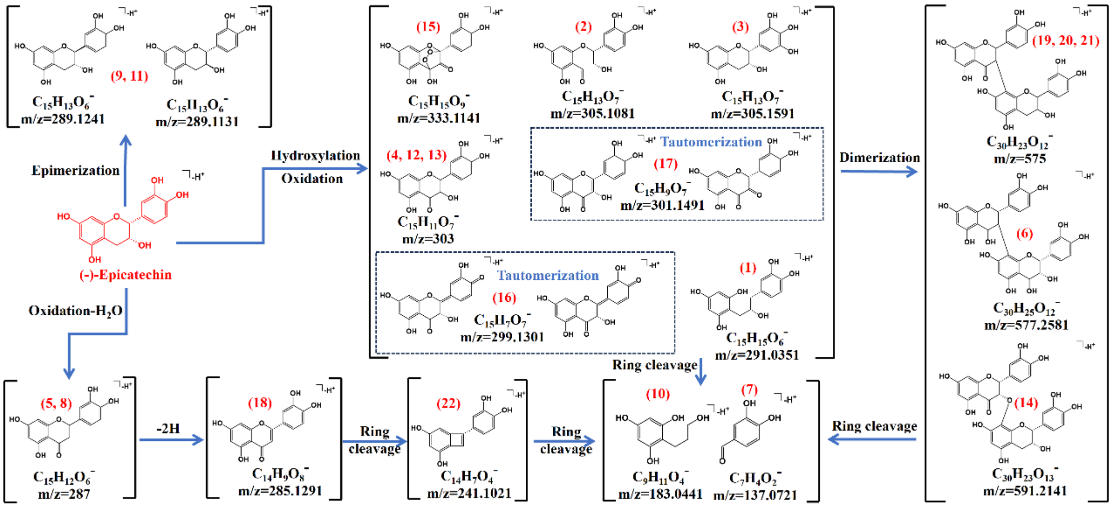

Figure 1: Proposed degradation pathways of EC in boiling aqueous solution.

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Autonomous Vehicles as an innovative monitoring strategy in environmental studies

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Water quality monitoring constitutes a challenge for authorities, due to the vulnerability of current strategies attributed to unpredictable and hazardous incidents, such as sewage discharge and agricultural runoff. Autonomous equipment such as Unmanned Surface Vehicles (USVs) and Aerial Unmanned Vehicles (AUVs) offer multiple advantages regarding real time monitoring and approach of geographical zones not easily accessible. The principal characteristics of such vehicles comprise remote control systems and customized sensors. Unmanned Surface Vehicles (USVs) can greatly enhance the speed, easiness and effectiveness of sampling, as demonstrated in the study of the sea Surface Microlayer (SML), a thin layer (1-1000 μm) representing the boundary between the atmosphere and ocean. SML is distinct from subsurface water due to its unique biological, chemical, and physical properties and tends to accumulate chemical pollutants such as metals and polycyclic aromatic hydrocarbons (PAHs). Despite its significance, SML still remains a generally understudied environmental compartment, due to difficulties so far characterizing its laboring and time consuming sampling. In this context, a new autonomous Unmanned Surface Vehicle (USV) was designed and constructed in the present work, in order to be applied in the study of SML and generally in the elaboration of environmental monitoring strategies, simultaneously allowing for samples collection. The vessel is remotely controlled via laptop, tablet, or smartphone and is equipped with four rotating glass disks for SML sampling, a peristaltic pump for subsurface water sampling, Teflon and amber containers, irradiance sensors and an anemometer.

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Innovative monitoring of emerging micropollutants in Psyttalia WWTP and the Saronikos Gulf Ecosystem

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Emerging micropollutants (EMPs) detection in wastewater & marine environment is of great concern for Athens Water Supply and Sewerage Company S.A. (EYDAP S.A.) harmonizing that way with the recast of the new urban wastewater treatment directive [1]. Pharmaceuticals, per- and polyfluoroalkyl substances (PFAS), industrial chemicals, pesticides, and many other pollutants are classified as EMPs. In this direction, the Horizon Europe ENVIROMED project aims to address the environmental impact of pharmaceuticals during their lifecycle. The case study is the Psyttalia WWTP and EYDAP is responsible for the monitoring campaigns of inlet, effluent and marine environment around the WWTP. The wide-scope target screening of more than 2,400 chemicals was conducted in the Laboratory of Analytical Chemistry, Department of Chemistry of NKUA leveraging complementary chromatographic techniques coupled to high resolution mass spectrometry (HRMS). This study presents the preliminary results from six seawater samples collected on May 21, 2024, from the Saronikos Gulf. Overall, 22 organic micropollutants were detected in the tested seawater samples. The most abundant class (36%) was the industrial chemicals, including PFAS, bisphenols etc. Another 27% of the detected contaminants were coffee and tobacco related contaminants, while 18% of the detected contaminants were classified as pesticides. Lastly, pharmaceuticals and artificial sweeteners were detected, both at 9%. Regarding the two pharmaceuticals detected, venlafaxine (antidepressant) was present in all samples, while cimetidine was detected in two samples but in the highest concentrations, ranging from 15.0 to 217 ng/L. In conclusion, EYDAP, is responsible for the development of a report, which will serve as feedback to the European Union, in order to better manage the presence of pharmaceuticals and their derivatives in waste and sea waters.

Acknowledgements:

ENVIROMED project has received funding from the European Union's Horizon Europe research and innovation programme under grant agreement No 101057844.

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SOA tracers in a background site in the Eastern Mediterranean: exploring formation pathways.

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Primary organic aerosol (POA) consists of directly emitted organic compounds, of biogenic (i.e., isoprene, monoterpenes, sesquiterpenes) or anthropogenic (i.e., benzene, naphthalene) origin, referred to as Volatile Organic Compounds (VOCs). POA undergoes numerous transformation processes and forms the Secondary Organic Aerosol (SOA), containing carboxylic acids, alcohols, carbonyls, organosulfate and organonitrate esters. It is important to elucidate the mechanisms of SOA formation and its influence on atmospheric processes. Furthermore, the chemical composition of the SOA must be determined to assess the effect on human health and the environment and define its toxicity.

A one-year-long field study has been conducted at an urban site of Nicosia, Cyprus (NICTRA) to outline the background levels of 118 SOA compounds in the Eastern Mediterranean region. Nearly 200 PM2.5 and PM1 samples have been analyzed for the determination of 92 organosulfates (OS) and organonitrates (ON) (method A) and 26 organic acids (OA) (method B) respectively. Results show statistically significant ($p<0.05$) differences between the distribution of SOA compounds in PM2.5 and PM1 particles. PM2.5 show higher SOA yields. For the organosulfate load of both PM clusters, lactic acid sulfate (LAS) and glycolic acid sulfate (GAS) are found to be the most abundant SOA, believed to derive from various sources and to associate with isoprene's transformation mechanisms, followed by OS with m/z 211, 213 and 215, generated from the isoprene epoxydiols oxidation mechanisms. Among the organic acids, azelaic acid exhibits the highest concentration in PM1 particles, whereas in PM2.5 particles, *β*-caryophyllinic acid is the most abundant. Statistical analysis tools have been applied to investigate correlations between the compounds' spatiotemporal distributions, indicative of possible common primary sources. Principal Component Analysis showed strong correlation between the majority of isoprene-OS and glycolic acid and lactic acid sulfate suggesting Isoprene as a common precursor VOC. The data were cross-examined with conventional pollutants' distributions to examine secondary formation pathways. In both PM clusters, a strong correlation is found between monoterpene-derived OS and NO_x levels ($R^2=0.83$ for PM1 and $R^2=0.86$ for PM2.5). Also, there is a strong correlation between SO_2 concentrations and ON levels ($R^2=0.96$ and $R^2=0.96$ for PM1 and PM2.5 respectively). On the other hand, GAS, LAS and isoprene-derived OS correlate with O_3 levels, which makes ozone the primary oxidant for their formation.

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Lab-made conductive filament for the 3D printing of ready-to-use multiplexed electrochemical sensors

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In the last decade, Fused Deposition Modeling (FDM), a state-of-the-art 3D printing technology, has been increasingly adopted in the production of electrochemical sensors, facilitated by the availability of commercially available conductive filaments, such as PLA loaded with carbon-based materials, which can be easily converted to electrodes [1,2]. Utilizing these commercially available carbon-based conductive filaments, the as-printed sensors exhibit poor electrochemical performance and require chemical or electrochemical surface activation or post-fabrication surface modification with external functional materials in order to improve their operational properties [3,4].

In this presentation, we report a novel biodegradable conductive PLA filament doped with Bi_2O_3 and CuO, which was synthesized and used for the 3D printing of multiplexed sensors [5]. The as-printed sensors do not need any surface treatment or activation and serve as multifunctional transducers for the direct and sensitive detection and quantification of two heavy metals (Pb and Cd) and two significant health biomarkers: glucose and uric acid. Lead and cadmium are voltammetrically determined through the formation of alloys with Bi nanoparticles, electrogenerated from Bi_2O_3, with limits of detection (LODs) of 0.39 μg L^{-1} for Pb and 0.68 μg L^{-1} for Cd. The electrochemical determination of the above-mentioned health biomarkers does not require the presence of any enzyme, as glucose oxidation is catalysed by Cu(III) electroformed from embedded CuO, while uric acid undergoes direct oxidation at the sensor. Glucose was determined amperometrically with a LOD of 0,182 mg dL^{-1} and uric acid was detected by Differential Pulse Voltammetry (DPV) with a LOD of 1,1 μmol L^{-1}. The validation of the sensors was performed by the analysis of samples with satisfactory recoveries ranging from 96% to 103%. The new generation multifunctional filament represents an important advancement toward the development of low-cost, environmentally friendly, multiplexed 3D printed sensors.

Acknowledgements: *I thank the Special Account for Research Grants of National and Kapodistrian University of Athens for the financial support.*

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Metabolic Responses to Acute Wine Consumption: A Time-Dependent Nutri-Metabolomic Study of Phenolic Metabolites using High-Resolution Mass Spectrometry.

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Wine has been extensively studied over the past few decades to better understand its potential health benefits from its consumption, including antioxidant, lipid-regulating, and anti-inflammatory effects [1], [2]. These benefits are believed to arise from the combined action of alcohol, micronutrients, and polyphenols, particularly the over 100 polyphenolic compounds identified in red wine, including flavonoids and non-flavonoids[3].

To gain a deeper insight into wine’s biological effects, it is crucial to understand not only its phenolic composition but also the bioavailability and metabolism of these compounds in the human body. Our study aims to investigate the time-dependent plasma changes in phenolic metabolites following wine consumption, offering novel evidence on the bioavailability of wine's phenolics and their potential health impacts.

We conducted a cross-over study involving 10 healthy male participants, with four separate daily trials. Each participant consumed a standardized meal accompanied by red wine, white wine, ethanol solution, or water. Blood samples were collected before (-15 min), immediately after consumption (0 min), and at multiple intervals over the following 6 hours (30, 60, 90, 120, 150, 180, 210, 240, 300, and 360 min). Plasma samples were analyzed using LC-qTOF-MS, employing both data-dependent acquisition (AutoMS, DDA) and data-independent acquisition (bbCID, DIA) methods. A suspect screening approach was applied, using an in-house list of 125 phenolic metabolites derived from extensive literature research [4].

This study aims to clarify the metabolic changes in phenolic metabolites caused by acute red wine consumption, compared to ethanol and white wine. It is the first to examine time-resolved alterations in these metabolites, offering insights into the metabolic pathways of wine phenolic compounds.

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Trigonal Planar Chromium(II) N-Heterocyclic Carbene Complexes as Potential Mononuclear Single Molecule Magnets

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During the last 30 years, a large number of multinuclear metal complexes have been shown to exhibit slow magnetisation relaxation and are referred to as single molecule magnets (SMMs). However, due to their small magnetic anisotropy, recent research efforts have been focused to mono- and bi-nuclear 3*d*- or lanthanide- based SMMs [1]. Among the 3*d*-systems, only a handful of high-spin ($S = 2$) Cr(II) complexes have been identified to date as mononuclear SMMs [2].

The [Cr{N(SiMe$_3$)$_2$}(Bn)(IPr)] complex (**1**), IPr = 1,3-bis(2,6- iPr$_2$C$_6$H$_3$)imidazol-2-ylidene, Bn = CH$_2$C$_6$H$_5$ (Figure 1), was obtained by the thermolysis of [Cr(IPr)Bn$_2$] in HN(SiMe$_3$)$_2$. A combined study by high-frequency and -field EPR spectroscopy, AC magnetometry and ab initio quantum chemical methods revealed that complex 1 is the first trigonal planar Cr(II) mononuclear SMM, which, interestingly, also contains a Cr–C$_{NHC}$ bond. Along these lines, the structural and magnetic properties of additional trigonal planar and T-shaped Cr(II) complexes will be presented and discussed.

We are grateful to the Special Account for Research Grants of the NKUA for financial support.

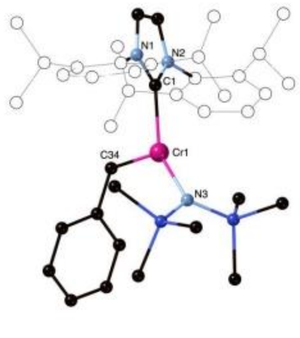
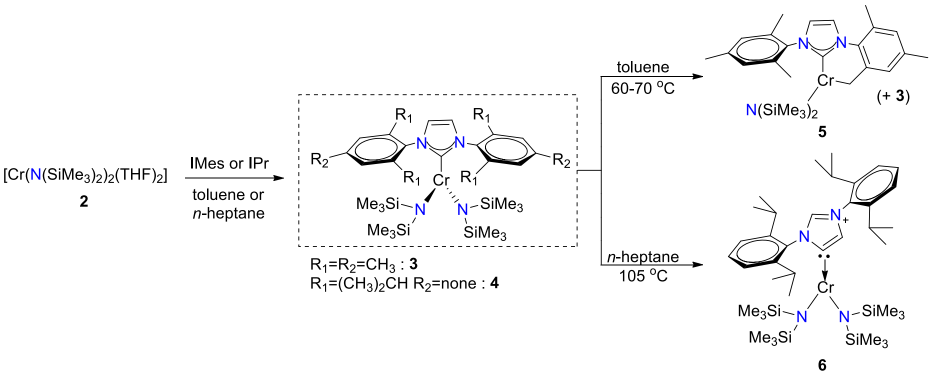


Figure 1. The molecular structure of **1**



Scheme 1: The synthesis of 3-coordinate Cr(II) complexes of this work

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The stability and degradation products of polyhydroxy flavonols in boiling water

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Polyhydroxy flavonols readily degraded during thermal processing. In this study, the UPLC-Q-tof-MS/MS was applied to explore the stability of dietary polyhydroxy flavonols, myricetin, kaempferol, galangin, fisetin, myricitrin, quercitrin and rutin, in boiling water. The decomposition of flavonols was mainly caused by the heterocyclic ring C opening to form simpler aromatic compounds. The degradation products mainly included 1,3,5-benzenetriol, 3,4,5-trihydroxybenzoic acid, 2,4,6-trihydroxybenzoic acid and 2,4,6-trihydroxybenzaldehyde, etc. Compared with myricetin with a pyrogallol-type structure on the ring B, the glycoside in myricitrin slightly affects the stability. However, the glycosides in rutin and quercitrin dramatically improved the stability in water. During the boiling process, flavonols underwent a series of chemical reactions, such as hydroxylation, dehydroxylation, deglycosidation, deprotonation, and C-ring cleavage.

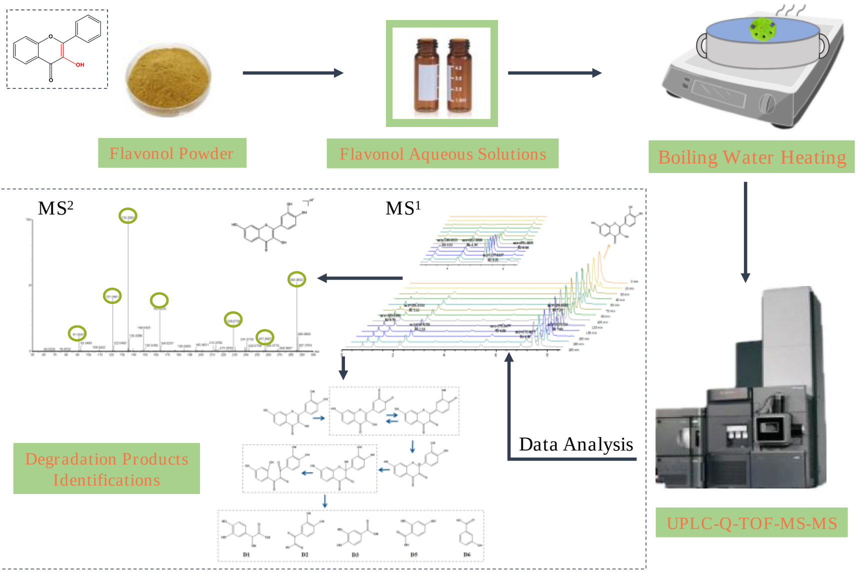

Figure 1. Flow diagram demonstrating the stability of flavonols during heating.

Microwave-assisted and base-dependent synthesis of γ-lactones or esters using N-heterocyclic carbenes as organocatalysts

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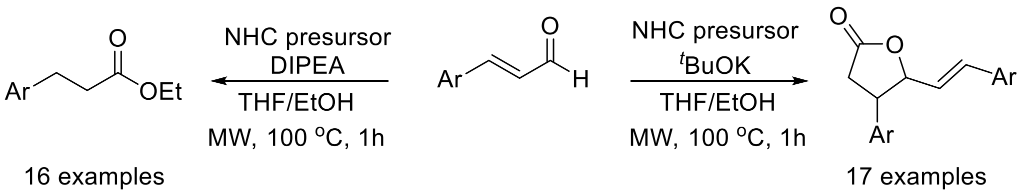
γ-Lactones are natural products found in plants, marine fungi and microorganisms and are used as intermediates for the synthesis of other added-value chemicals, but also in the flavoring and fragrance industry thanks to their aromas. γ-Decalactone has a peach-like scent, while whiskey and cognac γ-lactones give their distinctive scent to the corresponding drinks. The reactivity of γ-lactones is due to the lactone ring that undergoes ring-opening reactions to yield valuable compounds for further chemical transformations. N-heterocyclic carbenes (NHCs) are reactive species that are used as ligands in organometallic catalysts such as Grubbs' second-generation catalyst or more recently as stand-alone organocatalysts.

Our group has worked on the NHC-catalyzed, MW-assisted synthesis of hydroxymethylketones starting from aliphatic or aromatic aldehydes and paraformaldehyde, while the NHC precursors were either salts that yielded the NHC by using a suitable base or protected NHCs that were deprotected *in situ* due to the reaction conditions [1-3]. Inspired by the work of Bode *et al.* [4-5] we decided to use NHCs and MW irradiation for the synthesis of γ-lactones. In this work we will present a series of novel NHCs that were used together with commercially available NHCs in the microwave-assisted and base-dependent synthesis of γ-lactones starting from cinnamaldehyde analogues. Depending on the base used to generate the NHC either the γ-lactone or the corresponding saturated ester of cinnamic acid analogue was formed. The scope of these reactions will be discussed in detail.



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ERAP1 as a regulator of the immunopeptidome, proteome and cellular homeostasis of cancer cells

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Endoplasmic reticulum aminopeptidase 1 (ERAP1) metabolizes peptides inside the ER and shapes the peptide repertoire available for binding to Major Histocompatibility Complex Class I molecules (MHC-I), also known as the immunopeptidome. Moreover, it may have additional effects on cellular homeostasis, which have not been thoroughly explored. To address these questions, we utilized genetic silencing of ERAP1 expression as well as a selective allosteric ERAP1 inhibitor to probe changes in the immunopeptidome and proteome of the A375 melanoma cancer cell line. We observed significant immunopeptidome shifts for both methods of ERAP1 functional disruption, which were distinct for each method. Both methods of inhibition led to mild enhancement of cancer cell killing by stimulated human PBMCs from a healthy donor. ERAP1 functional disruption also resulted in significant proteomic alterations in pathways related to metabolism and cellular stress. Similar proteomic changes were also observed in the leukemia cell line THP-1. Biochemical analyses suggested that ERAP1 inhibition affected endoplasmic reticulum stress, reactive oxygen species production and mitochondrial metabolism. Although the proteomics shifts were significant, their potential in shaping immunopeptidome shifts was limited since only 15.8% of differentially presented peptides belonged to proteins with altered expression and 5.0% of proteins with altered expression were represented in the immunopeptidome shifts. Taken together, our findings suggest that modulation of ERAP1 activity can generate unique immunopeptidomes, primarily due to altered peptide processing in the ER, but also induce changes in the cellular proteome and metabolic state which may have additional effects on cancer cells.

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New Pyridine Dicarbene Pincer Ligands with Ring Expanded N-Heterocyclic Carbene Donors and their Transition Metal Complexes

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Imidazol-based N-Heterocyclic Carbenes (abbr. NHCs) are without doubt one of the most prominent and well-explored class of the NHC family and exploited as ancillary ligands[1]. Conversely, Ring-Expanded NHCs (abbr. RE-NHCs), despite displaying as ligands superior σ-donor characteristics and distinct steric effects, have been less explored and rarely employed as donors in ligand architectures[2]. Attracted by the versatility of the rigid Pincer architecture and the increased thermal stability of their transition metal complexes[3], two novel pyridine dicarbene Pincer ligand precursors with RE-NHCs were synthesised (Figure 1).

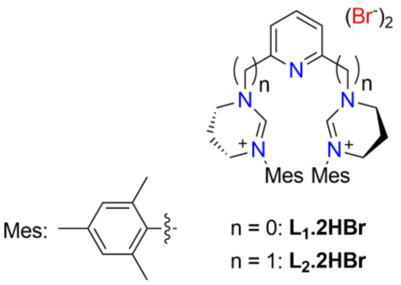

Figure 1: Ligand Precursors $L_1 \cdot 2HBr$ & $L_2 \cdot HBr$.

In situ generation of the free dicarbene **L_1** by deprotonation of the **$L_1 \cdot 2HBr$** and concomitant reaction with suitable metal precursors, or metalation of the **$L_1 \cdot 2HBr$** by aminolysis with metal bis(trimethylsilyl)amide metal precursors, afforded the complexes depicted in Figure 2. However, the coordination chemistry of **L_2** has not yet been studied due to its inherent instability. The complexes **Ni_1** and **Cr_1**, when activated with MAO, were catalysts of moderate activity for the oligomerisation and polymerisation of ethylene, respectively. Experimental data supported by DFT calculations showcased that compared to imidazolylidene analogues, **L_1** acts as a stronger electron donor and can indirectly modulate geometries and electronic structures of metals by sterics effected through the arrangement of wingtips[4].

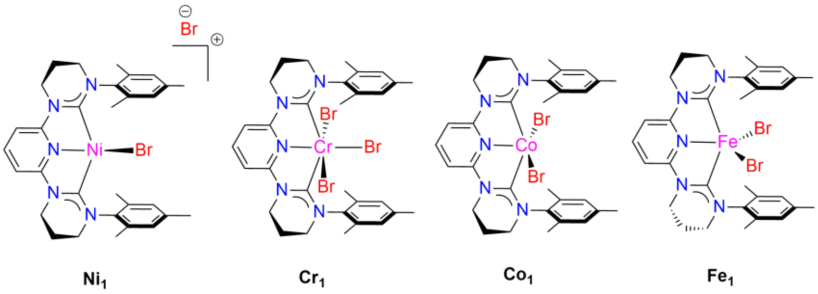

Figure 2: Metal Complexes of L_1.

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Exploring New Tripodal *N*-Heterocyclic Carbene Ligands Towards High- and Low-Valent Iron Complexes

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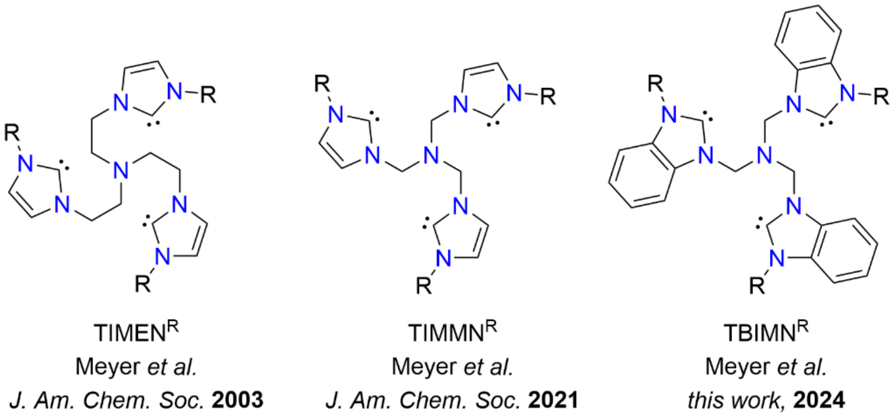
High-valent complexes of iron with terminal imido, nitrido and oxo ligands have been identified as active intermediates in both enzymatic and industrial catalytic processes of great interest, including the synthesis of ammonia.[1] The understanding of their molecular and electronic structures and reactivity, by means of isolating and studying well-defined model compounds, remains a challenging research topic. Towards that end, the utilization of tailored multidentate ligands (Scheme 1) with *N*-heterocyclic carbene (NHC) donors has been a milestone, allowing the structural characterization of once though to be elusive high-valent iron complexes, and the recent spectroscopic observation of an iron(VII) nitride.[2,3] In this work, we have employed different carbene donors to replace the classic imidazol-2-ylidenes and construct the new *tris*-carbene ligand scaffolds TBIMN^R (R = Mes, CH_2Cy). Their coordination to iron centers in different oxidation states has been probed following various synthetic strategies, and preliminary spectroscopic results on the characterization of the resulting complexes are reported.



Scheme 1: Nitrogen-anchored tripodal chelates established in metal coordination chemistry.

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POLYUREA-CROSSLINKED BIOPOLYMER AEROGELS - NOVEL NANOSTRUCTURED MATERIALS FOR DIVERSE APPLICATIONS

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Biopolymer aerogels are attractive materials because they come from natural resources, are biocompatible, biodegradable and non-toxic, are prepared in water, bear a large number of functional groups available for coordination to metal ions, hydrogen bonding, functionalization etc., and some of them, may be converted pyrolytically to carbon aerogels. However, the main drawback of most biopolymer aerogels is that they are mechanically weak materials. This issue was rectified recently with the synthesis of polyurea-crosslinked biopolymer (X-biopolymer; Figure 1) aerogels [1]. For example, X-alginate aerogels can be as strong as the best organic aerogels at half or one third of their density, and extremely stable in all aqueous environments with pH in the range of 3-9. The material properties of X-biopolymer aerogels can be tuned by a number of factors, including the nature of the biopolymer, the chemical identity of the triisocyanate, their relative concentrations, and the synthetic parameters, according to the specific applications.

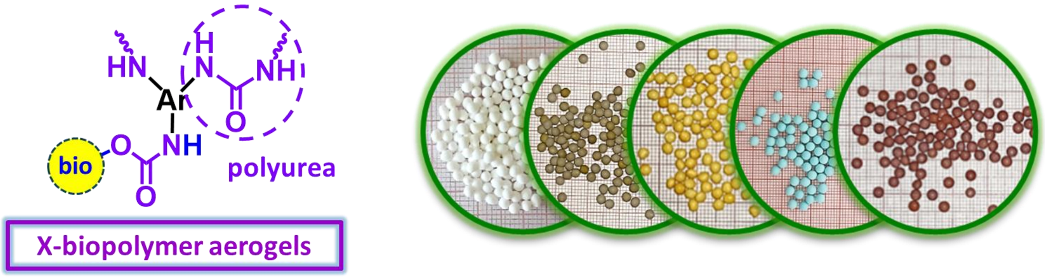

Figure 1

Acknowledgements

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Revitalisation of Group IV metal-oxo clusters: Synthetic approaches, structural motifs and applications

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Group (IV) metal oxo clusters garner a lot of attention due to their unique and interesting electronic properties, which can lead to different applications including catalysis, sensing, medicine and other industries.[1,2] In marked contrast to polyoxometalates (POMs) which are a well-studied and diverse series of clusters based primarily on group V & VI metals in their highest oxidation state, group IV clusters are comparatively less explored. These clusters exhibit distinctive structural features, chemical reactivity, and electronic structure. Nevertheless, their full potential has yet to be fully realized due to the lack of deeper understanding regarding their structure and formation mechanisms, inherent traits, and intricacies in their design, which could ultimately enable significant customization of their properties and overall behaviour. Considering the recently observed reignited interest in the chemistry of Group IV molecular species, the scope of this work is to bring onto the readers the main chemical characteristics of the family of titanium, zirconium, and hafnium-based clusters, their structural features and their potential in future applications.

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Goat milk proteins as a promising ingredient for functional food

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The development of functional food and sustainable food production are two main challenges facing food scientists and food technologists nowadays. Consumers are aware that a healthy diet can prevent hypertension, diabetes, heart disease, and cancer. To meet consumers' demands and protect the environment, food scientists are seeking bioactive compounds from food waste and their valorization through incorporation into functional food. Cow milk proteins are among the most widely used proteins as functional ingredients in many food products due to their good techno-functional properties. However, about 3% of the human population shows an allergy to cow's milk, and the production of cow's milk has a higher environmental impact compared to goat milk. Thus, the replacement of cow's milk protein with goat's milk protein can be a promising strategy for the development of functional food ingredients. Recently, it has been demonstrated that goat milk proteins can serve as carriers of bioactive compounds derived from medicinal plant extracts, edible mushrooms, grape pomace, bee pollen, as well as prebiotics and probiotics [1,2]. Functional food products based on goat milk proteins, grape pomace, and edible mushroom extracts have shown antioxidant, anti-inflammatory, wound-healing, and anticarcinogenic properties, as well as antibacterial, antifungal, and antibiofilm properties, owing to the bioactive compounds in grapes and mushrooms [1,3]. Furthermore, goat milk proteins have demonstrated good protection of bioactive compounds against severe conditions during *in vitro* gastrointestinal digestion, enabling their targeted delivery to the lower part of the intestine or the colon. This review will present recent results on the characterization and functional properties of goat milk-based functional food ingredients.

Keywords: Goat milk proteins, bioactive compounds, nanocarrier, functional properties, *in vitro* digestion

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Statistical copolymers of N–Vinyl Pyrrolidone and 2–Chloro Ethyl Vinyl Ether via Radical RAFT Polymerization as scaffolds for the synthesis of complex macromolecular architectures

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This study involves the synthesis of statistical copolymers of N–Vinyl Pyrrolidone, NVP, and 2–Chloro Ethyl Vinyl Ether, CEVE, via Radical polymerization utilizing the Reversible Addition–Fragmentation Chain Transfer, RAFT, technique. The initial phase of the research was dedicated to promote radical copolymerization of the two monomers, since radical polymerization of Vinyl Ether monomers, VEs, has not been previously reported in the literature in the absence of additives. Following the optimization of the copolymerization conditions, a series of statistical copolymers with varying ratios of monomer supply, were purposely synthesized at low conversions, thus enabling the calculation of the reactivity ratios. These findings, in conjunction with the statistical structure analysis of the P(NVP–stat–CEVE) copolymers, demonstrated that they possess a pseudo–diblock structure. The thermal properties of the copolymers were investigated, and the outcomes were evaluated in comparison with the behaviour of the corresponding PNVP and PCEVE homopolymers. In conclusion, the presence of pendant chlorine groups attached to the copolymer chain enables their use as scaffolds for the synthesis of complex macromolecular architectures, as they can be efficiently substituted by other groups, including hydroxyl groups and azides. These groups can be exploited for the formation of graft copolymers, utilizing the “Grafting From” and “Grafting To” techniques, respectively.

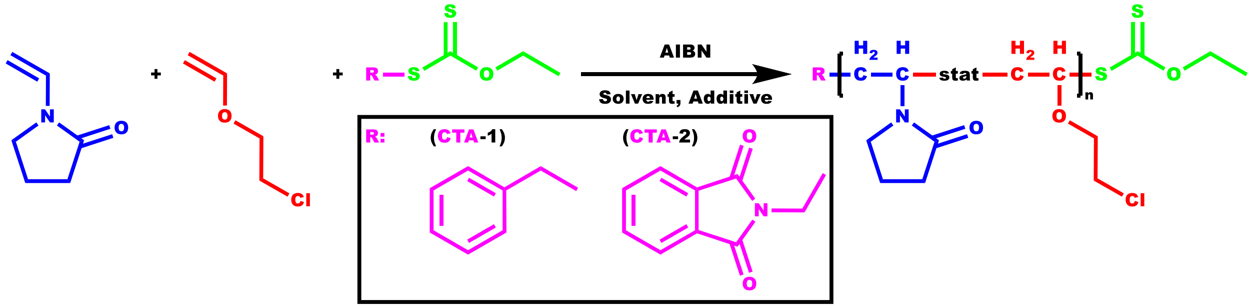

Figure 1. Synthesis of P(NVP–stat–CEVE) via RAFT polymerization technique.

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Complexation of anticancer Pt-drugs on Polymers containing poly(L-Histidine)

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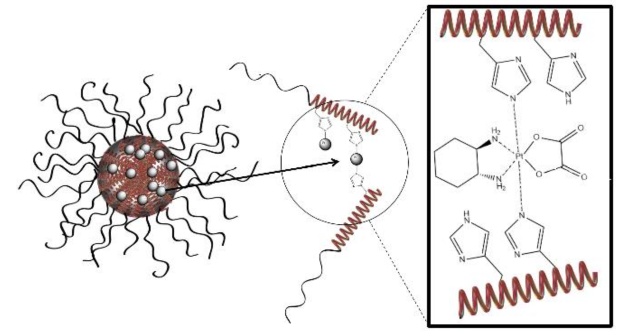

Figure 1: The suggested mechanism of conplexation

This research focuses on the complexation of the anticancer drug oxaliplatin and its verification through NMR spectroscopy. Oxaliplatin is primarily utilized in the treatment of colorectal cancer.[1,2]
To encapsulate the drug, polypeptides and hybrid copolymers based on poly(L-Histidine) were synthesized. Poly(L-Histidine) contains an imidazole group, granting it pH sensitivity and the ability to act as a ligand for metal ions like Zn and Pt. [2,3] These properties qualify the nanoparticles as a drug delivery system for metal based anticancer drugs.
A novel aspect of this study is the use of the protonated solvent 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) to investigate the complexation of poly(L-Histidine) and oxaliplatin via Nuclear Magnetic Resonance (NMR) spectroscopy. HFIP serves as an effective solvent for poly(L-Histidine), and the use of d6-DMSO capillaries was essential for the measurements. The study concluded with an analysis of drug encapsulation in hybrid copolymers using NMR spectroscopy in D_2O and D_2O Buffer (pH=5). Results showed the complexation of the platinum-based drug with the imidazole group of poly(L-Histidine), highlighted by the disappearance of the hydrogens at the -NH position of the imidazole ring and changes in the shifts of poly(L-Histidine). Additionally, the pH responsiveness of the nanoparticles was confirmed through NMR spectroscopy, indicating their suitability for in vitro testing. Furthermore, Thermogravimetric Analysis (TGA), Circular Dichroism (CD), and Transmission Electron Microscopy (TEM) were employed for a comprehensive characterization of the nanoparticles.

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A conformation and substrate-selective small molecule inhibitor of IRAP provides insight into the intricacies of the enzyme's catalytic cycle

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Insulin-regulated aminopeptidase (IRAP) is an enzyme with important biological functions and the target of drug-discovery efforts. We combined in silico screening with a medicinal chemistry optimization campaign to discover a nanomolar inhibitor of IRAP based on a pyrazolylpyrimidine scaffold. This compound displays an excellent selectivity profile versus homologous aminopeptidases, and kinetic analysis suggests it utilizes an uncompetitive mechanism of action when inhibiting the cleavage of a typical dipeptidic substrate. Surprisingly, the compound is a poor inhibitor of the processing of the physiological cyclic peptide substrate oxytocin and a 10mer antigenic epitope precursor but displays a biphasic inhibition profile for the trimming of a 9mer antigenic peptide. While the compound reduces IRAP-dependent crosspresentation of an 8mer epitope in a cellular assay, it fails to block in vitro trimming of select epitope precursors. To gain insight into the mechanism and basis of this unusual selectivity for this inhibitor, we solved the crystal structure of its complex with IRAP. The structure indicated direct zinc(II) engagement by the pyrazolylpyrimidine scaffold and revealed that the compound binds to an open conformation of the enzyme in a pose that should block the conformational transition to the enzymatically active closed conformation previously observed for other low-molecular-weight inhibitors. This compound constitutes the first IRAP inhibitor targeting the active site that utilizes a conformation-specific mechanism of action, provides insight into the intricacies of the IRAP catalytic cycle, and highlights a novel approach to regulating IRAP activity by blocking its conformational rearrangements.

ICHTHYS: Optimization of novel value chains for fish and seafood by developing an integrated sustainable approach for improved quality, safety and waste reduction

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ICHTHYS (OptImization of novel value CHains for fish and seafood by developing an integraTed sustainable approacH for improved qualitY, safety and waSte reduction) aims to optimize novel value-chains for fish and seafood products for the EU and international markets. It develops an integrated sustainable approach to improve quality and safety, while reducing product loss in the whole supply chain. ICHTHYS is an intersectorial project and focuses on two essential parts of the value chain, postharvest processing and packaging, integrating novel modern techniques and molecular biology tools in the evaluation of the quality and safety of fish and shellfish, including their allergenic capacity. New nonthermal processing methods, i.e. high pressure, pulsed electric fields and high-intensity pulsed light are investigated together with active and intelligent packaging and smart labels and biosensors for monitoring safety and shelf life enriched with novel data from "omics" analysis. The implementation of ICHTHYS will offer the industrial partners the opportunity to translate scientific research into well-defined knowledge-based end products and analytical tools. ICHTHYS aspires to provide cross-cutting intersectorial and interdisciplinary knowledge exchange and training for academics and commercial partners to improve their employability and career prospects. The project will contribute to the knowledge-based economy and society and boost regional and European competitiveness and growth, food exports and job creation.

Acknowledgment

This research has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie Grant Agreement no 872217 (ICHTHYS) https://www.ichthys-eu.org/about).

Evaluation of Fe:Eu nanoparticles as imaging probes of cervical cancer cells

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The purpose of this work is the synthesis of bimetallic hybrid Fe:Eu nanoparticles, their structural and morphological characterization as well as their biological evaluation. The combination of iron oxide nanoparticles' superparamagnetic properties and europium's optical properties could lead to a plethora of biological applications including imaging of cancer. Nanoparticles' development was carried out through the *co*-precipitation method performing synthesis of magnetic iron oxide nanoparticles coated with citrate and subsequently addition of europium at different Fe:Eu ratios (1:3, 1:1, 1:0.25). For the structural and morphological characterization of the nanoparticles, different techniques were carried out. DLS results confirmed the colloidal stability of the nanoparticles.[1] FT-IR and PXRD analyses confirmed the formation of magnetite and indicated the presence of europium hydroxide rods.[2] Elemental analysis by TEM proves the coexistence of iron and europium in the nanoparticles, whilst PL measurements demonstrate the fluorescence capability of the nanoparticles. Biologically, it was affirmed that the nanoparticles' internalization enhanced the *in vitro* fluorescence of cervical cancer cells. Moreover, nanoparticles of Fe:Eu ratio 1:3 appear to be biocompatible with the healthy human embryonic kidney cells, whereas they lead cervical cancer cells to apoptosis due to excessive ROS production.

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Unexpected Reactivity of a Low Valent Titanocene with Azides.

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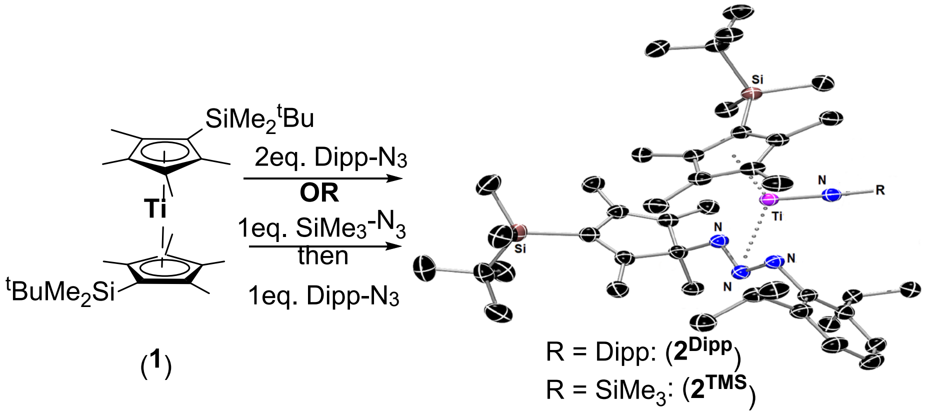
Metallocenes play a pivotal role in the development of organometallic chemistry [1], even after more than 70 years from the disclosure of ferrocene's structure [2]. Titanocenes in particular have been instrumental in understanding fundamental aspects of organometallic chemistry, leading to widespread applications such as olefin oligomerization/polymerization [3]. Of this important class of organometallic complexes, the first ever structurally authenticated Ti(II) complex $[\mathrm{Ti}(\eta^5\text{-Cp}^s)_2]$ (**1**) ($\mathrm{Cp}^s = [\mathrm{C_5Me_4SiMe_2}{}^t\mathrm{Bu}]^-$) [4] (Scheme 1) was an important development in the area, but its chemical reactivity has been barely explored. In this talk, we present our research efforts in expanding the chemistry of (**1**). During our investigations, we discovered that reaction of (**1**) with Dipp-N_3 (Dipp = 2,6-diisopropyl-phenyl) results in the formal insertion of one azide to a Ti-C(Cp^s) bond furnishing the Ti(IV) imido complex ($\mathbf{2}^{\mathbf{Dipp}}$) featuring a new triazenido ligand (Scheme 1). Computations suggest that the formation of ($\mathbf{2}^{\mathbf{Dipp}}$) proceeds *via* a Ti(IV) terminal imido complex, which has been confirmed experimentally by the synthesis of its congener ($\mathbf{2}^{\mathbf{TMS}}$) (Scheme 1). Detailed NMR studies show that ($\mathbf{2}^{\mathbf{Dipp}}$) & ($\mathbf{2}^{\mathbf{TMS}}$) display fluxional behavior in solution. Finally, the reactivity of (**1**) with other substrates will be presented to showcase its potential to induce reductive transformations.



Scheme 1: Reactivity of (**1**) with organic azides.

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Breaking covalent bonds in the context of the many-body expansion

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The Many-Body Expansion (MBE) is a concept based on combinatorial mathematics and is usually employed to count the number of elements in the union of finite sets. In 1970 was applied for the first time to chemical physics problems considered individual water molecules as "bodies" connected via hydrogen bonds as it was used to estimate the non-additive three-body term by partitioning the energy of a water trimer.[1]

The purpose of the MBE in quantum chemistry is twofold: in analysis, to understand the composition of interatomic and intermolecular interactions, and in practice, to facilitate calculations of large systems.[2-3] The application of MBE in covalent structures, especially metallic ones, is full of challenges due to the complex electronic structure and short-range interactions exhibited by such systems. Both dynamic and non-dynamic correlation may be necessary to capture the multi-coordinated bonding of metals, in addition to considerations of different spins among the intermediate structures of open shell metals.[4]

In this presentation, a novel implementation of the MBE to account for the breaking of covalent bonds is analyzed. The central concept of the new implementation is the *in situ* atomic electronic state of an atom in a molecule that casts the one-body term as the energy required to promote it to that state from its ground state.[5] The rest of the terms correspond to the individual diatomic, triatomic, etc., fragments. Here, the MBE for the 1st and 2nd group metals and for the XH_n series, X = C, Si, Ge, Sn and n = 1–4) is examined and analyzed via coupled cluster, perturbation theory, and multireference configuration interaction methodologies.[5-7]

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Taming arenes: A comparative and systematic study

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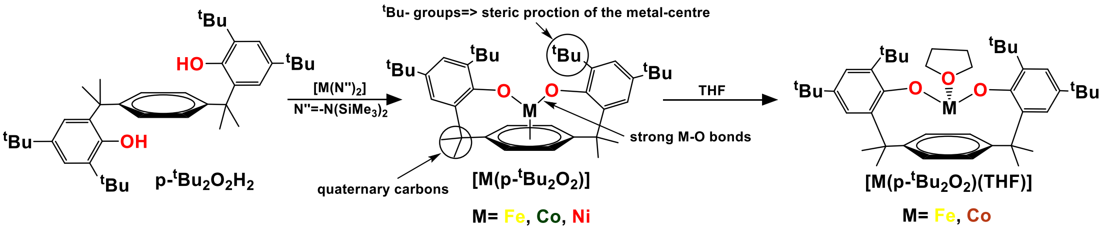
Multidentate ligands featuring a central arene (tethered arene) in an apical position poised to interact with metal centres, have been shown to be advantageous supporting architectures towards promoting multielectronic small molecule reduction. Specifically, when coordinated to heavier transition metals[1] or f-block elements[2], arenes can be formally reduced even twice. Hence, complexes of reduced tethered arenes react with small molecules promoting electron transfers with electrons originated from both the arene and the metal centre. Nevertheless, this reactivity has not been widely expanded to the cheap and readily available 3d metallic centres. Thus, we derived the ligand p-^{t}Bu$_2$O$_2$H$_2$ (Scheme 1), a potential L$_3$X$_2$ donor, which has the above attributes and is used to implement the concept of “arenes acting as electron reservoirs’’ in 3d-metals, with ultimate goal to develop (electro)catalytic processes. The phenolate donors secure strong M-O bonding and the quaternary benzylic carbon atoms, adjacent to the anchor arene, hinder acid-base reactions, making the above ligand a suitable candidate to chase this cause.



Scheme 1: The synthetic route towards [M(p-^{t}Bu$_2$O$_2$)] and [M(p-^{t}Bu$_2$O$_2$)(THF)] complexes by using the ligand p-^{t}Bu$_2$O$_2$H$_2$. The color code used reflects the true color of the isolated compounds.

Up to now, we were able to isolate three hitherto unknown complexes [M(p-^{t}Bu$_2$O$_2$)] (M= Fe, Co, Ni), along with their THF adducts [M(p-^{t}Bu$_2$O$_2$)(THF)] (M= Fe, Co) and characterized them spectroscopically and structurally. IR serves as a qualitative proxy to identify the degree of the metal-arene interaction, while cyclic voltammetry studies on both the solvated and non-solvated species, indicate a possible correlation of the M-arene interaction with the reduction potential of the complexes.

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Multicomponent Reactions: Creating Complexity via Sustainable Catalytic Transformations

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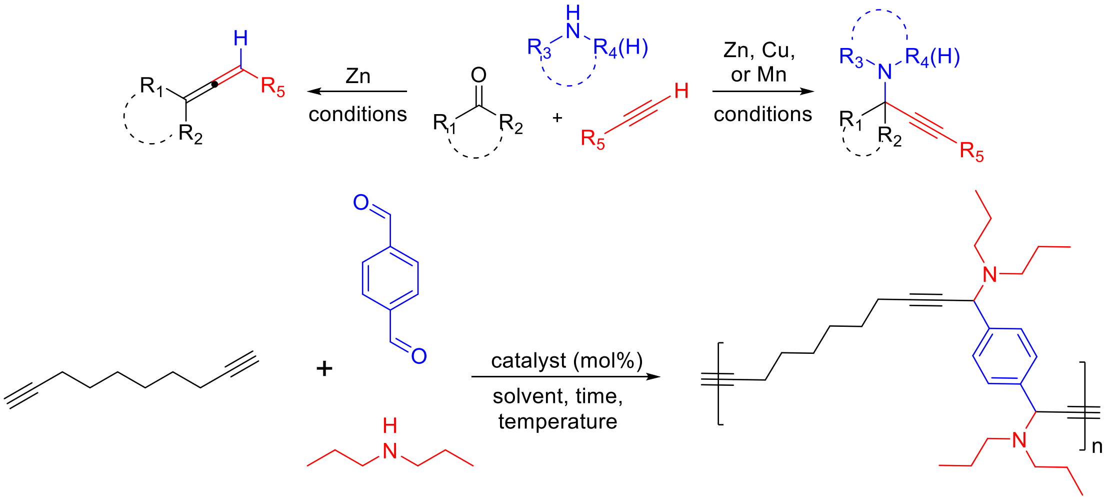
Sustainable catalysis is one of the most active research fields, both in industry and academia [1,2]. After a brief introduction to our research group and current projects/interests, some recently developed sustainable catalytic protocols, employing Cu, Zn, Mn, or N-heterocyclic carbene (NHC) catalysis, will be presented. These include the multi-component reactions between ketones, amines, and alkynes, leading to propargylamines, allenes, or polymeric scaffolds [3-9].



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Comprehensive liquid biopsy analysis for monitoring NSCLC patients under second-line osimertinib treatment

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The aim of this study was to perform a comprehensive LB analysis for monitoring NSCLC patients under second-line osimertinib treatment, by combining plasma-cfDNA and CTC analysis to identify molecular alterations at resistance and potential targets for subsequent treatments. Peripheral blood from 30 NSCLC patients was collected before treatment (baseline) and at disease progression (PD). Plasma-cfDNA was analyzed for DNA mutations (*EGFR*, *PIK3CA*, *KRAS*-G12C, *BRAF*-V600E) using digital PCR and for DNA methylation (*RASSF1A*, *BRMS1*, *SLFN11*, *RASSF10*, *APC*, *RARβ*, *FOXA1*, *WIF-1*, *SHISA3)* using methylation specific PCR. CTCs were enriched from identical blood draws using Parsortix (Angle, UK). CTC-derived gDNA was analyzed for the same DNA mutations and methylation markers. CTCs were analyzed for *HER2* and *MET* amplification with FISH. RT-qPCR was performed in CTCs-derived mRNA for *CK-8*, *CK-18*, *CK-19*, *VIM*, *TWIST-1*, *AXL*, *ALDH-1*, *PD-L1*, *PIM-1*, *B2M* genes. PD-L1 was detected in CTCs enriched using ISET (Rare cells, France) using immunofluorescence (IF). *EGFR* mutation analysis in plasma-cfDNA and CTCs have shown complementary information; T790M was detected only in CTC from three patients at PD, but not in paired plasma-cfDNA. *PIK3CA* mutations were detected only in plasma-cfDNA but not in CTCs. *KRAS*-G12C and *BRAF*-V600E were not detected in any sample. *MET* amplification was detected in CTCs of two patients at baseline whereas *HER2* amplification was detected in CTCs of three patients at baseline and in one patient at PD. DNA methylation between CTCs and cfDNA revealed low concordance. Data from IF and RT-qPCR for the presence of PD-L1 positive CTCs in matched samples revealed high detection rates suggesting a theoretical background for immunotherapy in EGFRm NSCLC patients. PD-L1, *PIM-1* and *AXL* expression in CTCs indicate a potential benefit of targeted therapies for NSCLC patients who relapse following osimertinib treatment. Our results indicate the importance of complementary information obtained through parallel analysis of CTC and ctDNA. Comprehensive LB analysis efficiently represents the heterogeneous molecular landscape and provides prominent information on subsequent treatments for NSCLC patients progressing with osimertinib based on different druggable molecular alterations.

Detection rate for *ESR1* mutations is significantly higher in CTC-derived gDNA than in paired plasma-cfDNA samples as revealed by ddPCR

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Plasma-cfDNA analysis to track *ESR1* mutations is highly beneficial for the identification of tumor molecular dynamics and the improvement of personalized treatments for patients with metastatic breast cancer (MBC) [1]. Plasma-cfDNA is established up to now as the most frequent liquid biopsy analyte to evaluate *ESR1* mutational status. CTCs enumeration and molecular characterization analysis provides important clinical information in patients with MBC. In this study, we investigated whether analysis of CTCs and ctDNA provide similar or complementary information for the analysis of *ESR1* mutations. We analyzed both plasma-cfDNA (n=90) and paired CTC-derived gDNA (n=42) from MBC patients for seven *ESR1* mutations. Eight out of 90 (8.9%) plasma-cfDNA samples, tested using the ddPLEX Mutation Detection Assay (Bio-Rad), were found positive for one *ESR1* mutation, while 11/42 (26.2%) CTC-derived gDNA samples were found positive for at least one *ESR1* mutation. Direct comparison of paired samples (n=42) revealed that the mutation rate for *ESR1* mutations was significantly higher in CTC-derived gDNA (11/42, 26.2%) than in plasma-cfDNA samples (6/42, 14.3%), (Concordance: 31/42 (73.81%), $p<0.152$, chi-squared test). Our results, using this highly sensitive ddPLEX assay, reveal a higher percentage of mutations in CTC-derived gDNAs than in paired ctDNA in patients with MBC. CTC-derived gDNA analysis should be further evaluated as an important and complementary tool to ctDNA for identifying patients with *ESR1* mutations and for guiding individualized therapy.

Pyrimidine-dependent UV-mediated crosslinking magnifies minor genetic or epigenetic changes in clinical samples

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Detection of minor DNA allele alterations is becoming increasingly important for cancer early detection, monitoring, and treatment selection. As applications increase, so does the need for methodologies that provide improved sensitivity combined with robust performance and specificity. We describe a new method that uses ultraviolet light to eliminate wild-type DNA alleles and enables improved detection of minority genetic or epigenetic changes in tissues and liquid biopsies [1]. Pyrimidine-Dependent UV-based Minor-allele Enrichment (PD-UVME) employs oligonucleotide-probes that hybridize to wild-type (WT) sequences and incorporate a UVA-sensitive molecule (CNVK) placed directly opposite interrogated pyrimidines, such as thymidine (T) in targeted DNA. Upon UVA illumination CNVK crosslinks with T, preventing subsequent amplification of WT DNA strands. Mutations that remove the T escape crosslinking and are readily amplified and detected. Similarly, when CNVK is placed opposite cytosines in CpG dinucleotides it discriminates between methylated and unmethylated cytosine, enabling direct enrichment of unmethylated DNA targets. PD-UVME was applied for detecting *BRAF* V600E mutations in model systems, thyroid patient cancer samples and plasma-cfDNA from melanoma patients. When PD-UVME was applied in serial dilutions of mutated *BRAF* V600E DNA into WT DNA, the mutation abundance changed from 0.01%, 0.1% and 1% to 1.74%, 3.41% and 25.6% respectively. Out of 9 thyroid cancer tissue samples, PD-UVME applied prior to ddPCR revealed a low-level mutation in 1 of the samples classified as negative by conventional ddPCR. Similarly, when 7 plasma circulating-free DNA (cfDNA) samples from melanoma patients were examined for *BRAF* V600E mutations, PD-UVME-ddPCR identified 6 positive samples versus 1 positive sample detected via conventional ddPCR. All 10 plasma-cfDNA samples obtained from normal volunteers were negative via both approaches. PD-UVME mutation/methylation enrichment performed prior to ddPCR magnifies signals from low-level mutations or epigenetic changes and can increase confidence in the results.

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NALCN promoter methylation as a biomarker for metastatic risk in a cohort of NSCLC patients

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Liquid biopsy enables real-time monitoring of tumor development and response to therapy through the analysis of CTCs and ctDNA [1]. NALCN is a sodium leak channel that is frequently involved in tumor evolution and immunity and acts as a tumor suppressor. Deletion of Nalcn has been shown to increase cancer metastasis and the number of CTCs in peripheral blood [2]. In this study, we investigated for the first time NALCN promoter methylation in a) Aza-treated cell lines (A549, TE671, BT20, MDA-MB-468), b) paired NSCLC tissues (n=22) and c) plasma cell-free DNA (cfDNA) from patients with NSCLC (early stage n = 39, metastatic n = 39) and 10 DNA from healthy donors (HD) using a newly developed highly specific and sensitive real-time MSP method. Treatment with 5′-aza-dC induced the expression of NALCN only in the A549 cell line, suggesting that DNA methylation regulates its expression in certain cancers. mRNA NALCN expression levels were quantified in NSCLC and adjacent non-cancerous tissues and it was found to be underexpressed in 54.5% of tumor tissues, with significantly higher expression (P=0.009) in recurrence-free patients compared to those who relapsed. NALCN methylation level was negatively correlated with corresponding expression (P=0.439), while Kaplan–Meier analysis showed an association of NALCN promoter hypermethylation with worse disease-free intervals (DFI) (P=0.017). Evaluation of NALCN methylation in cfDNA revealed that it was detected in 5.1% of early and 10.2% of advanced cases. Our results strongly suggest that epigenetic inactivation of NALCN may be a predictor of metastasis in NSCLC. Our results should be further validated in studies based on a larger patient cohort to further explore whether DNA methylation of the NALCN promoter could serve as a potential prognostic DNA methylation biomarker and predictor of metastasis in NSCLC.

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Evaluation of PCR-enhancing approaches to reduce inhibition in wastewater samples and enhance viral load measurements

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Molecular-based assays are the most commonly used methods for the detection and quantification of viruses in wastewater. The variety of inhibitory substances present in the complex matrix of wastewater hinders downstream analysis and often leads to false negative results and underestimation of viral load [1]. The development of robust and inhibitor-tolerant detection methods is necessary in the context of wastewater-based epidemiology, a valuable tool that has gained further importance since the emergence of the Covid-19 pandemic. Various strategies are used to mitigate inhibition in the polymerase chain reaction (PCR) with the most prevalent of all: the dilution of the sample and the inhibitor removal kits [2]. In this study, we first indicated the presence of inhibitors in wastewater samples and the evaluation of eight different PCR enhancing strategies were further performed using reverse-transcription PCR (RT-qPCR) protocol. False negative results were eliminated through four approaches evaluated, a 10-fold dilution of the extracted sample, addition of T4 gene 32 protein (gp32), addition of Bovine Serum Albumin (BSA), and using an inhibitor removal kit. Among the methods that removed inhibition, the most significant for the removal of inhibition was the addition of gp32 (at a final concentration 0.2 μg/μl). This optimized protocol was further applied to wastewater samples tested for Severe Acute Respiratory Syndrome Coronavirus 2 (SARS-CoV-2) and a direct comparison study was further performed with reverse-transcription droplet digital PCR (RT-ddPCR). The detection frequency of both methods was 100% and the obtained viral concentrations were higher by RT-ddPCR; the optimized RT-qPCR assay showed a good correlation (Intraclass Correlation Coefficient: 0,713, p-value < 0,007) with RT-ddPCR. This is the first study to directly compare common strategies for eliminating inhibition in wastewater and demonstrates the importance of developing robust assays to accurately assess the recovery rates and viral loads of the targets tested, in a simple, cost-effective and high-throughput manner.

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Combining Metabolomics and Liquid Biopsy to Identify Diagnostic and Prognostic Biomarkers in Patients with Non-Small Cell Lung Cancer

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Lung cancer is considered the deadliest form of cancer, primarily due to late diagnosis and lack of early detection methods, with non-small cell lung cancer (NSCLC) representing over 85% of all lung cancer cases and is generally associated with poor prognosis in advanced stages. In this study, we investigated changes in circulating metabolite levels in NSCLC patients versus healthy controls, and between NSCLC patients with different disease stages (ongoing versus progressive disease). Sixteen NSCLC patients were enrolled in the study (eight ongoing and eight PD) and five healthy controls. Plasma metabolite levels were assessed using untargeted metabolomics employing UHPLC-tims-Q-ToF-MS in both electrospray ionization modes. A clear discrimination between the different groups was achieved using multivariate chemometrics techniques and univariate statistical analysis. The study revealed five elevated and seven reduced metabolites in patients versus healthy controls, while in relapsed patients, one metabolite was upregulated and five metabolites were downregulated. The primary discriminatory and differential metabolites included D-lactic acid, D-glucose, L-arginine, L-cystine, L-tryptophan, Glutamine, Creatine, Betaine, Glycerophosphocholine, Indoleacrylic acid, 5-acetylamino-6-formylamino-3-methyluracil, 2,6 dimethylheptanoyl carnitine, 6-keto-decanoylcarnitine, Oleic acid and Choline. These results suggest disruptions in the metabolic pathways of glucose, amino acids, and phospholipids in patients with lung cancer. In conclusion, metabolomics identified distinct metabolic profiles in patients with NSCLC, offering potential diagnostic and prognostic biomarkers.

Keywords: biomarkers; lung cancer; metabolomics; liquid biopsy; mass spectrometry

In-Depth Investigation of Organic Micropollutant Burden in the Dnipro River Basin During Wartime Using HRMS-Based Workflows

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Anthropogenic activities significantly contribute to the introduction of organic micropollutants such as priority pollutants and emerging contaminants into the environment. Man-made environmental disasters, such as oil spills and the destruction of infrastructure during wartime, significantly increase the chemical burden on the environment. Thus, systematic monitoring after ecological disasters is of utmost importance. On 6 June 2023, an explosion destroyed the Nova Kakhovka dam in southern Ukraine, causing an ecological disaster. The collapse resulted in a massive release of water, sediments, and, subsequently, organic micropollutants into the Black Sea through the Dnipro River, potentially impacting these ecosystems [1,2].

The present study aims to investigate the occurrence of organic micropollutants in the Dnipro River basin and the Black Sea following the collapse of the Nova Kakhovka dam. In this framework, surface water, seawater, groundwater, and sediment samples were collected during a monitoring campaign conducted immediately after the dam breach and the ensuing flood. The analytes were extracted from the environmental matrices using generic sample preparation protocols, whereas the instrumental analysis included complementary chromatographic techniques and ionization modes, coupled with high-resolution mass spectrometry (LC-ESI-QToF MS and GC-APCI-QToF MS). The post-acquisition data treatment consisted of two steps. First, wide-scope target screening was conducted to investigate the presence of more than 2,500 organic micropollutants from various categories, such as pharmaceuticals, per-and polyfluoroalkyl substances (PFAS), industrial chemicals, and plant protection products, and their transformation products (TPs). Second, suspect screening was performed for 95,000 environmentally relevant organic micropollutants [3–5]. Afterwards, the post-disaster sampling campaign results were compared with data from previous sampling campaigns, conducted in 2019 and 2020. In total, 146 organic micropollutants from various chemical classes were identified in the water and sediment samples. The nitroaromatic explosive 4-Nitrotoluene was present in all analyzed water samples and in 7 out of the 8 sediment samples. The comparative analysis of pollutant levels in the area revealed a discernible upward trajectory, with notable shifts observed in Plant Protection Products and Industrial Chemicals.

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The impact of 4D metabolomics and wide-scope screening methodologies for the investigation of Greek bee products' bioactive content

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In recent years, a growing scientific interest in the analysis of bee products has been developed, due to their high nutritional and financial value. Propolis and royal jelly have gained particular attention because of their promising beneficial properties. Propolis is a wax-like mixture, mainly consisted of resin and secretions from the salivary glands of the bees (*A. mellifera*). It also contains smaller amounts of other compounds, such as aromatic and essential oils, pollens, and phenolic compounds [1]. Royal jelly is a gelatinous and creamy secretion produced by the glands in the hypopharynx of young honeybee workers, called nurses. It represents the food source for all honeybee larvae during the first three days following birth, and the exclusive food of the queen bee for her entire life [2]. Due to their positive health impact, numerous pharmaceutical companies have promoted products such as food supplements, and cosmetics, using propolis and royal jelly as the main ingredients. Thus, further investigation of their bioactive components is of utmost importance.

For the determination of bee products' bioactive compounds, a novel analytical methodology has been developed, using Ultra High-Pressure Liquid Chromatography (UHPLC) coupled with Trapped Ion Mobility Spectrometry – Quadrupole Time of Flight Mass Spectrometry (TIMS-QTOF-MS). A Vacuum Insulated Probe Heated Electrospray Ionization (VIP-HESI) was used as the ion source offering several key analytical benefits, including increased sensitivity, and robustness, and decreased thermal degradation, resulting in zero loss or fragmentation of sensitive compounds [3]. Moreover, the incorporation of TIMS in High-Resolution Mass Spectrometry (HRMS) workflows provides an extra dimension of identification, introducing the Collision Cross-Section value (CCS value). This 4D metabolomics approach integrating qualifier ion, Retention Time (RT), fragmentation ions, and CCS values increases the identification confidence of the analytes, resulting in the separation of isomeric and co-eluted analytes [4]. Target and suspect screening workflows were followed, to allow the detection of several polyphenols. To the best of our knowledge, it is the first time that this powerful cutting-edge methodology is used to determine phenolic compounds in bee products.

Thirty-six propolis and twenty-two royal jelly samples from different regions across Greece were collected and analyzed achieving a comprehensive characterization of their phenolic content. In royal jelly samples, target screening allowed the identification and quantification of 35 bioactive compounds while in propolis 48 analytes were determined. In addition, following a thorough literature review, information on bioactive compounds previously mentioned in bee products was gathered, and a suspect database of 190 compounds was created. Suspect screening results revealed the presence of more than 110 compounds in propolis and 70 compounds in royal jelly. Based on the results, quinic acid was among the dominant compounds in royal jelly, while galangin and pinocembrin were dominant in propolis. The findings of this work are important for analytical and food chemistry. The capabilities of the technique UHPLC-VIP-HESI-TIMS-QTOF-MS were explored, while the identification of more than 100 analytes resulted in the widest chemical characterization of royal jelly and propolis based on their bioactive composition that has never been conducted.

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Investigation of the presence and removal of emerging contaminants at various stages of industrial wastewater treatment

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Nowadays, an ever-increasing number of pollutants are entering the environment due to various human activities, posing serious risks to human health and ecosystems. In the past, global research primarily focused on the study of priority pollutants, due to their known persistent, bioaccumulative, and toxic (PBT) properties. However, priority pollutants represent only the "tip of the iceberg," as many other compounds have neither been legislated nor sufficiently studied [1].

In recent decades, the development of new, more sensitive analytical techniques has revealed the presence of many other potentially hazardous substances known as "emerging contaminants." Emerging contaminants are organic compounds that are not included in routine monitoring or existing legislation [1]. Nonetheless, concern about them is growing due to their frequent detection in the environment and the often-unknown threats they pose. Industrial activities are one of the main sources of these pollutants, and the disposal of industrial wastewater poses a significant threat to ecosystems and human health due to its high toxicity and complex composition [2].

Taking all the above into account, the present study aims to develop reliable and effective analytical workflows for the determination of emerging contaminants and to investigate their presence and removal at various stages of industrial wastewater treatment.

For this purpose, the technique of choice was ultra-high-performance liquid chromatography coupled with ion mobility spectrometry and high-resolution mass spectrometry (UHPLC-TIMS-QToF-MS). Specifically, high-resolution mass spectrometry was used for targeted analysis across a wide range of compounds (wide-scope target screening), as it offers the capability to identify numerous compounds that differ minimally in their mass. Furthermore, an internal database containing over 2,400 emerging pollutants, priority pollutants, and their biotransformation products was utilized for data processing.

The identification of the compounds was conducted using strict parameters related to mass error, retention time shifts, isotopic patterns, and the presence of qualifier ions. Additionally, the incorporation of ion mobility spectrometry allows for the inclusion of collision cross-section (CCS) as an additional orthogonal identification parameter, which often resolves the issue of separating isomers and isobars. Filtering based on time and ion mobility also provides cleaner MS and MS/MS spectra.

Finally, the aforementioned technique was applied to samples of industrial wastewater, which were pretreated using a generic sample preparation protocol. Numerous compounds from various categories were detected, including personal care products, plant protection products, and pharmaceutical compounds.

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Optimization and validation of a method for the determination of PFAS in soil

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Perfluoroalkyl and polyfluoroalkyl substances (PFAS) are ubiquitous anthropogenic contaminants in the environment due to their widespread use in various industrial applications and as compounds in everyday products. As the carbon-fluorine bond is one of the strongest, these synthetic chemicals are highly resistant to degradation leading to their persistence in the environment. The complexity of PFAS lies in their ability to be produced with varying chain lengths, side chains, and functional groups, leading to a vast array of possible combinations. Because of these properties PFAS are also known as "Forever Chemicals' and pose significant risks to both the environment and human health due to their persistence, bioaccumulation and toxicity. Studies have discovered significant amounts of them in blood and soils of remote areas, without the presence of industries and human activities in the wider area. Different sources including air, water and landfill lead to the concentration in soils, while some may end in plants through roots. Although several methods have been developed for the determination of PFAS in water and foods, not enough studies have been in soils so it is crucial to ensure accurate, sensitive, and reliable analytical results. The aim of this study is to develop, optimize and validate a method for the determination of more than fifty PFAS in soils. At this presentation the development and optimization of the method will be shown. During the optimization process a number of parameters like extraction technique, extraction solvent and weight of the sample have been tested. For the separation and quantification have been used state of the art technology liquid chromatography-tandem mass spectrometry (LC-MS/MS) Sciex QTRAP 6500+.

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An Innovative Toolkit for Enhanced Water Quality Monitoring of Water Supply Network

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Global challenges like climate change and emerging pollutants are increasingly affecting drinking water supply and treatment. In response, Athens Water Supply and Sewerage Company S.A. (EYDAP S.A.) is continuously improving its water quality monitoring processes, from source to treatment, in line with the updated EU Drinking Water Directive 2020/2184 [1]. As part of this effort, EYDAP is testing the innovative Toolkit from the Horizon Europe project “ToDrinQ.” The Toolkit is demonstrated at Lake Yliki, in boreholes (e.g., Mavrosouvala), and throughout the water supply network to the Polydendri Water Treatment Plant (PWTP). Specific challenges have been identified, to be investigated using hard sensors (for Nitrates, Lead and Total Bacteria) and soft sensors (for Chlorophyll-a, algal bloom events and nutrients runoff). Additionally, EYDAP’s Unmanned Surface Vehicle (USV) operates seasonally in Lake Yliki collecting thousands of data points for real-time monitoring and for calibrating soft sensors. In July 2024, after a long period, Lake Yliki resumed supplying water to the PWTP, enabling an integrated monitoring strategy. EYDAP’s strategy involved: i) the USV to collect data and samples, ii) analyzed them in the laboratory (LD) and iii) online sensors along the canal, allowing adaptation to real-time changes in water quality and ensuring the continuous delivery of high-quality drinking water to consumers.

Table 1: Innovative Monitoring Strategy for the Water Supply Network combining Data from Laboratory Analyses (LD) and Unmanned Surface Vehicle (USV) from Lake Yliki and PWTP, July 2024

Sampling Point/ Parameter	Method	Centre Lake Yliki	Earth Dam of Artificial Lake	Artificial Lake Yliki	PWTP Influent (LD)
Chl-a (µg/l)	USV	1.5 – 3.9	5.1 – 10	11 – 28	N.A.
EC (µS/cm)	USV	434 – 484	490 – 520	530 – 660	365 – 390
pH	USV	8.12 – 8.22	8.21 – 8.32	8.33 – 8.41	7.86 – 8.07
O2 (µg/l)	USV	7.22 – 7.95	8.10 – 8.45	8.80 – 9.45	N.A.
TN (mg/l)	LD	< 1.2	< 1.2	1.2	N.D.
NO_3^- (mg/l)	LD	≤ 0.56	N.D.	< 0.5	0.7 – 1.1
Pb (µg/l)	LD	N.D.	< 2.4	< 2.4	< 2.4
Total Bacteria	LD	1500 – 2900	N.A.	N.A.	15 – 8200

N.D.: Not Detected, N.A.: Not Analysed

Acknowledgements

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Development and validation of analytical methodology for the determination of per– and poly–fluoroalkyl substances (PFAS) in fish feed samples using modified QuEChERS and LC– HRMS.

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Per- and polyfluorinated alkyl substances (PFAS) contain a large number of compounds widely used in a variety of industrial and consumer products due to their properties such as resistance to high temperatures, thermal and chemical stability, water repellant properties etc. However, due to their high persistence, also called ‘’*forever chemicals*’’, they have been detected in various environmental matrices and biota tissues. PFAS have been also recently detected in fish feed samples, thus they that can be transferred and accumulated to fish and consequently to humans. It is therefore necessary to consider the quality control of the whole food production chain, including fish feed. To this purpose, a targeted method for the determination of PFAS in fish feed has been developed and fully validated in the current work using a modified "Original" QuEChERS extraction and liquid chromatography – high resolution linear ion trap-Orbitrap mass spectrometry (LC–HR-LTQ-Orbitrap-MS). Variations of sample amounts (2 and 5 g), sonication treatment times (15 and 30 min) and clean-up sorbent and protocols (Z–sep$^+$ (Method A), Z–sep$^+$ and PSA (Method B), EMR–Lipid (Method C) were tested to recover 18 PFAS from the fish-feed matrix. The optimum parameters were 2 g initial sample amount, 30 min sonication time and EMR–Lipid clean-up. The validation included the assessment of linearity, recovery, matrix effects, accuracy, intraday/interday precision, limits of detection and quantification, reporting limits and measurement uncertainty. Method validation was performed at two concentration levels (0.2 and 50 ng/g) showing good performance as follows: linearity ($r^2 > 0.99$), recovery (51.1% – 101.2%), precision (RSD <20.7%), limit of detection (LOD: 0.01 – 0.15 ng/g) and quantification (LOQ: 0.03 – 0.50 ng/g), decision limit (CC_α: 0.01 – 0.09 ng/g), detection capability (CC_β : 0.03 – 0.16 ng/g), matrix effects (ME: -50 to -12.4%), and measurement uncertainty (MU: 24.56 – 57.66 ng/g) at the lowest concentration level of 0.2 ng/g. The validated method was applied to 30 fish feed samples of different origin revealing the presence of PFOA in one sample (concentration of 0.34 ng/g) and the PFOS in two samples (concentrations of 0.60 ng/g and 0.77 ng/g, respectively).

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Greece 2.0
NATIONAL RECOVERY AND RESILIENCE PLAN
Funded by the European Union
NextGenerationEU
ΕΛΙΔΕΚ
Ελληνικό Ίδρυμα Έρευνας & Καινοτομίας

Destressing the Mediterranean Sea from chemical pollution: application of innovative technologies in the Thriasio Wastewater Treatment Plant

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Athens Water Supply and Sewerage Company S.A. (EYDAP S.A.) aspires to destress the marine environment of the Elefsis Gulf from chemical pollution, aligned with EU Mission 'Restore our Ocean and Waters by 2030' [1] as well as the requirements of the recast of the urban wastewater treatment directive [2], the Water Framework Directive, and the Marine Strategy Framework Directive. EYDAP intends to adopt an innovative technological solution in Thriasio Wastewater Treatment Plant (TWWTP) to remove 'forever chemicals', namely PFAS, heavy metals, PCBs, PAHs, and pesticides, from wastewater before they enter the Elefsis Gulf. The innovative GREEN DUNE® Photobioreactor system [3] developed in the RHE-MEDiation project will be applied in TWWTP to optimize the treatment process by using microalgae technology, since microalgae have demonstrated the ability to remove a wide range of environmental inorganic and organic contaminants. The photobioreactors, to be placed after secondary treatment, are of prismatic shape, which ensures increased microalgae productivity, wastewater treatment capabilities and enhanced water quality. Preliminary analyses of Thriasio wastewater sampled in April-May 2024 identified a significant number of substances of interest, namely 61 Pharmaceuticals, 24 PAHs, 20 PCBs/DDTs/Pesticides, 12 Plant Protection Products, 11 Industrial Chemicals, 11 PFAS, 10 Metals, 9 Surfactants, 4 Drugs of Abuse, 3 Insecticides, 1 Coffee related compound, 1 Naturally Occurring Substance, and 1 nonsteroidal anti-inflammatory drug. Seawater analyses from the Elefsis Gulf identified 44 Pharmaceuticals, 17 Plant Protection Products, 12 Industrial Chemicals, 8 Coffee & Tobacco related compounds, and 4 Surfactants. The RHE MEDiation technology can constitute a tailored approach to remove undesired chemicals as well as both a centralized and decentralized solution.

Acknowledgements

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Development and validation of methods for the determination of a new mitochondrial antioxidant (TPP-Hydroxytyrosol) in cerebellum and liver of mice.

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Mental illnesses are among the top 10 global causes of health loss. Anxiety and depression disorders, being the most widespread of the mental illnesses, affect all ages and are equally located to all geographical areas. It is estimated that 301 million people are suffering from the abovementioned conditions in modern societies. When not treated properly and timely, they could potentially lead to the manifestation of the generalized anxiety disorder. Psychological stress causes oxidation of the mitochondrial pathways. Intense research is conducted on pharmaceutical interventions, which intends to ameliorate this condition. Therefore, innovative approaches that currently followed, include substances that target mitochondria bearing an antioxidant moiety.

In the terms of this study, a newly synthesized antioxidant comprised of triphenyl phosphine, a six carbon alkyl spacer and hydroxytyrosol (TPP-HT) was administered to mice orally through drinking water. Cerebellum and liver samples were collected, and analyzed employing liquid chromatography tandem triple quadrupole mass spectrometry (UHPLC-MS/MS), aiming to assess the levels of the TPP-HT to the respective tissues.

The samples preparation involved the extraction with appropriate solvents (acidified MeOH, and an aq. mixture of ACN for the cerebellum and liver samples, respectively), as well as a preconcentration step to accomplish the required for the analysis methods sensitivity. Both methods were validated in terms of selectivity, linearity, accuracy, precision and levels of detection and quantification. The performance criteria for the methods were evaluated, proving their fitness of purpose. Furthermore, extensive chemometrics characterization was applied in terms of multiple model comparison enhancing the data validity and establishing of a novel workflow for quantitative data treatment. Results reveal that TPP-HT penetrates the blood brain barrier, at an average level of 11.5 ng/g in the cerebellum, whereas in liver revealed an average content of 4.8 ng/g was detected.

Could MS/MS-based molecular networking be an alternative to multivariate analysis in omics studies? The saffron trimming case.

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In the last 20 years, -omics technologies have dominated, gaining popularity over traditional analytical techniques. The metabolomics approach is widely employed in the construction of mathematical models, the exploration of biomarkers, and the investigation of biochemical processes. Molecular networking has emerged as a key method to visualize and exploit the chemical domain in non-targeted mass spectrometry data treatment. The acquired information from the MS/MS data was further utilized for the construction of a Feature-Based Molecular networking (FBMN). To fulfil this task, the Global Natural Products Social Molecular Networking (GNPS) theory employing the Mass2Motif algorithm has been used to create the network's nodes. These nodes compile the total GNPS network based solely on MS/MS information.

Besides the annotation utility of these networks, it is intriguing to exploit them as statistical entities based on the graph theory in an attempt to offer a new approach for treating omics data. Aiming to examine this hypothesis, saffron which is subjected to several authenticity studies, has been utilized as the case study. The chemical analysis was performed via UPLC-QToF-MS, and the derived MS/MS data were analyzed using GNPS. Regarding the saffron, in Iran the trimming process according to their length dictates the different varieties. Among them, Sargol, Negin, Pushal are the most valuable red varieties, while adulteration often occurs through their selective mixing. Alignment and comparison of the network's families have been studied. Various metrics have been evaluated, like the community and centrality measures. Extracted Ion Chromatograms of MS/MS spectra from the nodes corresponding only to a single trim (i.e. only in Negin) have been evaluated in order to verify the validity of the approach.

^{1}H-NMR and UHPLC-HRMS based chemical profiling of Cypriot carob syrups

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Carob is recognized for its beneficial effect in metabolic disorders and potent antioxidant activity, attributed to polyphenols, carbohydrates, and specific substances such as D-pinitol. Carob syrup is a product linked with the tradition of Cyprus, offering distinctive nutritional benefits alongside its pharmacological properties. Lately, carob syrup presents commercial potential, since there has been a continuous increasing demand for carob-based products. The aim of this study was the chemical characterization of commercial and traditionally prepared Cypriot carob syrups through the detection of their metabolites, highlighting both its unique nutritional worth and medicinal potential. Specifically, commercial (n=12) and traditionally prepared (n=19) carob syrup samples from Cyprus were analyzed using Ultra-High Performance Liquid Chromatography-Quadrupole Time-of-Flight Electrospray Ionization Mass Spectrometry (UHPLC-QTOF-ESI-MS) and Nuclear Magnetic Resonance (NMR) spectroscopy. Initially, NMR-based metabolic profiling revealed through Principal Component Analysis (PCA) the differentiation between commercial and traditionally prepared carob syrups. The clustering of the two groups was initially attributed to the peak region of sugars as expected, including sorbitol, D-xylose, D-glucose, D-lactose, and sucrose. After excluding the variables corresponding to the sugars, PCA analysis facilitated group clustering based on the distinctiveness of the aromatic and aliphatic regions of the spectra. In parallel, more than 48 metabolites were detected by LC-MS, out of which 21 were quantified using analytical standards. These included: a) amino acids (n=13), b) fatty acyls/fatty acids and conjugates (n=6), c) sugars (n=9), d) flavonols and flavonoids (n=7), e) organic acids (n=9), f) nucleotides and nucleotide derivatives (n=3), and g) alkaloids (n=1). Commercial carob syrups were rich in alanine (mean concentration=16.2 mg kg^{-1}) and D-glucose (mean concentration=12.4 mg kg^{-1}), while traditional syrups in alanine (mean concentration=14.7 mg kg^{-1}) and L-serine (mean concentration=10.8 mg kg^{-1}). In conclusion, NMR and UPLC-QToF-MS analyses contributed to the determination of carob syrups chemical profile and set the basis for further investigation on distinguishing commercial from traditionally prepared products.

Title: Time series untargeted metabolomics to investigate the impact of blood transfusion in patients with thalassemia

Metabolomics markers of red blood cell transfusion in thalassemia

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Abstract text:

Thalassemia is a group of inherited blood disorders characterized by insufficient production of hemoglobin. This deficiency leads to anemia and the treatment strategies depend on the severity of the condition. Patients with moderate or severe symptoms require regular blood transfusion (BT) to maintain sufficient hemoglobulin levels. However, the therapeutic effect of BT is compromised by adverse outcomes that affect the morbidity and mortality of the patients over the years. Iron overload is the most common side effect, characterised by iron accumulation in the body leading to damage of vital organs (heart, liver). Moreover, patients often exhibit allergic reactions, or other complications due to immune response to donor's blood.

Acknowledging that the research on the short- and long-term effects of BT on thalassemia patients is limited and that Greece shows hight rates of transfusion-dependent thalassemia (TDT) due to the prevalent genetic traits, the current study aims to contribute to the deeper comprehension of the biochemical alterations occurring due to BT from the metabolomics point of view.

Therefore, an untargeted metabolomics methodology, employing the cutting-edge HRMS instrumention *timsTOFpro2* and DIA MS acquisition was optimized and applied in plasma sample of TDT patients. In collaboration with the Expertise Centers for Hemoglobinopathies of the Hippokration and Laikon General Hospitals of Athens, blood samples of TDT patients were collected in three time points, i.e., pretransfusion and at two posttransfusion time points. A thorough statistical workflow including methods as ANOVA, ASCA, MEBA and post-hoc analyses was designed to identify timeseries trends and to determine metabolites related to the intervention.

The results revealed several metabolites with significant variance during BT time points. The altered metabolites suggested extended dysregulation of methionine’s and cysteine’s biosynthesis, alteration in sugars and their derivatives, as well as metabolic markers of oxidative stress.

Preliminary evaluation of trace elements content and sulfur speciation of wines produced in Greece

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The occurrence of trace elements and sulfur plays a significant role in the vinification process, may affect the organoleptic features of wines, can be related with the possibility of discrimination among different wine types and exerts a potential impact on human health [1,2]. Under this perspective and considering the currently increasing trend of wine consumption, the element profiles, together with copper and sulfur species were determined in 6 samples of white and 22 of red wines produced form Greek varieties. A total of twenty-three (23) macro constituents (Ca, K, Mg, Na) and trace elements (Ag, Al, As, Ba, Cd, Co, Cr, Cs, Cu, Fe, K, Li, Mn, Ni, Pb, Rb, Sr, V, Tl, Zn) were measured employing inductively coupled plasma mass spectrometry (ICP MS). The determination of sulfur speciation was performed electrochemically by linear sweep voltammetry (LSV), used for the first time worldwide in wine samples, while labile copper was determined by differential pulse anodic stripping voltammetry (DPASV). Despite the strong variation characterizing the trace element content of the Greek wine samples examined herewith, this was generally higher in red in comparison to white wines, with most of the values not exceeding the maximum acceptable limits imposed by legislation, being in accordance with values reported in literature. Further investigation is however required, in order to elucidate their potential connection with variety and geographical origin. Regarding sulfur, principally occurring in wines as SO_2, it was measured at higher levels in white wines in comparison to red ones, with its inert forms prevailing in white wine samples, whereas its labile forms in red ones. Respectively, copper levels detected in red wines significantly exceeded those measured in white ones. The lower percentages of labile copper in terms of total in wines indicate a significant copper complexation with SO_2 [3]. The results obtained were comparable to those reported in pertinent literature, albeit rather limited regarding copper and sulfur speciation in wines.

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Total mercury in the water column of the coastal zone in the Red Sea, the Gulf of Aqaba, and the Arabian Gulf

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The aim of this study is to provide a baseline assessment for the environmental status of the Saudi Arabian Red Sea and Arabian Gulf coastal zone, including the Gulf of Aqaba, related to mercury (Hg) pollution. Under the framework of the Field Surveillance Task (Task 6) conducted by the Marine and Coastal Environment Protection Initiative (MCEP; https://mcep.kaust.edu.sa), 15 coastal sites and 1 offshore were selected in the Red Sea along with 3 hotspot areas in the Arabian Gulf [1]. Total Hg (THg) concentrations in the water column, determined according to EPA Method 1631 [2] were obtained from overall 81 sampling stations during a campaign in the summer of 2021 and are presented herein. This survey constitutes the first geographically comprehensive study of Hg within the Saudi Arabian coastal waters providing baseline information in this developing area. The THg levels in the Arabian Gulf were significantly higher than those in the Red Sea. Among the Red Sea sites, the Jeddah Lagoon System, the adjacent area Jeddah Mena, and the King Fahd Port in Yanbu presented the highest concentrations. A significant positive relationship ($p < 0.001$) was detected between Hg and other anthropogenic metals (Pb, Cd, Cu, Ni, As, Zn) analyzed by the Hellenic Centre for Marine Research (HCMR) [3]. The concentration of Hg in the surveyed areas fall well below the threshold values set by both the Saudi Arabia National Environmental Standards for Ambient Water Quality (< 0.1-0.4 μg/L) and the EU standards (< 70 ng/L, Directive 2013/39/EU) [4].

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Waste tire char valorization by preparing Ni-Cu carbocatalyst for applications in sulfate radicals based advanced oxidation processes (SR-AOPs) : Degradation of metronidazole emerging pollutant

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Waste tire amounts have continuously increased in the last decades presenting a great potential for harmful effects to the environment. Pyrolysis was applied lately as an effective recycling method in order to recover energy and produce valuable products. Tire char (TC) represents an attractive by-product that can be modified to produce adsorptive and catalytic materials of significant industrial relevance. In this study, a series of Ni-Cu-TC catalysts with different weight ratios was synthesized and applied towards the degradation of metronidazole (MTZ) by advanced oxidation processes (AOPs), through activation of peroxymonosulfate (PMS, HSO_5^-) and peroxydisulfate (PDS, $S_2O_8^{2-}$) oxidants. MTZ was studied as a model emerging pollutant since it is one of the widely used antibiotics worldwide, with high solubility and diffusion in aqueous media, frequently detected in various wastewaters. Physicochemical characterization of TC catalysts was performed by scanning electron microscopy (SEM), X-ray diffraction (XRD), ATR-FTIR spectroscopy, Raman spectroscopy, porosimetry, and elemental analysis. XRD pattern of TC_10%Cu was ascribed to cubic Cu_5Zn_8 with diffraction peaks at 43.37°, 50.46°, 74.14° and 89.96°. Three characteristic diffraction peaks of TC_10%Ni appeared at 37.25°, 43.28° and 62.88°, which are indexed as (111), (220) and (220) planes, correlated to NiO cubic structure. The best catalytic systems were tire char with 10% (w/w) loading Cu (TC_10%Cu/PDS) and 10% (w/w) loading Ni (TC_10%Ni/PMS), with 100% degradation of MTZ in 30 min and 15 min, respectively. The optimal dosage of PMS, PDS and Ni-Cu tire carbon catalyst, was 100 mg/L, 250 mg/L and 500 mg/L, respectively. In order to identify the major reactive species generated, scavenging experiments have been conducted. For PMS/10%Ni-TC system singlet oxygen ($^1O_2$) was revealed as the dominant species followed a non-radical mechanism, while for PDS/10%Cu –TC system $SO_4^{\bullet -}$ radicals were the major oxidative species. Finally, mass spectrometry (LC-HR-MS) analysis was followed to identify transformation products (TPs) during MTZ catalytic degradation by TC_10%Cu and TC_10%Ni, and TP with *m/z*=128.0450 Da was the major one. Further experiments on characterization of the catalysts were in progress (e.g. XPS analysis, contact angle) in order to correlate catalytic performance and mechanisms with surface properties of the prepared catalysts.

Screening of a marketed drug library identifies dantrolene as an activator of the antioxidative enzyme paraoxonase-1

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Objectives: Human paraoxonase 1 (PON1) is a hydrolytic enzyme, which is bound to high-density lipoprotein (HDL) in serum. This enzyme can hydrolyze a variety of substrates displaying activities of paraoxonase, arylesterase and lactonase. The hydrolysis of pro-atherogenic oxidized phospholipids represents the major function of PON1, thus contributing to the antioxidant and antiatherogenic properties of HDL. Reduced PON1 activity has been associated with an increased risk for cardiovascular disease.

Methods: In the present study, a library of commercially available drugs (956 compounds) was screened to identify small molecules that can increase the HDL-associated PON1 activity. Screening was performed by a kinetic absorbance assay in a 96-well plate using human HDL as enzyme source, and paraoxon and phenyl acetate as substrates to measure paraoxonase and arylesterase activities of PON1 respectively. In addition, we studied the effect of certain compounds on the activity of specific PON1 variants (polymorphisms 192Q/R, 55L/M and mutation M127R). Furthermore, mechanistic investigation of the effect of compounds on enzyme activity was performed using recombinant human wild-type PON1 and the PON1[L55M] variant associated with reduced activity in humans, as well as molecular docking of drugs onto the structure of PON1.

Results: Library screening led to the identification of seven compounds that increase the paraoxonase activity, four of which also increase the arylesterase activity of PON1. Analysis of the effect of these compounds on the activity of PON1 variants showed that dantrolene is an activator of all enzyme variants studied, inducing the stronger activation to PON1[L55M]. Further analysis showed that dantrolene, at a low μM concentration, has the capacity to activate dose-dependently both WT PON1 and PON1[L55M] by primarily increasing the V_{max} of the enzymatically catalyzed reactions. Molecular docking suggested that dantrolene binding to PON1 can result to direct stabilization of Ca(II) atoms that either participate in catalysis or stabilize the protein.

Conclusion: Our findings support that existing drugs, such as dantrolene, can increase HDL-associated PON1 activity and pave the way for new therapeutic approaches for atherosclerosis and cardiovascular disease.

Aggregated α-synuclein in erythrocytes as a potential biomarker for idiopathic Parkinson's Disease.

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Mostly known for its implication in synucleinopathies, including Parkinson's disease (PD), α-synuclein is predominantly expressed in the nervous system [1]. Most of the peripheral α-synuclein is found in erythrocytes, and several studies have examined a possible association between erythrocytic α-synuclein and PD [2-4]. We have used a recently developed ELISA that selectively detects fibrillar and oligomeric α-synuclein to measure aggregated α-synuclein in red blood cells (RBCs) collected from PD patients and age/sex-matched control individuals (n=35). The PD group included patients without any common mutation (genetically undetermined group, GU-PD, n=56) as well as mutation carriers in the α-synuclein gene (A53T-PD, n=28) and glucocerebrosidase gene (GBA-PD, n=24). We found that the concentration of aggregated α-synuclein in erythrocytes was significantly increased in GU-PD patients compared to controls. A53T-PD and GBA-PD patients exhibited similar levels of erythrocytic aggregated α-synuclein as the control group. The levels of fibrillar/oligomeric α-synuclein in RBCs were reduced in respect to the age of control individuals suggesting that the observed increase in the GU-PD cohort was not due to normal aging. Parallel assessment of monomeric α-synuclein revealed that aggregated, but not total, could discriminate PD patients from control individuals. The elevation of aggregated α-synuclein in PD erythrocytes, which is not related to aging, suggests that these forms may be indicative of PD pathology and possibly accumulate upon disease establishment. As such, aggregated α-synuclein in RBCs could be a potential biomarker for PD diagnosis.

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The inhibition of α-synuclein aggregation using marine-derived bacterial metabolites as a novel neuroprotective approach for Parkinson's Disease

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Inclusions consisting of aggregated α-synuclein (α-syn), an abundant neuronal protein, are the most common histopathological finding in Parkinson's Disease (PD). The species thought to compromise the viability of neuronal cells are the soluble high molecular weight oligomers resulting from monomeric α-syn multimerization. The identification of therapeutic targets in PD is crucial, given the current lack of a definitive cure and the limited symptomatic relief provided by available medications. The marine environment, hosting a vast largely unexplored biodiversity, offers an enormous untapped resource for the discovery of novel biochemicals with diversified chemical structures containing new or uncommon functional groups thereby exhibiting more potent biological activities. In this work, we have screened a panel of marine-derived bacterial extracts to discover agents that can drive the removal of aberrant α-syn assemblies. Initially, the homogenates of marine-derived bacteria were selected by their ability to hinder the elongation of pre-formed fibril seeds *in vitro* using a specific thioflavin T fluorescence assay[1]. The most potent extracts were subsequently administered in a well-established SH-SY5Y cell system in which the inducible expression of α-syn results in oligomer formation and cell death. The effects of the marine extracts in the levels of aggregated α-syn were assessed by an aggregate-specific ELISA assay[2]. The secondary metabolites isolated from the most potent marine extracts were administered to SH-SY5Y cells to assess which compounds contain anti-aggregation activity in a cellular context. Our results demonstrated that the extract BIO904 and its component BIO904-09, a 2,5-diketopiperazine, exhibited a significant dose-dependent decrease in the levels of aggregated α-syn.

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Failure of major proteostatic mechanisms and lysosomal malfunction in p.A53T-αSyn PD patient iPSC-derived astrocytes

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The accumulation of aggregated alpha-Synuclein (αSyn) is typical in Parkinson's disease (PD)-patients' brains and the prion-like spreading hypothesis is gaining ground. However, the astrocytic contribution in PD pathology is understudied, despite PD-related mechanisms including neuroinflammation and aggregate resolution pathways may involve non-cell autonomous components. Dysregulation of neuronal autophagy is known to cause accumulation of aggregated αSyn. Here, we aimed to investigate how the p.A53T-αSyn mutation affects proteostasis in astrocytes, using our previously established induced pluripotent stem cell (iPSC) model derived from PD patients harboring the p.A53T-αSyn mutation. Ventral midbrain astrocytes differentiated from PD iPSCs (PDa) displayed accumulation of protein aggregates, including the pathological phosphorylated form of αSyn. Proteome profiling of PDa versus Ha revealed endocytosis and protein catabolic processes, including autophagy, among the most affected pathways. Upon investigation of the endocytic capacity of Ha and PDa treated with neuronal conditioned medium, we observed that unlike Ha, PDa have diminished capacity to uptake neuronal αSyn. Moreover, proteasome activity was reduced in PDa and autophagy was disturbed, as revealed by increased LC3II levels and reduced autophagosome to autolysosome transition. Additionally, PDa exhibited decreased LAMP1 levels, reduced lysosomal acidity and enzymatic activity, alongside with increased number of lysosomes and altered lysosomal positioning, essential for proper autophagosome-lysosome fusion. These observations couple dysregulated autophagy with impaired lysosomal integrity in PDa. Overall, our data demonstrate that the p.A53T-αSyn mutation causes intrinsic malfunctions in astrocytes, related to proteostasis and clearance mechanisms that may have a critical contribution in PD pathology. **Funding:** HFRI Project 1019-DiseasePhenoTarget; GSRI Project TAA TAEDR-0535850 - Brain Precision.

Copper(II) and nickel(II) complexes with coumarin derivatives: Structure and biological evaluation

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Transition metals and, especially, their metal ions count several years of research and scientific interest focused on their biological role.[1] Transition metal complexes of different drugs have been shown to significantly improve their biological activity, showing at the same time new therapeutic potential. Copper(II) and nickel(II) compounds have shown bacteriostatic, antineoplastic, anticancer, antifungal, antiviral, antioxidant and cytotoxic activity.[2,3]

The aim of the study was to synthesize novel metal complexes of the biologically interesting coumarin derivative coumarin-3-carboxylic acid, in order to characterize their structure and examine their biological activity. We conducted the synthesis of Cu(II) and Ni(II) with the ligand coumarin-3-carboxylic acid, in the absence or presence of the nitrogen-donor co-ligands 1,10-phenanthroline (phen) and imidazole (Himi).

The characterization of the newly-synthesized complexes was carried out by spectroscopic and physicochemical techniques. The structural determination for two of the complexes was accomplished by single-crystal X-ray diffraction. The *in vitro* biological study of the complexes involved their interaction with calf-thymus (CT) DNA, bovine and human serum albumins (BSA and HSA) and the evaluation of their antioxidant activity.

The complexes were found to bind to CT DNA tightly *via* intercalation as monitored by UV-vis spectroscopy and viscosity studies and *via* their ability to displace ethidium bromide (EB) from its adduct with CT DNA. In addition, the complexes bind tightly and reversibly to both serum albumins studied. The complexes have shown noteworthy scavenging activity towards DPPH and ABTS radicals and the ability to reduce H_2O_2.

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Development of bio-MOFs as drug delivery systems for cancer treatment

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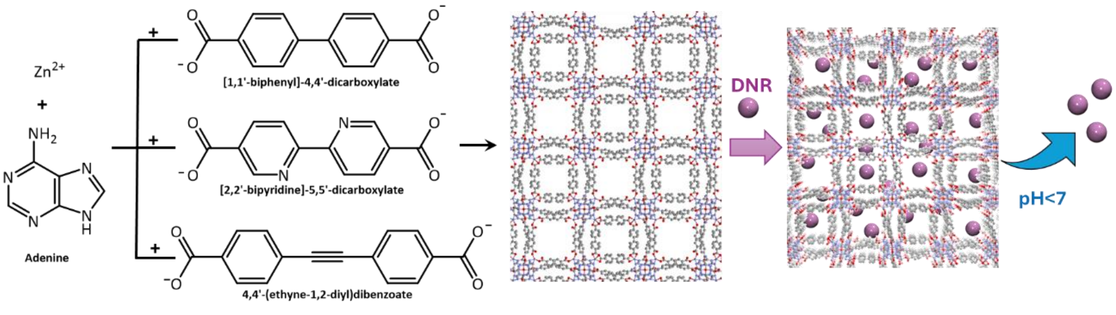
The need for highly targeted cancer therapies has led to the development of biological Metal-Organic Frameworks (bio-MOFs) as promising drug delivery systems. These frameworks are ideal carriers for anticancer agents due to their biocompatible components (metal ions and organic linkers), and structural advantages including large cavities and functionalized frameworks. These features enable the precise encapsulation and controlled delivery of therapeutic drugs directly to cancer cells while minimizing side effects. The purpose of this work is the development of bio-MOFs and the evaluation of their efficacy as drug delivery systems for cancer treatment. We synthesized both well-known bio-MOFs (such as Bio-MOF-1 [1], nano-Bio-MOF-1 [2], and Bio-MOF-100 [3]) and novel bio-MOFs with innovative linkers, including 2,2'-Bipyridine-5,5'-dicarboxylic acid and 4,4'-(Ethyne-1,2-diyl)dibenzoic acid (Scheme). All materials were thoroughly characterized by combination of PXRD, FT-IR, TGA, SEM, EDS, NMR and porosimetry. Daunorubicin (DNR) was used as model drug for encapsulation, and its release was studied under varying pH conditions simulating healthy and tumor environments.



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GreenSynthesisofcarbon Quantum dotsforGeoenvironmentalApplications

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The purpose of this work is the synthesis of economic and environmentally friendly nanoparticlesfrom cotton waste, through probiotic microorganisms,which will be used in agriculture and environment.In particular, carbon quantum dots (CQDs)exhibit important optical and electrochemical properties, such as high fluorescent quantum yield, excellent biocompatibility, low-toxicity, and aqueous solubility forimproving crop yields and restoring problematic soils.The transmissionelectron microscopy(TEM)confirms the morphological characteristics and dynamic light scattering results confirmed the hydrodynamic diameter ($d_{H,}$DLS)as well as the colloidal stability of the CQDs.[1] FT-IR, fluorescence and UV-analysis confirmed the propertiesand the existence of functional groups and the nature [2].

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Synthesis of Fused-Cyclic Aryl Amino Carbene Ligand Precursors

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Since the introduction of singlet state, thermally stable and crystalline **C**yclic-**A**lkyl-**A**mino **C**arbenes (**CAACs**) by Bertrand *et.al.* (**Figure 1**)[1], suffice to say that this type of 2e$^-$ donor ligands have made their indelible mark in diverse areas of chemistry[2]. This is due to their enhanced σ-donation and π-acidity, which can stabilize low-coordinate, as well as electron-rich species, respectively. **F**used **C**yclic-**Ar**yl-**A**mino **C**arbenes (**F-CArACs**)[3] take these advantageous attributes even further, especially regarding their π-acceptor properties thanks to conjugation built in their design (**Figure 1**). To this end, we present new synthetic routes leading to the preparation of expanded **F-CArAC** ligands' azolium precursors, incorporating ancillary arene or SiR_3 moieties in their architecture (**Figure 1**). We envisage that including these groups (R_2 in **Figure 1**) into the **F-CArAC** ligand scaffold will offer steric protection, engender further stabilisation *via* dispersion forces and additionally, in the case when R_2 is an arene, provide a second site for metal centres to form an M-arene π-complex.

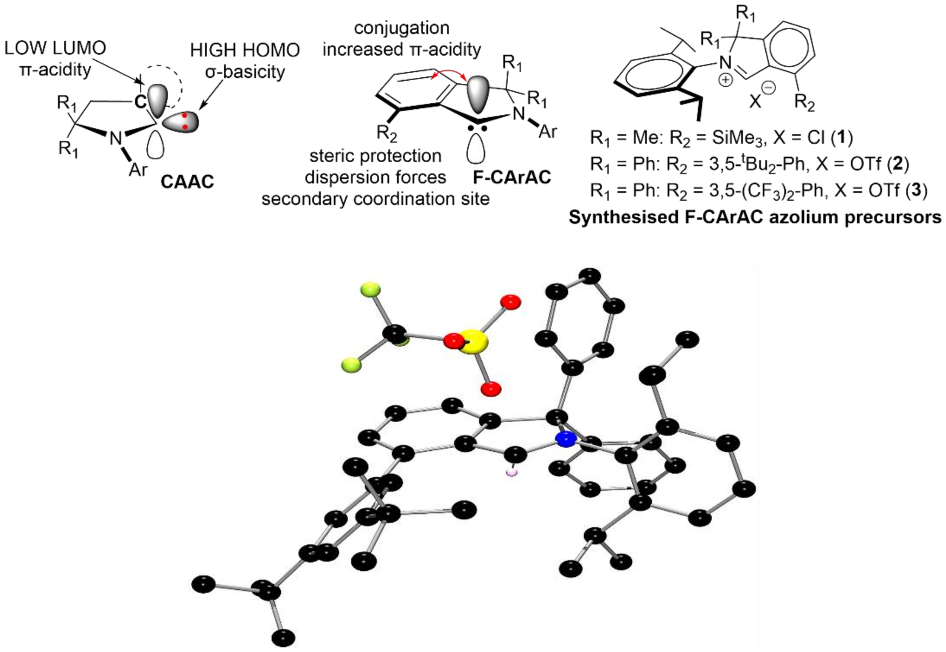

Figure 1: Top: From left to right: CAAC, F-CArAC, synthesised F-CArAc azolium precursors; Bottom: Molecular structure of F-CArAc azolium precursor (**2**).

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POLYUREA-CROSSLINKED ALGINATE AEROGELS WITH NO NEED FOR SUPERCRITICAL DRYING

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One of the most critical steps in the synthetic procedure of aerogels is the drying step, as this step must ensure the preservation of the porous network of the wet gel into the dry object, and thus the unique material properties of aerogels. The best drying method is drying from supercritical CO_2. In the frame of developing new sustainable processes and aerogel products, research has been intensified for biopolymer-based aerogels and towards replacing supercritical drying with more conventional and more green drying methods. In this work, polyurea-crosslinked M-alginate (X-M-alginate, M: Ca, Cu, Zn, Ag) have been prepared via the reaction of pre-formed M-alginate gels with an aliphatic triisocyanate derived from isophorone diisocyanate. Crosslinking with polyurea has proven to be an efficient way to increase the mechanical strength and the stability of alginate aerogels [1,2], improving therefore their application potential. X-M-alginate gels were dried from (a) supercritical CO_2 (SCD) or (b) low vapor pressure solvents. SCD provided macroporous/mesoporous X-M-alginate aerogels with BET surface areas in the range of 300-500 $m^2\ g^{-1}$ and porosities >90% v/v, while drying from low vapor pressure solvents provided mostly mesoporous aerogels with BET surface areas in the range of 300-400 $m^2\ g^{-1}$ and porosities in the range of 75-90% v/v. The fact that aerogels obtained from conventional drying retain high surface areas and porosities can be attributed to the rigid structure of the aliphatic polyurea.

Acknowledgements

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Antitumoral effect and Mechanisms of action of Silver Nanoparticles on Breast Cancer cells

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Breast cancer is a leading cause of mortality among women worldwide since conventional therapies for this type of cancer are often limited due to severe side effects. In this study we synthesised silver nanoparticles (Ag NPs) coated with tannic acid (TA) and explored their effects on two breast cancer cell lines, MDA-MB-231 and BT474. MDA-MB-231 cells are a model of highly invasive and metastatic triple-negative breast cancer (TNBC), while BT474 cells are used to study HER2-positive tumours. The structural characterisation of the Ag NPs was acquired through transmission electron microscopy (TEM) images but were also further analysed by UV spectroscopy and nanosight analysis. The antitumor effects of Ag NPs were evaluated using various biological assays and their mechanisms of action were investigated through Western Blot analysis and real time PCR. The results showed that Ag NPs significantly reduced cell viability in a dose-dependent manner in MDA-MB-231 cells, while in BT474 cells their cytotoxic effect was more moderate. Furthermore, Ag NPs were shown to inhibit angiogenesis and cell migration. Western Blot analysis revealed an increase in oxidative stress, producing reactive oxygen species (ROS) and lipid peroxidation, mediated by the activation of the p38 MAPK signalling pathway.

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Sorption study of two amide-based MOFs towards heavy metal cations in aqueous environment.

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Metal-Organic Frameworks (MOFs) are coordination polymers consisting of metal ions acting as nodes and organic ligands acting as edges.[1] Main characteristics of these materials are their crystallinity and high porosity. Due to the variety of the metal centers and the organic functional groups, these polymers can be used to various applications such as gas storage and separation, catalysis and wastewater purification from organic and inorganic pollutants.

Heavy metal cations such as Pb^{2+}, Hg^{2+}, Cd^{2+} are hazardous for living organisms, so it's important their capture from water streams. For that reason, the materials that will act as sorbents should be water-stable and contain suitable functional groups (such as -COOH groups).[2] One famous MOF for its water and pH stability is UiO-66-NH_2, which is consisted of Zr_6 nodes connected with amino-terephthalates (NH_2-BDC^{2-}). In this work we modified the organic ligand using chlorides, ending up with two amide ligands containing a free carboxylic group. In a second step, the ligands reacted with a Zr salt, and the final products identified as UiO-66 analogues. The sorption studies conducted using Pb^{2+} solutions and the results are quite promising.

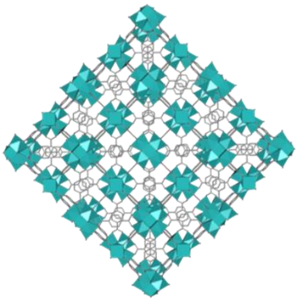

Figure 1: The 3D crystalline structure of UiO-66 (***fcu*** topology).

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Bioinspired Electrocatalysts for Hydrogen Evolution Reaction

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Reducing the carbon footprint is an emerging challenge in addresing the energy crisis. The reliance on platinum (Pt) group catalysts for hydrogen/proton interconversion can be challenged by hydrogenases. These natural catalysts offer exceptional activity with minimal overpotential requirements.[1] Although O_2-tolerant [NiFe]-hydrogenases, are more favourable for H_2 oxidation, they are often hindered by the H_2 product itself. [NiFeSe]-hydrogenases, which contain selenocysteine in place of cysteine at the nickel active center and exhibit unique attributes in water splitting, paving the way for new Ni-Se catalysts. This class of enzyme category demonstrates enhanced proton reduction regardless of H_2 presence, positioning them among the most active molecular H_2 evolution catalysts.[2] Consequently, the use of a biomimetic electrocatalyst paves the way for a more sustainable and cyclic fuel economy. The abundance and affordability of nickel is crucial to the development of efficient catalysts to be used for hydrogen generation.[3] Moreover, the non-innocent nature of biomimetic ligands coordinated to a nickel-metal center leads to complexes with significant electrocatalytic activity into hydrogen evolution reaction (HER).[4]

Herein, we present the synthesis, characterisation and electrocatalytic performance of mixed dithiolene-diselenolene nickel complexes. We tailored their properties by substituting the groups on the diselenolene ligand and compared them with various heteroleptic dithiolene complexes synthesized and studied in our laboratory.[5,6]

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Synthesis Antimicrobial and Photocatalytic applications of TiO_2@CuO nanoparticles

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Titanium dioxide (TiO_2) nanoparticles are pivotal in sustainable nanocomposite research, particularly in UV-driven photocatalysis due to their significant surface area, stability, and cost-effective synthesis. [1] Incorporating noble metal nanoparticles can heighten TiO_2 photocatalytic ability by improving electron-hole separation and extending absorption into the visible spectrum. [2]

In this study, spherical TiO_2 nanoparticles were synthesized through a revised sol-gel process, with high yield and monodispersity. Hybrid Cu@TiO_2 Nps were fabricated by embedding Cu Nps on the surface of TiO_2 Nps in the presence of hydrazine. The nanocomposites were characterized structurally by FT-IR and XRD, while their morphology was determined by SEM, TEM and colloidal stability was assessed through DLS. The photocatalytic activity was systemically evaluated through UV-Vis spectroscopy by studying the photodegradation of methyl orange (MO), after visible light irradiation.

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Synthesis and characterization of a Cu(II) and a Ni(II) complex with a curcumin derivative. Study of their interaction with CT-DNA and BSA.

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Curcumin, a polyphenolic pigment of the rhizome of turmeric or Curcuma longa L., has received considerable attention because of its bioactive effects, pharmaceutical, biotechnological and medicinal applications [1, 2]. Despite all these facts, the utility of curcumin is limited by its low bioavailability and chemical stability [2]. Structural modifications have been implemented in curcumin to overcome these obstacles and enhance its overall anticancer activity. These modifications are aimed to increase bioavailability and stability and elevate selective toxicity against cancer cells [1, 3]. Among them, the synthesis of metal complexes of curcumin derivatives have been found to exhibit better pharmacological properties and photo induced anticancer activity against different types of cancers [4]. In our work, the Copper (II) and Ni (II) complexes with a curcumin derivative were synthesized and characterized. Also the interaction with CT-DNA and BSA were investigated. Characterization of both the ligand and the complexes was carried out using the following spectroscopic techniques: mass spectroscopy (MS), nuclear magnetic resonance (NMR), fluorescence, infrared (IR) and ultraviolet-visible (UV-Vis) spectroscopy. Then, the interaction of these compounds with CT-DNA and BSA was studied by means of cyclic dichroism (CD), ultraviolet-visible (UV-Vis) spectroscopy, fluorescence, and viscometry. The results of this study showed the ability of both the ligand and the complex to interact with DNA and BSA. Based on the structure of the ligand and the experimental data in the JOB method, we have the formation of a Cu(II):curc stoichiometry complex = 1:1 and a Ni(II):curc stoichiometry complex = 1:1 as well as a Ni(II):curc stoichiometry complex = 2:1. From spectrophotometric titration the binding constants Kb of the complexes with CT-DNA were found to be in the range of 10^5-10^6 M^{-1}. From the competitive activity studies with Ethidium Bromide, the complexes were found to act competitively. The cyclic dichroism spectra showed an intense ICD effect and the interaction of the complexes with DNA causes a conversion of the B structure of DNA to A. The hydrodynamic method of viscometry confirms the interaction by intercalation for ratios up to about 0.2. The complexes interact with BSA with a binding constant value of 10^5 M^{-1}, within the range of 10^4-10^6, so that the protein is a good transporter of the drug.

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New Novel Metal-Organic Frameworks
Based on Polynuclear Rare-Earth Metal Clusters

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Metal-Organic Frameworks (MOFs) are porous crystalline materials created through the coordination of metal ions or clusters with organic bridging ligands [1]. These frameworks can form one-dimensional (1D), two-dimensional (2D), or three-dimensional (3D) networks, each containing potential voids or pores. For example, MIL-53 and CAU-10 result by the combination of an aluminum rod with simple ligands such as terephthalic or isophthalic acid respectively. In another case, the polymerization of the hexanuclear cluster, Zr_6, by a dicarboxylate ligand can result in a variety of MOFs, with UIO-66 being a prominent example due to its water stability, porosity, and ease of synthesis. Similarly, Rare-Earth (RE) metals can form analogous clusters with F/OH bridges, leading to the development of RE-UIO-66 analogs [2]. These analogs are notable for their stable and positively charged frameworks.

Our approach was to investigate whether additional MOFs can be synthesized using simple dicarboxylate ligands and known clusters. We also explored which other polynuclear Rare-Earth (RE)-based clusters can serve as secondary building units (SBUs) for the formation of these structures, leading to the isolation of a new series of RE-based MOFs with different nuclearities.

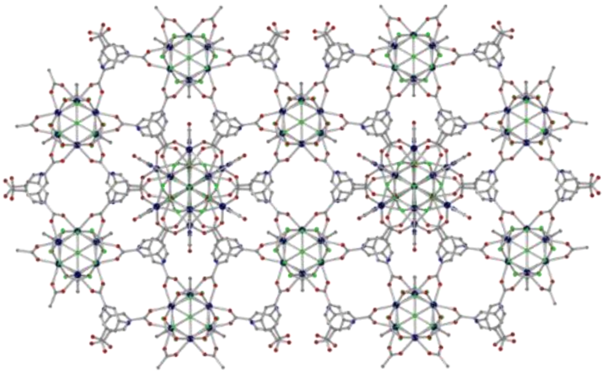

Figure 1: The 3D crystalline structure of our new MOF down the crystallographic axis c.

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Copper Single Atom-diimine Catalytic centers immobilized on TiO_2 for water purification under-visible-light irradiation.

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Titanium dioxide (TiO_2) is the most investigated nanomaterial due to its excellent photocatalytic properties, non-toxicity, chemical stability and low cost. It exhibits a large band gap of ~3.2eV, which limits its absorption capacity in the UV light spectrum. To enhance the catalytic efficiency of TiO_2 for water purification, it is crucial to reduce its bandgap. This modification enables the material to effectively harness sunlight, including the visible light spectrum, thereby improving its photocatalytic performance. [1]

Single-atom catalysts (SACs) exhibit remarkable catalytic efficiency due to their unique electronic structure and maximum utilization of individual atoms, which improves selectivity and activity in various chemical processes. Cu-based SACs (Cu-SACs) can expose more accessible active sites which are utilized more efficiently. When combined with TiO_2 the photocatalytic performance is improved due to the transfer of electrons on the Cu SACs and the suppression of exciton recombination. [2,3].

In this study, we employed an innovative approach for the modification of the Cu SACs centers on TiO_2 by bonding them with various diamine ligands. A variety of analytical techniques were used for characterizing the generated TiO_2 oxide nanoparticles, including X-ray diffraction (XRD) and thermogravimetric analysis (TGA) to determine the crystal structure and composition. Optical properties were assessed using UV-DRS, while spectroscopic characterization were performed using IR-ATR and Raman techniques. The resulting Cu SAC:[diimines]/TiO_2 nanoparticles demonstrated high degradation efficiency under LED visible light for the removal of toxic dyes from water, such as Methylene Blue (MB) and Rhodamine B (RhB).

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Photocatalytic hydrogen production via bioinspired heteroleptic* Nickel catalysts

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Amid the global energy crisis, the demand for alternative energy resources aimed at achieving a greener and more sustainable future is rapidly increasing. In this context, hydrogen technologies emerge as a promising zero-emission energy source with significant potential for energy storage. To address the energy barrier of the water-splitting redox reaction [1], we draw inspiration from NiFe-hydrogenase enzymes to develop biomimetic catalysts[2]. Additionally, NiFeSe-hydrogenase[3], which incorporates selenocysteine instead of cysteine at the enzyme's active site, opens new avenues for synthesizing a diverse range of catalysts that include either selenium or both selenium and sulfur in their ligand frameworks.

Furthermore, the well-established non-innocent character of these ligands enhances the stabilization of their complexes due to the ligands' aromatic coordination structures. These natural catalysts achieve the highest known yield for the electrochemically reversible reaction of proton/hydrogen interconversion[4]. Light-driven hydrogen evolution through photocatalysis under LED lamps ($\lambda \geq 400$ nm) creates conditions conducive to artificial photosynthesis (AP), paving the way for a greener and more circular energy economy[5]. In this study, we present the synthesis and characterization of a series of new heteroleptic Ni complexes as catalysts, along with their efficiency in visible light-driven hydrogen production. Furthermore, the role of the ligands' substituents is examined.

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CHITOSAN-DERIVED CARBON AEROGELS: EFFECT OF CROSSLINKING STRATEGY AND PYROLYSIS CONDITIONS ON TEXTURAL AND MATERIAL PROPERTIES

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Carbon aerogels (CAs) show unique properties, which make them promising materials for different applications. In addition to their well-studied application as adsorbents or as supercapacitors, CAs show potential as advanced catalyst carriers, since they exhibit a multiscale porosity, which has the potential to enhance the catalytic efficiency in comparison to commercial solutions (e.g., activated carbons). In particular, they have high microporous specific surface areas (for the anchoring and dispersion of nanoparticles, e.g., metal nanoparticles) and meso/macroporosity for the efficient transport of products and reactants, and they provide electrically conductive materials [1]. The production of CAs involves pyrolysis of organic aerogels, which is performed under an inert atmosphere (e.g., N_2) and at high temperatures. Due to the outstanding textural properties of the products, tailorability and high pyrolysis yield, polycondensated resorcinol-formaldehyde (RF) gels have been the most common starting materials in the polymer-to-carbon aerogel route since the 1990s [2,3]. A green alternative to RF as starting material is the use of biopolymer aerogels, which can be derived from abundant resources, e.g., from alginate, cellulose or chitosan, the latter showing the advantage of having naturally incorporated nitrogen containing functions. Even though first works have already shown that biopolymer aerogels can be successfully converted to carbon aerogels, the pyrolysis yield is generally still significantly lower as compared to RF-based routes [4]. Due to changes of the pore network during pyrolysis, also the challenge to preserve the textural properties during pyrolysis arises. In this study, our objective is to elucidate the crucial factors for preserving the pore structure during pyrolysis, examining both the processing parameters and those pertaining to the aerogel-based starting material. Our main findings focus on the role of different crosslinking strategies and chemical stabilization during aerogel synthesis, as well as on the effect of different final temperatures/heating rates during pyrolysis.

Acknowledgements

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The influence of the solvent on the growth of zinc oxide

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Zinc oxide (ZnO) is one of the most important and widely used metal oxides with applications ranging from catalysis, electronics and energy harvesting to cosmetics and biomedicine. ZnO has attracted worldwide research interest due to its low toxicity, biocompatibility and diverse morphology [1,2]. Morphologically different ZnO nanostructures enable a wide range of applications, as the behavior of ZnO depends on its size and morphology. ZnO also serves as a biocompatible, antibacterial and antiviral agent, which enables its use in biomedical applications [3]. Among the various synthesis methods, the solvothermal method is attractive due to its simplicity and excellent control over particle size, shape and dispersibility [4]. The development of a surfactant-free solvothermal synthesis route, characterized by the presence of a small number of reactants, provides a deeper insight into the formation mechanism of ZnO nanoparticles and the control of reaction pathways. The kinetics of nucleation and growth of ZnO nanoparticles strongly depend on the properties of the solvent. The alcoholic solvent and the intermediate species formed during ZnO synthesis can selectively bind to different crystal facets of polar ZnO or suppress its crystal growth, leading to preferential crystal growth. In the present work, zinc oxide particles were prepared by solvothermal synthesis with different alcoholic reagents and in aqueous media. The nucleation and growth process of ZnO nanoparticles were investigated by X-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM). The results of the X-ray diffraction analysis show that the use of 1-butanol alone as a solvent leads to a rather isotropic crystallite shape, while the ZnO nanoparticles grow predominantly in the *c*-direction in the presence of all other alcohols used as well as in aqueous media. The alcohols of different size and polarity act both as solvents and reactants and as controlling agents for crystal growth by providing different bonding interactions that are involved in both the nucleation processes and the preferential growth of the ZnO nanoparticles. On the other hand, the differences in the nucleation processes in aqueous solution determine the two subsequent growth processes, primary ZnO nanosubstructures and potential hierarchical microstructures. A synergistic effect between the I_{002}/I_{100} values and the crystallite size on the photocatalytic activity was found.

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New terephthalate 3D-MOF based on Y_6 cluster

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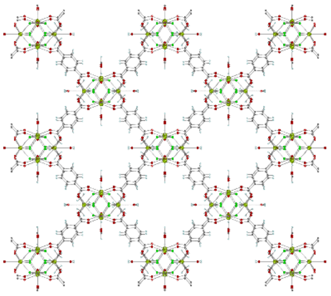
MOFs are crystalline, porous materials that consist of metal ions or clusters (SBUs) connected by organic molecules acting as bridging ligands. These create 2 or 3 – dimensional coordination networks which are of great scientific importance due to their pores being able to absorb various molecules, and thus have multiple applications. UiO-66 is one of the most well-known MOFs in the field of coordination chemistry. It is formed by 12-coordinated Zr_6 clusters that are bridged by the dianions of terephthalic acid (BDC).[1] What sets it apart from most other MOFs is its porous network which results in a high surface area and exceptional thermal stability, as well as the ability to use various BDC derivatives (usually NH_2-BDC), making it highly modular.[2]

In our laboratory we have been working a lot with isophthalic acid, since no MOFs have been reported to utilize it alongside the Zr_6 cluster. Thus, we wondered what would happen if we combined both isophthalic and terephthalic acid, intending for them to simultaneously react with the hexanuclear cluster. The difference is that Yttrium was used instead of Zirconium to form the hexanuclear cluster, as it is easier to obtain single crystals with it. As a result, we obtained a new MOF based on the Y_6 clusters which are bridged only by terephthalates, whereas the isophthalic acid acts as a modulator. Its role seems to lead to a new structure, depending on the reaction conditions as well, while some of the other products we obtained were known structures such as the Yttrium analogues of UiO-66.



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A novel $CuNaTi_3O_8$ Freudenbergite-type photocatalyst for efficient water purification under visible light irradiation

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In the field of heterogeneous photocatalysis, TiO_2 nanoparticles occupy a prominent position. Nevertheless, the main drawbacks of TiO_2, - specifically, its inability to absorb visible light and the rapid recombination of excitons - overshadow its great advantages, such as chemical stability and low toxicity, thereby limiting its uses as a widely used photocatalyst [1]. Recently, composite materials based on the modification of the crystal structure of titanium dioxide have garnered interest in photocatalysis. The framework of TiO_2 can accommodate cations such as Na^+, leading to sodium titanate, a material with interesting optical ad physical properties. To maintain charge balance, other cations, such as Fe^{3+}, Cr^{3+}, and Ni^{2+}, can also be incorporated into the lattice, resulting in Freudenbergite ($FeNaTi_3O_8$)- like structures that exhibit intriguing physical and optical properties [2], [3].

Herein, we report the synthesis of a novel $CuNaTi_3O_8$ nanoparticulate semiconductor through sol-gel chemistry. Several techniques have been employed to characterize this new material including powder X-ray diffraction (XRD), electron microscopy (SEM, TEM), dynamic light scattering (DLS), IR-ATR, UV-Vis, and Raman spectroscopies. The photocatalytic performance of this material was systematically evaluated under visible light irradiation using low-energy LED lamps, demonstrating significant degradation of Methylene Blue and Rhodamine B dyes. To elucidate the underlying photocatalytic mechanism, scavengers such as isopropanol (IPA), ethylenediaminetetraacetic acid (EDTA), and sodium sulfate (Na_2SO_4) were utilized to identify the active species involved in the degradation process. These findings highlight the potential of $CuNaTi_3O_8$ as an efficient photocatalyst for water purification under visible light conditions.

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Activation of TiO_2 nanoparticles with N-doped CQDs for photodegradation of Methylene Blue and reduction of H_2

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TiO_2 nanoparticles are regarded as highly promising photocatalysts due to their strong chemical stability and photocatalytic efficiency. However, their large band gap (3.0–3.2 eV) restricts their activation to UV light, which constitutes only a small fraction of sunlight. Additionally, the rapid recombination of electron-hole pairs and the limited absorption of visible light hinder their photocatalytic activity. A successful strategy to overcome these limitations is the formation of nanocomposites with carbon nanostructures, which enhances their photocatalytic performance in the visible light spectrum[1,2].

Carbon Quantum Dots (CQDs) have emerged as a significant class of quantum dots owing to their unique characteristics and eco-friendly nature. Typically less than 10 nm in size, CQDs are known for their strong photoluminescence (PL) properties. They offer advantages such as water solubility, low toxicity, chemical stability, and easy surface modification, making them highly useful in fields such as biomedical research, targeted drug delivery, and therapeutic applications[3]. Incorporating nitrogen into CQDs enhances their electrical properties due to charge imbalance and electron distribution resulting from the differing electronegativities of the constituent elements[4].

Herein, we report the synthesis and characterization of nitrogen-doped carbon quantum dots and the creation of nanocomposites with TiO_2 in different ratios (5% and 50%). The photocatalytic activity of the nanocomposites was tested for the degradation of Methylene Blue (MB) under a visible light source (LED lamps, 20 W) and for hydrogen production under full light spectrum radiation (Xe lamp, 300 W).

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Association of the Oxazine Azo Dye C.I. Basic Blue 3 with Humates

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The textile processing industry is the second largest consumer of water, following agriculture. The disposal of textile effluents and organic waste into land and water systems facilitates the movement of synthetic dyes through agricultural soils. Azo dyes, in particular, reduce microbial populations and decrease enzyme activity, richness, and diversity, negatively impacting soil environment and hindering plant growth; additionally, they can enter the food chain. When textile dyes are released into water bodies, they alter their color, causing aesthetic damage, and reducing photosynthesis and dissolved oxygen levels, further harming aquatic life.

Humic substances (HS) play a crucial role in ecosystems as a significant reservoir of recalcitrant organic carbon and nitrogen. They have a beneficial impact on soil structure and properties; they support physiological and metabolic processes in plants acting as growth promoters, biostimulants, and stress relievers. Due to their diverse surface functionality, HS can associate with a wide range of inorganic and organic substances, including metal ions, soil minerals, oxides, hydroxides, and xenobiotics, through complexation and chelation. This ability enhances nutrient bioavailability by binding HS to immobile nutrients, while chelation with toxic metals and persistent hydrophobic organic contaminants reduces their toxicity.

C.I. Basic Blue 3 (C.I. 51004) is a chloride salt commonly used for coloring paper and dyeing polyacrylonitrile fibers. The interactions between this cationic dye and three humate salts, each containing different levels of humic acid, were studied using spectroscopic techniques. All humates demonstrated high adsorption efficiency (~1 g dye/g HS). Factors influencing the adsorption were also evaluated. Several adsorption models were applied to the experimental data.

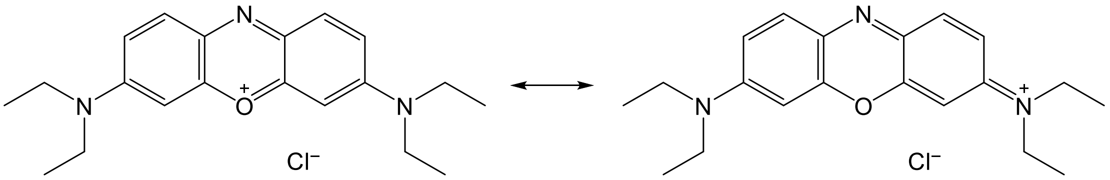

Figure 1: Structural formulae of C.I. Basic Blue 3.

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POLYUREA-CROSSLINKED ALGINATE AEROGELS WITH ANTIBACTERIAL PROPERTIES

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Alginate aerogels are among the most well-studied biopolymer-based aerogels. Their preparation is simple, inexpensive and environmentally friendly, and they can incorporate several metal cations. Therefore, they have found several applications, including a wide range of biomedical applications. The main disadvantage of alginate aerogels is that they are mechanically weak. This has been rectified recently, by applying the X-aerogel technology, initially developed for silica and other inorganic aerogels, in order to prepare polyurea-crosslinked alginate (X-alginate) aerogels [1-3], via reaction of a preformed alginate network with a triisocyanate that was introduced, post-gelation, to the pores of the wet gel *via* diffusion. Crosslinking with polyurea has proven to be an efficient way to increase the mechanical stability and hydrophobicity of alginate aerogels, improving therefore their application potential. For example, X-Ca-alginate aerogels (Ca-alginate crosslinked with polyurea derived from aliphatic triisocyanate Desmodur N3300) have been found suitable for implants in tissues [4]. In the present study, the potential antibacterial activity of X-M-alginate (M: Cu, Ag, Zn) aerogels has been studied against pathogenic microorganisms, such as *Staphylococcus aureus*.

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Application of Response Surface Methodology for the optimization of natural compounds' extraction from pomegranate seed oil using acoustic cavitation technology

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Natural compounds play a significant role in the organoleptic and nutritional features of fruits with polyphenols, fatty acids, carotenoids and vitamins being mostly abundant, not only in the edible, but also in the non-edible parts. Especially pomegranate and its by-products – including its seed oil (PSO), albedo and peels - have gained a lot of attention because of their health promoting role, linked to these compounds[1,2]. To recover them from fruit products, different extraction techniques, mostly conventional such as Soxhlet, maceration, percolation etc., have been implemented. However recently, "green" technologies, that consider environmental and economic protection have been proposed, with acoustic cavitation being one of them. In our study, we evaluated the effect of different extraction parameters, such as the extraction solvent (EtOH-H_2O ratio), extraction time and solvent-to-solid ratio, to the responses of PSO' yield and total phenolic content by using response surface methodology (RSM), by utilizing an ultrasonic bath. The optimum variables were later used to extract PSO which was characterized for its phenolic, flavonoid, and tannin content, as well as for its antioxidant activity. Additionally, LC-QTOF-MS and GC-FID were used to detect and quantify phenolic compounds and fatty acids. Response surface methodology identified that a 1/57 solvent-to-solid ratio, a 49/51 EtOH-H_2O concentration and an extraction time of 94 minutes, were the optimum variables for achieving highest yield (21.14%) and TPC (7.41mg GAE/g oil) simultaneously. Additional experiments confirmed the effectiveness of the experimental design achieving a yield of 21.13 ± 0.96% and a TPC of 9.0 ± 0.59mg GAE/g oil. Results have shown that PSO exhibited high antiradical activity of 91.64%, flavonoid content of 1.18 ± 0.32 mg CE/g oil and tannin content of 6.51 ± 1.07 mg TT/g oil. Finally, several polyphenols and fatty acids were.detected through chromatographic analysis.

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Antifungal Efficacy of SiO_2@Ag/CeO_2 core-shell nanoparticles against *Aspergillus niger*.

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Fungi such as *Aspergillus niger*, produce harmful mycotoxins like ochratoxin A, which can cause serious health risks to humans, including nephrotoxicity and other kidney-related diseases [1]. Unfortunately, like bacteria, fungi have started to be more resistant to the existing antifungal agents, such as azoles, a strong antifungal agent [2]. Developing new antifungal agents has become a priority in the scientific community, with a particular focus on metal-based nanoparticles, including silver (Ag) and silica (SiO_2). Combining SiO_2, which is an excellent carrier material for metal nanoparticles, with Ag and CeO_2, enhances the stability of the nanoparticles and their antimicrobial properties [3]. In the current study, the antifungal efficacy of SiO_2@Ag/CeO_2 core-shell nanoparticles were examined against *A. niger*. A screening method based on agar diffusion binary responses was applied to identify the minimum inhibitory concentration (MIC) of the nanoparticles against *A. niger* which was then validated using optical density (OD at 600 nm) measurements. Core-shell nanoparticles of SiO_2@Ag/CeO_2, demonstrated antifungal activity at concentrations of AgNPs and CeO_2 equal to 0.03 mM and 0.3 mM, respectively. However, comparing SiO_2@Ag/CeO_2 with SiO_2@Ag core-shell nanoparticles, reveals that *A. niger* was inhibited similarly, with a minimal difference in the effective concentration of 0.05 µL/mL. Additionally, the presence of CeO_2 appeared to stabilize the SiO_2@Ag core-shell nanoparticles, as was indicated by the lack of colour change after 6 days of incubation at 25°C, whereas the SiO_2@Ag nanoparticles without CeO_2 and AgNPs became noticeably darker over the same period and temperature. Validation of these observations with OD600, resulted in identifying the MIC of CeO_2, AgNPs, SiO_2@Ag, and SiO_2@Ag/CeO_2 at 0.5 mM, 0.11 mM, 0.07 mM, and 0.1mM, respectively. Overall, it can be concluded that core-shell nanoparticles have good stability properties and are effective antifungal agents.

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Multi-mycotoxin detection in dried and fresh fruits

Occurrence of mycotoxins in food commodities in the Greek market

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Mycotoxins are gaining global attention due to their frequent contamination of food supplies and serious health risks to humans and animals. Fruits, with their high sugar and moisture content, are particularly vulnerable to spoilage fungi, especially during pre- and post-harvest phases, which increases mycotoxin production potential.[1] While European legislation regulates established mycotoxins like aflatoxins (AFs) and Ochratoxin A (OTA) in dried fruits, information on *Alternaria* and *Fusarium* mycotoxins in fresh and dried fruits is limited, classifying them as emerging threats.[2,3] Their rising incidence underscores the need for more sensitive methods for multi-mycotoxin detection. The purpose of this work was to develop a reliable and rapid method for the simultaneous determination of 13 mycotoxins (AFB1, AFB2, AFG1, AFG2, OTA, Alternariol (AOH), Alternariol methyl ether (AME), Zearalenone (ZON), Deoxynivalenol, Fumonisin B1, Fumonisin B2, T2-toxin, HT-2 toxin) and to study their occurrence in 18 dry and 3 fresh fruits in the Greek market, followed by UHPLC–(ESI)MS/MS analysis. Comparison of two sample preparation methods (QuEChERS and Immunoaffinity Columns, IAC), was carried out and the most suitable and efficient one was chosen for the extraction of each mycotoxin. QuEChERS was used for the determination of AME, AOH, HT-2, ZON and DON while IAC was used for the determination of AFs, OTA, T-2, Fumonisins and DON. The results indicated that AOH, HT-2, ZON and DON were absent (<LOD) in both dried and fresh fruits while AME was detected in 3 samples at very low concentrations (0.02-0.08 ng/g). No AFs were detected in fresh fruits but they were detected in 3/18 of dry fruit samples at concentrations 0.03-1.06 ng/g and OTA was detected in half of the investigated samples at concentrations 0.06-0.79 ng/g. None of the mycotoxins investigated in both substrates were found above the legislative limits (MRL); instead, they were 0.5 to 40 times below the legal threshold.

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Investigation of the presence of zearalenone and fumonisin in cereals from the Greek market applying rapid immunological detection methods (ELISA)

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The purpose of this study was to investigate the presence of two mycotoxins, fumonisin (FUM) and zearalenone (ZEN), produced by *Fusarium* spp., in cereals and cereal products, seeds, and herbs intended for human consumption or animal feed. In total, 34 samples were collected from Greek retail markets including oat, wheat, rice bran, maize, barley, and hops. The analysis was performed using a validated indirect competitive enzyme-linked immunosorbent assay (ELISA). The method had a limit of detection of 5 μg/kg and a limit of quantification of 10 μg/kg for zearalenone while the respective values for fumonisin were 0.015 and 0.05 mg/kg.

Of the 34 samples tested, 31 were found to be contaminated with ZEN. The three samples that tested negative for ZEN (< 10 μg/kg), were a raw barley sample and two different varieties of barley malt used in beer production. Maize had the highest average ZEN level (682.98±401.80 μg/kg), followed by oats, rice, wheat, and malt. A significant amount of ZEN was detected in the different varieties of hops (407.33±182.21 μg/kg). Two samples of maize intended for human consumption and two samples of maize flour exceeded the EU legal limits (350 μg/kg for raw maize and 75 μg/kg for processed cereals) and were deemed unfit for human consumption.

The results for FUM showed that the mycotoxin was absent in several cereal samples, including oat, malts, wheat flour, sunflower seeds, wheat pellets, soft wheat, durum wheat, rice, and barley. A total of 14 samples tested positive for FUM, with levels ranging from 0.05±0.03 mg/kg in oat flour to 10.46±1.14 mg/kg in maize kernels. Other positive samples included maize flour (5.76±0.54 mg/kg), all tested hops (max. 3.42±0.96 mg/kg), and rice bran (max. 0.12±0.01 mg/kg). It is noteworthy that no studies were found specifically investigating fumonisin levels in hops. The detection of fumonisins in all tested hops samples highlights a potential area for further research, as the presence of these mycotoxins in this commodity has not been extensively explored. The investigation of these mycotoxins in a wider range of cereal crops and conditions will help ascertain the impact of weather variability, in view of the emerging climate crisis.

The present work was supported by FunShield4Med project financed from the European Union's Horizon Europe Research and Innovation Programme (Grant Agreement 101079173).

Effect of wood alternatives origin and size on the chemical composition and aging of tsipouro.

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Abstract

Tsipouro, a traditional Greek spirit made from grape marc, is typically consumed as a clear, unaged distillate. However, aging practices using oak barrels have introduced "aged tsipouro," which offers a distinctive aromatic profile from both varietal and wood-derived aromas. In response to growing consumer demand for innovative spirits, alternative aging methods using wood fragments, such as oak toasted chips, has gained attention [1]. This study aimed to investigate the impact of different wood fragment sizes (thin wood sheets, dominoes and sticks) from American oak (AO), French oak (FO), Greek oak (GO), and Greek chestnut (GC) on tsipouro aging. While extensive research has examined the influence of oak chips on various beverages like wines, beers, whiskies, and brandies [2], there is limited knowledge on their application in tsipouro maturation. Gas Chromatography–Mass Spectrometry (GC-MS) was used to analyze extracts from tsipouro aged with these wood fragments. Our findings revealed that syringaldehyde, vanillin, acetovanillone, and guaiacol were present in all samples, irrespective of wood species or dimensions. Among these, syringaldehyde consistently exhibiting the highest concentrations, ranging from 12.18 mg/L in FO thin wood sheets to 1.68 mg/L in GC dominoes. FO thin wood sheets yielded the highest extraction efficiency, followed by sticks and dominoes, while sticks were more effective for AO. Similarly, sticks were optimal for GC, while dominoes were more effective for GO. It is noteworthy that GO exhibited satisfactory performance compared to AO and FO, irrespective of fragment size. Moreover, although chestnut wood produced fewer compounds, it was still considered suitable for tsipouro aging. In general, the findings contribute to a deeper understanding of how wood type and fragment size affect the physicochemical and organoleptic properties of tsipouro, offering insights into potential advancements in the production of this traditional spirit.

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Assessment of Ochratoxin A levels in Thessalian wines and evaluation of consumer exposure

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Abstract

Wine has been a key part of human culture for nearly 10,000 years and is still widely consumed. While moderate consumption offers health benefits, it may also contain harmful substances, such as ochratoxin A (OTA). OTA, a mycotoxin produced by fungi like *Aspergillus carbonarius* and *Penicillium verrucosum,* is commonly found in wines, from Mediterranean regions [1]. It is classified as a Group 2B carcinogen by the International Agency for Research on Cancer (IARC), posing potential cancer risks. The European Food Safety Authority (EFSA) has set a tolerable weekly intake (TWI) of 120 ng OTA/kg body weight [2]. This study aimed to evaluate OTA contamination in wines from Thessaly, Central Greece, using 100 samples from both Greek and international grape varieties. OTA levels were determined using the enzyme-linked immunosorbent assay method (ELISA kit), known for its cost-effectiveness, speed, and sensitivity, making it an innovative tool for rapid in situ assessment in wineries. The results revealed that 7% of the wine samples were contaminated with OTA, with concentrations ranging from 0.78 to 1.95 μg/L. The microclimate of specific regions in Thessaly appears to influence OTA presence, highlighting the need for ongoing surveillance of OTA levels in wine. Importantly, only 1% of the samples exceeded the regulatory limit of 2 μg/L. Based on OTA occurrence and wine consumption patterns, consumer exposure was considered negligible. The study underscores the importance of effective vineyard management and winemaking practices to minimize OTA contamination and safeguard public health.

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NON INTENTIONALLY AND INTENTIONALLY ADDED SUBSTANCES SCREENING TESTS IN FOOD CONTACT MATERIALS

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Abstract

Foods, before their final consumption, come into contact with many materials and objects during their production, processing, storage, preparation and supply, which are called "food contact materials" and may be made of plastic, metal, paper or glass with or without the addition of other materials, e.g. adhesives, inks, coatings, in order to protect and / or improve the appearance of packaging materials. More specifically, in the production of materials and objects in contact with food, intentionally added substances (IAS) are used, which help to improve the properties of the material. However, in addition to these substances that are intentionally added, food contact materials also contain NIAS (Non Intentionally Added Substances), such as impurities and contaminants in raw materials, as well as by-products in the production process. Materials can transfer their components (IAS and NIAS) to food through the migration phenomenon, with the potential for high exposure to certain substances, which may be harmful to human health. Tsakalidis Analysis & Testing, with a team of specialized and experienced scientists, supported by the appropriate modern equipment, has developed methods of non-targeted screening tests in order to check the migration of both IAS and especially NIAS. A private library has been set up for NIAS with spectra of identified substances and at the same time the risk of exposure to them is being assessed and evaluated. This paper presents a mapping of packaging materials related to the identification and risk assessment of IAS and NIAS that have been analyzed in the last decade in Tsakalidis Analysis & Testing laboratories.

Keywords: NIAS, IAS, migration, food contact materials

Title: Assessing the antifungal resistance of silver nanoparticles against *Aspergillus niger* isogenic mutants

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Nanotechnology is currently one of the most expansive fields of research, with diverse applications across various disciplines (He & Hwang, 2016). In the field of food microbiology, metal nanoparticles, particularly silver nanoparticles, are predominantly employed to inhibit the development of microorganisms within different systems (Li et al., 2017). This study investigates the antifungal effects of silver nanoparticles on six *Aspergillus niger* mutants. The mutants, N402, TLF39, TLF93, TLF95, TLF96, MA2.34, were exposed to varying concentrations of silver nanoparticles, and comparisons were drawn based on the presence or absence of specific genes (van Leeuwe et al., 2020). The diameter of the fungal mycelium was measured every 12 hours until the entire Petri dish of the control was colonized, about 7-10 days. The slope of the mycelium diameter increase over time was used to determine the growth rate (Sardella et al., 2017, 2019). Additionally, this research placed significant emphasis on evaluating the "work to be done", which refers to the amount of work that a cell has to perform to adapt to new environment of the silver nanoparticles (Ag NPs)(Swinnen et al., 2004). Notably, among the six studied mutants, the TLF95, which exhibits the most extensive gene deletions (ΔkusA::DR-amdS-DR, ΔagsA, ΔagsE) (van Leeuwe et al., 2020) affecting the fungal cell wall, demonstrated the highest "work to be done," whereas the wild-type strain N402 exhibited the lowest. To conclude, the antifungal effects of silver nanoparticles on *Aspergillus niger* mutants are influenced by their genetic composition, with TLF95 showing the highest adaptation effort and N402 the least. Gene deletions, particularly affecting the cell wall, play a key role in nanoparticle susceptibility.

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Electronic structure of the MoLi, MoBe, and RuB molecules: Ground and Low-Lying States

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Transition metal compounds play significant role in many research fields such as Organometallic Chemistry, Catalysis, Surface Science and Astrophysics.[2] The accurate theoretical description of these molecules is a demanding task, because of their computational complexity due to their high density of states and the high space-spin angular momentum of the transition metal atom. As a result, the understanding of the chemical bond between a transition metal element and a main group element is not an easy task.[2]

In the present work, the electronic structure of three diatomic molecules, i.e., MoLi, MoBe, and RuB have been studied employing accurate ab initio methodologies. The complete active space self-consistent field (CASSCF) and the multireference configuration interaction plus single and double excitations (MRCISD) methodologies in conjunction with the aug-cc-pV5Z(-PP) basis sets have been used. The dissociation energies, bond lengths, dipole moments and usual spectroscopic data have been calculated for all studied states. Their potential energy curves of all low-lying electronic states have been plotted. Finally, their bonding has been analyzed. MoBe presents specific interest due to the type of bonds that form the Be atom, while the ground state of the RuB presents a quadruple bond.

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Clustering Studies in Peripheral Collisions between Heavy Nuclei

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Fermionic systems may occur in a crystalline phase or exhibit quantum liquid properties [1]. However, finite nuclei transiently behave as clusters of protons and neutrons. At present, there is a strong interest in clustering phenomena, both experimental and theoretical [2]. While the origin of nuclear clustering is deeply connected with the effective nuclear interaction, the detailed mechanism of clustering remains elusive.

In this work, we studied the momentum distributions of projectile-like fragments from the reaction of an ^{40}Ar beam with a ^{64}Ni target at 15 MeV/nucleon, using experimental data obtained by our group with the MARS spectrometer at the Cyclotron Institute of Texas A&M University [3,4]. Here, we focused our attention to the products that correspond to the removal of an alpha particle cluster, ^{4}He.

As a first step, we compared the experimental momentum distributions with calculations performed with the Deep Inelastic Transfer model (DIT) [5] and the Constrained Molecular Dynamics model (CoMD) [6] followed by the de-excitation code GEMINI [7]. Further on, using the primary results of the CoMD calculations, an attempt was made to count the alpha-particles ejected during the reaction and the projectile-like and target-like nuclei that may have resulted from alpha particle pickup or removal. We observed that some of the parameters that we varied in the CoMD calculations, namely enhancement of the Pauli constraint, as well as the nuclear compressibility, have a significant effect on the calculated distributions and provide a rather good description of the cluster breakup and/or transfer.

We think that peripheral collisions of heavy ions offer the proper conditions (i.e., gentle excitation of the reaction partners) so that clustering may develop, and cluster transfer may be favored. We therefore believe that further studies will deepen our understanding of clustering in collisions in the Fermi energy regime (15-35 MeV/nucleon).

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Computational study of the copper-catalyzed α-alkylation of aryl acetonitriles with benzyl alcohols

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Considerable efforts have been made towards achieving step and atom economy in organic synthesis focusing on environmentally benign processes, through the use of abundant, low cost transition metals.[1-2] Recently, a highly efficient, in-situ formed $CuCl_2$/TMEDA catalytic system (TMEDA = N,N,N',N'-tetramethylethylene-diamine) for the cross-coupling reaction of aryl acetonitriles with benzyl alcohols was reported, where the use of a low catalyst loading and a catalytic amount of base leads to the synthesis of α-alkylated nitriles in up to 99% yield. A mechanistic pathway was proposed based on the experimental findings.[3]

In this presentation, the computational study of the copper-catalyzed α-alkylation of aryl acetonitriles with benzyl alcohols is presented. DFT methodology was employed to study the Cu-catalytic reaction mechanism. The computational study investigates possible reaction steps proposed for the formation of the aldehyde from the corresponding alcohol. A variety of different Cu^{II} complexes were used, and the preferred reaction pathway has energy barriers of up to 24 kcal/mol. The homolytic cleavage of the $C(sp^3)$–H bond of the benzyl alcohol is favored energetically, and the release of H_2 is very likely to occur. DFT calculations provide further insight in the experimental data, confirming the proposed, unprecedented reaction mode for this transformation.[3]

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Probing the Production of Neutron-Rich Nuclei Towards the r-Process Path via Multinucleon Transfer Reactions

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The production and study of nuclides at the extremes of nuclear stability toward the neutron dripline have become a central focus in the nuclear physics community to understand various astrophysical processes, most notably the rapid neutron capture process (r-process), which plays a significant role in the production of half of the abundance of nuclides heavier than iron [1]. Along the lines of these studies, we investigated medium-mass heavy-ion reactions at energies of 15–25 MeV/nucleon to access nuclides with high neutron excess [2,3].

In this contribution, we present experimental data from two representative reactions analyzed using different spectrometers. Specifically, we studied the reaction of ^{70}Zn (15 MeV/nucleon) + ^{64}Ni with the use of the MAGNEX large-acceptance spectrometer at the INFN-LNS in Catania, Italy, as well as the reaction of ^{86}Kr (15 MeV/nucleon) + ^{64}Ni by employing the MARS spectrometer at Texas A&M University, USA. The experimental data were compared with theoretical model calculations.

Through this parallel contrast of the results from both reaction systems, we aim to gain insights into the optimum experimental conditions that may enhance our understanding of exotic nuclei production, ultimately contributing to a deeper exploration of nucleosynthesis processes, particularly those associated with the rapid neutron capture (r-process) pathway.

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Photophysical properties of Donor-Acceptor (D-A) fluorescent sensors

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Organic donor-acceptor (D-A) molecules possess a common motif with both an electron-donating and electron-withdrawing group separated by a conjugated π system. Such D-A type molecules are widely employed in the fields of chemical and biological sciences, providing unique metal-free control over their reactivity and behavior with low-energy, visible light.[1]

Fluorescent dyes based on the BODIPY core have been the focus of intensive research because of their interesting photophysical properties.[2-5] Depending on the specific chemical environment and how it is used, it can exhibit characteristics of both donors and acceptors. Important photophysical characteristics of BODIPY include high fluorescence quantum yields, narrow absorption and emission bands, good solubility in a variety of solvents, high photochemical stability and relatively good biological uptake.[2-5]

In this presentation, a series of D-A molecules as well as fluorescent sensors based on BODIPY are studied via DFT methodology. Their photophysical properties are analyzed and their potential as molecular logic gates is investigated. Theoretically, the effect of the used methodology on accurate results is investigated.

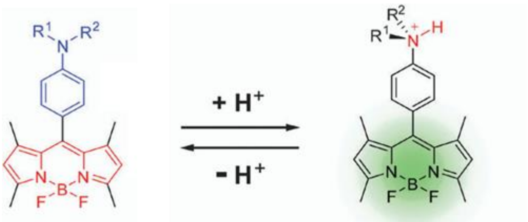

Figure 1. Bodipy Derivative.

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A MOLECULAR DYNAMICS SIMULATION METHOD FOR THE REPRODUCTION OF THE MOTION OF FLEXIBLE MACROMOLECULES IN ION MOBILITY SPECTROMETRY

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In the present study, using a Nonequilibrium Molecular Dynamics Simulation method [1], we study the effect of the temperature on the structure of flexible macromolecules in inert gases under the influence of an electric field. Specifically, we examine the behavior of the vibrational motion and transport phenomena of flexible molecules at various temperatures and field strengths that apply ion mobility spectrometry. Because experimentally it appears that the flexible peptides have different structures at low and high temperatures [2], the question was raised whether a single intermolecular potential is sufficient to describe the appearance of the structures at all temperatures or the temperature is modifying permanently the structures, thus requiring the consideration of two or more potentials for the description of the motion.

We have calculated the average velocity and the cross sections of the ions in the gas, as well as other molecular properties. We observed that, although one ion-atom intramolecular potential can describe well the transport through the drift tube, the use of two different potentials for the vibration of the peptides reproduces the experimental results much better.

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Carbenes to tune 2D metal organic frameworks

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Two-dimensional metal-organic frameworks (2D MOFs) have emerged as highly tunable materials with promising applications in catalysis, electronics, and nanotechnology.[1] However, controlling their surface properties through functionalization remains a significant challenge. We will present a strategy for the use of N-heterocyclic carbenes (NHCs) to fine-tune the electronic properties of 2D MOFs. While NHCs are widely studied for their role in catalytic metal surface functionalization for medical and luminescent applications, their integration into solid-state materials like MOFs remains underexplored.[2] Based on recent findings that demonstrate the reversible binding of prototypical NHCs to surface single-atom sites in a square planar coordination environment,[3] we propose to use the electron-donating capabilities of different NHC ligands as dopants of 2D-MOFs. In particular, we propose NHCs of varying electron-donating character in order to exemplary modulate the band structure and work function of a 2D MOF, namely of the semiconducting single layer $Cu_3(C_6O_6)$ on Cu(111) (figure 1).[4] A suitable experimental investigation under ultra-high vacuum (UHV) conditions to ensure atomically precise surfaces will be outlined. The structural and thermal stability of NHC-functionalized MOFs will be characterized using temperature-dependent scanning tunneling microscopy, while the band structure and work function will be evaluated through scanning tunneling spectroscopy and Kelvin-probe force microscopy. The outcomes of this research will provide critical insights into the design of flexible nanomaterials with optimized surface and electronic properties, offering broad implications for future applications in catalysis, electronics, and nanotechnology.

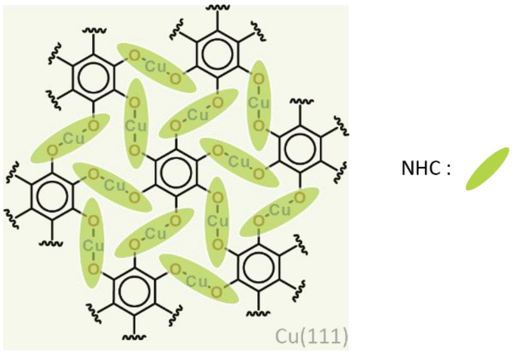

Figure 1. 2D MOF $Cu_3(C_6O_6)$ on Cu(111) functionalized with NHCs bonded to the MOF Cu atoms.

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Properties of projectile-like fragments from peripheral nuclear collisions of ^{86}Kr (25 MeV/nucleon) on ^{208}Pb

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Multinucleon transfer in peripheral reactions is of great interest to the nuclear physics community as it is a useful tool to produce neutron-rich nuclei. Notably, neutron-rich nuclei from Fe (Z=26) and above take part in the astrophysical rapid neutron capture process (known as r-process) which is mainly responsible for the production of elements above iron[1].

In this work, we studied the mass and momentum distributions of projectile-like fragments from the reaction of an ^{86}Kr beam with a ^{208}Pb target at 25 MeV/nucleon. The experimental data were obtained in previous works of our group [2] with the MARS spectrometer at the Cyclotron Institute of Texas A&M University.

Experimental mass and momentum distributions of the fragments were compared with calculations performed with the Deep Inelastic Transfer model (DIT) [3] and the Constrained Molecular Dynamics model (CoMD) [4] followed by the de-excitation code GEMINI [5]. We included in our distributions the primary excited projectile-like fragments calculated from the theoretical models. Our calculations provided an overall satisfactory description of the experimental distributions, indicating also directions for possible improvements.

We think that the systematic study of the yields and momentum distributions of the products from peripheral heavy-ion collisions can provide valuable information regarding the mechanisms of nuclear reactions in the Fermi energy regime (15-35 MeV/nucleon). This, in turn, can give guidance to the production and study of neutron-rich nuclides participating in the r-process nucleosynthesis.

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The solvent and nitrogen geometry effect on the absorption spectra of a ferrocene-naphthalimide derivative

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The ability of molecules to process information similar to electronic systems was proposed in 1993. [1] Molecules respond to changes in their environment resulting in alteration of the absorption spectra. [2] These types of molecules are designed according to the principles of photoinduced electron transfer systems. Recently, we studied theoretically the photophysical properties of a 3-input AND molecular logic gate (MLG) [3], which had been synthesized by Magri et al. [4], and presented an enhanced fluorescence spectrum. The fluorophore is the 4-amino-1,8-naphthalimide, the terminal fragment is a piperazine unit which easily is protonated and acts as a proton receptor and a crown ether group. Here, we are focusing on the truncated molecule of this 3-input AND MLG, without the crown ether. The inclusion of two different solvents explicitly and implicitly was studied via DFT/TD-DFT calculations. The N atom of piperazine towards ferrocene presents a crucial role, and its geometry affects the absorption spectrum of the molecule. The effect of the geometry of the N was studied.

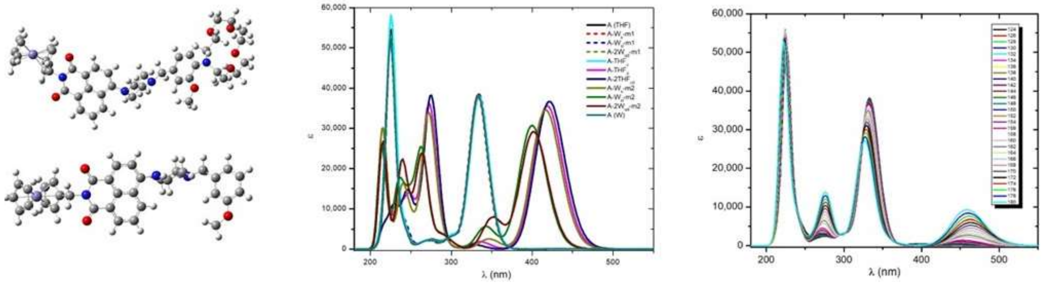

Figure 1: Calculated minimum structure of the initial *(top left)* and truncated MLG *(bottom left),* absorption spectrum in THF and water *(middle)* and absorption spectrum of the structure upon changing N dihedral angles in THF at PBE0/6-31G(d,p) *(right)*.

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Synthesis and characterization of hybrid cadmium compounds exhibiting intense fluorescence

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In recent years, considerable research has been carried out on hybrid compounds of halogenated metals that exhibit a structure similar to perovskites. The design of these compounds provides the possibility to combine organic and inorganic elements at the molecular level to prepare materials with excellent desirable properties [1]. Such materials, mainly based on lead, have been used for the fabrication of photovoltaics, LEDs, photosensors and other devices. However, due to the instability and toxicity of these compounds as well as to broaden their potential applications, research was extended to similar materials with different metal.

Compounds of this type with cadmium have been little studied although they present interesting properties [2,3].

In this work we synthesized and characterized compounds of the AxCdX2+x type (A: benzylamine and X: Cl, Br,I). In order to achieve an increase in the fluorescence of these compounds we introduced structural defects by partial replacement of divalent Cd with trivalent Sb. Based on this methodology we prepared materials with intense and relatively broad fluorescence spectra.

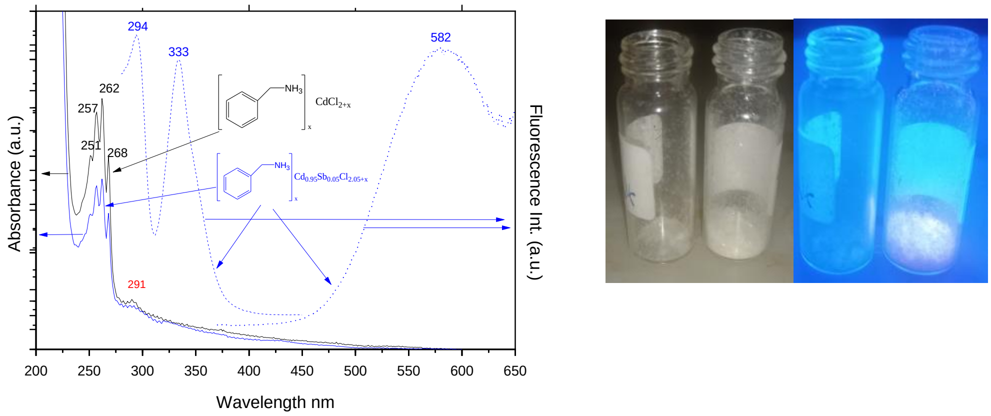

Figure 1: Absorption, fluorescence and excitation spectra (left) and photographs under normal light and under UV for the pure and the Cl. "doped" material (right)

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GENERATION AND STUDY OF A NOVEL DNA BASE LESION

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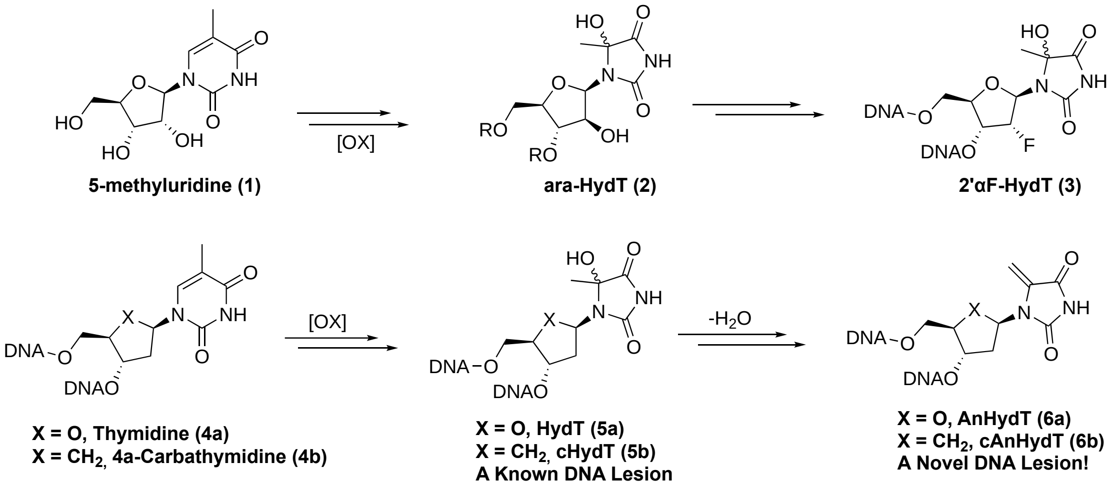
In aerobic organisms, oxidative stress occurs when the balance between Reactive Oxygen or Nitrogen Species (ROS/RNS) production and antioxidant defenses is severely disrupted. This imbalance may lead to DNA damage through the oxidation of nucleobases and sugar moieties in nucleotides. The main DNA base alteration repair mechanisms include Base Excision Repair (BER) and Nucleotide Excision Repair (NER), which may operate simultaneously on the same lesion.[1] Within our laboratory, research has been focused on the role of these mechanisms in cell function, with studies, utilizing synthetic nucleotides with oxidized bases, linked to the sugar through stable BER-resistant glycosidic bonds, that allow the study of NER processes.[2,3]



We present herein the synthesis of a BER-resistant derivative of 5-hydroxy-5-methylhydantoin (**3**), a DNA lesion derived from thymidine (**4a**) oxidation, together with the first observation of a previously unreported lesion which have been termed AnhydroHydantoin (AnHydT, **6a**). This lesion results from an unexpected dehydration of HydT (**5a**), leading to the formation of an exocyclic double bond. AnHydT displays an enhanced reactivity as a Michael acceptor. Details are provided on the isolation, characterization, and derivatization of both the carbacyclic and natural forms of the novel AnHydT lesion.

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DABCO-Catalyzed Synthesis of Thiazolidine-2-thiones: System Development and Mechanistic Insights

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The unique structure of propargylamines, encompassing a nucleophilic amine adjacent to an electrophilic alkyne moiety, renders them versatile building blocks for the preparation of numerous valuable organic structures and compounds of medicinal interest.[1-7] Among the plethora of synthetic strategies employing their derivatization, significant emphasis has been placed on their reactivity with heteroallenes, such as carbon dioxide, aiming at heterocycles featuring an exocyclic carbon-heteroatom bond.[8,9]

A base-catalyzed protocol for the construction of unprecedented 1,3-thiazolidine-2-thione scaffolds from carbon disulfide and α-tertiary propargylamines is reported. The reaction proceeds efficiently under ambient temperatures in the absence of solvent. The purification of the products is achieved without column chromatography. The reaction mechanism is also investigated experimentally.

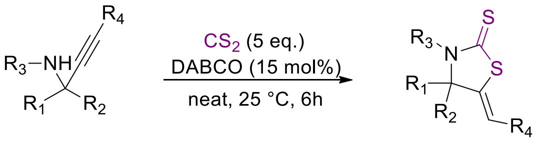

Figure: DABCO-catalyzed synthesis of thiazolidine-2-thiones from propargylamines and carbon disulfide.

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Synthesis and functionalization of step-growth polymers prepared by the A^3 multi-component coupling reaction

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Multicomponent reactions offer a streamlined method for synthesizing organic compounds in a one-pot manner. The A^3 or KA^2 coupling of aldehydes or ketones with amines and alkynes is an efficient route to propargylamines, compounds with diverse chemical properties.[1] Extending this strategy to polymer synthesis enables the production of polymers with varied properties and applications. This study presents a sustainable, air-tolerant approach for synthesizing novel polymeric propargylamines using a highly-reactive, widely available copper catalyst, yielding excellent results.[2] The post-functionalization of polymers is vital for developing functional materials. Our work further explores two post-functionalization strategies of A^3 polymeric propargylamines to create poly-electrolytes and diverse polymeric structures with unique physical and chemical characteristics.[3]

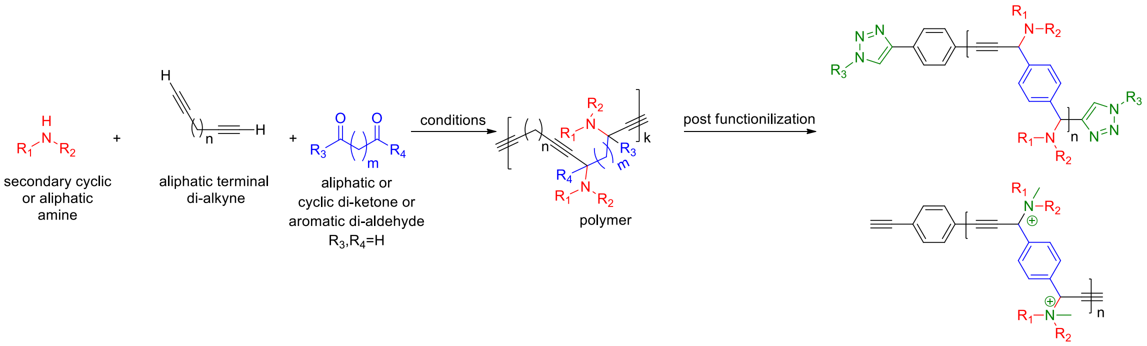

Figure: Step-growth polymerization reaction and post functionalization strategies.

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The research project was supported by the Hellenic Foundation for Research and Innovation (H.F.R.I.) under the "1st Call for H.F.R.I. Research Projects to support Faculty Members & Researchers and the procurement of high-cost research equipment grant" (Project Number: 16).

ΕΛ.Ι.Δ.Ε.Κ.
Ελληνικό Ίδρυμα Έρευνας & Καινοτομίας

Studies Towards the Synthesis of Natural Products Ornosol and Insularoside

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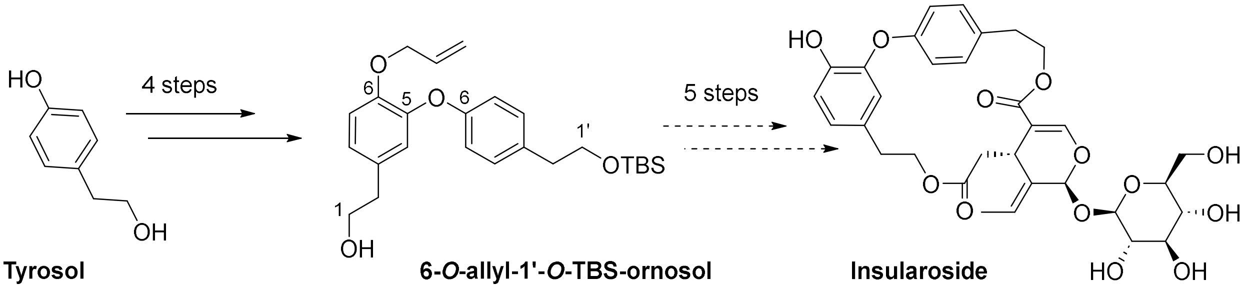
Insularoside and ornosol are bioactive natural products isolated from the *Fraxinus* species.[1] Specifically, insularoside, also known as ornoside, a secoiridoid glucoside from the leaves of *Fraxinus insularis*, was identified as an oleoside-type glucoside containing ornosol, a dimeric tyrosol derivative, isolated from the bark of *Fraxinus ornus*.[1] Naturally occurring ornosol forms a macrocyclic lactone, linked via ester bonds to an oleoside moiety (Scheme).[2] Both natural products are known for their antioxidant and anti-inflammatory properties and contribute to the *Fraxinus* bioactive constituents. Their role in drug discovery is underscored by the significance of natural compounds in developing effective therapeutic agents.[3,4]

We present herein our studies towards the synthesis of ornosol and insularoside, through a regioselective process constituted by three key steps. The commercially available natural product tyrosol (2-(4-hydroxyphenyl)ethanol) was successfully transformed in four steps to a protected derivative of ornosol, via a copper-catalyzed Ullmann reaction.[5] The elaboration of the insularoside skeleton involves a five-step sequence, including a selective esterification between the protected ornosol and the 7-carboxylate of a tetraacetyl derivative of oleoside. Oleoside is derived from oleuropein, itself isolated from olive leaves, in two steps. A key intramolecular macrolactonization reaction together with a series of deprotection reactions have been designed in order obtain the final natural product. The proposed methodology provides a strategic approach for synthesizing other natural products in the secoiridoid family that incorporate the tyrosol moiety.



Scheme 1. Key intermediates in the synthesis of insularoside.

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Investigating the interactions of a new set of quaternary propargylamine derivatives with monoamine oxidase enzymes.

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INTRODUCTION

MAO inhibitors (monoamine oxidase inhibitors) are crucial in treating neurodegenerative disorders. The aim of this study is the design of novel not terminal propargylamines using Molecular Docking and Dynamics and Toxicity studies.

MATERIALS AND METHODS

We synthesized a diverse group of quaternary propargylamines and assessed their inhibitory effects on both hMAO-A and hMAO-B enzymes, finding them to be notably effective. These compounds adhere to Lipinski's rule of five and show no predicted toxicity. Their binding interactions were explored through molecular docking, all-atom classical molecular dynamics (MD) simulations, and MM/GBSA binding free energy calculations. Overall, the propargylamines described in this study hold significant promise as potential treatments for conditions such as depression, Parkinson's disease, and Alzheimer's disease.

RESULTS

All synthetic propargylamines studied demonstrated sub-micromolar inhibition of both hMAO-A and hMAO-B through molecular docking. Molecular dynamics (MD) simulations revealed that compounds 4j and 4k had Root Mean Square Deviation (RMSD) fluctuations below 4 Å, indicating their stability and consistent binding with the target protein. These compounds also showed significant inhibitory activity, with IC50 values ranging from 765.6 to 861.6 nM for hMAO-A and 152.1 to 164.7 nM for hMAO-B. The Binding Free Energy analysis for compound 4k was calculated at -63.07±5.40 kcal/mol, suggesting a stronger binding affinity for hMAO-B compared to selegiline. MM/GBSA calculations indicated favorable binding for all compounds with both hMAO-A and hMAO-B. Additionally, these propargylamines appear to have good intestinal absorption and comply with Lipinski's rules, showing no predicted toxicity.

CONCLUSIONS

These molecules hold significant promise for treating neurodegenerative diseases. This is the first instance where a propargylamine scaffold with an internal alkyne, as opposed to a terminal one, has demonstrated such biological activity. New compounds are currently under evaluation, and the most effective ones will undergo in vivo testing to further assess their potential benefits.

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Synthesis of Carbasugar Derivatives as Potential Inhibitors of Glycogen Phosphorylase

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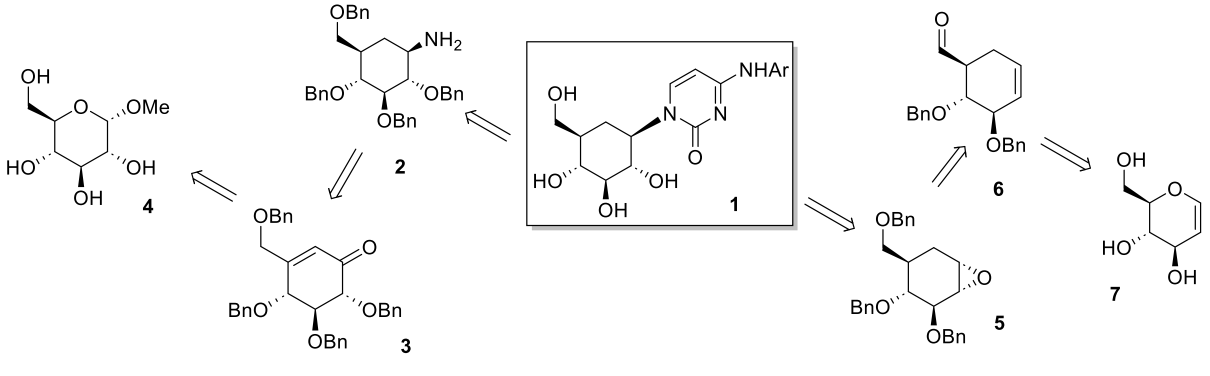
Glycogen phosphorylase (GP) is a key regulatory enzyme involved in maintaining glucose homeostasis by catalyzing the breakdown of stored glycogen in the body. Inhibition of GP presents a promising therapeutic strategy for the treatment of type II diabetes mellitus, as well as other pathological conditions, including cancer. In our laboratory, several N^4-aryl-N^1-(β-D-glucopyranosyl)cytidines, potent nM inhibitors of GP have been synthesized and studied in recent years.[1] The primary objective of the current study is to synthesize 5a-carbasugar analogs (**1, Scheme**) of the above strong inhibitors, that target specifically the enzyme's catalytic center, with desirable pharmacokinetic profiles, including smooth transport across the cell membrane, that would enhance inhibitory potency *in vivo.*

Initially, 1-*O*-methoxy-glucose (**4**) served as the starting material, which after a series of transformations and a Swern-Horner-Wadsworth-Emmons reaction,[2] in the key step, led to **2**. The carbocyclic compound **3** was subsequently converted stereoselectively into amine **2**, through multiple steps, and was then coupled with uracil to yield, after a final three-step sequence, the desired inhibitors **1**. To enhance the synthetic process, we also explored an alternative route that involves fewer steps and a simplified intermediate handling. The process begins with D-glucal (**7**) and features a Claisen reaction,[3] as the pivotal step, converting the sugar into carbocyclic compound **6**. Later epoxidation to **5** followed by subsequent substitution with uracil is under study, in order to produce the same inhibitors in fewer steps and enhanced yields.



Scheme: The two retrosynthetic routes for the synthesis of carbocyclic GP inhibitors (**1**).

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β-Lactones and β-lactams: Design and synthesis of novel antimycobacterial compounds

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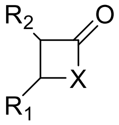
β-Lactones are potent serine hydrolase inhibitors which are important for the survival and proliferation of bacteria and mycobacteria, including Mycobacterium tuberculosis (*M.tb.*) that causes tuberculosis. Tuberculosis was the leading cause of death from a single infectious agent prior to the Covid-19 pandemic [1]. The most important β-lactone in the market is Xenical® or tetrahydrolipstatin that inhibits the activity of human digestive lipases and is prescribed against obesity.

Our group works on the design, synthesis and antimycobacterial study of β-lactones bearing an aliphatic carbon atom chain, saturated or unsaturated, at the α-position and a small propyl chain at the β-position [2]. In this work, we present novel β-lactones that bear a fluorine atom for the improvement of the activity and the pharmacokinetic properties, along with synthetic routes to their synthesis. Also, we present β-lactones that bear a terminal alkyne at the α-position that may be used as chemical probes for the identification of the target enzymes in mycobacteria. The synthesis of β-lactams based on the structure of the most promising β-lactones is also disclosed. Finally, a synthetic methodology for the synthesis of the most active β-lactones in optically pure form is discussed.



The chemical structure of α,β-disubstituted β-lactones (X=O) and
β-lactams (X=NH).

This research work was supported by the Special Account for Research Grants of the National and Kapodistrian University of Athens (SARG/NKUA) and the Centre National de la Recherche Scientifique (CNRS), Aix Marseille University.

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Synthesis of phosphinic pseudopeptidic inhibitors of M1 aminopeptidases using a late-stage diversification strategy

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M1 aminopeptidases ERAP1, ERAP2 and IRAP is a group of Zn-metallopeptidases that participate in several biological functions and are involved in human immune responses. Numerous recent studies have shown that these enzymes are important therapeutic targets which prompted the development of inhibitors [1]. Among these inhibitors, phosphinic pseudopeptides are particularly promising due to the high specificity for target enzymes, which derives from their weaker binding affinity to the Zn atom, as compared to other types of inhibitors, allowing a more significant contribution of secondary non-covalent interactions.

After the development of phosphinic pseudopeptide DG013A by our research group [1], a very potent but non-selective inhibitor of ERAPs/IRAP, further attempts towards the improvement of selectivity have been carried out following synthetic strategies that focus on the late-stage diversification of their P_1, P_1' and P_2' positions. Among these, synthetic tools targeting the P_1 position, which, according to studies, is believed to be crucial for selective inhibition of ERAP1, has been less studied compared to methodologies aiming at P_1' and P_2' positions. For this reason, we decided to investigate the synthesis of stereochemically defined phosphinic pseudopeptidic inhibitors suitable for late-stage diversification of P_1 position. In this presentation, the application of a synthetic protocol based on a facile oxidative Heck reaction, which afforded such pseudotripeptides functionalised at the P_1 position, is described [2].

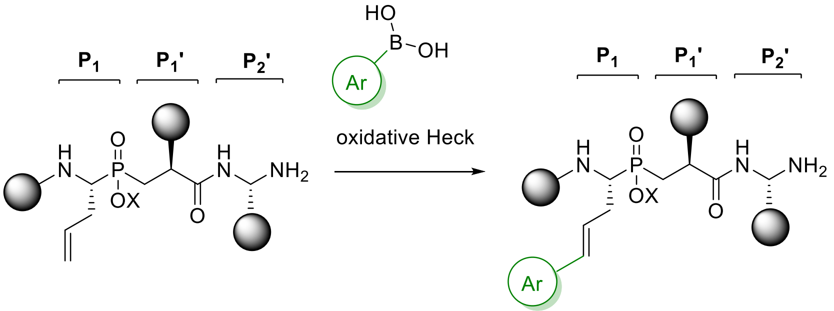

Figure 1: General structure of phosphinic pseudopeptidic substrates

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Halogen-Bonded Complexes (XBCs) in Solution: A Spectroscopic and DFT Study

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Halogen bonding (XB) refers to interactions of halogen atoms with electron-rich compounds, leading to the formation of XB complexes (XBCs).[1] Recently, XBCs have played a substantial role in inducing photochemical organic reactions.[2] In this work,[3] we study the formation of XBCs between tertiary amines and CBr_4 in solution, employing DFT, TDA-DFT (Tamm-Dancoff approximation), UV-Vis, and NMR studies, in order to understand the ability of XBCs generation. It is known that the formation of a XBC can be observed via UV-Vis spectroscopy by the appearance of a new band shifted to higher wavelengths, upon mixing the two components.[4] However, no systematic study of XBC generation between tertiary amines and CBr_4, using ^{13}C NMR spectroscopy has been conducted so far. ^{13}C NMR spectra of a solution of CBr_4 alone and the corresponding mixtures of CBr_4-amine were recorded, indicating clear shifts for the CBr_4 carbon atom. Additionally, ^{13}C NMR studies were performed in order to determine the association constant of some of the studied XBCs. Furthermore, DFT and TDA-DFT studies were performed in ACN to calculate the binding energies, the involved S_0 and T_1 states and their properties and their theoretical UV-Vis spectra. Lastly, DFT and UV-Vis studies were carried out for the case of DABCO with different halomethanes, in order to determine if CBr_4 is a better XB donor. The XBC generation concept was implemented for the light-mediated amide formation. According to the acquired results, all tertiary amines may form halogen bonds with CBr_4, however the properties of such a bond seem to vary.

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H.F.R.I.
Hellenic Foundation for Research & Innovation

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Modular Synthesis of Azines Bearing a Guanidine Core from *N*-Heterocyclic Carbene (NHC)-Derived Selenoureas and Diazo Reagents

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N-Heterocyclic carbene (NHC)-derived selenoureas comprise a fundamentally important class of NHC derivatives, with significant relevance in coordination chemistry and for probing the electronic properties of NHCs. Despite the extensive reactivity of chalcogen-containing compounds, the utilization of NHC-derived selenoureas as versatile organic building blocks has remained largely unexplored.

The present contribution introduces a novel, straightforward transformation leading to azines bearing a guanidine moiety, through the reaction of a wide range of NHC-derived selenoureas with commercially available diazo compounds, in the presence of triphenylphosphine. This transformation offers a new approach to such products, having biological, materials chemistry, and organic synthesis applications. The guanidine-bearing azines are obtained in excellent yields, with all manipulations taking place in air. A reaction mechanism is proposed, based on both experimental mechanistic findings and density functional theory (DFT) calculations.

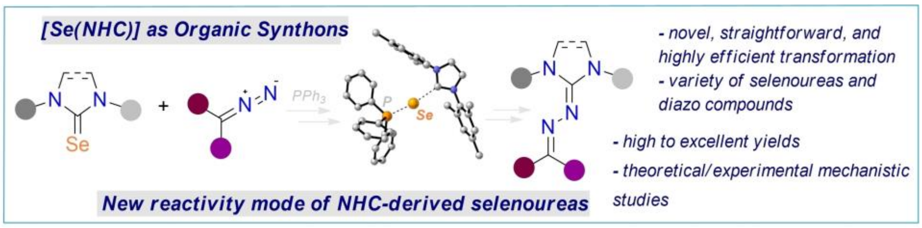

Figure: Synthesis of azines bearing a guanidine moiety.

Reference:

E. Tonis, N. V. Tzouras, N. Bracho Pozsoni, M. Saab, S. Bhandary, K. Van Hecke, D. J. Nelson, F. Nahra, S. P. Nolan, G. C. Vougioukalakis, *Chem. Eur. J.* **2024**, *30*, e202401816.

The research project was supported by the Hellenic Foundation for Research and Innovation (H.F.R.I.) under the "1st Call for H.F.R.I. Research Projects to support Faculty Members & Researchers and the procurement of high-cost research equipment grant" (Project Number: 16 – Acronym: SUSTAIN). The Research Foundation–Flanders (FWO) is acknowledged for a Fundamental Research PhD fellowship to NVT (11I6921 N) and research grant G0 A6823 N to SPN.

ΕΛ.Ι.Δ.Ε.Κ.
Ελληνικό Ίδρυμα Έρευνας & Καινοτομίας

Docking studies of drugs acting on Myasthenia Gravis

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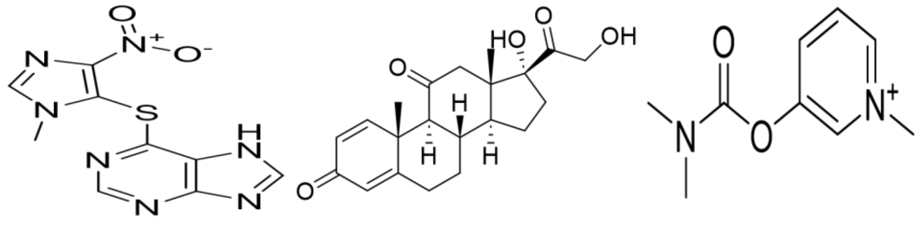
In the present study and evaluation of commercially available drugs acting as inhibitors of specific enzymes used to reduce the symptoms of Myasthenia Gravis was performed in order to evaluate their interaction and consequently their action with target protein molecules. Myasthenia Gravis is a chronic autoimmune disease for the treatment of which mainly drugs targeting acetylcholinesterase are administered. Computational chemistry programs based on Molecular Binding were used in the preparation of this thesis to evaluate the binding of pyridostigmine, azathioprine and prednisone to target proteins. Specifically, the binding of molecules in twelve classes of enzymes to a binding site of each enzyme was studied: Human acetylcholinesterase (4EY7), Human butyrylcholisterase (5DYW), Human adenosine A1 (5UEN), Cathepsin K (1YK8), Carbonic anhydrase (4XIX) , Dehydrogenase (3D4N), Thimidine kinase (4UXJ), Cannabinoid CB1 (5XR8), Sars-Cov-2 (6LU7), Alkaline phosphatase (1ALK), Carbonic anhydrase XII (1JD0), Carbonic anhydrase VII (6H37). Using two computer programs, the types of bonds developed during the interaction of the binding molecules with the protein of each receptor were visualized. Studies on the stability and molecular interactions developed during protein-binding interaction, Molecular Dynamics simulations on the compounds that gave the strongest bindings and spectroscopic studies to verify the validity of the results were performed.



a b c

Figure 1: The chemical structure of Azathioprine (a), Prednisone (b) and Pyridostigmine (c).

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"Synthesis of Star-Shaped Poly(n-hexyl isocyanate) Homopolymers via Coordination Polymerization and Core-First Methodology Using Multi-Functional (Half-)titanocene Alkoxy Complexes "

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In this work, the synthesis and characterization of star-shaped poly(n-hexyl isocyanate), PHIC, homopolymers with three, four, six, and eight arms are presented. The polymers were synthesized via the core-first methodology, utilizing tri-, tetra-, hexa-, and octa-functional (half-)titanocene alkoxy complexes as coordination polymerization multifunctional initiators. These complexes served as the cores, from which the PHIC chains were grown, leading to the formation of star-shaped structures with precise arm numbers.

A significant challenge in this work was the synthesis of the multi-functional (half-)titanocene alkoxy complexes, as severe solubility issues emerged between the ligands and the primary complex $[(\eta^5\text{-}C_5H_5)TiCl_3]$. Overcoming these solubility problems between these various ligands and the primary complex required extensive optimization of the experimental parameters, making the synthesis of the initiators particularly demanding.

The resulting star-shaped PHIC homopolymers were thoroughly characterized using various techniques. Size exclusion chromatography (SEC), was employed for the study of their molecular characteristics, NMR spectroscopy to verify their star-structure as well as the composition of the (half-)titanocene alkoxy complexes, thermogravimetric analysis (TGA) in order to study their thermal degradation behavior and stability. Additionally, viscosity measurements were performed to determine the intrinsic viscosity of the polymers. This information, in combination with the weight average molecular weight of the star homopolymers from static light scattering (SLS) measurements, provided valuable data leading to the calculation of the number of branches of the star-shaped polymers.

This study demonstrates the successful application of the core-first methodology using (half-)titanocene alkoxy complexes via coordination polymerization to synthesize well-defined star-shaped PHIC homopolymers, highlighting their potential for advanced materials with tunable properties.

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Deposition of fragrances on carriers with different physicochemical parameters

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Fragrances are usually liquid mixtures of volatile chemical compounds with different structures, which are characterized by a pleasant scent. As a result, they find a wide range of applications, especially in the cosmetics industry, where they are used in almost all types of cosmetic products, including perfumes, hand and body wash products, as well as skin and hair care formulations. However, fragrances have a relatively short shelf life due to the fact that their components exhibit high volatility and reactivity in the presence of light, heat, moisture, and oxygen. The widely accepted method for stabilizing fragrances is deposition in suitable carriers and encapsulation [1]. This allows easier handling of fragrances during formulation, as well as ensures controlled release of fragrance in finished products. Fragrance carriers can be inorganic, such as silica-based materials, as well as organic, with natural polymers, such as alginate, gelatin, or chitosan, and semi-synthetic or synthetic polymers.

Within the framework of the presented research, natural thyme (*Thymus vulgaris*) essential oil (TEO), which exhibits antioxidant and antimicrobial activity, which can be beneficial especially in cosmetic products for the aging or acne-prone skin [2], as well as a lemon flavor for flavoring foods, such as tea, were used. The carriers applied for the deposition of TEO and lemon flavor were mesoporous silica and alginate microcapsules. Deposition on the silica was carried out by liquid-phase adsorption, while the polymer capsules were prepared by ionic gelation, during which an emulsion consisting of alginate and a fragrance of appropriate concentration was dropped into a $CaCl_2$ solution at a specified rate. In the next stage of the study, the gradual release of the fragrances from the carriers into the water-alcohol environment at different pH values was tested, using UV-Vis spectroscopy and gas chromatography. The obtained release profiles indicate a clear effect of the pH of the environment and the type of carrier used on the rate of release of fragrances.

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Cross-Linking of PVA-Based Coatings for Antifouling Applications

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Under IMO regulations, antifouling materials for marine applications are deemed necessary for the protection of aquatic environments and for the reduction of fuel consumption in shipping. [1,2] Cross-linked poly(vinyl alcohol) (PVA) based films can offer antifouling properties due to its hydrophilicity, by creating a water barrier that can block protein physisorption deriving from intermolecular interactions.[3] In this study instead of standard cross-linking agents such as glutaraldehyde that might show toxicity when degraded [4], polyoxometalates (POM's), well known for their attractive redox properties, were investigated. Photo-patternable, PVA/POM films spin coated on silicon wafers were investigated and it was demonstrated that they can effectively hinder protein physisorption. The PVA/POM films were cross-linked under UV radiation by Diels-Alder reactions.[3]. Different molecular weights and different hydrolysis percentages of commercially available PVA influenced the required processing conditions including post-applied (PAB) and post-exposure baking (PEB) temperatures as well as UV exposure dosage. Results showed that PVA with higher molecular weight required lower temperature processing. The research aims to develop new cross-linking agents for PVA films with effective antifouling properties, suitable for large-scale applications, including in the marine industry.

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Synthesis and characterization of statistical and block copolymers comprising of allyl– and dodecyl–isocyanate via titanocene–mediated coordination polymerization as scaffolds for complex macromolecular architectures.

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This study is focused on the synthesis and characterization of novel statistical and block copolymers consisting of allyl isocyanate (ALIC) and dodecyl isocyanate (DDIC) via coordination polymerization. In particular, the chiral half–titanocene complex [C_pTiCl_2(O–(S)–2–Bu)] was selected as the initiator in order to induce optical activity in the synthesized polymers. The statistical copolymerizations were conducted in five distinct monomer feed ratios, with the conversion intentionally maintained at a low level to facilitate the calculation of the reactivity ratios using a variety of linear graphical methods, along with the COPOINT computational program. In addition to the P(ALIC–co–DDIC) and P(ALIC–b–DDIC) copolymers, the corresponding homopolymers PALIC and PDDIC were also synthesized and subjected to a comprehensive analysis of their thermal stability and the kinetics of thermal degradation. For this purpose, thermogravimetric analysis (TGA) and differential thermogravimetry (DTG) were employed within the framework of Ozawa–Flynn–Wall (OFW) and Kissinger–Akahira–Sunose (KAS) isoconversional methods. Finally, the ALIC–based polymers were employed as scaffolds for the preparation of functional polyisocyanates via a thiol–ene click reaction with thiophenol, exploiting the presence of the double bonds at the side groups. The products of the click reaction were subjected to the same thermal analysis, which revealed that the introduction of aromatic rings into the polymer structure resulted in enhanced thermal stability.

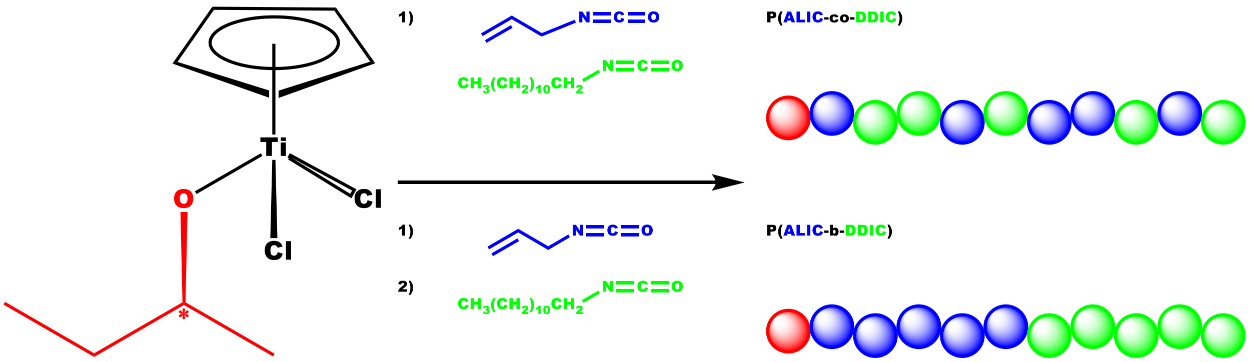

Figure 1: Synthesis of P(ALIC–co–DDIC) and P(ALIC–b–DDIC) via coordination polymerization.

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Modification of fluoropolymer surfaces using ultraviolet irradiation

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Surface modification techniques are crucial for tailoring polymer properties to suit various applications, especially in biomedical science. The key goal is to alter the polymer's surface by introducing functional groups that improve its performance, without compromising its bulk properties. These modifications can be achieved through physical, chemical, or biological methods. Recently, physical methods, such as plasma and radiation-induced treatments, have gained prominence. Radiation, divided into ionizing and non-ionizing types, includes UV irradiation, which has become popular for non-ionizing polymer surface modification due to its simplicity and the accessibility of UV lamps in laboratories. Fluoropolymers, in particular, possess exceptional properties, including high thermal stability, low dielectric constant, chemical resistance, low friction, and surface energy, making them indispensable in industries like aerospace, automotive, electronics, and medical devices. This study focuses on modifying fluoropolymers using UV irradiation to examine its effects on protein adsorption.

The fluoropolymers investigated in this study were poly(tridecafluoroheptyl acetal ethyl methacrylate) homopolymer and its copolymer with poly(methyl methacrylate), both synthesized via ATRP. The monomer used has a fluorinated side chain that can be cleaved in acidic conditions and thus by incorporating a photoacid generator in the polymer solution and exposing to UV irradiation the polymeric film, surface chemistry modification can be achieved. The change of the biomolecule adsorption capacity of the prepared films after UV irradiation was showed and evaluated, showcasing the innovative use of optical lithography and fluorinated polymers to create well-defined areas on substrates where biomolecules are selectively attached. This study is expected to have potential applications in site-specific biomolecule immobilization for biological research.

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Development of sustainable mixed matrix alginate membrane substrates for gas separations

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The growing demand for sustainable and efficient gas separation technologies has driven research into innovative materials. In line with green chemistry principles, there is a strong emphasis on reducing or completely eliminating hazardous materials. Therefore, this study aims to evaluate the potential of alginate, a natural, biodegradable, gel-forming linear biopolymer extracted from brown algae [1], as a viable and eco-friendly alternative to conventional polymeric substrates that utilize toxic solvents in gas separation processes, particularly for CO_2 capture and natural gas sweetening. To address the fragile nature of alginate and improve its low permeance, various carbon nanomaterials were integrated to enhance its gas permeation properties, resulting in a green and sustainable substrate while upholding environmental sustainability.

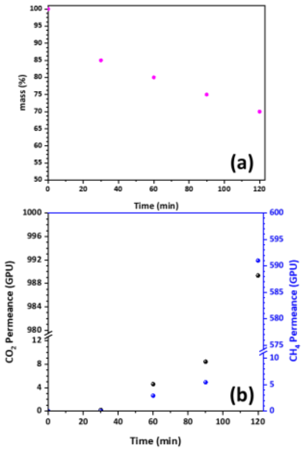

Figure 1: (a) Temporal variation of mass weight and; (b) corresponding changes in CO_2 and CH_4 permeance for the alginate/10 wt.% MWCNTs membrane substrate.

In this study, we developed several flat sheet membranes using alginate as the polymeric matrix, incorporating graphene nanoplatelets (GNPs) and multi-walled carbon nanotubes (MWCNTs) within the alginate. We optimized the filler content to achieve a balance between mechanical strength and permeance. This approach not only harnesses the eco-friendly properties of alginate, but also takes advantage of the selective adsorption capabilities of the fillers, leading to improved gas performance. As shown in Figure 1a, there is a continuous weight loss over time, indicating the presence of residual water or moisture in the membrane and suggesting that water gradually evaporates from its matrix. This moisture hinders gas permeation, reducing the initial permeance by making it difficult for CO_2 to pass through easily. Over time, the increase in CO_2 permeance, depicted in Figure 1b, is likely attributed to both structural changes within the membrane and the gradual evaporation of moisture. As CO_2 interacts with the alginate, it may cause slight swelling or plasticization of the polymer matrix, increasing the free volume or spaces between the polymer chains [2,3]. In addition, the membrane undergoes structural modifications, such as reduced hydration of the polymer chains, which further frees up diffusion pathways and enhances gas permeation.

The findings demonstrate that the development of a mixed matrix alginate substrate is feasible and offers significant potential for gas separation technologies, successfully merging sustainability with effective performance. This study contributes to the growing field of green materials by showcasing alginate-based membranes as a promising solution for efficient gas separation substrates, paving the way for further research in environmental applications.

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Stereoselective synthesis of chiral cyclopentanols towards macrocyclic natural products of the *Jasminun* species

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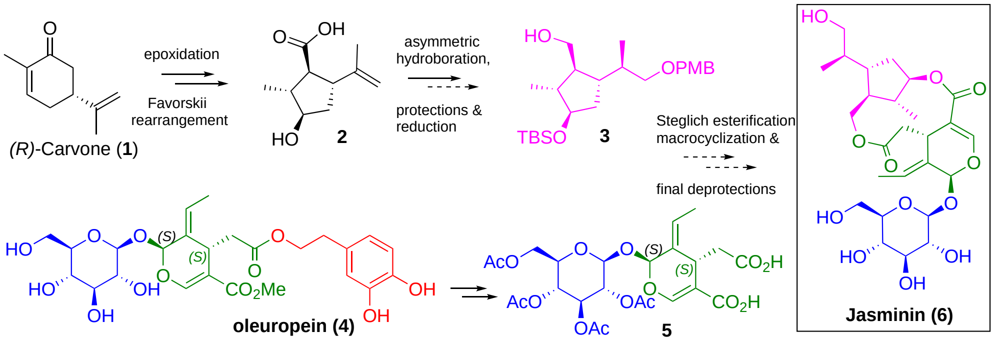
Functionalized cyclopentanols, prevalent in natural products and pharmaceuticals, offer valuable scaffolds for drug discovery due to their rigid frameworks and advantageous pharmacokinetic properties.[1] Certain secoiridoid natural products contain such a cyclopentapyran core, derived from iridoids. They are found in members of the *Oleaceae family*, notably the *Jasminum* species *J. azoricum*, *J. sambac*, *J. nudiflorum and J. mesnyi*.[2] There are around forty reported secoiridoids with a triol or tetraol cyclopentane ring decorated with five contiguous stereocenters, which are considered to be an interesting but synthetically demanding target,[8] with various biological and pharmaceutical activities, including antioxidant and antimicrobial effects.[3] Jasminin (**6**, Scheme 1), the main member, is found in the leaves of Primrose Jasmine, an evergreen shrub found in China, India and Nepal. These leaves are also rich in jasmoside, jasmesoside, oleuropein and other secoiridoids and are used for their antioxidant and anthelmintic potential.[4]



Scheme 1. Key intermediates involved in synthesis of Jasminin.

In this work, a synthetic methodology is being developed for accessing such cyclopentanols stereospecifically, with the initial final target of the synthesis being jasminin (**6**).[7] The synthesis commences with *(R)*-carvone undergoing epoxidation, Favorskii rearrangement followed by orthogonal protections, hydroboration–oxidation and reduction in order to get the suitably protected triol **3**. The synthesis concludes with a macrolactonization with protected oleoside **5**, derived from oleuropein, a valuable bio-renewable synthetic building block with diverse biological activities and potential therapeutic applications,[5] found in abundance in olive leaves.

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Synthesis of pH-Responsive Hybrid Copolymers and Their Conjugation with Protein to Combat Myasthenia Gravis

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The primary objective of this study is to effectively encapsulate a protein in order to enhance its half-life within the body and to investigate its activity through *in vivo* experiments.[1]

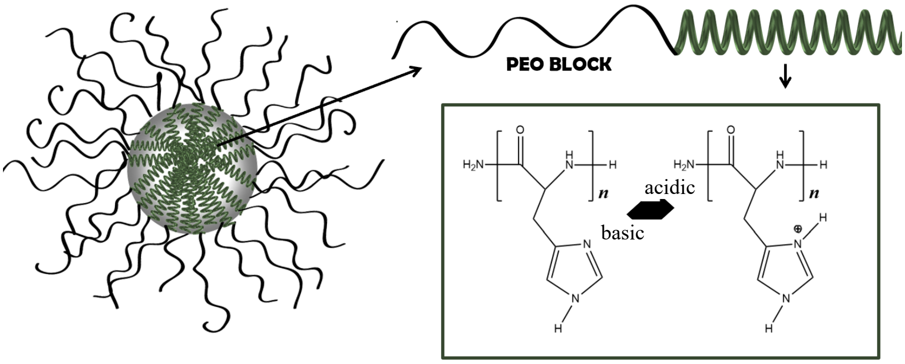

Figure 1: Poly-histidine conformations in acidic and basic environments.

A soluble mutant form of the extracellular domain of the a1 chain of AChR (a1-ECDm), which represents most of the auto-epitopes involved in Myasthenia Gravis (MG), was used.[2] To achieve efficient transport of the protein, via the systemic route , a hybrid polypeptide of the type poly(ethylene oxide)-b-poly(L-histidine) (PEG-b-PHIS) was synthesized as shown in Figure 1.[3] The property of self-organizing into crown-core micellar structures was exploited.[4] It was then investigated whether its intravenous administration to rats could safely and effectively treat the autoimmune disease. The in vivo experiments confirmed the existence of the protein incorporated into the nanoparticles, as it showed activity. It was studied by electrophoresis by incubating the nanoparticles at various pH, with imidazole to release the protein and with DMSO. However, it was observed that the incubation step of the protein in DMSO affects its shape. The samples were also studied by radioactivity to determine the amount bound.

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Car-washing formulations based on biosurfactants – synthesis and characterization

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The concept of sustainable development of personal care products, household detergents, as well as industrial and institutional cleaners is gaining increasing interest among consumers and industry representatives not only because of current trends but also because of the recommended implementation of the European Green Deal. The design of sustainable formulations encompasses all stages of their production and use, from the way raw materials are sourced and processed, through technological processes during production, to the selection of packaging, distribution, and disposal [1,2]. On the other hand, the constant growth in the automobile sector leads to an increase in the number of car washing centers, raising concerns about their impact on the environment, as the cleaning agents (detergents) used to wash cars can have harmful effects on the environment, especially on aquatic organisms [3]. A possible solution to this problem seems to be replacing synthetic surfactants in the car-washing formulations with biosurfactants, which not only possess good surface tension-reducing properties, but also have high biodegradability and reduced toxicity as they are produced by microorganisms, plants, and animals, or obtained by enzymatic synthesis [4].

Therefore, the purpose of our research was the development of biodegradable car-washing shampoos based on biosurfactants. The obtained formulations should be characterized by appropriate physicochemical parameters, good washing properties, and the ability to produce stable foam. In the framework of the presented research, the basic physicochemical parameters, i.e. pH, viscosity, and density of the shampoos obtained were evaluated. The contact angle was also measured using the droplet image analysis method. Moreover, the stability of the foam was assessed by applying the manual shaking technique, as well as the Static Multiple Light Scattering (SMLS) measurement with the Turbiscan^{LAB} analyzer. Our research showed that we have developed two formulations with physicochemical parameters typical for products of this type, but with components that exhibit very high biodegradability according to the OECD 301B test procedure and low toxicity to aquatic organisms. In addition, the formulations obtained showed high application potential as shampoos for car washing.

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