Università di Pisa
Dipartimento di Chimica
e Chimica Industriale

Doctorate
School in
Chemistry
and
Materials science

CFF '25

# CHEMISTRY FOR THE FUTURE

International Conference
7-9 July 2025

Via Giuseppe Moruzzi 13 - 56124
Pisa, Italy
cff25@dcci.unipi.it

# BOOK OF ABSTRACTS

UNIVERSITÀ DI PISA

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Scientific Equipment
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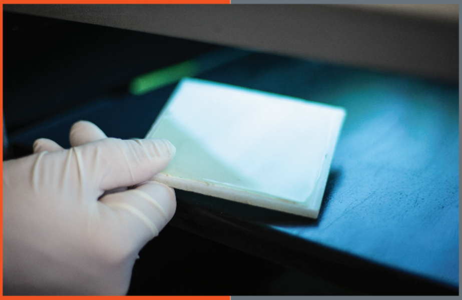
Stoccaggio



# TAKEDA ITALIA: PRODUZIONE DI VALORE

Presente in Italia dal 1982 con la sede commerciale di Roma, Takeda conta anche due siti produttivi, a Rieti e a Pisa. Pionieri nella produzione di terapie plasmaderivate, ogni giorno, nel centro produttivo di Rieti, leader nella raccolta del plasma e considerato una delle migliori realtà produttive mondiali nel campo del frazionamento alcolico del plasma, lavorano oltre 730 dipendenti. Il sito di Pisa conta oltre 250 dipendenti ed è dedicato alla produzione di albumina. Entrambi sono parte di un network mondiale composto da 7 siti.

## FATTI CHIAVE - UNA RETE DI ECCELLENZA

**Roma** – Sede commerciale presente in Italia da più di 40 anni. Takeda è tra le prime 15 aziende farmaceutiche del Paese

**Rieti** – Sito produttivo specializzato nel frazionamento alcolico del plasma da cui si ricavano intermedi quali l'albumina, le immunoglobuline e i fattori della coagulazione, necessari per la produzione di terapie plasmaderivate.

**Pisa** – Sito produttivo dedicato alle fasi di formulazione finale del bulk, inattivazione virale, riempimento asettico e l'ispezione visiva.

**+ di 1300 dipendenti**

**+54 Prodotti nelle aree:** Oncologia, gastroenterologia e infiammazione, malattie rare, ematologia, vaccini (dengue) e cure primarie

**+20 Programmi di supporto ai Pazienti** affetti da malattie rare in varie aree terapeutiche comprese le malattie da accumulo lisosomiale, l'emofilia, le immunodeficienze e l'angioedema ereditario.

## UN PEZZO DI STORIA ITALIANA

| | |
|---|---|
| 1978 — | Takeda arriva in Europa. Prima in Francia, poi Germania e nel 1982 in Italia |
| 1984/ 1985 — | Perfezionata la "microsphere technology" che permetterà la formulazione di un "deposito" a rilascio controllato dell'analogo del Gn-RH per la terapia del cancro alla prostata, cancro al seno, fibromi uterini, endometriosi, pubertà precoce, FIVET. |
| 1995 — | L'inibitore della pompa protonica (PPI) per il trattamento della gastrite viene lanciato in Italia e diventerà uno dei più usati nel mondo. |
| 1997 — | L'antagonista dell'angiotensina II è commercializzato in Italia. |
| 2001 — | Lancio del pioglitazone in Italia. |
| 2010 — | Mifamurtide è disponibile in Italia. Il farmaco ha dimostrato negli ultimi dieci anni di aumentare la sopravvivenza nei pazienti affetti da osteosarcoma. |
| 2016 — | Diventa disponibile anche in Italia il primo e unico farmaco biotecnologico a selettività intestinale approvato per il trattamento di adulti con malattie infiammatorie intestinali. |
| 2017 — | Takeda acquisisce ARIAD Pharmaceuticals. Si rafforza la presenza nell'area di onco-ematologia e dei tumori solidi con nuove e innovative terapie mirate. |
| 2019 — | Grazie all'acquisizione di Shire, Takeda diventa un'azienda biofarmaceutica globale presente in oltre 80 Paesi. In Italia vengono acquisiti gli stabilimenti produttivi di Rieti e Pisa. |
| 2021 — | Takeda rende disponibile in Italia la formulazione sottocutanea di vedolizumab, farmaco biotecnologico per le malattie infiammatorie croniche intestinali. |
| 2023 — | Takeda Italia lancia un antivirale usato contro le infezioni post-trapianto da cytomegalovirus (CMV) ed un nuovo vaccino che protegge dalla febbre virale dengue. |

01/01/2025

# *PRESENTAZIONE AZIENDALE*

Laborchimica Srl si occupa dal 1977 di Forniture per Laboratori di Analisi e Ricerca.

Oltre a **reagenti** e prodotti chimici commercializziamo **consumabili**, plastiche, vetreria e **strumentazioni** dalle più semplici alle più complesse e tutti quei servizi essenziali per soddisfare tutte le necessità dei laboratorio moderni.

Ci occupiamo della **progettazione di nuovi laboratori** fornendo anche gli arredi, comprensivi di banchi, cappe e armadi di sicurezza. Oltre alla ampia gamma di prodotti che siamo in grado di offrire, stiamo lavorando ogni giorno di più per perfezionare quelli che sono i nostri servizi. In primis il nostro reparto di service si impegna a garantire **assistenza tecnica**, **manutenzione** e **installazioni** per tutti gli strumenti da laboratorio. In fase di ispezione valuteremo il problema e ci organizzeremo assieme per risolvere al più presto. Ove sarà necessario contattare direttamente la casa madre, aggiungere prodotti necessari per il lavoro oppure organizzare spedizioni o trasferte da parte di altri tecnici, Laborchimica si occuperà direttamente del lavoro e della logistica, presentando un preventivo finale completo di tutte le spese.

Sempre in ottica di venire in contro al cliente siamo in grado anche di offrire attività di magazzino. Quando il nostro cliente ha dei consumi regolari di uno o più prodotti e li acquista con cadenza, pianifichiamo delle consegne e facciamo trovare il materiale sempre disponibile al nostro magazzino per creare una **safety stock personalizzata** e sopperire quindi ad ogni bisogno, necessità, picchi di produzione o altro. Necessitiamo solo di prodotti e quantità per formulare la nostra offerta, mantenendo il prezzo fermo per l’intera durata della fornitura.

Per tale servizio non saranno applicati sovraccosti né verrà richiesto alcun pagamento anticipato. L’emissione della fattura avverrà ogni volta che ci sarà una consegna.

Facendo di ***flessibilità ed adattabilità*** la nostra forza, anche questo servizio viene cucito addosso al cliente ed è variabile, in quanto a consegne e quantità, anche in corso d'opera Per garantire consegne sicure e regolari provvederemo a tenere a magazzino due mensilità successive del materiale pattuito. Facendo così potremmo Rispondere in tempi celeri a quelle che sono le esigenze del nostro cliente.

Se vuoi conoscerci o chiederci informazioni sui nostri prodotti e servizi non esitare a contattarci e a visitare il nostro sito **www.laborchimica.com**

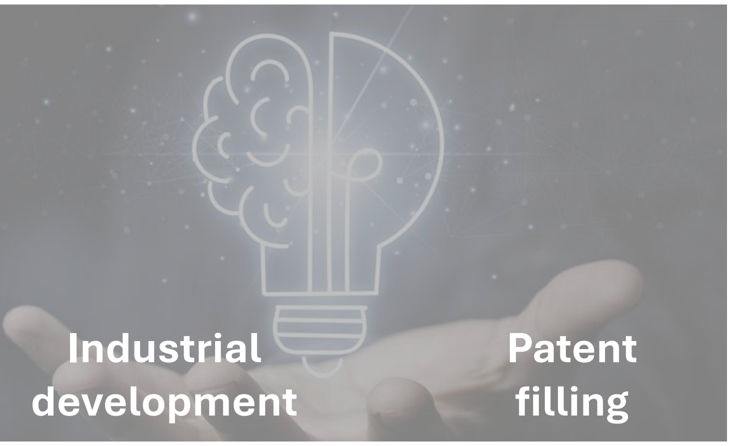
SPINPET

R&D for sustainable materials

**Spin-PET** develops **advanced solutions in the field of polymeric materials**, with a strong focus on **recycled polymers**. Our expertise lies in the **compatibilization** of different types of polymers and in **tailoring specific final properties** to meet the needs of various applications.
We offer both **theoretical consultancy and practical support** through our fully equipped laboratory.

With over a decade of experience, Spin-PET operates as an **innovative SME**. Originally a **spin-off of the University of Pisa**, we proudly maintain the **spin-off label** to reflect our ongoing collaboration and academic roots. We bring **creativity, problem-solving skills, and the generation of original IP** to companies seeking **innovation in material science.**

## OUR WORKING METHOD



**Research and development** activities are divided 4 steps:

**Feasibility study**

**Process/Product design**

**Industrial development**

**Patent filling**

## OUR EQUIPMENT

Thermal analysis:
Thermogravimetic Analysis (TGA)
And DSC

Chemical and optical analysis:
IR spectroscopy
UV-vis spectroscopy
Selective solvent extractions
Raman spectroscopy
Colorimeter (CIELab, CIEXYZ, CIELabCh)

Extrusion and rheological tests:
Pilot-scale twin-screw corotating extruder (Prism)
Lab-scale single-screw extruder (Brabender)
Discontinuous mixer (Brabender)
Melt Flow Index (MFI) Analysis

Preparation and mechanical analysis:
Injection molding and flat plate press
Tensile and flexural analysis
Hot set test
Impact Analysis (IZOD)

Reactor:
MONOWAVE 400 R microwave reactor

Other:
Viscosity determination
Density determination
SHORE hardness
GLOSS
UL94 flammability test
Pellet Extruder 3D printer

**Research and development of new polymeric and composite materials.**
**Industrial chemical consultancy.**
Quality management system UNI EN ISO 9001:2015

Vogliamo essere la migliore azienda per cui lavorare, in cui investire e da cui acquistare. Vogliamo avere un impatto positivo sulla società in cui viviamo ed essere un esempio per il nostro ecosistema.

100th SAPIO GRUPPO

*Breathing the future*

Nel presente
per garantirti il futuro

## Il nostro lavoro...garantirvi ogni giorno
## Il valore della qualità e della sicurezza

Proteggiamo l'acqua, non solo all'origine, ma anche durante la sua distribuzione, mantenendo in efficienza gli impianti di trattamento, rinnovando le strutture ed ottenendo un monitoraggio continuo ed accurato.

Il Laboratorio di Analisi ASA, nel 2023, nell'ambito dei controlli sulle acque destinate al consumo umano e dei controlli gestionali sulle acque reflue restituite all'ambiente, ha registrato complessivamente **10.884** campioni sui quali ha determinato **82.030** analisi, inclusi **8.392** parametri per garantire la validità dei risultati di prova.

**82.030 analisi**

**Oltre a quelle effettuate da ASL e ARPAT**

## La garanzia del nostro lavoro

| Acqua potabile<br>**56.322** analisi | Acqua di depurazione<br>**17.316** analisi | **10.884** campioni | **32** Comuni SII |
|---|---|---|---|

Conosci la qualità della tua acqua **www.asaspa.it**

Olefins & Polymers
Europe

**INEOS** is a global chemical company
Our products touch every aspect of modern day life.

**INEOS has a strong commitment to research, innovation and sustainability**

## OUR BUSINESS

The flagship of the company is the FEX, a group resource dedicated to defining and implementing corporate research and development plans in the European and global polyolefin sector.

## OUR FUTURE

We don’t stand still, we continue to be ambitious and the pilot plant in Rosignano plays a key role in developing new products and production processes.
We are engaged in developing our sustainable agenda to improve our operations and to implement sustainable solutions.

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https://it.linkedin.com/company/ineos-manufacturing-italia s.p.a

Never waste
**MOPI** S.r.l.
Always use

**MOPI** find new applications for all waste, scraps or by-products of industrial processes, as well as post-consumer plastics and rubbers, to reintroduce them as new raw materials into the production cycle, generating a circular economy.

## Technological analyses

Ring & Ball
Penetration
Cold Bend
Cleveland open cup

## Rheological analysis

Viscosimeter Brookfield
Melt Flow Index (MFI)
Rheometer with oscillating disc
Rotational viscometer Mooney

## Flame Retardant Properties

Laboratory scale B roof (CEN/TS 1187)
Vertical Burning tests (DIN4102B2)

## Thermal and molecular analysis

Fluorescence Miscoscope
Thermogravimetric analysis (TGA)
Infrared Spectroscopy (FT-IR)
Differential scanning calorimeter (DSC)

## Processing

Oxiboost reactor
High sheat mixer
Laboratory roller mixer (calender)

## Mechanical properties

Mechanical properties in bending
Mechanical properties in traction

Waters
TA
OPTIKA MICROSCOPES ITALY
MENESTRINA dal 1895
BROOKFIELD AMETEK
SILVERSON HIGH SHEAR MIXERS/EMULSIFIERS

***Equipment from the best brands***

SYSTEM CERTIFICATION
ISO 9001
SGS

SCAN ME

ECOPOL

BIODEGRADABLE HYDROSOLUBLE POLYMERS

Ecopol is a global leader in the production of biodegradable and water-soluble films and delivery systems.

Our commitment to sustainability and innovation has positioned us as a compelling ecological alternative to traditional packaging materials, offering a significant reduction in environmental impact.

Our biodegradable films and delivery systems empower leading consumer goods companies to significantly cut carbon emissions and decrease the use of water in their supply chains.

Since our inception, we have been relentless in our pursuit of excellence, consistently delivering superior quality to our customers, and we strive to ensure a more sustainable future for our employees, business partners, and communities.

Our mindset of continuous improvement and focus on innovation empowers us to invest in the most advanced technologies and to nurture truly collaborative relationships with our customers when it comes to researching and developing the next generation of sustainable delivery systems.

www.ecopol.com

Laviosa, a fourth-generation family-owned business, is one of the leading companies in the world in the research, extraction, processing and marketing of bentonite. Laviosa is active and present in worldwide markets and has production plants located in Italy, France, Turkey and India.

Research, development and innovation are the foundations of the company combined with the respect for the environment.

**www.laviosa.com**

## OUR MAIN ASSETS AND SKILLS ARE:

- **Raw material control**
- **Worldwide localized production**
- **Customer-oriented approach**
- **Constant innovation and product application knowledge**

TECHNOLOGY COMPANY
iPOOL
DESIGN
MATERIAL

provides technical information and comparative studies in order to evaluate the chemical-physical properties for each specific material following the most requested regulations and standards

## Flame Retardant Properties

- Vertical Burning tests (DIN4102B2)
- Limiting Oxygen Index (LOI)
- UL-94
- Smoke emissions

## Mechanical properties

- Mechanical properties in bending
- Mechanical properties in traction
- Tear Strength Test (Tear Strength)
- Peeling test
- Impact Tests (Izod)

## Processing polymeric materials

- Laboratory roller mixer (calender)
- Laboratory single screw extruder
- Co-kneader (Buss)

## Thermal and molecular Analysis

- Differential scanning calorimeter (DSC)
- Thermogravimetric analysis (TGA)
- Infrared Spectroscopy (FT-IR)

## Rheological analysis

- Melt Flow Index (MFI)
- Rheometer with oscillating disc
- Rotational viscometer Mooney
- Viscosimeter Brookfield

SYSTEM CERTIFICATION
ISO 9001
SGS

SCAN ME

**FAVS** di Gnudi Andrea e Antonella S.r.l. nasce nel 1939 con l'azienda **Gnudi**, fabbrica di soffieria a mano per la lavorazione del vetro.

Negli anni questa attività è cresciuta, dando vita alla società **F.A.V.S.** - Forniture Apparecchiature Vetrerie Scientifiche, alla cui produzione si affianca anche la commercializzazione di altri materiali da laboratorio, ciò che differenzia i loro prodotti in quel settore.

Oggi FAVS gestita dai figli Andrea e Antonella, opera a livello nazionale ed internazionale nel commercio di strumentazione scientifica, vetreria e arredi da laboratorio, armadi di sicurezza, prodotti chimici, articoli monouso, ecc...

**CONTACT US**

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**Via Seragnoli, 5 - 40138 Bologna**

**FAVS**
**Scientific Equipment**
di Gnudi Andrea e Antonella S.r.l.

www.favs.it

**AZIENDA CERTIFICATA UNI EN ISO 9001:2015**

FAVS vanta una clientela diversificata e di alta qualità, tra cui Aziende, Facoltà ed Enti di ricerca scientifica che operano secondo elevati standard qualitativi e che da tempo utilizzano la nostra azienda come fornitore.

INNOVAZIONE ED ALTA QUALITÀ PER LABORATORI DI RICERCA, UNIVERSITÀ, CNR, INDUSTRIA E FARMACEUTICA

STRUMENTAZIONE, CONSUMABILE, PRODOTTI CHIMICI E ARREDI DA LABORATORIO DELLE MIGLIORI MARCHE

Kartell ASEM WTW
BRAND VELP SCIENTIFICA BOLA witeg
GVS MACHEREY-NAGEL SciLabware
GIORGIO-BORMAC CHEMISAFE VACUUBRAND
OPTIKA heidolph Asynt
CHRIST Merck
DWK LIFE SCIENCES

# SCIENTIFIC PROGRAM

# Monday – July 7th

| *Schedule* | *Speaker* | *Affiliation* | *Activity* |
|---|---|---|---|
| 13:30 – 14:15 | | | ***Registration*** |
| 14:15 – 14:30 | | | ***Welcome and Opening*** |
| **Session 1 – chair: Arianna Ghelardi, Luca Melega** | | | |
| 14:30 – 15:10 | **Prof. Silvia Bordiga** | University of Torino | ***Plenary lecture*** |
| | *Optical spectroscopy as a “Swiss army knife” in understanding catalysts* | | |
| 15:10 – 15:35 | **Andrea Giovanelli** | University of Pisa | ***Keynote lecture*** |
| | *Synthesis and Characterization of Polymers for Ion and Gas Separations* | | |
| 15:35 – 16:00 | **Francesca Nerli** | University of Pisa | ***Keynote lecture*** |
| | *Switchable cooperative $CO_2$ adsorption mechanism in multivariate fluorinated metal-organic frameworks* | | |
| 16:00 – 16:30 | | | ***Coffee break*** |
| **Session 2 – chair: Amanda Arcidiacono, Elena Betti** | | | |
| 16:30 – 17:10 | **Prof. Paolo Carloni** | Forschungszentrum Jülich | ***Plenary lecture*** |
| | *Multiscale simulations of neuronal receptors: from quantum to coarse grain* | | |
| 17:10 – 17:35 | **Ivan Giannì** | University of Pisa | ***Keynote lecture*** |
| | *Approaching excited state energies for medium size Multi-Reference systems* | | |
| 17:35 – 18:00 | **Patrizia Mazzeo** | University of Pisa | ***Keynote lecture*** |
| | *Electrostatic embedding machine learning for ground and excited state molecular dynamics of complex systems* | | |
| 18:00 – 19:00 | **Benedetta Bertoncini, Samuele Botticelli, Simona Braccini, Mariastella Cascone, Matteo Cei, Mattia Fausti, Marta Filomena, Giuseppe Fulvetti, Claudia Ghelarducci, Federico Paolino** | | ***Flash presentations*** |
| 19:00-20:00 | | | ***Poster session + happy hour*** |

# Tuesday – July 8th

| *Schedule* | *Speaker* | *Affiliation* | *Activity* |
|---|---|---|---|
| **Session 3 – chair: Caterina Campinoti, Ludovica Dei** | | | |
| 09:00 – 09:40 | **Prof. Kevin Lam** | University of Greenwich | ***Plenary lecture*** |
| | *Your Chemistry has “Potential” Highly Reactive intermediates without the “bang”* | | |
| 09:40 – 10:05 | **Luca Gherardi** | University of Pisa | ***Keynote lecture*** |
| | *Conformational freedom of single stranded oligonucleotides* | | |
| 10:05 – 10:30 | **Marco Bazi** | University of Pisa | ***Keynote lecture*** |
| | *Hairpin-shaped RE/$Pt_2$ Heterometallic Complexes* | | |
| 10:30 – 11:00 | | | ***Coffee break*** |
| **Session 4 – chair: Cecilia Campi, Mariano De Cristofaro** | | | |
| 11:00 – 11:40 | **Dr. Diego Tamburini** | The British Museum | ***Plenary lecture*** |
| | *Chemistry for the Past – from neo-Assyrian writing boards to Tahitian natural dyes* | | |
| 11:40 – 12:05 | **Alberto Cerchiai** | University of Pisa | ***Keynote lecture*** |
| | *An innovative solid-state sensor for hydrogen leak detection for a safe energy transition* | | |
| 12:05 – 12:30 | **Elena De Gregorio** | University of Pisa | ***Keynote lecture*** |
| | *Nanomaterial-based electrochemical sensors for clinical applications* | | |
| 12:30 – 14:00 | | | ***Lunch break*** |
| **Session 5 – chair: Luca Soldati, Chiara Zappelli** | | | |
| 14:00 – 14:40 | **Prof. Ipsita Roy** | University of Sheffield | ***Plenary lecture*** |
| | *Natural and Sustainable Polymers of Bacterial Origin and their Biomedical Applications* | | |
| 14:40 – 15:05 | **Lorenzo Bonaldi** | University of Pisa | ***Keynote lecture*** |
| | *Thermochemical and catalytic processes for the sustainable production of biofuels through biomass conversion* | | |
| 15:05 – 15:30 | **Vanessa Matteucci** | University of Pisa | ***Keynote lecture*** |
| | *Sustainable asphalt binders: effects of chemical modifications on terminal blend rubberized asphalt* | | |
| 15:30 – 15:55 | | | ***Coffee break*** |

| **Session 6 – chair: Lorenzo Sembranti, Luca Melega** | | | |
|---|---|---|---|
| 15:55 – 16:20 | **Matilde Benedettini** | University of Pisa | ***Keynote lecture*** |
| | *Development of hydrophobic and grease resistant fluorine-free modifiers for paper* | | |
| 16:20 – 16:45 | **Stefania Volante** | University of Pisa | ***Keynote lecture*** |
| | *Energy storage devices: performance and safety assessments in* $LiFePO_4$ *batteries and development of sustainable materials for supercapacitors* | | |
| 16:45 – 17:00 | **Matteo Pietrini** | Doctor Resin & Chemicals | ***Sponsor*** |
| | *Epoxy Resins in the Stone Industry* | | |
| 17:00 – 17:15 | **Stefania Viganò** | Takeda Pharmaceuticals | ***Sponsor*** |
| | *Plasma Fractionation process* | | |
| 17:15 – 20:00 | | | ***Poster session*** |
| 20:00 | | | ***Social dinner*** |

# Wednesday – July 9th

| *Schedule* | *Speaker* | *Affiliation* | *Activity* |
|---|---|---|---|
| **Session 7 – chair: Chiara Zappelli, Elena Betti** | | | |
| 09:00 – 09:40 | **Prof. Angela Casini** | Technical University of Munich | ***Plenary lecture*** |
| | *Frontiers in Medicinal Inorganic Chemistry: Unconventional Design Concepts for Therapy and Imaging* | | |
| 09:40 – 10:05 | **Sara Benetti** | University of Pisa | ***Keynote lecture*** |
| | *Exploring reactivity pathways to access new organodiiron complexes for aqueous applications* | | |
| 10:05 – 10:30 | **Matteo Pugliesi** | University of Pisa | ***Keynote lecture*** |
| | *Exsolution-Driven Formation of Ultrasmall $Co_3O_4$ Nanoparticles from CoMo-LDH for Enhanced Water Oxidation Performance* | | |
| 10:30 – 11:00 | | | ***Coffee break*** |
| **Session 8 – chair: Joel Santos, Amanda Arcidiacono** | | | |
| 11:00 – 11:40 | **Prof. Alberto Credi** | University of Bologna | ***Plenary lecture*** |
| | *Light-driven nonequilibrium operation of artificial (supra)molecular motors* | | |
| 11:40 – 12:05 | **Alberto Santonocito** | University of Pisa | ***Keynote lecture*** |
| | *Magnetic Modulation of Light Using a Gires–Tournois Metasurface* | | |
| 12:05 – 12:30 | **Piermarco Saraceno** | University of Pisa | ***Keynote lecture*** |
| | *From Complexity to Specificity: First-Principles Simulations of Light-Harvesting in Plant Antennas* | | |
| 12:30 – 14:00 | | | ***Closing and final remarks*** |

# PLENARY LECTURES

# Optical spectroscopy as a “Swiss army knife” in understanding catalysts

S. BORDIGA

*Department of Chemistry, NIS Center and INSTM Reference Center, University of Turin,*
*Via Quarello 15, 10135, Turin, Italy*
silvia.bordiga@unito.it

The study of heterogeneous catalysis is crucial for advancing industrial processes in energy, chemicals, and environmental applications. Spectroscopic techniques have emerged as powerful tools to investigate the complex phenomena occurring at the catalyst surface during reaction processes. These methods provide detailed insights into the structural and electronic properties of catalyst materials, as well as their dynamic behavior under reaction conditions. Techniques such as infrared (IR), Raman, ultraviolet-visible (UV-Vis) and X-ray Absorption (XAS) spectroscopies, just to mention some of them, enable the observation of key intermediates, reaction mechanisms, and changes in the active sites of catalysts. However, though some spectroscopic tools (e.g. IR or UV-vis) are nowadays broadly available, their fundamentals are often not fully handled by the final user, sometime leading to gross errors in their application and reporting of results. In the meantime, operando spectroscopies, which allow measurements under actual catalytic reaction conditions, have greatly enhanced our understanding of catalyst behavior in real-time. However, to be properly applied, they need devoted advanced experimental tools to measure and to analyze the results. The combination of these spectroscopic and molecular modelling approaches has been instrumental in unraveling the molecular-level interactions between catalysts and reactants, identifying reaction pathways, and guiding the design of more efficient, selective, and durable catalytic systems. The present contribution aims to illustrate potentialities and limits of spectroscopies, in characterizing zeolites and Metal organic Frameworks, selecting a few case studies.

**References:**

Carlo Lamberti et al., Chem. Soc. Rev., ,39 (2010) 4951
Silvia Bordiga et al., Chem. Soc. Rev., 39 (2010), 4885
Silvia Bordiga et al., Chem. Soc. Rev., 44, (2015) 7262
Elena Groppo et al., Chem. Rev., 123, 21, (2023) 12135

# Multiscale simulations of neuronal receptors: from quantum to coarse grain

P. CARLONI

*Computational Biomedicine, Institute for Neuroscience and Medicine INM-9, Forschungszentrum Jülich GmbH, 52428 Jülich, Germany*
p.carloni@fz-juelich.de

We will present recent computer simulations from our laboratory on G-protein-coupled receptors (GPCRs), which are important for several neuronal functions, including synaptic transmission and the chemical senses. Our findings shed light on various aspects of GPCRs biology, including ligand binding, activation, and signaling pathways. We will conclude our presentation by discussing how the combined use of machine learning and hybrid quantum mechanical/classical mechanics simulations can greatly improve the accuracy of the simulations.

# Frontiers in Medicinal Inorganic Chemistry: Unconventional Design Concepts for Therapy and Imaging

A. CASINI

*Chair of Medicinal and Bioinorganic chemistry, Department of Chemistry, School of Natural Sciences, Technical University of Munich (TUM), Lichtenbergstrasse 4, 85748 Garching, Germany*
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The field of medicinal inorganic chemistry is a burgeoning subfield of medicinal chemistry that focuses on the development of metal-based diagnostic and therapeutic agents for different diseases. In this lecture, I highlight recent strategies in the area of metallodrug design which I consider particularly intriguing, also from a mechanistic perspective, based either on catalytic pathways or purely relying on noncovalent interactions of organometallic compounds with different pharmacological targets.

For example, gold-based complexes, either as molecular species or integrated into supramolecular entities will be presented, providing insights into their reactivity in biological environments and unique mode of pharmacological action. In addition, in the nuclear medicine domain, the emerging field of supramolecular (radio-)theranostics will also be addressed, in which the classical radiopharmaceutical design is revisited and implemented by self-assembly strategies (Figure 1).

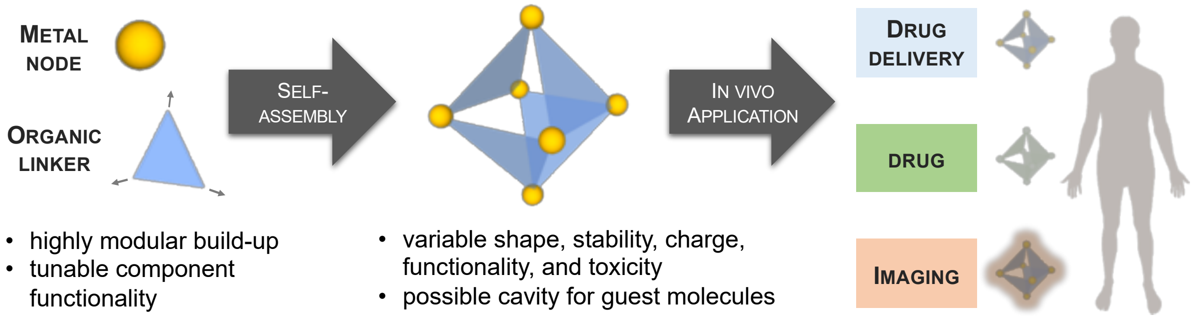

**Figure 1**. Example of unconventional drug design concept: self-assembly of 3D-metallacage structures and their possible applications in medicine.

# Light-driven nonequilibrium operation of artificial (supra)molecular motors

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The design, synthesis and investigation of artificial molecular machines has formidably stimulated the creativity of chemists in the past three decades. The directionally controlled motion, activated by energy inputs, of molecular components is key to realize nanometer-scale motors that could perform tasks. By implementing energy ratchet mechanisms with topologically non-trivial molecules, such as rotaxanes and related systems, we have realized prototypes of artificial molecular pumps powered by light. Here we will describe the design and evolution of these devices, and discuss the conceptual and pratical challenges associated with the use of light energy to drive chemical systems away from chemical equilibrium. Besides the interest for fundamental science, synthetic molecular machines and motors have the potential to bring about radical innovation in catalysis, materials science, energy conversion, robotics and medicine.

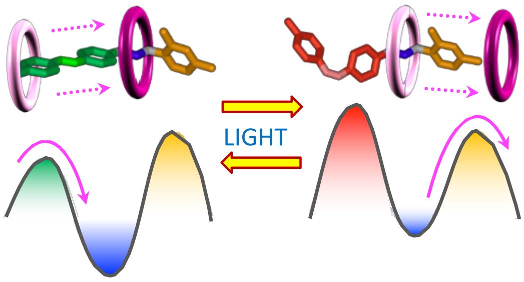

**Figure 1**. Operation scheme of a light-driven molecular pump based on a pseudorotaxane architecture.

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# Your Chemistry has “Potential”
## *Highly Reactive intermediates without the “bang”*

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Chemistry thrives on highly reactive intermediates - remarkable tools for building complex molecules. But one might ask: shouldn't their synthesis involve fewer risks than a special life insurance policy?

Synthetic organic electrochemistry, which has its roots in the pioneering work of Faraday and Kolbe on the electrolysis of aliphatic carboxylic acids, has become a powerful tool for sustainable chemical synthesis. Despite numerous successful industrial applications, its wider potential remains under-exploited. However, the increasing demand for greener, safer and more cost-effective synthetic methods has spurred the development of innovative electrosynthetic techniques.

In this talk, we will review novel, safe, green and economically viable electrosynthetic methods for the preparation of highly reactive organic intermediates, including iso(thio)cyanates, isocyanides, carbocations and diazo compounds. These methods significantly reduce the inherent risks associated with traditional synthetic approaches, while improving efficiency and sustainability. We will also highlight the scalability of these processes through flow electrosynthesis and their impactful real-world applications within the pharmaceutical industry, with case studies in collaboration with GSK, AstraZeneca and Johnson & Johnson.

# Natural and Sustainable Polymers of Bacterial Origin and their Biomedical Applications

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In this work we have focused on the production and use of bacteria-derived sustainable biomaterials for use in biomedical applications. Two main types of biomaterials have been focused on, including Polyhydroxyalkanoates (PHAs) [1] and bacterial cellulose (BC) [2]. PHAs are polyesters produced by a range of bacteria including *Ralstonia eutropha*, *Psuedomonas sp.*and *Bacillus subtilis*. These polymers are biodegradable in the soil and in the sea. In addition, they are also resorbable in the human body and are highly biocompatible. Hence the PHAs can be used for biomedical applications such as the development of scaffolds for hard and soft tissue engineering, medical devices, and drug delivery. BC can also be produced by a range of bacteria including *Gluconobacter xylinus and Sarcinia ventriculi.* BC is also a green polymer, is sustainable and degradable in the soil. It is also highy biocompatible and can be used in biomedical applications.

Polyhydroxyalkanaotes are polyesters with monomer chain length ranging between $C_4$ - $C_{16}$. They are divided in to two main types, short chain length PHAs (scl-PHAs) with monomer chain length $C_4$-$C_5$ and medium chain length PHAs (mcl-PHAs) with monomer chain length $C_6$-$C_{16}$.The scl-PHAs are normally hard and brittle whereas the mcl-PHAs are soft and elastomeric in nature. Hence, we have mainly used the scl-PHA, Poly(3-hydroxybutyrate), P(3HB), for bone tissue engineering [3], drug delivery [4] and medical devices development such as coronary artery stents, and the mcl-PHAs for cardiac, nerve, pancreas, kidney and skin regeneration. For bone tissue engineering we have used neat P(3HB) and composites of P(3HB) with Bioglass® [3], hydroxyapatite [8] and carbon-based materials [7]. The mcl-PHAs have been used for the development of cardiac patches [6], nerve guidance conduits [5], wound healing patch, bioartificial pancreas and bioartificial kidney. Processing techniques used include additive manufacturing, electrospinning and melt electrowriting.

Bacterial cellulose has also been produced under static culture conditions using *G. xylinus*. This is a highly nano-fibrillated structure and hence is an excellent substrate for cell attachment and growth. We have surface modified bacterial cellulose to create antibacterial bacterial cellulose [9]. We have also used BC as a filler for P(3HB) based composites since BC is one of the stiffest known materials. In addition, we have electrospun BC for a range of applications.

In conclusion, we have successfully used bacteria-derived sustainable biobased materials for a variety of biomedical applications. Both PHAs and bacterial cellulose have a lot of potential in the future as sustainable biomedical materials of choice.

**Acknowledgements:** This work was supported by ECOFUNCO (Grant agreement number: 837863); British Council Grant-BHF Cardiovascular Regenerative Medicine Centre led by Imperial College London, NEURIMP (Grant Agreement Number 604450), REBIOSTENT (Grant Agreement Number 604251), HyMedPoly (Grant Agreement Number 643050) and 3D BIONET and EPSRC.

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# Chemistry for the Past – from neo-Assyrian writing boards to Tahitian natural dyes

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The use of mass spectrometric techniques for the characterisation of organic materials in cultural heritage objects is a well-established research field. Nevertheless, conducting this research in a museum setting poses various challenges, from ethical sampling strategies to sourcing rare reference materials. This talk focuses on two cases studies from the British Museum's collection to showcase these challenges as well as the importance of collaborative research and multi-analytical approaches in heritage science.

The writing boards excavated from the Northwest Palace at the Assyrian city of Nimrud (modern Iraq) represent the first material evidence of cuneiform writing on wax (7th century BCE). Recent scientific investigation was conducted to characterise the materials used to produce them, including the wax paste, the pigments and the wood. By using Fourier Transform infrared spectroscopy (FTIR), pyrolysis-gas chromatography-mass spectrometry with *in situ* silylation (Py(HMDS)-GC-MS), gas chromatography coupled to quadrupole time-of-flight mass spectrometry (GC-QToF-MS), Raman spectroscopy and scanning electron microscopy (SEM), interesting comparisons were established with previous analyses conducted in the 1950s. In particular, the use of orpiment ($As_2S_3$) in the yellow wax paste appears to have played a role in the outstanding preservation state of the beeswax. The presence of a carbon black pigment suggests that some writing boards had a grey/black colour, indicating that the practice of adding soot or ashes to beeswax, which was common in Greek and Roman times, might have originated much earlier [1].

The British Museum also houses one of the few surviving examples of a Tahitian mourner's costume (*heva tu papa'u*) collected by Captain James Cook in 1774. Following a major conservation project, the costume was displayed in 2019. Some of the costume parts show a red colouration that proved particularly challenging to identify [2]. During a field trip to Tahiti, a visit to a local dyeing workshop enabled some precious reference samples to be collected. Analyses by high-performance liquid chromatography coupled to diode array detector and tandem mass spectrometry (HPLC–DAD–MS/MS) led to the creation of a molecular database and to the identification of the red colour as a local dye referred to as *mati*. The significance of this discovery for local communities is outstanding, as it represents an invaluable connection with their past and their ancestors, ultimately highlighting the importance of reciprocal knowledge exchanges between researchers and local practitioners as a key approach for accessing rare reference materials and reviving historic knowledge [3].

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# KEYNOTE LECTURES

# Hairpin-shaped RE/$Pt_2$ Heterometallic Complexes

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In recent decades, rare-earth complexes have been extensively studied for their luminescent properties, exploitable in many different fields [1]. Interest in their biomedical applications has grown, particularly for use as luminescent probes [2] due to their narrow emission bands and long luminescent lifetimes, making them well suited for interference-free live tracking. Moreover, platinum-based drugs have already been widely used for treating numerous diseases and extensively studied [3], following the discovery of cis-platin's biological activity by Rosenberg in 1964. Heterometallic compounds gained more and more attention for their unique properties, derived from the presence of two different metal centers within the same complex [4]. Among these, platinum/lanthanide heterometallic complexes have acquired significant interest for their medical application as theranostic agents [5], multifunctional molecules capable of simultaneously providing therapy and diagnosing diseases. This dual functionality leverages the therapeutic activity of platinum and the luminescence of the f center. Using a DTPA-based heterotopic ligand, hairpin-shaped RE/$Pt_2$ heterometallic complexes were synthesized reacting $RECl_{3(aq)}$ with the anionic Pt-based metalloligand, [$Pt_2L^{3-}$], prepared reacting the DTPA-bisanhydride with the platinum complexes with the pyridinaminopropylamine and pyridinaminohexylamine, [$PtCl_2L'$] and [$PtCl_2L''$]. The heterometallic complexes were characterized through $^1$H-NMR spectroscopy revealing that the Ln center was successfully bound by the Pt metallo-ligand and biologically studied for their application in theranosis.

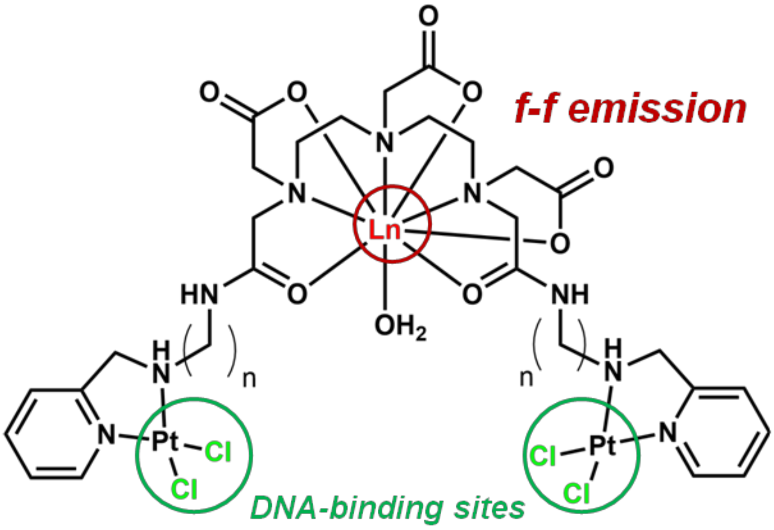

**Figure 1**. Structure of the [$Pt_2L(Ln)OH_2$] (n: 3; 6) heterometallic complexes.

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# Exploring reactivity pathways to access new organodiiron complexes for aqueous applications

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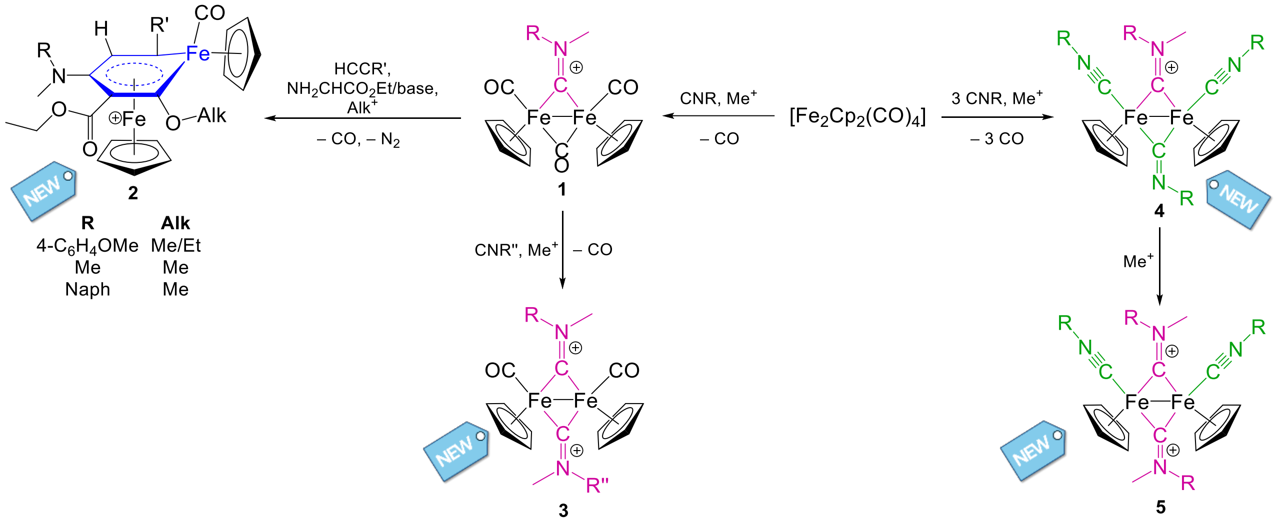
Considering the significant synthetic advantages offered by dimetallic molecular platforms,[1] the commercially available and cost-effective [$Fe_2Cp_2(CO)_4$] (Cp = $\eta^5$-$C_5H_5$) has been employed as a starting material to synthesize various diiron(I) complexes with bridging cationic hydrocarbyl ligands, including iminium ligands, alternatively viewed as aminocarbyne (Figure 1, structure **1**). These complexes are accessible through straightforward and multigram-scale procedures and display a rich and versatile chemistry accessible upon CO removal,[2] which was exploited to synthesize the first class of ferrabenzenes (**2**) via a multicomponent C-C bond forming process. Computational studies confirmed the aromatic nature of **2** and elucidated their formation mechanism. Furthermore, convenient synthetic pathways were developed to obtain novel mono- and bis-iminium diiron complexes with either isocyanides or CO as co-ligands (**3** to **5**). The physicochemical properties and *in vitro* cytotoxicity profiles of complexes **2-5** will be discussed. Specifically, complexes **3** showed potential for photo-activated chemotherapy due to their ability to release CO upon light activation.



**R''** = Me, Cyclohexyl, Benzyl

**R** = Me, Cyclohexyl, Xylyl

**Figure 1**. Synthetic pathways to iron-$\eta^6$-coordinated ferrabenzenes (**2**) and iminium and bis-iminium diiron complexes (**3-5**).

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# Thermochemical and catalytic processes for the sustainable production of biofuels through biomass conversion

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Fossil fuels continue to dominate the global energy supply, particularly in the transport sector, where around 70% of petroleum is used for fuel production [1]. In response, growing research efforts are concentrated toward sustainable alternatives. Among these, biomass, especially waste biomass from industrial, municipal, or lignocellulosic sources, stands out as a low-cost, abundant, and sustainable feedstock for the production of biofuels and value-added chemicals via catalytic or thermochemical conversion processes [2].

This work investigates the production of biofuel through the valorisation of low-value biomass, focusing on both catalytic and thermochemical conversion processes. The catalytic pathway centres on the synthesis of ethyl levulinate (EL), a promising bio-blendstock that can be used in both diesel and gasoline engines [3]. EL can be obtained via acid-catalysed alcoholysis of the polysaccharide fraction of biomass and easily purified. The study initially explored the conversion of model sugar compounds, achieving yields above 50 mol%. Then, the focus shifted towards real waste materials as potential low-value feedstock for an industrial EL production. Moreover, special emphasis was placed on the practical use of EL as diesel and gasoline additive. In particular, engine tests were also carried out to evaluate the impact of various gasoline-EL blends on engine performance and emissions. As a thermochemical approach, the study focused on the gasification of pulp and paper mill sludge (PPMS), a typical paper industry waste mainly composed of cellulose and $CaCO_3$. Experiments were carried out in a ≈100 $kW_{TH}$ downdraft fixed-bed reactor using either an $O_2/H_2O$ mixture or air as the gasifying agent. Specifically, key process parameters (temperature, substrate loading, and gas flow rates) were carefully optimised to maximise gasification efficiency and improve syngas composition, allowing to reach a high hydrogen-rich syngas composition (~40 mol%), ideal for energy recovery.

In conclusion, this work explored the production of a high-potential EL biofuel from low-value raw materials and evaluated its application as a bio-additive in gasoline engines. Additionally, it investigated gasification as an innovative and efficient method for valorising PPMS waste, leading to the generation of hydrogen-rich syngas suitable for energy production.

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# An innovative solid-state sensor for hydrogen leak detection for a safe energy transition

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Combating climate change is among the most urgent and relevant challenges of our time. A key aspect in this fight is represented by the gradual reduction of fossil fuel use and $CO_2$ emissions, in favour of renewable energies. Among the various options under evaluation by governments and scientific community, green hydrogen ($H_2$) has emerged as a promising clean energy vector. Hydrogen offers several advantages such as very high specific energy, high combustion enthalpy, and can be used both in direct combustion and fuel cells, yielding only energy and water as products [1]. However, its widespread use is still hindered by issues related to its production, storage, and, most critically, safety. $H_2$ is in fact a highly reactive gas, with wide flammability range in air and low autoignition energy. In this context, gas sensors will play a fundamental role in the future deployment of $H_2$ technologies, by enabling the rapid detection of leaks before dangerous concentrations are reached, preventing accidents, explosions, or even fatalities. The current state of the art includes a wide range of sensor technologies, such as catalytic, thermal, electrochemical or chemoresistive sensors, each with its own strengths and limitations, such as low selectivity, short lifetime and poisoning of active materials [2]. To overcome these limitations, we developed a solid-state electrochemical hydrogen sensor that eliminates all liquid components to enhance robustness and operational stability. The test of the sensor showed a linear relationship between the sensor response and the logarithm of hydrogen concentration, consistent with the Nernst equation. Interestingly, the measured sensitivity exceeds the theoretical Nernstian slope of 59 mV/decade, indicating that additional mechanisms may be enhancing the response. Furthermore, the sensor is able to maintain the same performance at elevated temperatures, thus highlighting its robustness across a range of thermal conditions.

The device was also evaluated according to current industry standards for ageing, demonstrating outstanding long-term stability, robustness, and reliability. Finally, it has been validated under real working conditions in a $H_2$ bio-production pilot plant in Treviso (TV), confirming its effectiveness in monitoring a safe and sustainable $H_2$ production process.

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# Nanomaterial-based electrochemical sensors for clinical applications

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Nanomaterial technologies have found widespread applications in sensing over the past decades. Due to the unique physicochemical properties -distinct from their bulk counterparts- and the large surface-to-volume ratio, nanomaterials can help overcome limitations such as low sensitivity and selectivity, that often limit sensor performance in real-world applications. In particular, 2D-Nanomaterials offer promising tools for electrochemical sensors, including both conducting (e.g. graphene, MXenes) and semiconducting (e.g. Transition metal dichalcogenides, TMDCs) materials, which can be tailored and functionalized.

This work focuses on integrating nanostructured materials -both inorganic (MXenes, 2D-$WS_2$) and biological (antibodies and aptamers)- for the development of electrochemical sensors aimed at detecting biomarkers associated with chronic kidney disease (CKD), and melanoma.

For CKD, monitoring biomarkers such as urea, creatinine and cystatin C is essential for diagnosis and tracking of disease progression [1,2]. In this perspective, a three-sensor platform for simultaneous electrochemical detection of these biomarkers in sweat was developed, designed to be further integrated into a wearable lab-on-chip device.

In the context of melanoma, the detection of circulating tumor cells (CTCs) in blood is crucial, as CTCs can cause the occurrence of metastases, even after the surgical removal of a tumor. Early detection of CTCs can thus be critical for prompt management of cancer [3]. For this purpose, an immunosensor based on titanium carbide MXene was developed for selective and sensitive detection of melanoma CTCs in blood samples.

This work was supported by Kermit (Kidney disease sweat sensor patch for early diagnosis and remote monitoring), Horizon-EIC-PATHFINDERCHALLENGES-01-04, Grant agreement 101115504, and the call PRIN 2022 (Project of National Relevance, Italy, code 20228LPFCA) from European Union – Next Generation EU.

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# Conformational freedom of single stranded oligonucleotides

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Therapeutic oligonucleotides have become a potent drug class that modulate cell function, through several interference mechanisms. Among them, antisense oligonucleotides, ASOs are single strand oligomers, typically containing 15 to 25 bases, designed for selectively binding mRNA sequences through Watson-Crick base pairing, which results in perturbing the expression of the protein coded by their target mRNA.

Accurately predicting the structure and dynamics of antisense oligonucleotides in solution is crucial for optimizing their therapeutic efficacy and understanding their interactions with target RNA sequences and cellular components. Single-stranded nucleic acids exhibit significant conformational flexibility, which plays a key role in their stability, target binding, and overall biological activity. However, existing molecular dynamics (MD) forcefields often impose excessive rigidity on backbone conformations, leading to deviations from experimentally observed structures and limiting the predictive power of simulations. [1,2]

In this work, we present a correction to the state of the art forcefield to more accurately reflect the conformational flexibility of single-stranded nucleic acid filaments in solution. Notably, this new forcefield is applicable to both canonical phosphodiester (PO, Figure 1a) linkages, which constitute the natural backbone of nucleic acids, and to phosphorothioate (PS, Figure 1b) modifications, that is most widely studied and therapeutically relevant modification in the field of antisense oligonucleotide research.

To validate these new parameters, we performed MD simulations and compared the resulting conformational ensembles with experimental NMR data, observing a significant improvement in the accuracy of the simulated structures compared to those generated by state of the art forcefields.

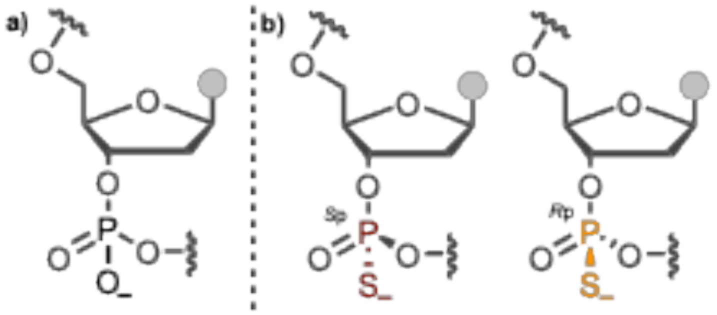

**Figure 1**. Representation of a) native phosphodiesther oligonucleoides structure, b) phosphorothioated modified oligonucleotides in the two possible configurations.

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# Approaching excited state energies for medium size Multi-Reference systems

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Multi-Reference systems are a family of chemical compounds that encompasses all the fields of application of chemistry. Some common examples are transition metal complexes, transition states in reaction pathways or the excited states of highly conjugated molecules. These systems show a rather complicated electronic structure due to near or proper degeneracies between frontier orbitals. Such condition causes a bad description of the system itself with single determinant methods (DFT, CC), since the occupancy of these orbitals is not apparent. To study this kind of systems, specific Multi-Reference methods have been devised and CASSCF[1] is probably the prime method of the MCSCF family. Unfortunately, CASSCF suffers from a double curse of dimensionality, both with the size of the basis set and with the number of active orbitals, that restricts the chance to apply this method to rather small systems with few active orbitals. To push forward the limit of applications of CASSCF, in this work we have developed an algorithm that exploits clever numerical strategies, such as the Density Matrix Renormalization Group (DMRG[2]) method and the Cholesky Decomposition (CD[3]) of the two-electron integrals. Both are rank reducing techniques that exploit the sparsity of the most memory consuming quantities in CASSCF, i.e. the electron-repulsion integrals (ERI) matrix and the FCI tensor, to produce more manageable quantities suited for the application of optimized BLAS routines. As a first application we applied our newly algorithm to the study of the electronic structure of Lutein[4], a carotenoid present in light harvesting systems.

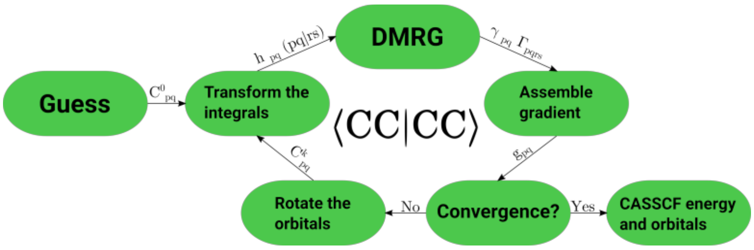

**Figure 1**. Our DMRG-CASSCF algorithm

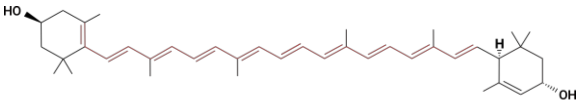

**Figure 2**. Chemical structure of Lutein

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# Synthesis and Characterization of Polymers for Ion and Gas Separations

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The emission of greenhouse gases from human activities is the main cause of climate change and global warming. To contrast this process, new alternative processes with low $CO_2$ emissions must be introduced to decarbonize the energy intensive sectors.

Functionalized polymeric membranes can play a crucial role in the green transition, because they can be optimized for the application in different fields such as gas separation [1], water electrolysis [2], hydrogen fuel cells [3], reverse electrodialysis [4] and $CO_2$ capture [1].

However, these materials do not meet the performance and costs that are required for the application on a large scale and thus further research is needed for them to be industrially relevant and competitive.

When developing new polymeric materials for advanced applications, most of the attention is commonly focused on pushing the performance of the material, but a complete characterization is in some cases missing.

Understanding the structural and phase properties of the material is essential to relate its macroscopic properties to their molecular origin. This acquired information can then be exploited to new materials with even more suitable performances.

In this presentation, we report the synthesis and characterization of ion exchange membranes for water electrolysis and polymers with intrinsic microporosity (PIMs) for the application in gas separation.

Our attention is mainly focused on the characterization of previously reported materials to gain further knowledge of structure-properties relationships. Most of the characterization has been performed using multinuclear NMR, both in solution and solid state.

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# Sustainable asphalt binders: effects of chemical modifications on terminal blend rubberized asphalt

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The terminal blend rubberized asphalt (TBRA) process is an innovative method designed to recycle large amounts of crumb rubber (CR) from End-of-Life Tires (ELTs), involving the depolymerization and devulcanization of CR under heat and high shear forces, with bitumen acting as the reaction medium [1]. In this study, the performance of TBRA binders is evaluated in comparison to a conventional paving-grade bitumen (B50/70), used as a benchmark. With the objective of potentially improving the long-term performance of asphalt mixtures incorporating TBRA binders, the effects of chemical modifications were investigated. Specifically, two oxidation techniques — air blowing and low-temperature aging [2] — and sulfur-based vulcanization [3] were examined, both applied individually and in combination. A series of modified TBRA binders were prepared under controlled conditions and subjected to rheological characterization through dynamic shear rheometry (DSR) and low-temperature testing using the bending beam rheometer (BBR). The results show that these chemical modifications effectively enhance the binder's properties, particularly when oxidation at 163 °C is combined with vulcanization, leading to a notable increase in complex modulus (G*) and improved flexibility at low temperatures, suggesting enhanced elasticity and thermal cracking resistance. These findings highlight the potential of this approach for producing high-performance and sustainable asphalt binders.

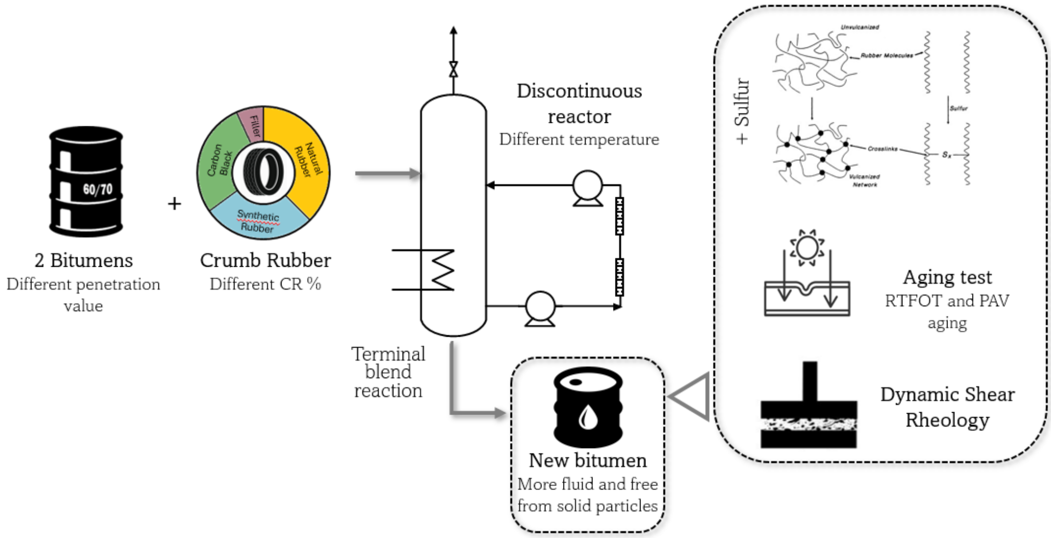

**Figure 1**. Schematic flowchart of materials preparation and their subsequent characterization

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# Electrostatic embedding machine learning for ground and excited state molecular dynamics of complex systems

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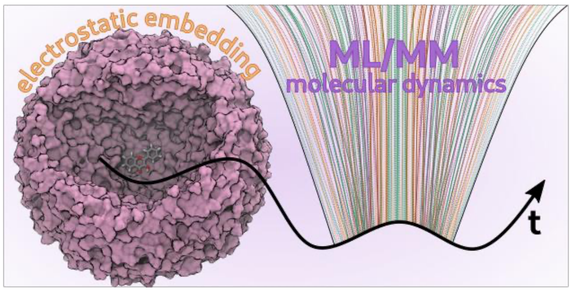
Modelling chemical processes in the condensed phase remains a significant challenge in computational chemistry due to the complex influence of the surrounding environment. This interplay is usually addressed using hybrid quantum mechanics/molecular mechanics (QM/MM) approaches, where a quantum description of the target region is conveniently coupled with a classical representation of the environment.[1] Although these methods balance accuracy and computational cost, their limitations become particularly evident in molecular dynamics (MD) simulations, where the computational cost remains a major challenge, limiting the accuracy of statistical sampling for both ground- and excited-state dynamics. Machine learning (ML) has proven highly useful in this field, providing a cost-effective alternative to QM calculations while preserving high accuracy. From the beginning, ML models for potential energy surfaces have been coupled to MD engines, in order to accelerate ab initio simulations.[2] However, most efforts have focused on isolated systems, with few attempts of including the environment effect for ground-state simulations.[3]

Here, we present two strategies for computationally efficient ML/MM simulations, designed to emulate ab initio QM/MM MD within the electrostatic embedding framework. The first method employs Gaussian process regression to estimate energies and forces by decomposing them into a vacuum contribution and an environment-induced shift, respectively accounting for the internal geometry of the QM part and for the polarization effect induced by the external MM charges.[4] The second approach leverages an equivariant graph neural network[5] that inputs atomic coordinates, atomic numbers, total charge, and environment potential, enabling a physically informed and generalizable treatment of electrostatics. These models facilitate accurate and transferable ML/MM simulations that closely emulate ab initio QM/MM MD while significantly reducing computational cost.



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# Switchable cooperative $CO_2$ adsorption mechanism in multivariate fluorinated metal-organic frameworks

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The concept of multivariate metal-organic frameworks (MTV-MOFs) relies on integrating diverse functionalities by combining multiple linkers, metals, or secondary building units within a single, well-ordered structure. The result is a fine control over tunable chemical environments and multifunctionality in a single material.[1]

In this study, we apply the mixed-linker MTV approach to the phase-change F4_MIL-140A(Ce) MOF, conducting a fundamental investigation into the structural factors driving its peculiar $CO_2$-responsive behaviour (Figure 1). Built from $Ce^{IV}$ and tetrafluorobenzenedicaboxylate linker (F4-BDC), F4_MIL-140A(Ce) exhibits a cooperative $CO_2$ adsorption mechanism linked to a concerted ring rotation, resulting in a non-hysteretic step-shaped adsorption isotherm. This phenomenon is not observed with $N_2$, $CH_4$, and $C_2H_2$, resulting in high $CO_2$ selectivities over these gases.[2]

Our recent findings reveal that removing a single fluorine atom from the MOF ligand suppresses the observed $CO_2$-induced flexibility. This reduced steric hindrance in the less fluorinated linkers enhances access to the $Ce^{IV}$ sites, thereby eliminating the need for cooperative ring rotation to accommodate $CO_2$. Consequently, the partially fluorinated F*x*_MIL-140A(Ce) ($x$ = 2, 3) exhibit conventional Langmuir $CO_2$ adsorption profiles.[3]

However, it remains unclear whether the $CO_2$-induced concerted ring rotation relies on a specific threshold of fluorination or if the position of fluorine atoms on the aromatic ring influences this behaviour. To explore this, we developed a series of F4:F*x*_MIL-140A(Ce) MOFs by systematically varying the F4:F*x*-$H_2$BDC ratios ($x$ = 1, 2, 3), allowing precise control over the degree of fluorination at the molecular level. The PXRD analysis confirmed that all samples formed single-crystalline MIL-140A phases, indicating successful solid solution formation. $CO_2$ adsorption studies showed that the cooperative adsorption is maintained when fluorination exceeds 80%, with the pressure at which the adsorption step occurs remaining consistent regardless of the co-linker used.

Altogether, our results show that the perfluorinated structure of the linker is key to driving cooperativity in MIL-140A(Ce). By adjusting the level of fluorination, this responsive behaviour can be selectively switched on or off, enabling tailored gas adsorption properties.

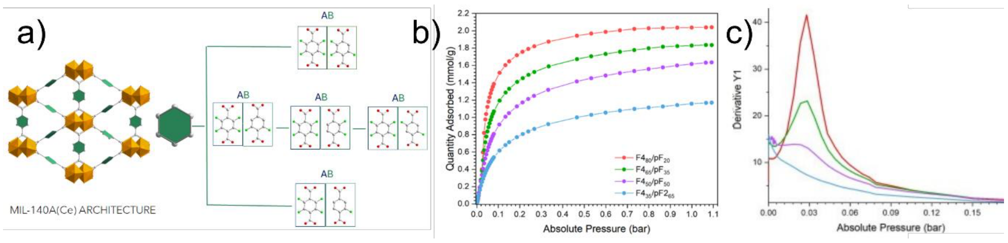

**Figure 1**. Mixed-linker F4:F*x*_MIL-140A(Ce).

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# Epoxy Resins in the Stone Industry

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Thanks to their unique combination of properties, Epoxy Resins are widely used in the stone industry. From blocks extraction in the quarries to the final tiles or panels installation, Epoxy Resins are effectually used for gluing, providing structural consolidation or even for aesthetical treatment of natural stones.

The aim of this presentation is to introduce main Epoxy Resins properties, with special attention to the features making them successful in the stone industry. Furthermore, a brief overview of the industrial application processes will be given.

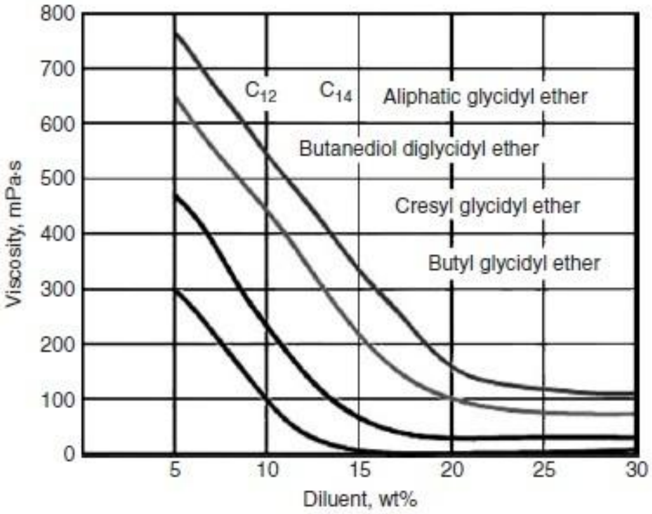

**Figure 1**. Viscosity reduction of a diglycidyl ether of bisphenol A (DGEBA) epoxy resin by reactive diluents. [1]

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# Exsolution-Driven Formation of Ultrasmall $Co_3O_4$ Nanoparticles from CoMo-LDH for Enhanced Water Oxidation Performance

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The development of efficient and cost-effective catalysts for water electrolysis is essential to advance the field of renewable energy.[1] Among transition metal-based systems, Co-Mo layered double hydroxides (LDHs) have garnered attention for their compositional tunability and redox-active sites.[2] In this contribution, we report the synthesis of a Co-Mo oxide composite via a one-pot exsolution-driven approach, involving scalable urea-assisted co-precipitation of Co-Mo-LDH followed by calcination under air. The thermal treatment induces the formation of ultrasmall $Co_3O_4$ nanoparticles (below 2 nm) homogeneously dispersed on an amorphous $CoMoO_x$ matrix, enhancing the electrochemical surface area and electron transport properties. Remarkable electrocatalytic performance was observed respect to monometallic $Co_3O_4$ system obtained by the same approach, as well as a benchmark $IrO_2$ catalyst. Comprehensive ex-situ structural analyses were carried out by transmission electron microscopy (TEM), powder X-ray diffraction (PXRD), Raman spectroscopy, $N_2$ physisorption, and inductively coupled plasma optical emission spectroscopy (ICP-OES).

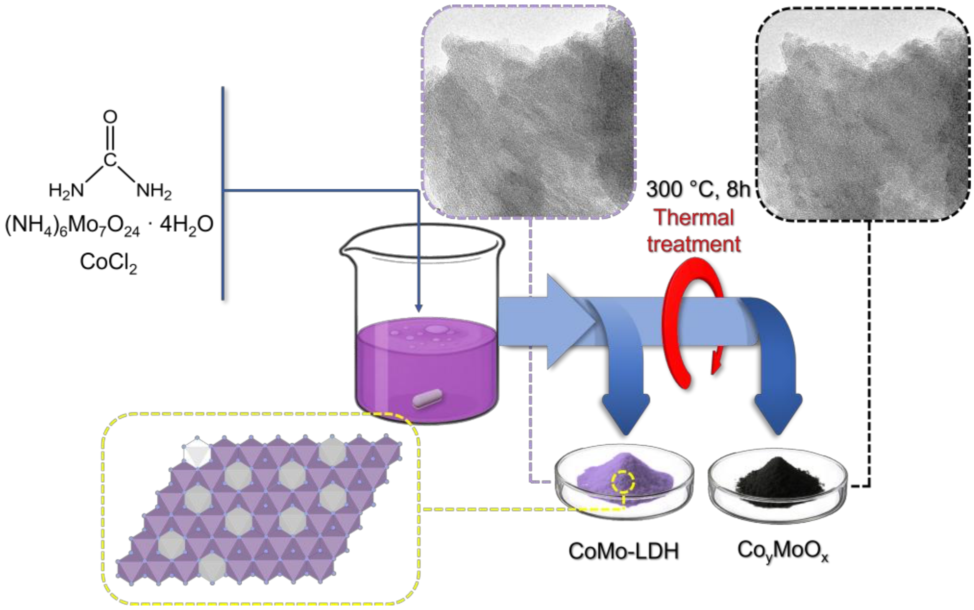

**Figure**. Synthetic approach for the synthesis of CoyMoOx system.

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# Magnetic Modulation of Light Using a Gires–Tournois Metasurface

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Metasurfaces offer remarkable control over electromagnetic wave propagation, and while static metasurfaces have been widely studied, fully realizing their potential in optical applications requires dynamically tunable structures that can adjust their optical properties in real time [1]. A promising strategy to achieve such tunability involves the use of external magnetic fields, which enable non-contact, fast, and reversible modulation of the optical response, without reliance on mechanical components. Notably, technologies generating strong, rapidly varying magnetic fields at sub-micron scales are already mature (*i.e.* hard disk drive write heads) [2]. To leverage this capability, we have designed and fabricated magnetically tunable Gires-Tournois (GT) metasurfaces [3], incorporating ferromagnetic materials into their architecture. These reflective metasurfaces are composed of a multilayer structure: a dielectric spacer separates a bottom reflective layer from an array of top-layer nanodisks, which serve as partially reflective elements. By tailoring the geometry and material properties of the nanodisks, along with the dielectric spacer and embedded ferromagnetic layers, we enable magnetic control over the reflectance spectrum, particularly under circularly polarized illumination. The interplay between the localized surface plasmon resonances (LSPR) of the ferromagnetic nanodisks and layers and the GT cavity resonances, enhanced by Bragg interference conditions, gives rise to rich and tunable optical behavior. This enables precise modulation of reflectance and phase delay at target wavelengths when subjected to external magnetic fields. Such dynamic control renders GT metasurfaces highly promising for a wide range of applications, including real-time intensity modulators, adaptive optical switches, beam shaping elements, and beyond (see Figure1).

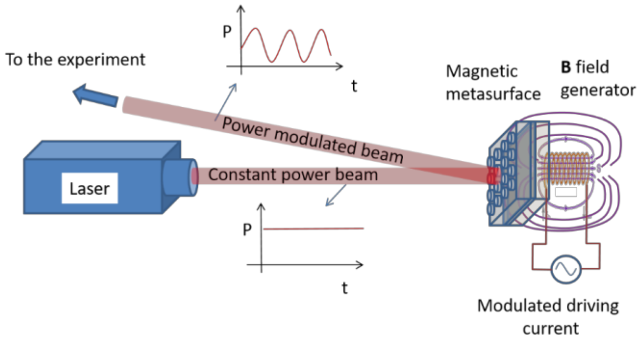

**Figure 1**. Schematic illustration of a Gires–Tournois metasurface operating as an optical intensity modulator.

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# From Complexity to Specificity: First-Principles Simulations of Light-Harvesting in Plant Antennas

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Photosynthetic light-harvesting relies on the precise arrangement of pigments in protein scaffolds to achieve efficient light absorption and excitation energy transfer (EET). Ultrafast spectroscopies, such as transient absorption (TA), are powerful tools to study these dynamics. However, the coexistence of multiple pigments with overlapping spectra and timescales hinders the identification of specific EET pathways. Simulations offer a way to disentangle these signals and connect observed dynamics to molecular structures.

In the first study, we explore CP29, a minor antenna complex found in Photosystem II. Thanks to the combination of quantum chemistry, exciton models, and Redfield–Förster dynamics, we simulate TA spectra, obtaining a good agreement with experimental data on wild-type and mutant complexes[1]. Analysing the underlying theoretical model, we map each kinetic component to specific EET channels, identifying the most important ones. The results show that EET in CP29 is robust against structural perturbations, highlighting the versatility of its pigments network[1]. The approach employed, though perturbative, allows the treatment of systems containing many pigments, each coupled to numerous vibrational modes.

In the second study, we focus on the strongly coupled chlorophyll pair a603–a609 in the Lhca4 subunit of Photosystem I. This system features few, highly coupled states, including low-lying charge-transfer (CT) states that, although inherently dark, become weakly UV-vis active through mixing with excitonic states. Previous calculations suggest ultrafast (~200 fs) dynamics involving these states, but direct experimental observation remains challenging[2]. We use the Hamiltonians calculated in a previous study[3] to simulate the excited-state dynamics with the numerically exact ML-MCTDH method. This allows us to characterize a coherent, non-adiabatic, sub-100 fs population transfer to the CT state. Importantly, the LE–CT energy gap, modulated by the protein environment, critically tunes the CT transfer efficiency. Our results clarify the nature of the emitting state and establish a connection between the red-shifted absorption band and the population transfer toward the CT state.

Together, these two studies explore complementary regimes: the first disentangles the interplay of several EET processes in a complex pigment network through direct comparison with experiments; the second focuses on a smaller system, where simulations offer a detailed view of an EET mechanism that experiments have so far been unable to detect. In both cases, the excitonic parameters are obtained directly from molecular structure, allowing a detailed and physically grounded interpretation of light-harvesting dynamics across different levels of complexity.

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# Plasma Fractionation process

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Human plasma is our raw material; it is collected from “Qualified” donors that have passed two sets of viral testing within 6 months. After release, frozen plasma units are pooled and thawed in a controlled environment at a temperature not to exceed 6°C. Liquid/solid separation of the thawed plasma pool is performed through centrifugation to remove the cryoprecipitate. The centrifugate is cryo-poor plasma, which is collected in a jacketed stainless-steel precipitation tank for further processing. Plasma Fractionation is a selective precipitation of desired proteins from human blood plasma through the careful control of the protein environment using a Cohn-Oncley [1] cold ethanol fractionation process (Figure 1). Five specific factors can be controlled in the fractionation process to achieve protein selective precipitation: ethanol concentration, pH, temperature, protein concentration, and ionic strength. By applying separation methods such as centrifugation, the liquid/solid phases are separated. Another separation method employed as industrial standard is filtration, which, through a filter press applying the principle of "dewatering," pumps the liquid out of the suspended solution, leaving behind a solid cake. Solid cake can be collected and subjected to additional purification steps, usually resuspension in specific buffer solution and additional treatment to increase concentration of target protein or remove elemental contaminant.

Purification process is for example realized through Ultrafiltration, which separates components based on molecular weight and size to isolate the compound of interest. Furthermore, Diafiltration involves adding a buffer to replace the liquid surrounding the target with one that is more suitable for storage stability. Human Albumin is one of the main products derived by plasma using the Cohn cold ethanol fractionation process, followed by specific purification process. The final product is heated at 60.0 ± 1.0°C for 10 to 11 hours for viral inactivation. The preparation contains sodium caprylate and N acetyl tryptophan as the stabilizer, and no preservatives or antibiotics.

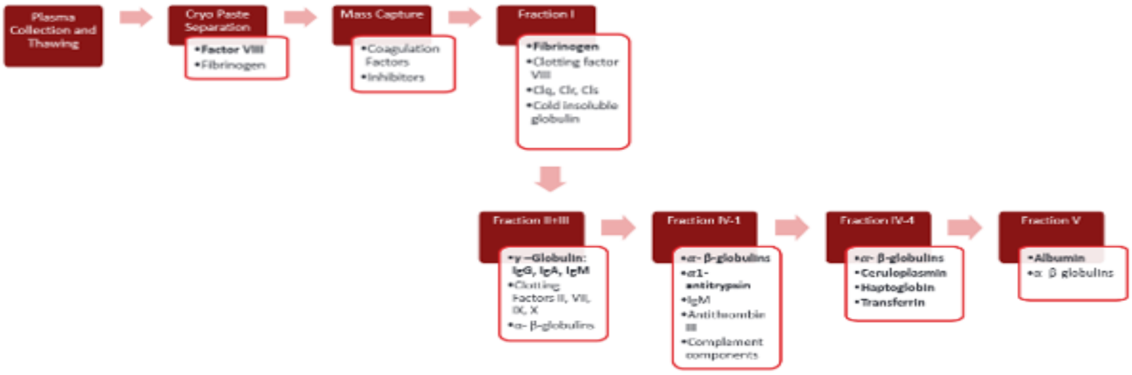

**Figure 1**. Plasma Fractionation process

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# Energy storage devices: performance and safety assessments in $LiFePO_4$ batteries and development of sustainable materials for supercapacitors

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The increasing deployment of energy storage systems across various sectors highlights the need for development of durable performances and sustainable electrode design to support the transition toward environmentally responsible energy solutions [1]. This work addresses two aspects of energy storage: i) the analysis of commercial graphite/$LiFePO_4$ (LFP) battery degradation under realistic cycling conditions and ii) the development of biomass-derived carbon materials for supercapacitor electrodes. Regarding the first aspect, LFP batteries are particularly attractive, due to their high thermal stability, theoretical capacity (170 mAh/g) and low toxicity. Nevertheless, under normal conditions, their degradation progresses over time, and incidents can still occur. While most studies focus on extreme conditions, such as overcharging, relatively little attention has been paid to battery aging working under standard operating conditions. In this regard, this work investigates the aging behavior of commercial LFP batteries under realistic cycling conditions, with the aim of understanding their degradation mechanisms and exploring potential secondary applications once their primary function becomes unfeasible.

The second aspect of our interest regards supercapacitors (SCs), which are attracting increasing interest due to their high-power density, long life and fast charging capability [1]. The primary challenges in SC research mainly include improving energy density, which is still lower than that of batteries, and developing high-performance electrodes [1]. Carbon-based materials, such as activated carbons (ACs), are widely used for electrode fabrication due to their cost-effectiveness, high conductivity and large surface area. Biomass, as a renewable resource, offers a sustainable route for producing carbonaceous chars through thermal processing. However, their limited specific capacitance ($C_s$) has encouraged the exploration of pseudocapacitive compounds (e.g. metal oxides), which allow for higher $C_s$ values [1]. Among them, CuO is particularly appealing, due to its high theoretical pseudo capacitance and favourable electrical conductivity [2]. This work focuses on synthesizing ACs from hazelnut shell waste biomass through different thermal treatments [3], followed by further improvement of the electrochemical performances through the addition of CuO. Our findings confirm the potential of these chars as sustainable SC electrodes, contributing to biomass valorization and supporting circular economy principles.

**Acknowledgment**
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# POSTER COMMUNICATIONS

# High molecular weight redox-active conjugated polymers from multipotent precursor approach

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Conjugated polymers have long been recognized as key materials in organic electronics, yet, in many instances, their processability remains challenging due to their inherent poor solubility and limited polymerization degrees, which limit the scope of several materials in device fabrication. In this study, we introduce a multipotent precursor strategy that enables the synthesis of high-molecular-weight conjugated materials incorporating either anthracene or anthraquinone units from a single precursor. These latter, based on 9,10-dihydroanthracene units, can be polymerized to high polymerization degrees and possess high solubility and processability, thanks to the flexibility of the main chain and the presence of sacrificial side chains. Different post-polymerization transformations allow the selective generation of conjugated polymers, preserving the polymerization degree and generating, from an identical precursor, different conjugated polymers characterized by a different chemical nature and different electronic characteristics.[1] Remarkably, these transformations can also be performed on the precursors in the solid state without affecting drastically their morphology.

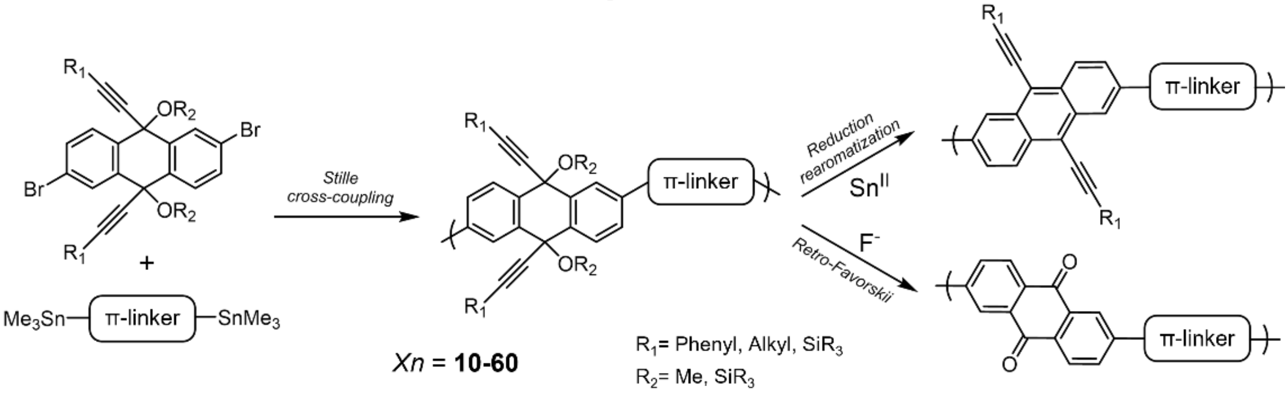

**Figure 1**. General procedure to firstly afford polymeric precursors, followed by post-polymerization reactions to obtain electronically complementary final polymers.

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# Esterification of hexanoic acid to hexyl hexanoate with heterogeneous Amberlyst resins: Optimization study on model compounds and grape pomace-derived fermentation crudes

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Esters are attracting great industrial interest, being exploitable for different applications (solvents, flavours, lubricants, plasticisers, biofuels, etc.) [1]. Esterification is an equilibrium reaction, needing of appropriate Brønsted acidity to overcome catalytic issues. Moreover, an excess of the alcohol is generally employed (typically, alcohol/carboxylic acid molar ratio higher than 4), and the removal of the produced water is sometimes carried out to maximize its production. In this context, hexyl hexanoate (HexHex) is industrially attractive as fragrance, lubricant, but also as oxygenated additive for diesel fuels [1]. As for other esters, mineral acids have been traditionally used to catalyse HexHex synthesis, but these show relevant environmental and work-up issues [2]. In this work, commercial sulfonic resins (Amberlyst) were employed for the HexHex synthesis, which was univariately optimized. Focusing on the most effective resin (Amberlyst-35), according to Figure 1, the catalyst loading was minimized, keeping a low alcohol/carboxylic acid molar ratio of 2, which is an effective choice for simplifying the next work-up. The in-situ use of a drying agent was also considered, to maximize the HexHex production. These optimized reaction conditions have been applied to the conversion of hexanoic acid-rich real feedstock, obtained by a novel biotechnological process of acidogenic fermentation of grape pomace, confirming the excellent results from the model compounds.

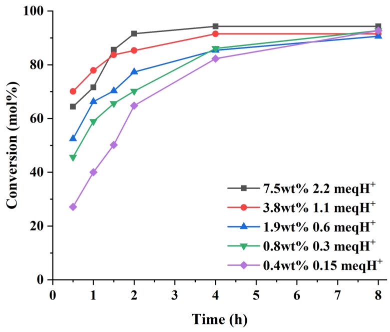

**Figure 1**. Kinetics of the HexHex synthesis at 120 °C, employing a constant alcohol/carboxylic acid molar ratio of 2, and different loadings of Amberlyst-35.

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**Acknowledgement:**

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# Water management of styrene-butadiene-based anion exchange membranes for energy application

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Hydrogen production and use through anion exchange membrane (AEM) water electrolysis and fuel cell (AEM-WE and AEM-FC) are promising approaches to aid the transition towards net-zero emissions. However, the fabrication of high-performing AEMs, in which the chemical, mechanical and electrochemical requirements are combined and optimized in a synergistic way, still represents a challenging task.[1]

A more precise understanding of water management and morphological properties is mandatory to help polymer scientists in the design and the development of highly conductive, yet mechanically robust, materials with superior durability in real working conditions both for water electrolyzers and fuel cells. More in detail, in this work we focused on surface morphology characterization and water management of AEMs prepared via radical functionalization reaction of a styrene-butadiene (SB) copolymer with vinyl benzyl chloride (VBC).[2,3] In particular, atomic force microscopy (AFM) technique was employed to investigate the presence of phase-separated morphologies for AEMs with different VBC FDs (15 and 27 mol%), while differential scanning calorimetry (DSC) analysis performed on wet samples was found to be effective for the determination of the amount of mobile (i.e freezable) water. Water transport measurements confirmed the positive effect of higher FDs when a water concentration gradient is applied, as in the case of AEM-FCs. Ion conductivity tests at different temperatures (20–80 °C) and relative humidities (50–100%) further highlighted the need for a minimum amount of ionic sites to effectively transport water under severe dehydration conditions. Finally, AEMs were tested both in fuel cell and in real water electrolysis working conditions (816 mA $cm^{-2}$, 55 °C) to gather further evidence of the benefits obtained from higher VBC FDs.

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**Acknowledgements:** The authors acknowledge the project “Membrane polimeriche a scambio anionico per la produzione di idrogeno verde – MOVE” co-funded by Regione Toscana and Enapter srl.
The Authors of the University of Pisa thanks for the partial financial support to this work the National Recovery and Resilience Plan (NRRP), Mission 4 Component 2 Investment 1.3 - Call for tender No. 1561 of 11.10.2022 of Ministero dell’Università e della Ricerca (MUR) (funded by the European Union – NextGenerationEU). Project code PE0000021, Concession Decree No. 1561 of 11.10.2022 adopted by Ministero dell’Università e della Ricerca (MUR), Project title “Network 4 Energy Sustainable Transition – NEST”

# Inkjet printing of electronic traces on nanopaper

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In recent years, sensors have gained a place in every aspect of life. From blood sugar measurement to complex arrays in modern cars, every aspect of life is controlled by one or multiple sensors. To simplify their application in some fields, like biomedical or food monitoring, flexibility of the substrate is required. Furthermore, with the growing attention to plastic pollution, an alternative to standard supporting materials is needed. Paper has already been proven a valid option for a flexible, renewable, recyclable and biodegradable substrate for electronic devices. In this work we evaluate the feasibility of nanopaper as an advanced material for electronic printing. The first step in this direction is to optimize the process to obtain cellulose nanocrystals from standard cellulose pulp, then comes the optimization of the nanopaper production from the obtained nanocrystals and finally the printing of electronic traces on the nanopaper.

To prepare the nanocrystals, we started from enzymatic processes already present in the literature[1,2] and we modified them to better suit the substrate we are working with. Given the dry nature of the cellulose pulp we are using, pretreatments were necessary to obtain better dispersion of the pulp and, therefore, higher yields. The tests involved the application of mechanical or chemical pretreatment, the optimization of reaction time and enzyme loading. This allowed an overall increase of the reaction yield.

Nanopaper was prepared depositing dispersions in water at various concentrations on microscope glasses. Both neutral cellulose nanocrystals and oxidized nanocrystals were used for this purpose, in the attempt of preparing a continuous and smooth film suitable for electronic printing.

Finally, inkjet printing tests of electronic traces were carried out on commercial ultra-refined paper (Sylvicta, Fedrigoni SpA), and on the nanopaper. The best results were obtained on the oxidized nanocellulose film thanks to the smooth and continuous layer.

This work poses the basis for further improvements in this field, showing promising results for the printing of electronics on nanopaper and nanocellulose-coated commercial paper.

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# Bi(or not too Bi)o plastics: environmental issues and analytical challenges

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In recent years, biodegradable and compostable plastics have become a part of everyone's daily lives[1]. They are an heterogenous family of complex materials with different properties and characteristics, which allow them to replace conventional plastic products in many applications. To improve their mechanical properties and to reduce their production costs, bioplastics are produced as blends. Non-biodegradable plastics, mainly polyethylene, are often also added to these blends. European standards currently regulate the requirements for materials to be considered or marketed as biodegradable. However, there are still no specific guidelines for bioplastics. Moreover, there are limited information on how bioplastics behave during the degradation process and once released in the environment. Many challenges need to be addressed. The presented work highlights the key aspects that should be explored to investigate bioplastics throughout their entire lifecycle. The aim is to develop new analytical methods to study bioplastics from the production step to the degradation process in natural, controlled, and composting conditions. Advanced analytical techniques such as analytical pyrolysis, gas chromatography and mass spectrometry play a fundamental role in this project. In fact, they have been proven to be effective and reliable for the analysis of polymers and their blends[2], [3]. The developed methods will be used to understand the characteristics of bioplastics and verify their compliance with the existing legislations, as well as improving our knowledge on what happens during their degradation. It is essential to focus on various aspects of bioplastics managing, starting with the quantification of the non-biodegradable fraction in the blends, then the study of the biodegradation process, and finally investigating the micro-bioplastics formation in composting plants. The answers to all these questions will be crucial for updating bioplastics legislations, developing new and efficient waste management strategies, and achieving the transition to a circular economy.

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# A quest for uncommon prostanoidic derivatives

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The isoprostanes (IsoPs) and congeners are naturally occurring compounds generated *in vivo* by the free-radical autoxidation of polyunsaturated fatty acids. Due to their mechanism of formation, the IsoPs are among the best biomarkers to assess oxidative stress (OS), a condition known to be involved at the onset and in the progression of several human and animal diseases.[1,2] For this reason, the availability of cheap IsoP standards is a strong current need in analytical and clinical studies.

Whereas a few prostanoidic compounds are included in the portfolio of specialized chemical suppliers, the vast majority of regio- and diastereomeric isomers expected to form via the oxidative radical cascade (*e.g.*, 32 enantiomeric pair in the autoxidation of arachidonic acid) are not commercially available and, in most cases, have never been described in the literature.

To fill this gap, in the past five years we endeavoured to develop some new and compact, stereocontrolled routes to the IsoPs, all relying as a key step in the [3+2] cycloaddition reaction of a trimethylene-methane (TMM) equivalent to a suitable cyclopentene derivatives.[3,4]

Building on these previous investigations, we report herein the recent efforts towards the preparation and characterization of selected regio- and diastereoisomers of the well-known and commercially available 15-$F_{2t}$-IsoP epimeric pair (**1**).

The possible identification of some of these novel IsoPs in biological fluids will be also briefly commented.

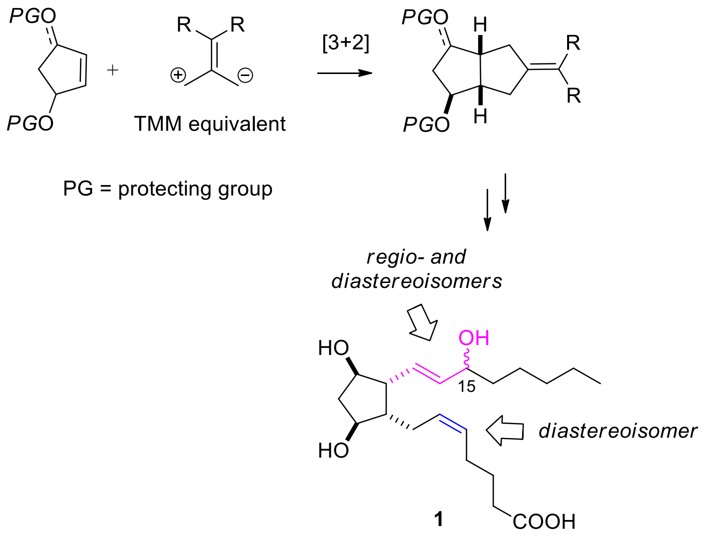

**Figure 1**. Approach to regio- and distereoisomers of 15-$F_{2t}$-IsoP (epimeric pair at C15).

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# Rhodamine-Loaded Smart Polymers for Visible Sensing: A Cost-Effective Approach to Optical Responsiveness

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In recent years, there has been significant growth in the study of optically responsive materials that react to various external stimuli. These so-called *chromogenic materials* typically consist of polymer matrices doped with active compounds capable of altering their optical properties—such as absorption, fluorescence, or refractive index—in response to environmental changes.[1] Their ability to transduce stimuli into visible optical signals makes them highly attractive for applications in sensing, smart coatings, and adaptive optical devices. These effects are generally associated with molecular or supramolecular changes, including aggregation or isomerization of the embedded chromogenic dyes.[2]

In this work, we explore the use of rhodamine-based molecular probes as efficient, low-cost, and multi-responsive chromophores for smart polymeric systems. Rhodamine derivatives are presented as a compelling alternative to traditional mechanophores like spiropyran, which suffer from complex, multistep synthesis and limited yields.[3] In contrast, rhodamine offers straightforward, high-yield synthesis and remarkable responsiveness, making it suitable for incorporation into diverse polymer matrices such as polyolefins, polyacrylates, and polyurethanes. These derivatives exhibit reversible isomerization between a non-fluorescent spirolactone (closed) form and a highly fluorescent zwitterionic (open) form, triggered by stimuli including pH changes, mechanical deformation, and photo-irradiation (Figure 1).[4] This structural switching leads to dynamic and reversible optical shifts, enabling real-time detection of external stimuli through visible signals. Our findings highlight the potential of rhodamine-functionalized polymers as cost-effective and versatile platforms for the development of next-generation smart materials and sensor technologies.

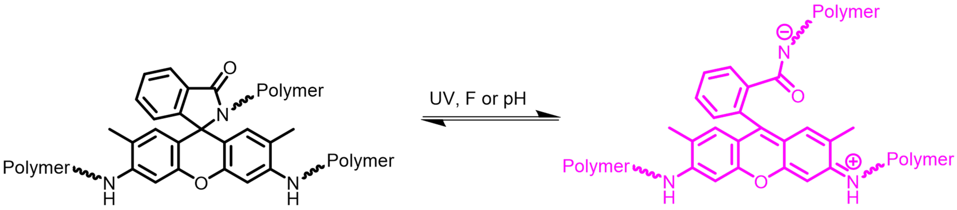

Figure 1: Multi-responsive behaviour of rhodamine derivatives.

**Acknowledgments:** This work was funded by the European Union (ERC, project MaMa, n.101097351).

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# Innovative Applications of Cellulose Nanocrystals in the Restoration of Historical Paper

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Today, thanks to innovations in materials science, new frontiers are opening for the preservation of Cultural Heritage. Nanocelluloses, and particularly cellulose nanocrystals (CNCs), are emerging as innovative materials for Cultural Heritage conservation, especially for paper artworks. [1] Their physical and chemical properties offer effective solutions for the consolidation of historical paper without the use of traditional adhesives. [2] CNCs are non-toxic materials, making their use safe for restorers and for the artwork itself. They can be applied directly to paper via an aqueous suspension and a simple brush. Once applied, CNCs form a transparent coating that does not alter the visual appearance of the work (Figure 1). They also offer good resistance to degradation, protecting the paper fibers over time.[3] Furthermore, the use of CNCs in paper consolidation represents a significant advance due to the reversibility, achievable by applying to the treated artwork a cleaning step performed with polysaccharide hydrogel. This last feature is pivotal for ensuring effective preservation of the artworks even from the degradation of the applied treatment. The project “SALVABIO - Sustainability and Biocompatibility for the Conservation of Book Heritage with Nanocellulose” is funded by the region of Tuscany under the FSE+ program 2021-2027. Tuscany, with its vast library holdings, has always been a bastion of cultural preservation, guardian of priceless works on paper. SALVABIO will support developing and refining nanocellulosic materials, including their compatibility with various solvents, that could revolutionize restoration techniques by providing sustainable and non-invasive solutions to preserve artworks and historical documents for future generations.

**Figure 1.** Images of pages and details from *Breviarium romanum ad usum fratrum minorum* treated with (A) water (pristine); (B) S_CNC; and (C) N_CNC.

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[3] Proposed standard terminology for cellulose nanomaterials from TAPPI WI 3021

# Evaluation of polyethylene content in bioplastic blends by microwave-assisted hydrolysis and analytical pyrolysis

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In the last years, the role of biodegradable and compostable plastics has become gradually more important. Their development has made it possible to progressively replace the use of non-biodegradable plastic products[1]. To improve their properties and reduce production costs, bioplastics are made of blends of several polymers among which it is also possible to find non-biodegradable polymers, mainly polyethylene. Current European standards (EN 13432:2002) establish that the content of non-biodegradable material within bioplastic blends must be lower than 1% by weight of the mixture itself. However, there are no guidelines on how to measure the content of this non-biodegradable components. Measuring the amount of non-biodegradable organics in biodegradable blends is fundamental both in control phases during production and in screening phases within composting plants. Advanced analytical techniques, such as analytical pyrolysis coupled with gas chromatography and mass spectrometry (Py-GC-MS), have proved to be effective for the study of polymers and copolymers[2,3]. However, the analytical approach can become complex when dealing with quantifying small fractions of components within complex blends. In addition, these methods cannot be suitable for routine screening investigations. Simpler, but at the same time reliable methods are required for routinary controls both during production and at the end of life of biodegradable materials. This work will present the development of an analytical procedure to isolate small amounts of polyethylene from complex biodegradable plastic formulations. The procedure is based on the use of microwave-assisted heating to degrade the biodegradable organic fraction and separate it from the non-biodegradable fraction. Formulations of bioplastics containing polylactic acid, polybutylene adipate-co-terephthalate, thermoplastic starch, calcium carbonate and polyethylene in known quantities are used to develop and test the method. Experimental design allow the optimal condition for degradation of the biodegradable part to be achieved. Once polyethylene is recovered from the matrix, it can be easily quantified by Py-GC-MS.

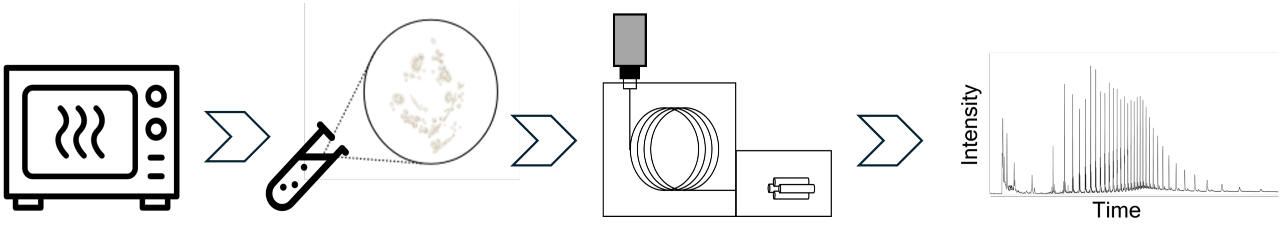

**Figure 1**. Matrix simplification scheme and analysis by Py-GC-MS.

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# Eco-Friendly Leather Tanning with Polyglycerols: Toward the Development of a More Sustainable Process

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Leather tanning is a chemical process of crucial relevance in the national industrial context, requiring chemical agents to stabilize the collagen matrix of animal hides. This set of treatments prevents the biological degradation of the raw hides, effectively transforming them into stable leather and enhancing the chemical-mechanical properties of the final product. Currently, alkaline chromium salts remain the most widely used tanning agents, but their use leads to significant environmental and toxicological concerns [1]. In this context, the INCANTO project ("INnovative Tanning Through New Types of Optimized Polyol-Based Tanning Agents") investigates the synthesis and use of polyglycerols as sustainable and metal-free alternative to conventional chromium-based systems. Polyglycerols are synthesized from glycerol feedstock, the main by-product of biodiesel production, thus supporting the circular economy approach of the same process. The hydroxyl groups in polyglycerols can facilitate the formation of hydrogen bonds with collagen, stabilizing the protein macrostructure [2]. Their functional behaviour is influenced by molecular structure (linear or branched) and the degree of functionalization [2]. Although branched polymers have been investigated in the literature for pre-tanning applications and/or for modifying wet-blue leather [3], the linear forms remain largely unexplored. In this context, our work focuses on the production of linear polyglycerols at high molecular weight starting from low molecular weight ones, which have been characterized for their degree of functionalization [4], in terms of OH groups and molecular weight distribution, in order to correlate the tanning performances with their chemical properties [5]. In this context, tanning tests have shown promising results for short-chain and linear polyglycerols, so now our ongoing research is focused on testing tanning performances of higher molecular weight polyglycerols. For this purpose, polymerization tests are in progress, employing *p*-toluenesulfonic acid or sulfuric acid as acid catalysts, aimed at modulating the degree of functionalization, molecular structure and chemical reactivity and, consequently, optimizing the physical and chemical performances of the resulting leather.

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# Boost of Oxygen Evolution Reaction (OER) by Chiral Spirobifluorene Additives

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The water splitting is becoming a new tool to produce green H$_2$. However, the oxygen evolution reaction (OER) remains a limiting step that prevents more efficient hydrogen production.[1] On the other hand, it has been demonstrated that chiral compounds can influence this reaction, reducing the overpotential that must be applied thanks to the chiral-induced spin selectivity (CISS) effect.[2]

For this reason, one of the main motivations of our research group is to obtain stable and robust chiral compounds to improve OER. Spirobifluorenes (SBFs) have shown to be compounds with a rigid skeleton and high conformational stability that present a chiral axial axis,[3] making them promising candidates for use as additives in OER.

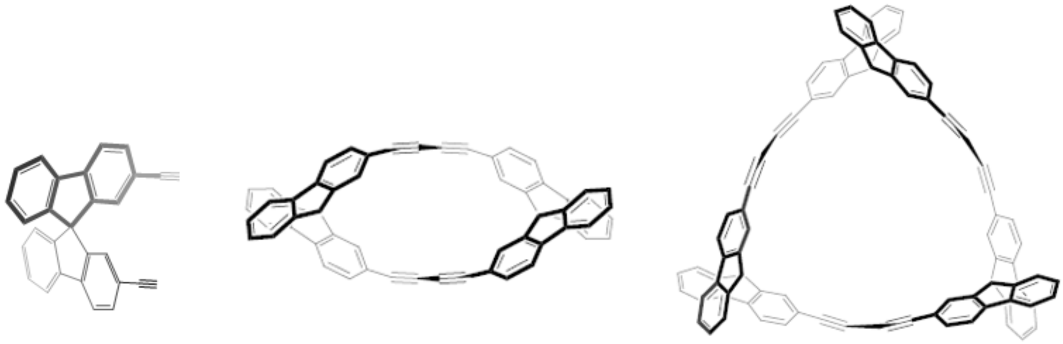

**Figure 1**. Homochiral structures from (P$_1$)-**DES$_1$**, (P$_2$)-**DES$_2$**, and (P$_3$)-**DES$_3$**.

In this study, chiral diethynylspirobifluorene (DES) ($P_1$)-**DES$_1$** and macrocyclic oligomers ($P_2$)-**DES$_2$**, and ($P_3$)-**DES$_3$** were employed to investigate their potential in electrocatalysis for alkaline OER (Figure 1). Nickel felt electrodes were functionalized with the chiral SBFs by drop casting and employed for OER. The results show that electrodes functionalized with ($P_2$)-**DES$_2$** and ($P_3$)-**DES$_3$** increase the catalytic activity compared with Ni felt alone while those functionalized with monomer ($P_1$)-**DES$_1$** worsens OER. Notably, both macrocycles, ($P_2$)-**DES$_2$** and ($P_3$)-**DES$_3$**, present significantly larger ECD and *g*-factor as compared to monomer ($P_1$)-**DES$_1$**, correlating the *g*-factor of the chiral additives with the overpotential reduction. We foresee that our results open new avenues for efficient of green H$_2$ production using chiral SBFs with improved g-factors, a goal we are currently working on.

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# Bis-chelated Palladium(II) complexes as an alternative to Platinum(II)-based compounds

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The aim of the present work is to evaluate new Pd(II) complexes as anticancer agents, due to their structural similarity to the platinum(II) clinically established complexes [1].

Since Pd(II) complexes hydrolyse much faster than their Pt(II) analogues, strong bidentate nitrogen ligands have been selected for achieving a sufficient kinetic stability [2].

Experimentally, the dichloride precursors 1a-c have been prepared starting from $PdCl_2$. Subsequently, compounds 2a-c have been prepared through the coordination of (1R,2R)-(−)-1,2-Diaminocyclohexane to the metal centre. (Fig. 1) [2,3].

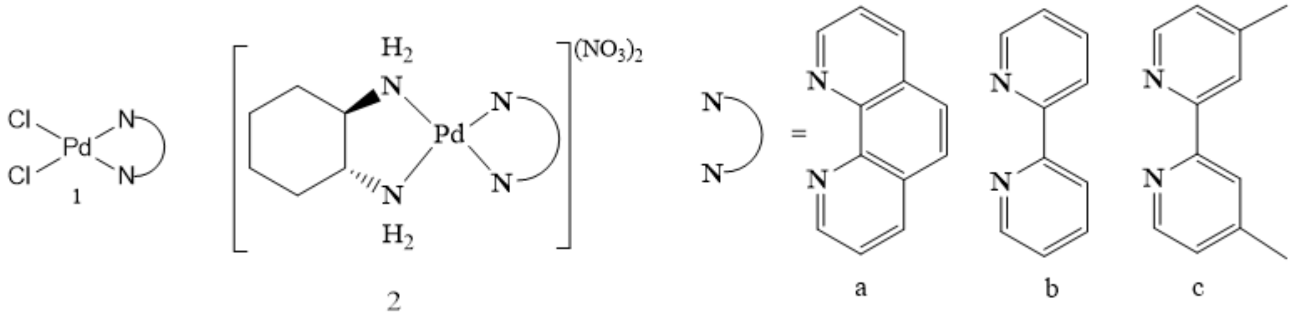

**Figure 1**. Chemical structures of the studied Pd(II) metal complexes

All complexes were characterized using spectroscopic methods ($^{1}H$- and $^{13}C$-NMR, FT-IR) and elemental analysis. Solubility and stability in physiological-like conditions will be evaluated.

Finally, these Pd-based compounds (1a-c and 2a-c) will be subjected to biological activity tests on tumour cell lines and, at least one normal cell line to evaluate cancer selectivity. Cell viability and the ability to induce apoptosis will be evaluated. Further studies will be conducted to investigate the possible mechanisms of action. Since DNA is a possible target for palladium(II) compounds, the interaction with natural calf-thymus DNA will be evaluated.[3]

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# Low-cost Inkjet-Printed nanostructured biosensor based on CRISPR/Cas12a system for pathogen detection

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The escalating global incidence of infectious diseases caused by pathogenic bacteria, especially in developing countries, emphasizes the urgent need for rapid and portable pathogen detection devices. As traditional techniques are time consuming, expensive and do not allow for a point-of-need analysis, biosensors represent a valid alternative, because of their low-cost, portability, ease of use and availability for point-of-care/need applications. This study introduces a sensitive and specific electrochemical biosensing platform utilizing cost-effective electrodes fabricated by inkjet-printing gold and silver nanoparticles on a plastic substrate [1]. The biosensor exploits the CRISPR/Cas12a system for detecting a specific DNA sequence selected from the genome of the target pathogen [2]. Upon detection, the trans-activity of Cas12a/gRNA is triggered, leading to the cleavage of rationally designed single-strand DNA reporters (linear and hairpin) labelled with methylene blue (ssDNA-MB) and bound to the electrode surface, leading to the decrease of the square wave voltammetry (SWV) MB associated signal. In principle, this sensing mechanism can be adapted to any bacterium by choosing a proper guide RNA to target a specific sequence of its DNA. The biosensor's performance was assessed for two representative pathogens (a Gram-negative, Escherichia coli, and a Gram-positive, Staphylococcus aureus), and results obtained with inkjet-printed gold electrodes were compared with those obtained by commercial screen-printed gold electrodes. Our results show that the use of inkjet-printed nanostructured gold electrodes, which provide a large surface area, in combination with the use of hairpin reporters containing a poly-T loop [3] can increase the sensitivity of the assay corresponding to a signal variation of 86%. DNA targets amplified from various clinically isolated bacteria, have been tested and demonstrate the potential of the proposed platform for point-of-need applications.

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# Assessing Vesuvine dyes degradation in historical textiles: solid-state modelling of aldehyde-induced interactions

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Environmental conditions play a critical role in the preservation of cultural heritage artifacts [1]. Assessing their impact is pivotal to heritage science, both for understanding the chemical processes underlying the ageing and degradation of organic dyes and for developing effective preservation strategies. Recent work by Chen et al. [2] has shown that volatile organic compounds (VOCs) emitted from support and conservation materials are key contributors to the degradation of the widespread dye Congo Red (C.I. 22120, Direct Red 28), with small aldehydes identified as the primary agents responsible for the fading of dyes containing disazo-naphthionyl moieties. In our investigation of a catalogue of silk threads dyed with basic colorants and produced in 1951 by the ACNA company (Milan, Italy) [3], several samples labelled as 'Vesuvina' (samples 65, 67, and 69) exhibited unexpected molecular profiles. These were characterised by the presence of unknown degradation products and the absence of the original dyes—Bismarck Brown Y (C.I. 21000, Basic Brown 1) and Bismarck Brown R (C.I. 21010, Basic Brown 4)—by suggesting that Vesuvine-based dyes are chemically unstable, undergoing significant molecular changes over time that complicate their identification in historical artifacts.

Due the chemical similarities between Vesuvine dyes and Congo Red, in this work we simulated the interactions between volatile aldehydes (i.e., formaldehyde, acetaldehyde, and benzaldehyde) and Bismarck Brown Y both in-solution (25 °C, 15 hours) and with the solid dyes cast on glass slides (25 °C, 6 months). The results achieved with liquid chromatographic techniques (HPLC-DAD, HPLC-HRMS) enabled us to broaden our understanding of the reactivity of disazo-naphthionyl moieties. We disclosed that Vesuvine dyes, consistently with the negative charge delocalisation of the nitrogen atoms involved in azo bond, react with aldehydes by forming six-membered rings and not imidazole-aldehydes products as reported for Congo Red [2]. In addition, besides the formation of monocyclic and bicyclic aldehydes-degradation products, further mechanisms as consequent oxidation processes of aldehyde-Vesuvine cyclic products were uncovered. The HPLC-DAD-ESI-Q-TOF database of molecular markers developed from model systems was subsequently used for shedding light on the ACNA 'Vesuvina' samples, allowing us to reconstruct the profile of Bismarck Brown Y in sample 65, Bismarck Brown R in sample 69, and a mixture of both dyes in sample 67.

These findings, along with the identification of a monoazo intermediate and its aldehyde-degradation products, underscore the chemical complexity of Vesuvine dyes and provide a framework for interpretating the degradation of these dyes in historical samples. Future works will extend our study on model systems through spectroscopic techniques, such as SERS and TLC-SERS, to pave the way for non-destructive investigation of Vesuvine-based historical samples.

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# Natural materials Development from Collagen-based Wastes – ArtDECOW: mild treatment and solubilization methods

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The leather industry presents a major environmental issue due to the large amounts of waste it generates. Developing a green approach for utilizing this waste can contribute to the sustainable recovery of proteins, transforming them into valuable bioresources.[1]

The ARTDECOW project focuses on developing eco-friendly methods for collagen treatment and solubilization, aiming to sustainably recover proteins from leather waste. This approach would enable the exploitation of collagen to create versatile, high-performance collagen-based biomaterials (CBBM).

In the first part of this study, vegetable-tanned leather waste was treated under mild experimental conditions using a green solvent system, Deep Eutectic Solvents (DES), highlighting a sustainable and gentle approach to the valorisation of leather waste. Successfully creating a biomaterial suitable for use as glue. In the second part, the same solvents systems were used to fully solubilize the leather and isolate collagen gelatine. The yields obtained were promising, especially compared to lower yields reported for not tanned leather waste in the literature. [2]

The vegetable tanned leather and the samples obtained from the developed methods were analysed by Fourier transform infrared spectroscopy (FTIR-ATR) to analyse the secondary structure of proteins [3], differential scanning calorimetry (DSC) to investigate more in detail the thermal behaviour of samples and thermogravimetric analysis (TGA) to characterize the thermal degradation of samples.

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# The Va3SCoDi project: historical scientific instruments for the valorization and dissemination of scientific knowledge

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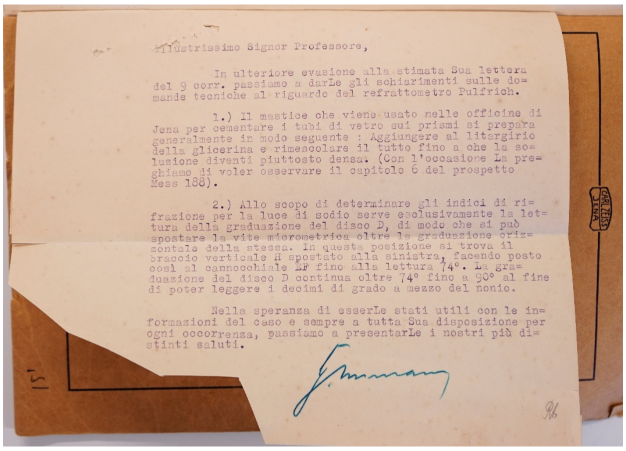
This poster will show the outline and first discoveries of the 'Va3SCoDi' research project, dedicated to the valorisation of historical scientific instruments through communication and dissemination of knowledge. Thanks to the grant bestowed by Regione Toscana it will be possible to document and catalogue the collection of historical scientific instruments of the Dipartimento di Chimica e Chimica Industriale (DCCI) of the Università di Pisa. This process will allow us to deepen our understanding of how historical scientific instruments can be used as educational tools, to use them to raise awareness toward scientific oriented studies and also to increase familiarity toward laboratory instrumentation and technical knowledge. The poster will portray some new archival sources, discovered inside the Archivio Generale of the university, about the formation of the collection and the acquisition of important instruments linked the scientific activities of important chemistry practitioners of the past like Raffaello Nasini and Camillo Porlezza. It will also show some of the historical practices used by scientific instruments maker in the creation and caring of these devices (*Figure* 2), comparing the sources with the original instruments (*Figure* 1) preserved inside the DCCI collection.

**Figure 1.** Carl Zeiss, Pulfrich's Universal Refractometrer



Illustrissimo Signor Professore,

In ulteriore evasione alla stimata Sua lettera del 9 corr. passiamo a darLe gli schiarimenti sulle domande tecniche al riguardo del refrattometro Pulfrich.

1.) Il mastice che viene usato nelle officine di Jena per cementare i tubi di vetro sui prismi si prepara generalmente in modo seguente : Aggiungere al litargirio della glicerina e rimescolare il tutto fino a che la soluzione diventi piuttosto densa. (Con l'occasione La preghiamo di voler osservare il capitolo 6 del prospetto Mess 188).

2.) Allo scopo di determinare gli indici di rifrazione per la luce di sodio serve esclusivamente la lettura della graduazione del disco D, di modo che si può spostare la vite micrometrica oltre la graduazione orizzontale della stessa. In questa posizione si trova il braccio verticale H spostato alla sinistra, facendo posto così al cannocchiale EF fino alla lettura 74°. La graduazione del disco D continua oltre 74° fino a 90° al fine di poter leggere i decimi di grado a mezzo del nonio.

Nella speranza di esserLe stati utili con le informazioni del caso e sempre a tutta Sua disposizione per ogni occorrenza, passiamo a presentarLe i nostri più distinti saluti.

**Figure 2.** Carl Zeiss instruction for the use of the instrument

# From Waste to Wealth: Eco-Friendly Extraction of Collagen and Polyhydroxyalkanoates for Industrial Applications

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The extraction of high-value biomolecules from natural sources represents a key strategy for the development of sustainable technologies, with applications in fields such as biomedicine, cosmetics, nutraceuticals, and biodegradable materials [1]. In a global context marked by increasing production of organic and agro-industrial waste, there is an urgent need to transform such residues into valuable resources, promoting approaches based on **circular valorisation of waste materials [2]**. In this framework, the present study focuses on two biomolecules of particular relevance: **collagen**, the main structural protein in animal connective tissues, and **polyhydroxyalkanoates (PHAs)**, a family of biodegradable polyesters synthesized by microorganisms. The main goal is to **optimize extraction processes** to improve efficiency, yield, and environmental sustainability.

Collagen was extracted from **fish scales**, a by-product of the seafood industry, using two different approaches: acidic solubilization and enzymatic hydrolysis. The process includes preliminary pretreatments to remove undesired components and obtain a cleaner matrix. This low-cost and abundant alternative source enables the valorization of organic waste and reduces the environmental impact of production. In parallel, PHAs were obtained from **bacteria cultivated on carbon-rich substrates**, including agro-industrial waste and organic effluents. Although chloroform is commonly used as an effective solvent for PHA extraction, its toxicity and low sustainability hinder industrial-scale application. Therefore, the study explored the use of **green solvent alternatives** capable of achieving significant yields and acceptable purity levels for future large-scale use.

The extracted biomolecules were **characterized using Fourier-transform infrared spectroscopy (FTIR)** to confirm their chemical structure and **thermal analysis techniques (TGA and DSC)** to assess stability and thermal properties.

This work contributes to the advancement of **sustainable bioextraction technologies**, highlighting the industrial potential of eco-friendly processes for the recovery and valorization of natural residual resources. The proposed optimizations open new perspectives for the integration of these biopolymers into innovative and environmentally responsible production chains.

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# Electrochemical biosensor for the quantification of Urea in dialysate and blood

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Since the invention of dialysis, patients with renal diseases have benefited from a noticeable increase in both quality of life and life expectancy due to the continuous progress of this therapy. In 1985, a group of researchers led by Gotch and Sargent introduced a parameter with the objective of assessing the adequacy of dialysis: **Kt/V** [1]. During this therapy, the concentration of uremic toxins in blood decreases exponentially. **Kt/V** is correlated with the concentration of urea in plasma pre- and post-dialysis and represents the exponential coefficient related to urea clearance. The efficiency of filtration also varies with molecular size, and urea is considered the ideal marker for assessing the removal of small molecules. For these reasons monitoring urea concentration in dialysate ensures effective hemodialysis and helps healthcare providers adjust treatment for optimal results. In this work, an enzymatic electrochemical biosensor for the detection of urea is proposed. The system, which requires minimal sample pretreatment, makes use of urease, a NAD/FAD independent enzyme, and a pH sensitive indoaniline derivative, can be used to perform live measurements in both dialysate or blood during treatment. The sensing mechanism is relatively simple. The ammonia, produced from the breakdown of urea by urease, originates a local variation of pH that is first measured by assessing the shift of an indoalinine derivative or riboflavine peak in square wave voltammetry (figure A), and then correlated to the urea concentration. Sensors with different dynamic ranges can be fabricated by varying the amount of enzyme during production (figure B), allowing sensor use in matrices with different concentration levels of the target analyte.

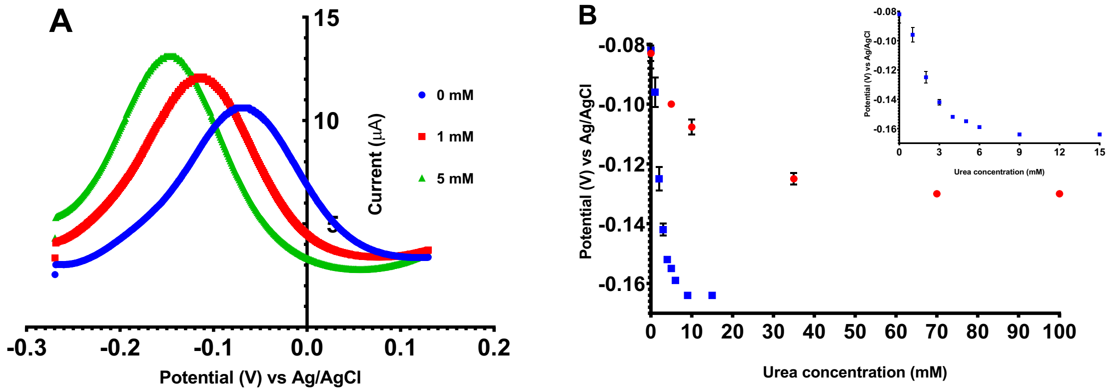

**Figure 1**. (A) Square wave voltammetries in PBS at varying concentrations of Urea. (B) Calibration curves of two sensors fabricated using different amounts of enzyme

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# A Design of Experiments-based approach in the synthesis of DNA-templated copper nanoclusters

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The growing demand for rapid, low-cost, eco-friendly, and simple bioanalytical assays is increasingly critical [1]. In this context, DNA-templated copper nanoclusters have garnered significant interest as fluorescent labels due to their remarkable properties: easy and fast synthesis, low cost, minimal environmental impact, and broad applicability in diverse chemical and biological assays [2]. However, limitations such as low fluorescence intensity and poor stability still hinder their performance compared to organic fluorophores [3]. To address these issues and better understand their formation mechanisms, Design of Experiment was employed to optimize synthesis conditions and develop a mathematical model linking fluorescence intensity and stability to key formation variables. An application in drug analysis is presented, along with future perspectives for enhancing (bio)chemical assays through insights gained from this approach.

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# From atomistic simulations to macromolecular aggregates: Understanding the structure of bulk liquids and the dynamics of molecular machines with AGGREGATE

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One of the main techiniques for sampling molecular conformations is Molecular Dynamics (MD) simulations. These simulations generate trajectories that can be analyzed using Statistical Mechanics to estimate macroscopic properties. However, standard MD analysis tools are often unable to directly detect macromolecular aggregates that may appear for short periods of time during the simulation. In this study, we present AGGREGATE[1], a new and systematic method to identify and classify these dynamic motifs, based on graph theory.

The effectiveness of this approach is evaluated by calculating thermodynamic populations in two illustrative systems. The first system models a phenol solution at varying concentrations [see Figure 1(a)], with trajectories in which all molecules diffuse throughout the simulation box, triggering the aggregation. Our method has already been shown[2] to effectively identify aggregates of varying sizes present in simulation, enabling accurate reproduction of the hydrogen bond bands in IR spectra of phenol solutions, and thus providing reliable estimates of aggregate populations.

Additionally, we explore a mechanically interlocked molecular architecture, specifically a [2]rotaxane [see Figure 1(b)]. This system consists of two components--a macrocyclic ring threaded onto a dumbbell-shaped molecule--that are not covalently bonded but are held together by steric hindrance from the two bulky groups at the axle ends, preventing dissociation[3]. We demonstrate how classifying unique aggregate conformers among the many possible configurations can be useful for tracking the dynamics of molecular machines and monitoring the conformational space explored during the simulation. By applying our approach to both systems, we show its ability to analyze non-covalent interactions and capture aggregate formation in both non-interlocked and interlocked molecular systems.

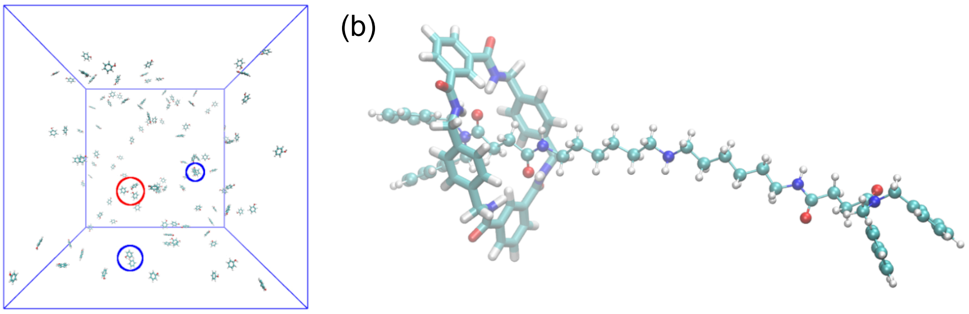

**Figure 1**. (a) Snapshot of a simulation box containing phenol molecules. Molecular aggregates are highlighted with coloured circles. (b) Atomistic model of the [2]rotaxane system investigated in this study.

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# 2D-Nanomaterial printing and electrode miniaturization for the development of sensors for chronic kidney disease biomarkers

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Kidney diseases represent a significant public health challenge due to their rising prevalence and long-term complications. Prompt and continuous monitoring of key biomarkers, including urea, creatinine, and cystatin c, is essential for early diagnosis and effective management of renal dysfunction. Wearable electrochemical sensors for sweat analysis are a promising technology, offering a non-invasive and sensitive approach to detect real-time changes in biomarker levels and enabling personalized kidney function monitoring [1]. In this study, we developed a printing processing method to fabricate nanomaterial-based electrodes to be integrated in wearable sensors.

An ink formulation based on $WS_2$ and ethyl cellulose as a binder [2] was employed to deposit $WS_2$ nanosheets onto the surface of the working electrode (WE) via inkjet printing. The correlation between the current response and the redox probe $K_3[Fe(CN)_6]$ concentration in PBS was investigated using cyclic voltammetry and electrochemical impedance spectroscopy. Moreover, a highly conducting ink based on titanium carbide MXene with cellulose nanocrystals as binder was formulated, and deposited with a “printed circuit board” printer. As the electrode size can highly impact sensitivity [3], we investigated the effect of electrode miniaturization. We designed screen-printed carbon electrodes with WE diameters ranging from 1 to 4 mm, keeping constant the working-counter electrodes spacing and the area ratios across all configurations (Figure 1). Lastly, we performed electrochemical studies and electroactive area assessment for all designs with $K_3[Fe(CN)_6]$ and $[Ru_3(NH)_6]Cl_3$.

The successful printing and characterization of the developed inks lay the basis for the integration of nanomaterial-based sensors for kidney health monitoring through sweat analysis. This work was supported by Kermit (Kidney disease sweat sensor patch for early diagnosis and remote monitoring), Horizon-EIC-PATHFINDERCHALLENGES-01-04, Grant agreement 101115504.

**Figure 1**. Screen-printed electrodes with 4, 3, 2 and 1 mm WE area, compared with 1 cent coin size.

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# Mechanicistic insights into BETA-3 adrenergic receptor modulation via molecular dynamics simulations

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G-protein coupled receptors (GPCRs) are key signalling proteins whose activation by agonists initiates numerous physiological processes [1]. The human β3-adrenergic receptor (β3AR) is a class A GPCR of therapeutic interest for vasodilation and metabolic disorders. Although mirabegron is recognized as a β3AR agonist [2], the activity of SR-59230A remains under debate, with evidence suggesting both antagonist and partial agonist behaviour [3] (Figure 1).

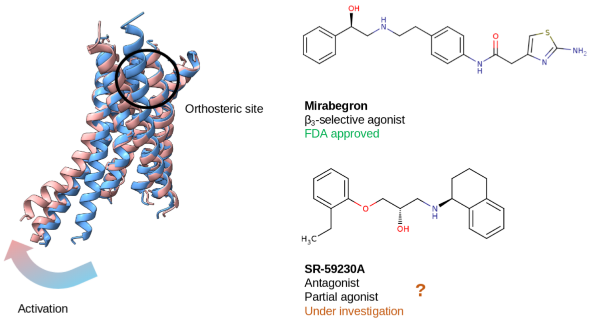

**Figure 1**. On the left the aligned active (red) and inactive (blue) states of the β3AR, on the right the ligands under study.

In this study, we elucidate the molecular mechanisms by which these ligands affect the configurational landscape of β3AR. Recently, the active structure of the human β3AR was determined by Cryo-EM [4]; however, its inactive conformation remains unresolved. To address this, we generated an inactive-state model via homology modelling using the available turkey β1AR structure [5].

Our molecular dynamics simulations of the apo receptor revealed an intermediate state characterized by a partial deactivation, evidenced by an inward movement of TM6. Incorporating the G-protein to maintain a fully active conformation, we performed ensemble docking to capture dynamic receptor fluctuations and obtain initial binding poses for both receptor states.

Notably, µs-long MD simulations demonstrate that SR-59230A-bound β3AR (in the absence of G-protein) persists in an active-like conformation, supporting its classification as a partial agonist.

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# Complete valorization of defatted Cynara cardunculus through a microwave-assisted biorefinery process

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Renewable resources such as lignocellulosic biomass are gaining interest as a sustainable alternative to fossil fuels, helping to reduce emissions and environmental impact. Cynara cardunculus is an interesting feedstock, being a perennial herbaceous crop that can grow on marginal lands. Up to now, the oil-rich seeds of the cardoon flower have found applications for bio-diesel production, whilst the cardoon residues called defatted cardoon (DC) are typically discarded despite its high polysaccharide content (37 wt%). This work presents the development of an innovative microwave-assisted biorefinery process of DC adopting a one-pot fractionation to obtain high-value chemicals and biofuels. An acidic biphasic organosolv pretreatment (water/n-butanol) was performed to easily isolate each biomass component: a solid cellulose-rich residue, an aqueous phase rich in xylose deriving from hemicellulose hydrolysis, and an organic phase containing solubilized lignin. The optimized organosolv pretreatment allowed the extraction of 72 wt% of lignin and 97 wt% of hemicellulose, enriching the solid residue up to 74 wt% in cellulose. This latter was used as substrate in a microwave-assisted one-pot butanolysis process catalyzed by H2SO4 to obtain n-butyl levulinate (BL), a promising bio-blendstock for Diesel [1]. Under optimized reaction conditions, a BL yield of 46 mol% was achieved, higher than that obtained from untreated biomass, demonstrating the benefits of the pretreatment in enhancing cellulose accessibility and reactivity. The aqueous phase rich in xylose were further processed by microwave heating to produce furfural,an important platform-chemical for the synthesis of a pletora of other added value products [2], via acid-catalyzed dehydration reaching the highest yield of 52 mol%. The use of a raw hydrolysate instead of a pure substrate makes this approach particularly attractive from an industrial perspective. Finally, lignin solubilized in the organic phase was separated by butanol, allowing its possible reuse in the organosolv pretreatment or as reagent in the butanolysis step. The recovered lignin was characterized by FT-IR and elemental analysis proving its high purity. In conclusion, the proposed valorization strategy allowed the effective exploitation of each DC fraction using microwaves as an efficient heating method according to a sustainable biorefinery process [3].

**Acknowledgements:**
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# Protein fishing with immobilized gold(I) complexes on 2-CTC resin for target identification

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Gold(I) complexes are well known for their potential anticancer activity, primarily attributed to the inhibition of thioredoxin reductase [1]. However, their precise mechanism of action is still not completely understood, due to the presence of various secondary targets.

In this frame, the present project is focused to the immobilization of two gold compounds onto suitable solid supports, allowing the fishing of proteomic targets related to the studied gold compounds. Experimentally, a gold-based compound is attached to a solid support and, when mixed with a cell lysate, it selectively binds to proteins with exposed cysteine or selenocysteine side chains. This allows to isolate target proteins from the rest of cell lysate.

The employed gold compounds were obtained by appropriately modifying the structure of two gold(I) complexes previously investigated.[2] Some attempts have been made to immobilize the two complexes on a 2-CTC resin by optimizing procedures reported in literature.[4] The functionalization reaction of the resin was carried out in DMF, in the presence of a base, for 24 hours. At the end of the reaction, the resin was capped to block the unreacted sites. The percentage of functionalization of the resin was determined through mineralization and subsequent ICP-MS analysis.

Experiments are currently ongoing to elucidate the affinity of the resin supported gold(I) complexes towards specific proteins.

**Figure 1.** The two complexes synthesized and analysed in this project.

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# Cholesky decomposition implementation of CCSD analytical gradients exploiting point-group symmetry

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In recent years, rank-reducing techniques have seen a surge of interest by the quantum chemistry community, due to them being able to mitigate the intensive computational cost associated with electronic structure methods, thus extending their applicability to larger molecular systems. In that regard, we exploit the Cholesky decomposition (CD) of the electron repulsion integrals (ERI) tensor [1], reducing the impact of its manipulation on the cost of quantum chemical calculations. CD is not only able to compress the information stored within the ERI tensor, making it possible to manipulate it without recomputing or reading the integrals from disk, but also affords a strict control over the accuracy of their representation, since the approximation error is bound to be lower than the predetermined threshold used for the decomposition. Here we applied the CD of ERIs and their derivatives to the computation of analytical geometrical gradients at the Coupled Cluster (CC) level of theory [2,3]. We present an efficient and parallelized implementation of CD, using a two-step algorithm [4] that can fully exploit Abelian point-group symmetry [5] and compute not only the Cholesky vectors, but also their derivatives with respect to nuclear displacements, also fully exploiting point-group symmetry. We use the Cholesky vectors and their derivatives to achieve an efficient and parallel implementation of the CC density matrices and for the intermediates in the Z-vector equations, along with their contractions with Cholesky decomposed differentiated integrals, yielding optimized molecular structures at the CCSD level. The capabilities of our new implementation are tested on a range of systems, for which we compute the energy and molecular structures.

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# Tailored Strategies to 3D Printing of Chitosan and its Derivatives for Biomedical Applications

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Chitosan (Cs) is a cationic polysaccharide derived from the deacetylation of chitin. It is studied for different biomedical applications due to its biocompatibility, biodegradability, antimicrobial activity, and ability to form hydrogels. One of the main limitations of Cs is a poor solubility in aqueous media, as well as a limited ability to support cell adhesion. In this study, scaffolds based on Cs or its derivatives were fabricated using a computer-aided wet-spinning (CAWS) technique [1] involving the extrusion of an aqueous polymer solution into a coagulation bath (**Figure 1**). Cs blended with a protein derivative containing the RGD sequence, i.e., methacryloyl gelatin (GelMA), was explored to enhance the ability of the resulting scaffold to support cell adhesion. An aqueous mixture of Cs, GelMA, and the photoinitiator lithium phenyl-2,4,6-trimethylbenzoylphosphinate (LAP) was printed and the scaffold was exposed to UV radiation to crosslink the protein derivative. In addition, carboxymethyl chitosan (CMCs) was obtained by Cs reaction with monochloroacetic acid in a strongly alkaline medium, using isopropanol as solvent [2]. CMCs scaffolds with enhanced hydrophilicity were stabilized in physiological environment using different types of crosslinking strategies, including ionic and polyelectrolyte complexation, or covalent crosslinking with glutaraldehyde (GA). In addition, on-going studies are aimed at printing a CMCs-methacrylate derivative prepared either with glycidyl methacrylate or maleic anhydride (mCMCs), then further photocrosslinked (i.e., with LAP).

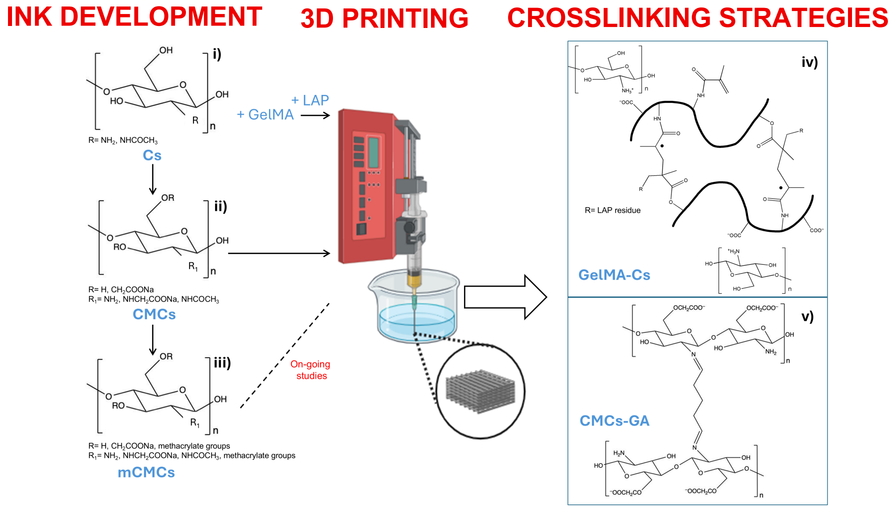

**Figure 3** . Aqueous ink development based on i) chitosan (Cs), ii) carboxymethyl chitosan (CMCs), or iii) carboxymethyl chitosan methacrylate (mCMCs); 3D printing; iv) photocrosslinking of GelMA-Cs and v) CMCs crosslinking with glutaraldehyde (GA).

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# Investigating the ET cascade in Cryptochrome 4 of different birds

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In the last few decades, Cryptochrome 4 (Cry4) has emerged as a widely accepted candidate for avian magnetoreception. Binding a FAD molecule next to a chain of four tryptophans, Cry4 has the possibility to establish an electron transfer (ET) cascade upon FAD's photoexcitation. This cascade, involving FAD and the tryptophan tetrad (Figure 1), results in the generation of a charge-separated radical pair, whose lifetime depends on the magnetic field (1).

Recent works have focused on robins' Cry4 (ErCry4) to experimentally elucidate its ET dynamics (2) and compare its magneto-sensitivity to that of other birds' Cry4, such as pigeons' ClCry4 (3).

In this work, we applied Marcus Model in combination with QM/MM(Pol) calculations to determine the rates of electron transfers along ErCry4's chain of FAD and tryptophans. The results we obtained provide us with a picture of how excited states' populations evolve and compare well with experimental transient absorption measurements (2). Given the biological soundness of such results, we then carried the same analyses on ClCry4, for which no experimental ET rates were available. In this way, we compared the two proteins, deriving a substantial agreement in the overall lifetime of radical pairs, and gaining a further insight on their similarities and differences at the structural level.

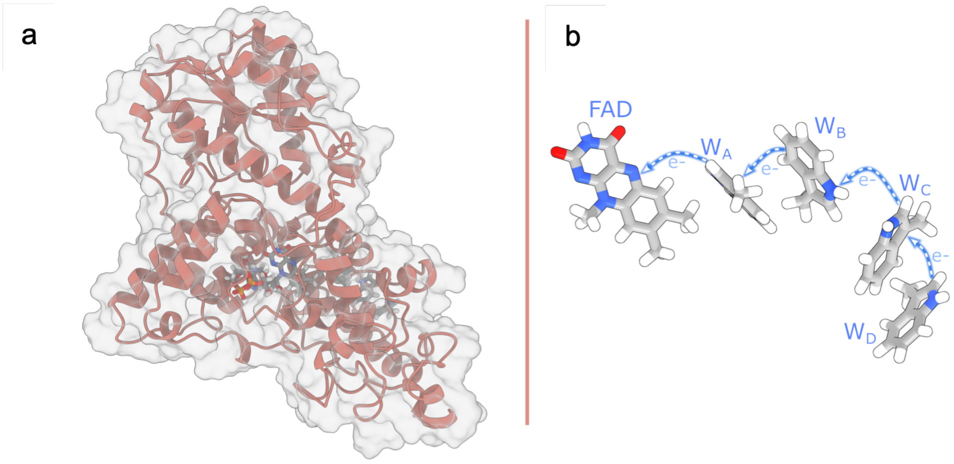

**Figure 1**. (a) Depiction of ErCry4's structure. (b) ET cascade involving FAD and the four Trp residues.

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# $Yb^{3+}$-Doped $CsPbCl_3$ Perovskite Nanocrystals: Quantum Cutting for Optoelectronic Applications

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Perovskite nanocrystals are emerging as a promising alternative material for optoelectronics and photovoltaic solar cells [1]. In particular, the incorporation of rare-earth ion $Yb^{3+}$ in lead halide perovskites boost the PLQY close to 200% thank to quantum cutting (QC) [2]. In QC the absorption of one photon at shorter wavelength is followed by the emission of two photons at higher wavelengths which arises from the forbidden f–f transition of rare-earth ions. Rather than common energy transfer mechanisms, the doping with ytterbium ions generates a vacancy in the lead lattice to compensate for the extra charge, leading to the formation of shallow trap states that mediate quantum cutting. This phenomenon has been proposed to increase the performance of standard Si solar cells since it rises the number of photons that can be converted in electricity (PLQY upon 200%) when perovskite is coupled to another photovoltaic material [2]. In this work, lead halide perovskites doped with trivalent rare-earth ions, specifically $Yb^{3+}$:$CsPbCl_3$, were synthesized and characterized using XRD, TEM, ICP, as well as absorption and photoluminescence (PL) spectroscopies under variable excitation power density [3]. The doped and undoped $CsPbCl_3$ NCs exhibit distinct emission characteristics since in the former the forbidden f–f transition of $Yb^{3+}$ ion (980 nm) is present alongside the host one. The PL spectra, recorded at increasing power densities, were analysed to qualitatively investigate the emission behaviour. Both signals show a linear increase with excitation power, although the 980 nm peak eventually reaches saturation. Further studies are ongoing to correlate these findings with the still debated theory for quantum cutting in Yb-doped perovskites and hopefully gain additional insight into the underlying mechanism. Italian MUR is acknowledged through PRIN 2022 PNRR project P20229723Z (CUP: B53D23025560001).

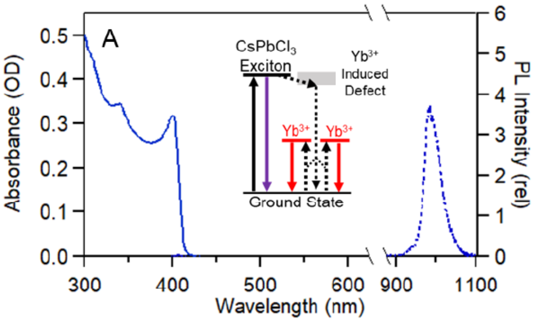

**Figure 1**: Room-temperature absorption (solid) and photoluminescence (dashed) spectra of 1.4% $Yb^{3+}$:$CsPbCl_3$ NCs suspended in hexane. Inset: Schematic energy-level diagram depicting $Yb^{3+}$ sensitization by quantum cutting [2].

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# Searching new pharmaceutical dual-drug solid-systems by combining solvent-based crystallization, mechanochemistry and solid-state NMR spectroscopy

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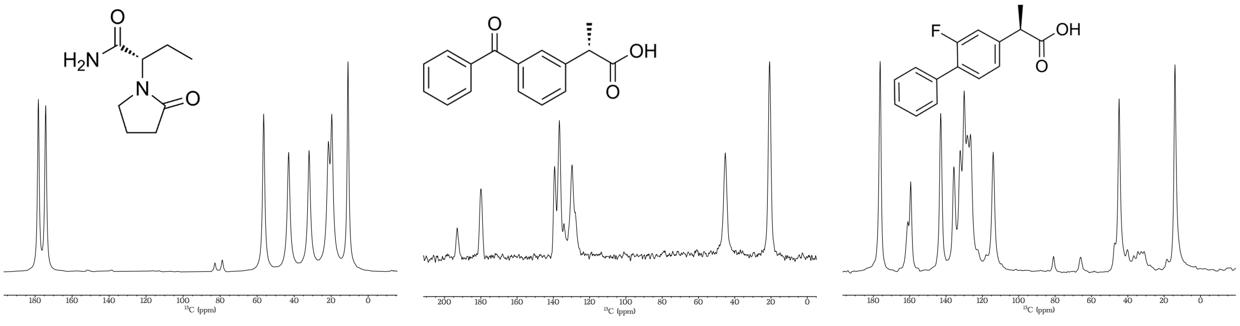
The solid-state chemical and physical properties of active pharmaceutical ingredients (APIs) play a crucial role in determining key characteristics such as solubility and stability[1]. Multi-component solid forms, including co-crystals, have emerged as effective strategies to optimize these properties without altering the molecular structure of the API [2]. Amorphous and co-amorphous systems also offer advantages, particularly in terms of bioavailability, although they often suffer from reduced stability [3]. In this study, we investigated the formation of dual-drug systems by combining pairs of three different APIs (Levetiracetam, (R,S)- or (S)-Ketoprofen, and (R,S)- or (R)-Flurbiprofen) via solution-based co-crystallization and mechanochemical synthesis (with and without solvent droplets). In these formulations, the use of two APIs as potential co-formers aims at improving not only the physicochemical properties but also the pharmacological efficacy of the formulation by combining different therapeutic effects, thus reducing the number of drugs required in specific treatment regimens. Solid-state Nuclear Magnetic Resonance (ssNMR) and Differential Scanning Calorimetry (DSC) were used to assess the nature of the obtained phases. High-resolution $^{1}$H and $^{13}$C ssNMR spectra were recorded and $^{1}$H spin-lattice relaxation times measured for both pure APIs (Figure 1) and their mixtures. This analysis led to the identification of a known co-crystal between Levetiracetam and Flurbiprofen, previously reported in the literature, but not yet structurally and dynamically investigated [4]. Additionally, two novel solid phases were individuated by observing chemical shift variations respect to the pure components.



(a) (b) (c)

**Figure 1**. $^{13}$C MAS ssNMR spectra of the pure Active Pharmaceutical Ingredients used in this work: (a) Levetiracetam, (b) (S)-Ketoprofen, (c) (R)-Flurbiprofen.

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# Modeling nonadiabatic dynamics with a semi-focused MASH

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Nonadiabatic dynamics are essential for understanding processes that involve transitions between electronic states, such as photochemical reactions, intersystem crossing and electron or energy transfer.

Although fully quantum methods such as Multi-Configuration Time-Dependent Hartree [1] and Variational Multi-Configuration Gaussian [2] do exist, significant attention is given to mixed quantum-classical methods, due to their lower computational cost. Among these, Tully's Fewest Switches Surface Hopping (FSSH) [3] is one of the most widely used but suffers from problems, such as internal incosistencies and the lack of quantum decoherence, that have to be addressed through ad hoc corrections [4].

Recently a new quantum-classical method, the "mapping approach to surface hopping" (MASH) [5], was introduced. Similar to FSSH, MASH evolves an ensemble of independent trajectories on adiabatic potential energy surface. However, unlike the stochastic FSSH algorithm, MASH determines the transitions between electronic states deterministically, based on the evolution of the electronic wavefunction. MASH can be derived from the classical quantum Liouville equation [5], and this provides clear rules for implementing velocity rescaling and handling frustrated hops. This also enables the incorporation of a quantum jump procedure to further enhance dynamical accuracy. MASH demonstrates improved accuracy over FSSH in two-state systems [5], with a comparable computational cost. Since the original MASH method is limited to two-state systems, two multistate extensions have been proposed so far: Multi-State MASH (MMASH) [6] and Uncoupled Spheres MASH (UNSMASH) [7].

Here we present a new multistate extension, the Semifocused Mapping Approach to Surface Hopping (SMASH). This expansion introduces a semi-focused sampling of the initial electronic amplitudes, confining the electronic population to a subset of electronic states. Like MASH, SMASH hops between electronic states are deterministic, guided by the wavefunction evolution. Moreover SMASH, like MASH, incorporates a decoherence correction based on the resampling of amplitudes. We benchmark SMASH against FSSH (with and without decoherence corrections) on various molecular systems. SMASH reproduces population dynamics with similar accuracy, while reducing unphysical transitions involving large energy gaps. These results highlight SMASH as a viable approach for simulating nonadiabatic molecular dynamics.

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# Study of tomato cutin as potential innovative biobased additive for Poly lactic acid.

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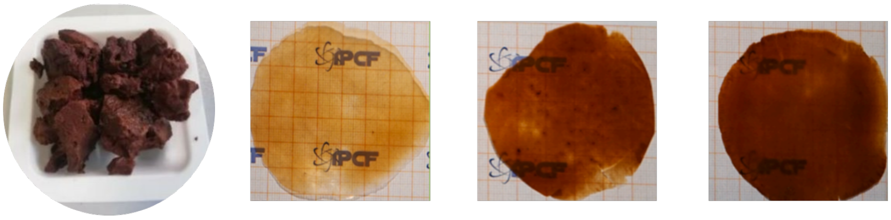
Innovative and green materials represent an important solution to environmental challenges also improving the sustainability of industrial processes. From this point of view, agri-food waste such as fruit peels and plant fibres can become valuable sources of additives or high-value chemicals. The by-products of the tomato industry represent the 5-13%wt on the whole production (peels and seeds). From these wastes, from the tomato peels, it is possible to extract a bio-polyester, known as Cutin, which is is mainly formed by esterified poly-hydroxylated fatty acids and epoxy hydroxylated fatty acid ($C_{16}$-$C_{18}$). The main features that make cutin interesting for eco-designed application on innovative materials are its non-toxicity, biodegradability, availability and excellent natural hydrophobicity. Despite these characteristics, the cutin applications are limited due to its poor solubility and low filmability. In this work the cutin extracted from the tomato peel, provided by an Italian start-up, has been mixed with Poly lactic acid (PLA) to obtain a self-standing material. PLA, one of the most commercialized biopolymers, is currently utilized in various applications as packaging and medical equipment. However, its low thermal stability, low environment degradation and low oxygen/water barrier limit the extensive applications. By combining agri-food waste and bioplastics it is possible to potential reduce the dependence on fossil resources and valorising others and/or the cost reduction of the final eco-designed products. The addition of cutin was evaluated in a range between 5 and 20%wt. The torque of the melt during the processing of the blends has shown a significant reduction compared to PLA; the same trend was observed for PLA average molecular weight depending on the amount of cutin. As far as the rheological data, the samples containing the highest amount of cutin (20 wt%) has shown a higher complex viscosity in the low-frequency region, even with respect to the PLA alone. This result was associated to the effect of the cutin 3D network. The water vapour permeability analyses have highlighted a reduction of the 8%–21% respect to the value of pure PLA film especially for the samples with the highest cutin content.



Cutin from tomato PLA Cutin 5%wt PLA Cutin 20%wt PLA Cutin 20%wt (pre-grinding)

**Figure 1**. Cutin extracted from tomato and PLA/Cutin film.

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# Nanostructured Electrochemical Immunosensor for the Detection of Circulating Tumor Cells

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Early detection of circulating tumor cells (CTCs) plays a crucial role in the clinical management of melanoma, one of the most aggressive forms of skin cancer. Indeed, CTCs can detach from the primary tumor, enter the bloodstream, and become activated, leading to the development of metastases and a drastic reduction in patients' survival rate [1]. However, due to their very low concentration in blood (1–100 cells/mL) [1], conventional diagnostic methods often lack sufficient specificity, sensitivity, and reproducibility [2].

Therefore, to overcome these limitations, we propose a lab-on-a-chip platform capable of isolating and counting CTCs from whole blood samples. Specifically, the immunosensor present in the platform is based on a gold screen-printed electrode, modified with 2D nanomaterials, which enhance the electro-active area and thus improve the signal-to-noise ratio. The working electrode's surface is further functionalized to allow stable immobilization of monoclonal antibodies specific for the *MCAM* antigens of CTCs (Figure 1, left). Electrochemical impedance spectroscopy is the signal transduction technique employed to detect the binding events, since binding is demonstrated by an increase in charge transfer resistance (Figure 1, right).

This project was funded under the call PRIN 2022 (Project of National Relevance, Italy, code 20228LPFCA) from European Union – Next Generation EU.

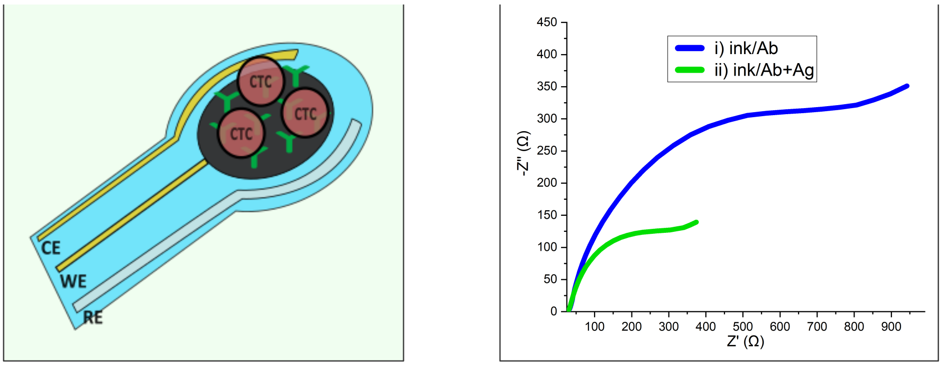

**Figure 1**. Left: schematic view of an electrochemical cell functionalized with antibodies (WE = working electrode, RE = reference electrode, CE = counter electrode). Right: Nyquist plot before (i) and after (ii) antigen binding to the antibodies.

**References:**

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# Sustainable Mechanochromic Polyolefins: Functionalizing Recycled Polypropylene for Stress Sensing Applications

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The development of mechanochromic materials—those that exhibit color changes in response to mechanical stress—has gained significant attention due to their potential applications in stress monitoring, sensors, and structural health monitoring. Such materials provide a visual indicator of mechanical deformation, enabling real-time detection of stress or strain. In this context, sustainable materials are particularly valuable, as they contribute to reducing environmental impact while offering innovative functionality. Recycled polypropylene (PP), obtained from pyrolysis, represents an excellent candidate for functionalization and material development.

In this study, recycled polypropylene (PP) was functionalized through a two-step process. First, pyrolysis was employed to generate terminal double bonds along the polymer chains. These reactive sites were then quantitatively converted into hydroxyl groups,[1] providing anchoring points for the subsequent grafting of pyrene derivatives.[2] The resulting functionalized polymer, referred to as PP-Py (see **Figure 1**), was structurally and spectroscopically characterized to confirm the successful grafting of the pyrene moieties and the aggregachromic characteristics. PP-Py was then blended with various polymeric matrixes, in particular HDPE, LLDPE and POE at different contents. Mechanical tests were conducted on the blends to evaluate their mechanochromic features. This work demonstrates the potential of recycled polypropylene-based materials for mechanochromic applications, successfully integrating sustainability with high functional performance for the visual detection of stress and strain.

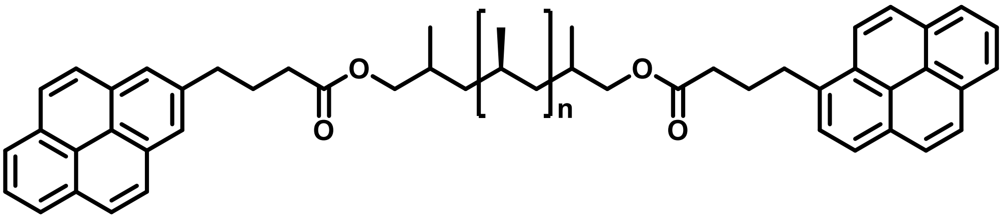

**Figure 1**. Structure of the PP-Py polymer.

**References:**
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# Multianalytical Approach to the Characterization of the Curing Process in Pre-Polymerized Oil Paints Containing Carbon Black

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Pre-polymerized oils are treated drying oils that have been widely used as painting mediums since the fifteenth and early sixteenth centuries. Their presence in paintings alongside raw siccative oils implies that artists made conscious choices about when and how to use them, as their physico-chemical properties differ in viscosity, adhesivity, and drying time.[1]

Despite the curing of raw linseed oils has been studied and characterized in detail [2,3], much less is known about the curing of pre-polymerized oils which depends on the type of treatment.

The aim of this work is to study the curing process of pre-polymerized oil paints combined with carbon black, which has an antioxidant effect and inhibits the radical chain propagation [4]. The paints were exposed to different ageing conditions in order to gain a better understanding of historical painting techniques and the stability of paint layers over time.

In this study three types of commercial pre-polymerized linseed oils were used. An heat-bodied oil (boiled in an inert atmosphere), a thickened oil (exposed to sunlight under air flow), and a catalyzed oil (heated in presence of lead oxide).

The oils were initially analysed by thermogravimetric analysis (TGA) under an air flow at a constant temperature of 80 °C, revealing distinct oxidation behaviours, oxidative degradation patterns, and differences in curing kinetics. In parallel, volatile species released over time from model paint layers upon oxidative degradation were investigated using SPME-GC/MS. The consistency between TGA and SPME-GC/MS results confirmed the differences in curing kinetics and enabled the identification of oxidative degradation products, whose relative abundance varied markedly across the samples.

Complementary information was obtained through EGA-MS analysis of naturally aged samples, which highlighted variations in cross-linking and thermal stability among the oils, based on their thermal degradation profiles.

These findings, integrated with upcoming HPLC-MS analyses designed to elucidate the initial oxidation state, are expected to enhance our understanding of the curing process in different pre-treated oils and provide new insights into the molecular characteristics of the resulting paint films.

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# Ligand-Dependent Cytotoxicity and DNA Interaction in Palladium(II) Complexes

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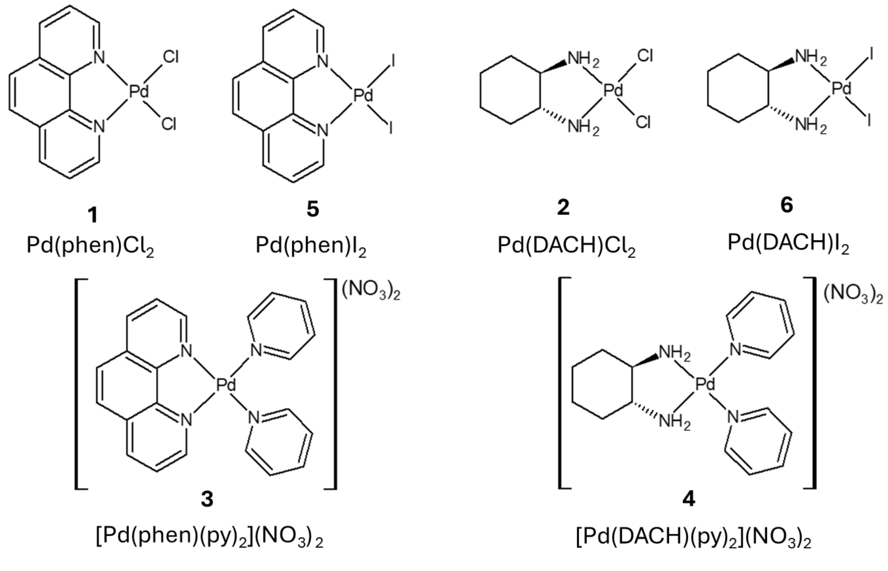
In recent years, the interest in palladium complexes as chemotherapeutics has been growing due to the necessity of overcoming the known limitations of clinically established platinum(II) anticancer compounds.[1] In this work, we synthesized a panel of six square planar palladium(II) complexes with a general formula [$PdAB_2$] and their biological properties were evaluated to identify trends linked to ligand variations. More precisely, two *N,N*-bidentate ligands were selected as A group, i.e. (1R,2R)-diamminocyclohexane (DACH) and 1,10-phenantroline (phen). On the other hand, chloride ($Cl^-$), iodide ($I^-$) and pyridine (py) were employed as B monodentate ligands. The complexes were synthesized following known experimental procedures and characterized by elemental analysis and NMR spectroscopy. DNA interactions were investigated through melting procedures and ethidium bromide (EB) displacement assay. These interaction studies highlighted covalent adduct formation as the preferential mode of binding for the DACH-containing complexes, whereas intercalation was predominant for the Phen-containing complexes. Notably, compound **1** appears to interact with DNA via both modes. Cytotoxic activity was evaluated on three ovarian cancer cell lines (A2780, A2780R, and SKOV3) as well as on a healthy control cell line (HSkM, human skeletal myoblasts). Significant cytotoxic activity was observed for Phen-containing complexes, with compound **3** showing also a good selectivity. Conversely, DACH-containing complexes were found to be biologically inactive.



**1** Pd(phen)$Cl_2$

**5** Pd(phen)$I_2$

**2** Pd(DACH)$Cl_2$

**6** Pd(DACH)$I_2$

**3** [Pd(phen)$(py)_2$]$(NO_3)_2$

**4** [Pd(DACH)$(py)_2$]$(NO_3)_2$

**Figure 1**. Molecular structures of the analyzed complexes.

**References:**

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# Protein Recognition by Cytotoxic *trans*-Pd(II) Complexes: A Ligand-Based NMR and UV–Vis Spectroscopy Approach

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Despite being among the most widely used anticancer agents, Pt(II)-based drugs suffer from several limitations in clinical application, including severe side effects, the development of intrinsic or acquired resistance, and the requirement for intravenous administration.[1] A promising strategy to overcome these drawbacks involves the design of novel complexes incorporating metal centers alternative to platinum. In this context, Pd(II) complexes have gained attention as potential antitumor drugs due to their coordination chemistry, which closely resembles that of Pt(II) compounds, and enhanced water solubility.[2] Although their mechanism of action is not yet fully understood, many *trans*-Pd(II) complexes have exhibited cytotoxic activity greater than or comparable to cisplatin against various cancer types.[3] On the other hand, their lower thermodynamic stability and higher kinetic lability than Pt(II) counterparts result in rapid ligand exchange reactions, which may prevent them from reaching target biomolecules within tumour cells.[2-4] Accordingly, a reproducible and accessible methodology was defined to investigate square-planar *trans*-Pd(II) complexes that, almost in principle, can be extended to the mechanistic study of other metal-based drugs.[5] To this aim, a series of compounds with the general formula *trans*-$PdL_2X_2$ (where L = pyridine or piperidine, X = Cl, Br, I) was synthesized and characterized. This rational combination of monodentate labile and spectator ligands could improve their stability during circulation inside the body (Figure 1). The interactions of these complexes with model proteins were studied by UV-Vis and NMR spectroscopy, and their *in vitro* activity against selected cancer cell lines was also investigated.

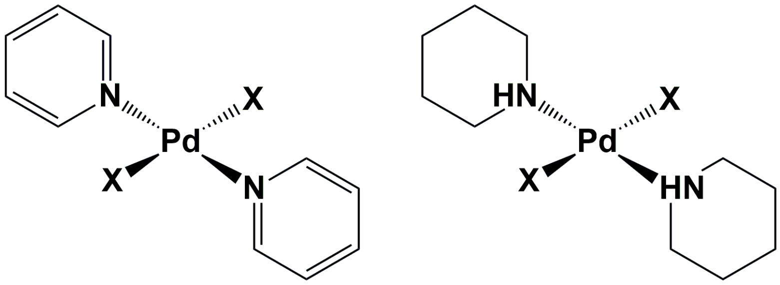

**Figure 1**. Molecular structures of the investigated *trans*-Pd(II) complexes

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# Ir-Eu Bimetallic Complexes For Electrochemically-Sensitized Circurarly Polarized Luminescence

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Circularly polarized luminescence (CPL) is an emerging frontier across various fields, ranging from optoelectronics [1] to bioanalytical sensing [2], offering new opportunities for advanced applications such as display technologies and bioanalytical sensors. In the latter, CPL represents a highly selective and innovative tool due to its unique ability to discriminate luminescent molecular probe–analyte interactions within complex environments.

Another phenomenon widely employed in the development of bioanalytical devices is electrochemiluminescence (ECL), which involves the generation of emissive excited states through electrochemical pathways [3]. ECL operates without the need for external light excitation, thereby minimizing interference from endogenous fluorescence in biological samples. This results in a low background signal and supports highly sensitive detection with excellent spatial and temporal resolution. The combination of CPL and ECL therefore represents a distinctive and promising strategy for chiral imaging and advanced biosensing applications.

The main objective of this project is the synthesis of chiral bimetallic complexes that can be electrochemically excited and are capable of emitting circularly polarized light. These complexes are composed of three key components: an Iridium metal center, essential for electrochemiluminescence (ECL); a Europium metal center, which can emit circularly polarized light in the red region (around 614 nm) with long excited-state lifetimes; and a bridging ligand capable of simultaneously coordinating both metal centers and facilitating efficient Ir-to-Eu energy transfer (**Fig.1**). In this context, the first examples of such complexes have been synthesized and subjected to spectroscopic characterization.

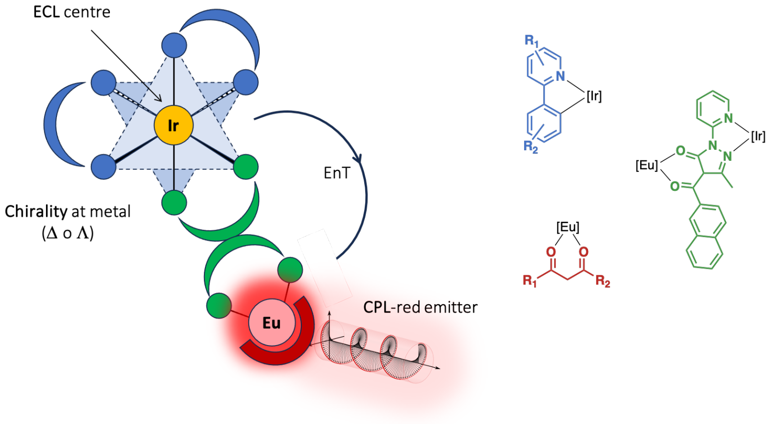

**Figure 1**. Schematic rappresentation of Ir-Eu bimetallic complexes (left) and proposed ligands (right).

**References:**
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# Smart Gels for Dry Eye Syndrome: A Natural Polymers Approach with Gellan Gum and Arabinogalactan

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Dry Eye Syndrome (DES) is a multifactorial disease characterized by tear film instability and ocular surface inflammation. Conventional eye drops often provide limited efficacy due to rapid clearance from the ocular surface and low bioavailability, underscoring the need for more advanced formulations [1]. This study focuses on the development of an ion-sensitive *in situ* gelling system composed of two natural polymers—low-acetylation degree Gellan Gum (GG-LA) and Arabinogalactan (AG)—for improved management of DES. This system is designed to be easily administered as eye drops and to form a stable 3D gel network upon contact with tear fluid, thereby increasing residence time and therapeutic efficacy. GG-LA, an ion-sensitive polysaccharide, undergoes sol–gel transition in the presence of tear fluid ions [2]. AG, a branched polysaccharide, contributes mucoadhesive properties and promotes epithelial regeneration [3]. Their combination allows the formulation to benefit from both the prolonged retention conferred by GG-LA's gelation and the mucoadhesive properties of AG. The ionic content of the polymeric solution was optimized to obtain the desired viscosity increase upon contact with tear fluid. Various GG-LA and AG concentrations were characterized for their viscosity and viscoelasticity, both before and after dilution with artificial tear fluid. A Design of Experiments approach was employed to identify the optimal formulation, balancing low initial viscosity ideal for instillation with a high post-gelation elastic modulus to ensure prolonged residence on the ocular surface. Response surface analysis revealed that GG-LA significantly influenced viscosity, while AG primarily modulated the gel's elastic properties. The most promising formulation underwent comprehensive physicochemical characterization, compatibility with tear fluid testing, and biocompatibility assessment on rabbit corneal epithelial cells, confirming its potential as an effective therapeutic approach for DES.

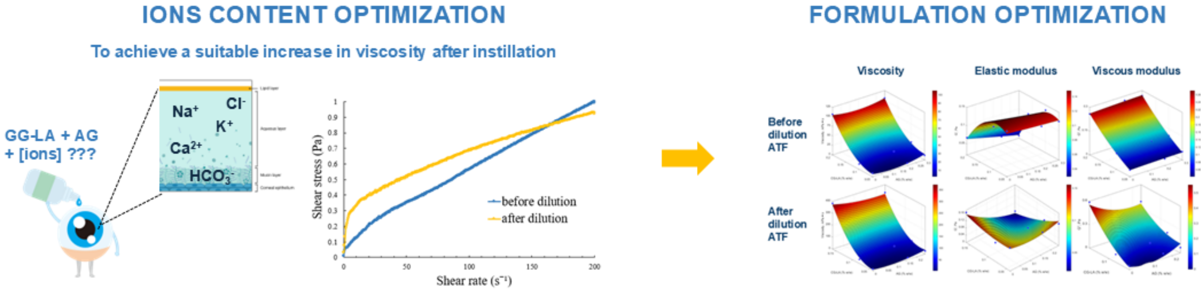

**Figure 1**. Schematic illustration of the preparation and optimization of an ion-sensitive *in situ* gelling eye drop formulation based on GG-LA and AG for DES treatment.

**References:**

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# Evaluating Atomic Oxygen as an Innovative Cleaning Technique for Cultural Heritage Preservation: A comparative Study with Laser Technology

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The surface cleaning is a crucial procedure for cultural heritage conservation. Usually, it involves the use of solvents (wet cleaning) or physical removal of dirt from the surface (dry cleaning). However, these methods have their limitations in terms of efficacy, safety and sustainability. Search for new approaches lead to the development of non-contact methods, which present significant advantages when working with solvent-sensitive and mechanically unstable heritage object surfaces. Such as the use of laser systems, that are versatile and allow to adjust parameters like laser source and pulse duration, even if this method has limitations too, specifically when applied to particularly sensitive surfaces.

In this regard recently, an alternative for cleaning the surface of works of art was developed based on the use of atomic oxygen (AO) in atmospheric pressure plasma. Its cleaning mechanism is based on the oxidation of the contaminants by atomic oxygen cold plasma. Given its mechanism of action, this technique is a promising non-contact technique particularly useful for cleaning carbon-based contaminants from porous, water-sensitive and fragile surfaces. The pioneering use of AO cleaning for cultural heritage conservation showed promise before [1]. However, before applying it to artworks, it is necessary to systematically study the chemical effects of AO on the substrate materials to evaluate the cleaning mechanism and carry out a systematic comparison to other established techniques. To this aim, this study systematically investigates the impact from AO cleaning and compares it to cleaning carried out with two types of lasers: Er:YAG[2], suitable for varnish thinning, and Nd:YAG[3], commonly used by conservators for soot removal. Experiments were performed on model oil paint layers (naturally aged for two years), consisting of ultramarine blue pigment and two different types of binders: linseed oil, used as oil binder since antiquity, and safflower oil, frequently encountered in modern paint formulations. Treated and untreated samples of identical composition were analyzed using a combination of analytical techniques such as SEM and optical microscopy to compare the surface morphology of the layers, ATR-FTIR and EGA-MS to assess the molecular changes undergone by the binder, and SPME-GC-MS [4] to monitor the evolution of VOCs released from paint layers over time.

In conclusion, the results show that AO cleaning is less invasive (ATR-FTIR, EGA-MS) compared to laser and, unlike the latter, it does not seem to cause long-term damage (SPME-GC-MS).

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# Diiron(I) Complexes for Biological Applications: Novel Structures and Behaviour in Aqueous Solutions

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Diiron(I) bis-cyclopentadienyl complexes represent a promising family of compounds for antitumoral applications, which have been widely investigated in recent years.[1] Specifically, complexes with a bridging aminocarbyne ligand have raised particular interest, showing promising values of selectivity and cytotoxicity on various 2D and 3D cancer cell lines, compared to cisplatin. Essential features for biological applications are stability and solubility in aqueous environment, as well as a balance between hydrophilicity and lipophilicity to ensure both a sufficient affinity to the physiological environment and the capability to cross the cell membrane. In this context, the dimeric metal moiety is particularly convenient since it provides a remarkable robustness to the structure, allowing the possibility of tuning the physical properties of the complex.[2] To clarify the relation between the influence of N-substituents and physico-chemical properties in aqueous solution, we synthesized and characterized a series of ethylated diiron aminocarbyne complexes bearing different N-substituents, counterparts of a previously reported methylated series. The synthesis procedure was carried out via substitution of a bridging carbonyl on the commercial precursor [$Fe_2Cp_2(CO)_4$] with an isocyanide ligand (CNR) and subsequent alkylation of the intermediate by electrophilic attack ($Et^+$) on the nitrogen. Stability and solubility properties in aqueous environment were evaluated, along with the octanol-water partition coefficient. These results were compared with those of the corresponding methylated analogues.

The mechanism of action of such compounds relies on the disruption of the complex inside the cell, leading to the release of oxidised Fe species and ROS, which cause *apoptosis*.[3] The kinetics of the disruption mechanism, though, are still to be clarified. Hence, experiments in water and cell culture medium were conducted on the selected compound [$Fe_2Cp_2(CO)_3(CNMe_2)$][$NO_3$], revealing a dependence of the decomposition rate on concentration, pH and environment.

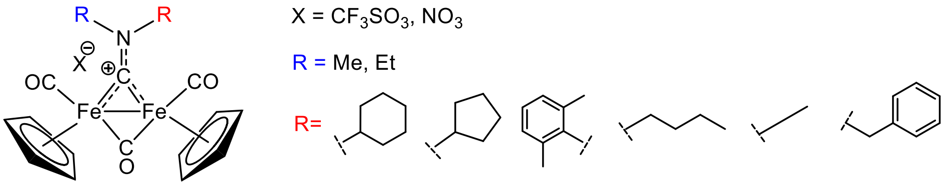

**Figure 1**. General structure of the diiron aminocarbyne compounds considered in the study.

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# Multiscale Modeling of Energy Transport for Light-Harvesting and Non-Photochemical Quenching in Higher Plants

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Photosystem II (PSII) light-harvesting complexes (LHCs) are able to collect sunlight and transfer energy to reaction centers with high efficiency through excitation energy transfer (EET). While the photophysics of isolated LHCs has been extensively investigated, their behavior in native assemblies remains poorly understood.[1–4] Recent ultrafast spectroscopy of the M-CP2 subdomain of PSII — comprising LHCII, CP29, and CP24—revealed its EET dynamics, but there is disagreement on how the assembly affects EET compared to isolated complexes.[5,6] These discrepancies highlight the challenge of disentangling overlapping EET processes experimentally.

We employ a multiscale computational approach combining molecular dynamics simulations with quantum mechanics/polarizable molecular mechanics (QM/MMPol) calculations to capture M-CP2's conformational ensemble in membrane.[7–9] To efficiently calculate excitonic parameters for this 67-chlorophyll system, we utilize machine learning models trained on QM/MMPol data, generating thousands of Frenkel exciton Hamiltonians that accurately capture environmental effects.[10,11] Following validation against absorption spectra, we simulate EET dynamics using Redfield-Förster theory.[12,13]

By comparing the full M-CP2 assembly with its isolated components, we reveal how supramolecular organization modulates energy transfer pathways and efficiency, providing mechanistic insights into this key PSII antenna subdomain involved in photoprotection.

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# Bacteriophages-based biosensors and orientation with electric field: an innovative method for the detection of bacterial pathogens

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Antimicrobial Resistance (AMR) represents one of the main threats to human health, aggravated by improper practices in the current use of antibiotics and traditional diagnostic limitations. Based on current estimates, AMR could cause up to 10 million deaths per year, making the development of innovative and efficient diagnostic strategies urgent [1]. Rapid and specific detection of pathogens is essential to limit the inappropriate use of antibiotics and contain the spread of resistance. In this context, electrochemical biosensors emerge as promising instruments that can rapidly detect pathogens responsible for an infection, allowing targeted treatments and limiting the use of broad-spectrum antibiotics, which are one of the main causes of the spread of AMR [2]. Bacteriophages (or phages), owing to their natural selectivity, stability, and low production cost, represent an ideal bioreceptor for point-of-care biosensors [3].

The present work describes the development of an impedimetric biosensor based on specific phages for *Escherichia coli* WG5, immobilized on gold electrodes through chemical functionalization (SAM of thiols, followed by activation of -COOH with EDC/NHS). Detection relies on Electrochemical Impedance Spectroscopy (EIS) measurements, evaluating the increase in Charge Transfer Resistance ($R_{ct}$) depending on bacterial concentration. At the same time, an experimental setup was developed to orient phages during immobilization. This is possible due to the application of an external electric field that allows a favourable orientation, utilizing the natural charge dipole characteristics of phages [4]. The objective of this step is to enhance phage bonding efficiency and the sensor's sensitivity.

Preliminary results suggest the feasibility of chemical functionalization and the sensor's effectiveness in detecting pathogens, confirming the increase in $R_{ct}$ values in response to bacterial concentrations. The electric orientation of phages, inspired by previous studies [5], is expected to improve system performance, reduce fabrication times, and increase sensitivity.

This approach contributes to the development of rapid, selective, and low-cost biosensors for pathogen detection, with significant implications for the diagnostic field and the fight against antimicrobial resistance (AMR). Further optimization in the orientation phase paves the way for even better performance and easier implementation in diagnostic devices.

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# Fluorescent labelling of anticancer gold(I) N-heterocyclic carbenes for metallomic studies

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In recent years, gold(I) complexes have attracted increasing interest as a promising alternative to classical Pt-based chemotherapeutic agents.[1] This interest especially stems from their different mechanism of action, exerted at the mitochondrial level, which has the potential to overcome the resistance mechanisms that often arise after treatment with standard Pt-based drugs.[2] In this context, a more in-depth understanding of the overall biological behaviour of gold(I) complexes is necessary for designing more effective anticancer compounds. This project aims to assess the intracellular profile of three gold complexes through the functionalisation with two different fluorescent tags. Therefore, a panel of three novel fluorescent complexes was synthesised and characterised, i.e. a N-heterocyclic monocarbene gold(I) complex and the corresponding biscarbene, both functionalised with an anthracenyl moiety, and a NHC gold(I) monocarbene bearing a BODIPY label. The compounds were characterised through 1H and 13C NMR, as well as elemental analysis. The crystallographic structure of the anthracenyl monocarbene was also obtained. The stability in DMSO and PBS, the spectrophotometric behaviour and the logP coefficient were determined for the three complexes. Interaction studies with human serum albumin through UV-Vis absorption spectroscopy and ESI-MS showed the ability to interact with the protein for the three complexes. Cellular uptake on cisplatin-sensitive and resistant A2780 ovarian cancer cells was determined using fluorescence-activated cell sorting (FACS) cytofluorimetry, highlighting strong cellular internalisation of all compounds. The cytotoxic activity of the complexes was evaluated on the same cell lines, showing good antiproliferative activity of the anthracenyl carbenes. Interestingly, the biological activity was higher in cisplatin-resistant cells rather than in sensitive ones. Intracellular biodistribution studies are currently being carried out using confocal microscopy. In order to gain a comprehensive understanding of the specific proteic targets, the protein content will be analysed using the MUltiDimensional Protein IdenTification technology (MudPIT).[3] Indeed, after the extraction of the proteome from each organelle and separation on 2D gel electrophoresis, the spots of interest will be detected by exploiting the presence of the fluorescence probes, and the corresponding proteins will be identified by LC-ESI-MS. This approach in its whole might represent a major breakthrough in identifying secondary targets of gold and in elucidating their overall mechanism of action in cancer cells.

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# Activation of Orange Carotenoid Protein Requires a photoisomerization

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The orange carotenoid protein (OCP) is a photoactive protein involved in the photoprotection of cyanobacterial antenna complexes [1]. Through two H-bonds in its C-terminal domain, OCP binds a keto-carotenoid (such as canthaxanthin) which is involved in the light-activation of OCP and finally acts as a quencher in the protoprotective mechanism. Absorption of blue light by the resting-state orange OCP ($OCP^O$) causes the translocation of the carotenoid into the N-terminal domain and ultimately the separation of the two domains and forming the active red $OCP^R$ state [2]. However, the photochemical mechanism that drives H-bond dissociation and carotenoid translocation is still unknown.

In a previous work, we proposed a trans-to-cis photoisomerization of OCP-bound canthaxanthin as a possible activation mechanism [3]. The cis isomer, however, is not observed in the structure of $OCP^R$ bound to the antenna complexes [4], therefore the chromophore must undergo to another isomerization once the active state is reached.

Here, we characterized the photoproduct with QM/MM simulations and we show that only the cis photoproduct possesses the spectroscopic features observed in transient absorption spectroscopy [2]. Then, by performing enhanced sampling simulations with the method umbrella sampling-replica exchanged molecular dynamics (US-REMD) [5], we demonstrate that the photoisomerization is a prerequisite for enabling carotenoid translocation. Finally, we explore the role of multiphoton absorption in facilitating the recovery of the all-trans canthaxanthin, by performing nonadiabatic QM/MM simulations of the final active state. [6]

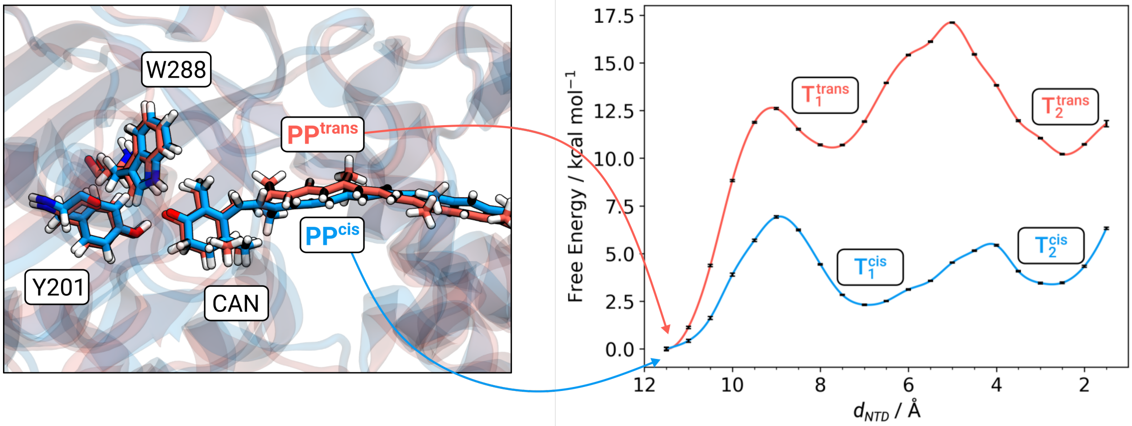

**Figure 1**. Representative structures of the cis and trans photoproducts with the H-bonded residues; free energy profiles of the carotenoid translocation for the cis and trans isomers.

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# Thermoresponsive amphiphilic random copolymers with alkyl and perfluoroalkyl side chains: synthesis, self-assembly, and drug encapsulation

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Single-chain polymer nanoparticles (SCNPs) has recently emerged as a promising class of functional polymeric nanomaterials, inspired by the folded structures of natural macromolecules, which enable complex functions through their three-dimensional arrangements.1,2 Among SCNPs, unimer micelles represent a distinctive subclass that is derived in aqueous solution via the self-folding of amphiphilic random copolymers through intramolecular hydrophobic interactions.3,4

In this study, a series of amphiphilic random copolymers were synthesized via ARGET-ATRP using a hydrophilic monomer, poly(ethylene glycol) methyl ether methacrylate (PEGMA), and varying the chemical nature of the hydrophobic co-monomer (including perfluorohexylethyl acrylate (FA) and a series of alkyl acrylates with different alkyl chain lengths). The self-assembly behavior of the copolymers in aqueous solution was investigated by using dynamic light scattering (DLS), DOSY NMR, and small-angle X-ray scattering (SAXS). These analyses revealed the formation of unimer micelles with hydrodynamic diameters (Dh) of 7–10 nm, via intramolecular chain folding. All copolymers exhibited LCST-type thermoresponsive behavior in water, characterized by a sharp increase in Dh (>600 nm), indicating the formation of larger, multichain aggregates above the cloud point temperature (TCp). To evaluate their potential for drug delivery applications, polymer/drug formulations were prepared using curcumin (Cu) as a model hydrophobic drug. Drug encapsulation efficiency was found to range from 60% to 80% and lead to a decrease in TCp, possibly due to the overall increase in hydrophobicity of the system after CU loading.

**Funding information**:
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# Searching and modeling microplastic transport in soil and aquifers

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Microplastics (MPs) are a widespread pollutant of the Anthropocene, yet reliable methods for their detection in soil and groundwater remain limited. The bilateral Italy–China ENCOMPASS project addresses this gap by studying MPs contamination and transport from agricultural soils to groundwater, using both mass- and particle-based quantification. Soil and groundwater were sampled in the agricultural land south of the coastal Lake Massaciuccoli, a reclaimed area of mixed sedimentary and peat soil composition. Analyses include mass-weighted (P.I.S.A.) [1] and number-weighted (flotation) approaches. In parallel, we are developing a digital percolation model using PMG 2.0 (Porous Microstructure Generator) [2] and MATBOX (Microstructure Analysis ToolBox) [3] to generate and characterize Soil Digital Analogues (SDA), which are then imported into COMSOL Multiphysics to simulate particle transport. Initial simulations in sandy matrices highlight preferential flow paths and particle trapping influenced by pore geometry and flow dynamics. Experimental validation with reference matrices (e.g. quartz sand) and MPs (produced by grinding and sieving) is planned. This integrated approach aims to advance our understanding of MPs behavior in agricultural systems and support mitigation efforts.

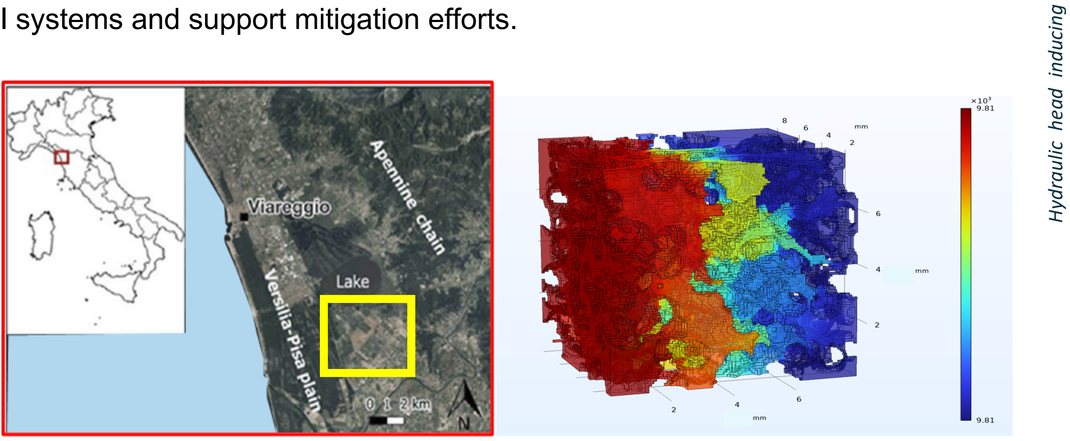

**Figure 1**. On the left, the sampling site near Massaciuccoli lake, On the right a simulated hydraulic parameter using generated SDA, imported in COMSOL Multyphysics

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# Asymmetric activation of tropos biphenolic moieties by isohexides: a combined computational-experimental approach

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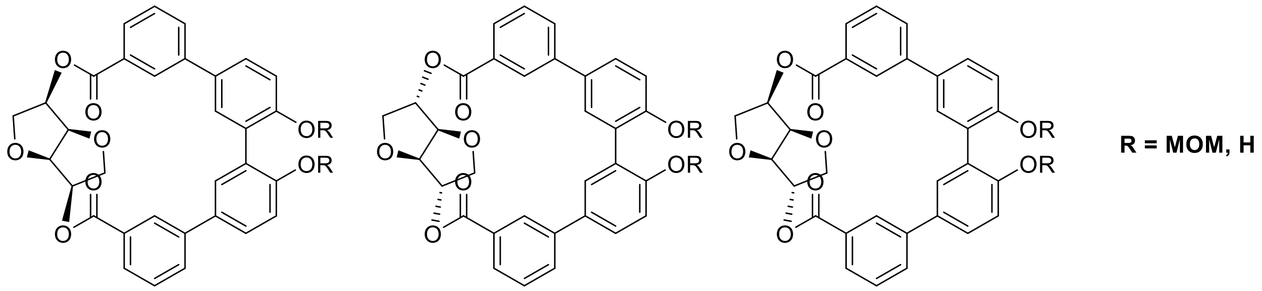
The asymmetric activation[1] of conformationally flexible 2,2'-dihydroxybiaryl units represents a promising strategy in enantioselective catalysis.[2,3] In this work, a novel class of chiral macrocyclic compounds was synthesized by covalently linking 2,2'-biphenol (BIPOL) derivatives, endowed with carboxylic groups, to isohexides, chiral molecules derived from D-mannitol and D-sorbitol, via esterification using EDC/DMAP-mediated coupling.[4] Density Functional Theory (DFT) calculations have been carried out to identify the optimal position of the carboxylic groups and to predict capability of the isohexides to induce a prevalent sense of twist on the BIPOL streogenic axis. All the compounds synthesized have been stereodynamically characterized with NMR and ECD spectroscopy, in combination with TD-DFT[5] calculations. It has been demonstrated that the cyclization reaction led to the formation of a prevalent diasteroisomer over the other, with the entity of this prevalence depending on the nature of the sugar.



**a** **b** **c**

**Figure 1:** chiral macrocycles derived from isomannide (**a**), isoidide (**b**) and isosorbide (**c**)

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# CASSCF Linear Response Theory for the calculation of molecular response properties

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Linear response (LR) theory is one of the most powerful and versatile tools in computational chemistry [1] as it enables the computation of excitation energies, oscillator strengths, and frequency-dependent molecular properties, providing thus a direct route to compare calculations with experimental measures.

When combined with multiconfigurational methods such as the Complete Active Space Self-Consistent Field (CASSCF) [2], LR theory is particularly effective for describing the response of systems with pronounced static correlation or near-degeneracy, including conjugated organic molecules and transition metal complexes.

We present a robust and efficient implementation of LR theory at the CASSCF level [3]. Our approach leverages the Cholesky decomposition of two-electron integrals [4], enabling the routine treatment of large molecular systems. The capabilities of our implementation are demonstrated through the calculation of (chiro)ptical properties—specifically optical rotation (OR) in different gauges, electronic circular dichroism (ECD), and UV-Vis spectra—using extensive basis sets, on a phycocyanobilin model system. These properties are key tools in stereochemical analysis, allowing for the determination of absolute configurations and conformational preferences in chiral molecules.

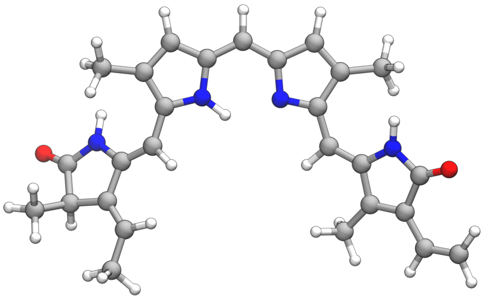

**Figure 1**. Molecular structure of the phycocyanobilin model system in the anti-syn-anti (asa) conformation.

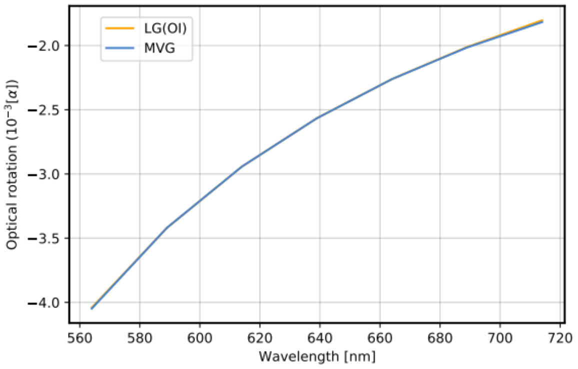

**Figure 2**. Optical rotatory dispersion of the asa conformer computed using the MVG and the LG(OI) gauges.

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# Synthesis and characterization of iron and zinc based ternary LTTM

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Deep Eutectic Solvents (DESs) and Low Transition Temperature Mixtures (LTTMs) have emerged as versatile and effective solvents for a wide range of applications.[1] While the characterization of binary DESs is well established and reported, ternary systems remain comparatively underexplored, with studies often prioritizing practical applications over fundamental understanding.

In this work, we conducted the synthesis of five ternary systems based on choline chloride, levulinic acid and either zinc chloride dehydrate or iron chloride hexahydrate. All the systems have been characterized through the measurement of their key parameters: density, viscosity, electrical conductivity and thermal behaviour. Differential Scanning Calorimetry (DSC) was used to characterize the thermal transitions and to better determine whether they should be classified as DES or LTTM. Thermogravimetric Analysis (TGA) and coupled TGA-FTIR spectroscopy were used to probe the thermal stability and decomposition profiles, also allowing us to have insights into the molecular interactions in our systems. Viscosity and electrical conductivity were further analyzed through the Walden Plot, in order to evaluate the mobility of ionic and non-ionic species.

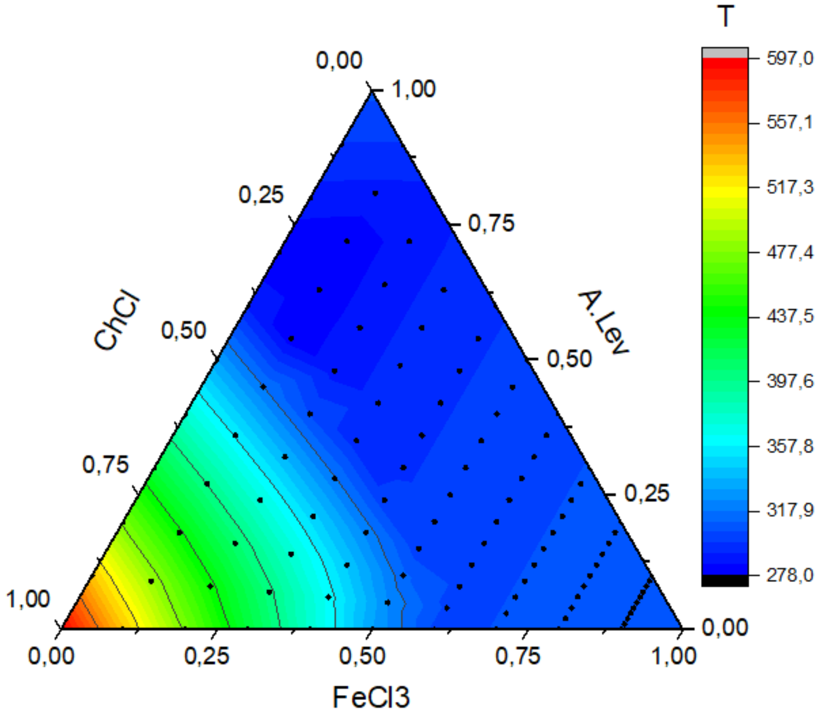

**Figure 1**. theoretical melting point for ternary systems made of $FeCl_3$, ChCl and Lev. A.

**References:**
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# Evaluation of the Applicability of Industrial UV-Vis and NIR Spectrophotometers for Real-Time Monitoring of Water Quality

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This study evaluates the applicability of industrial UV-Vis and NIR spectrophotometers for real-time monitoring of drinking water and wastewater quality (*Figure 1*). The main goal is to develop a smart, continuous monitoring system that functions as an Early Warning System (EWS), for the early detection of anomalies, such as chemical contamination or technical failures, thus enabling rapid intervention when issues are detected [1][2].

The research involved systematic sampling from water distribution network and various points in a wastewater treatment plant. Each sample was simultaneously analyzed using traditional chemical-analytical methods such as pH, conductivity, ion concentrations (by Ion Chromatography-Conductivity), metals (by Inductively Coupled Plasma Mass Spectrometry), volatile/semi-volatile organic compounds (by Solid Phase Micro Extraction Gas Chromatography-Mass Spectrometry) and spectroscopic techniques. UV-Vis and NIR spectra were recorded using both industrial and benchtop spectrophotometers with different optical path lengths.

This produced a large dataset used to identify spectral regions correlated with physicochemical parameters. Data processing involved spectral pretreatment (Standard Normal Variate (SNV) Multiplicative Scatter Correction (MSC) and Savitzky-Golay), Principal Component Analysis (PCA), and Partial Least Squares (PLS) regression, aimed at capturing the characteristic spectral fingerprint of water and developing robust predictive models for specific physicochemical parameters. These models, calibrated on real samples, help overcome the limitations of commercial spectroscopic systems, which are often not flexible in complex sample matrices. This approach supports the use of spectroscopy tools in environmental monitoring and helps improve water resource management systems.

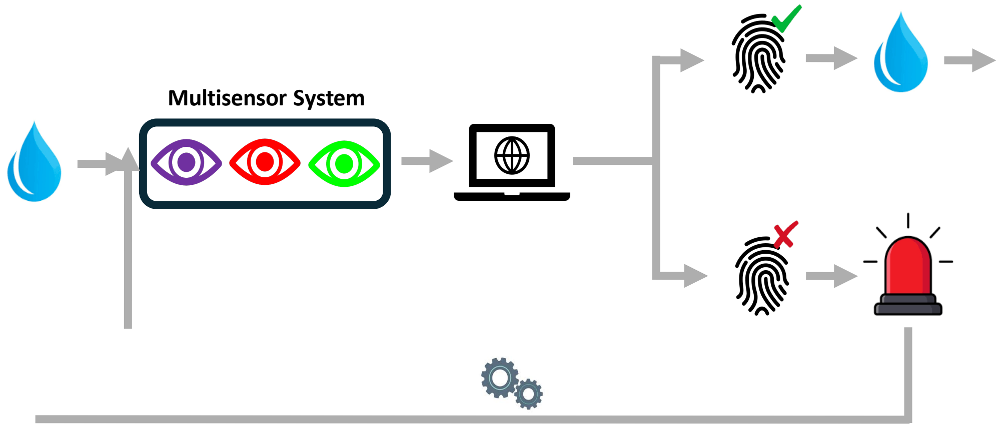

**Figure 1**. Early Warning System (EWS) scheme used to record a real-time water fingerprint

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# Airborne microplastic at its source: a quantitative analysis method for indoor microplastics by pyrolysis–gas chromatography/mass spectrometry

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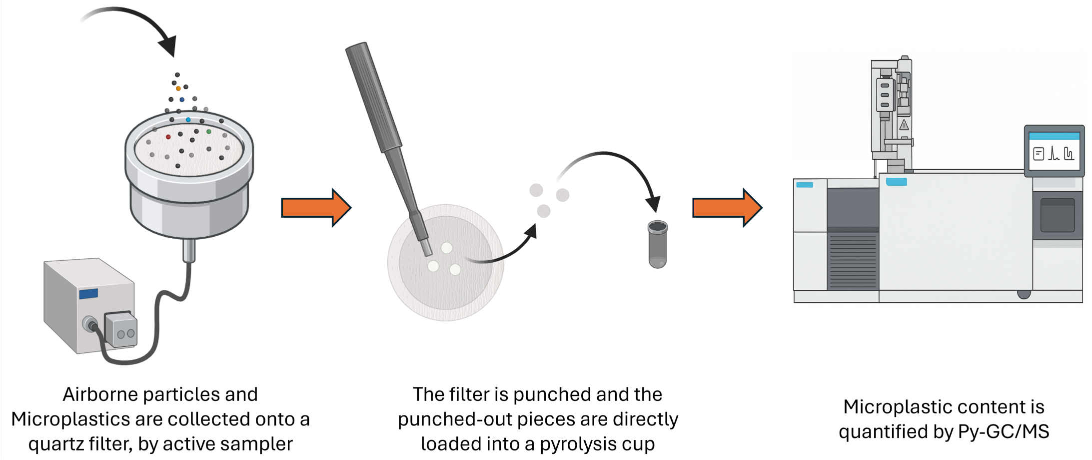
Microplastic (MP) pollution has raised growing concern among researchers due to their potential risks to both the environment and human health; however, limited attention has been paid to airborne MPs [1]. MPs can remain suspended in the air for days, be transported over long distances, and inhaled by humans, potentially leading to adverse health effects such as inflammation, lung damage, and oxidative stress [2]. These risks are especially relevant indoors, where MP concentrations are significantly higher [1]. This study aims to develop an active sampling method for indoor MPs using quartz filters, followed by direct quantitative analysis through pyrolysis–gas chromatography/mass spectrometry (Py-GC/MS) (**Figure 1**). Active and personal active samplers were employed in different types of facilities. In a mixed waste treatment facility, PP and PS concentrations ranged from 28–2 μg/m³ and 89–3 μg/m³, respectively, between the grapple crane sorting area and the bale storage. In a Plexiglass-processing plant, PMMA concentrations varied from 11–2 μg/m³ between the cutting area and the office, with personal samples reaching up to 35 μg/m³. Quantification was carried out using an external calibration with a standard mix of MPs. Significant levels of PMMA, PVC, PP, PS, and PE were detected in different work areas. Recovery tests were also performed by dispersing the MP standard in ethanol and collecting it on quartz filters using a filtration system. Results showed a strong variation in recovery rates depending on the polymer type, with underestimations ranging from 69% to 89% for most polymers, while other polymers like PVC, Ny6 and PE were subjected to overestimation.



Airborne particles and Microplastics are collected onto a quartz filter, by active sampler

The filter is punched and the punched-out pieces are directly loaded into a pyrolysis cup

Microplastic content is quantified by Py-GC/MS

**Figure 1**. Workflow scheme of the method including active sampling, sample processing and analysis.

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# Easy Access to tetrahydro-[1,4]diazepino-indoles Through Intramolecular Cyclization

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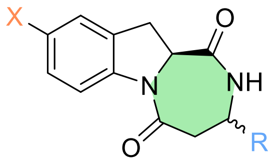
Diazepines are seven-membered heterocyclic compounds with two nitrogen atoms in different positions. Different bioactive compounds share this seven-member ring structure, often acting in the central nervous system, like the most famous benzodiazepines-based drugs.[1]

In this work, we propose an easy 2-steps synthesis to access a particular class of diazepines based on a chiral indoline moiety, (S)-tetrahydro-[1,4]diazepino-indole-1,5-dione, which was demonstrated to have some interesting activities in the central nervous system.[2] The efficient cyclization step to a seven-member ring is based on a common approach which uses the tendency of some amino acids to favor the *cis*-amide isomer of a peptide bond.[3,4] In our system we exploit the tendency of (2S)-Indoline carboxylic acid to favor the *cis*-isomer of the amide bond in polar solvents, a property that we understood through deep physical-chemical studies of the amide-isomer equilibrium.[5,6] The use of different $\beta^3$-amino acids in the diazepine synthesis offer the possibility of diversification in the side chain of the 7-member ring. Moreover, the feasible halogenation of the indole aromatic ring opens the way for further functionalizations through cross-coupling reaction, enhancing the chemical space to be explored in large libraries of compounds.



R= side chain of any Amino acid
X= halogen

**Figure 1**. (S)-tetrahydro-[1,4]diazepino-indole-1,5-diones.

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# The Role of Mordants and Dyes in the Ageing of Silk and Innovative Conservation Strategies

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Silk has long been considered one of the most valued textiles, used for over 5,000 years thanks to its natural luster and remarkable mechanical and thermal properties [1]. However, silk is delicate and prone to degradation over time. Conventional cleaning methods often present challenges in both cleaning and preserving silk-based heritage artifacts [2]. This work is part of the MOXY project, which aims to develop a novel, non-contact cleaning method based on the generation of a cold plasma of Atomic Oxygen (AO), applicable to delicate objects. Evaluating possible negative effects on silk of AO cleaning is a fundamental step towards the validation of the technique and its transfer to restorers and conservators. To this aim, it is essential to study natural aging and oxidation processes of silk to establish a clear understanding of its degradation pathways. To date, such detailed insight into silk degradation, particularly at the molecular level, remains incomplete in the literature. In this research, reference materials were subjected to artificial aging under different environmental conditions, leveraging the effects of UV-Vis light, elevated temperature, and relative humidity. In order to provide insights into the degradation patterns of silk, analytical pyrolysis has been adopted —EGA-MS and multi-shot Py-GC/MS—to assess the thermal stability of silk and obtain information at molecular level. Historical samples were also investigated using the same approach. The specific impact of dyes and mordants was assessed by including in the experimental set-up silk samples dyed with the natural dye Carminic acid (CA), using alum as a mordant, and Rhodamine B (RhB), a direct synthetic dye. The changes in aged silk proved to depend not only on environmental conditions but also on the dyes and mordants used. Interestingly, CA in combination with alum showed a protective effect, slowing down the aging process of silk. No detectable changes emerged when silk was treated with Atomic Oxygen. In parallel, the impact of both environmental conditions and exposure to AO on the dyes was also evaluated.

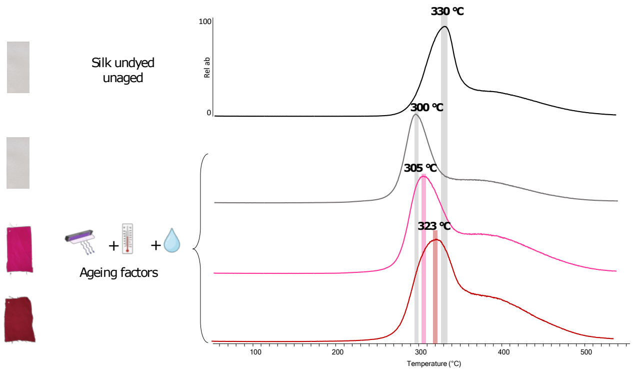

**Figure 1**. EGA-MS curves of silk undyed and unaged and of silk undyed, dyed with RhB and CA aged in Solarbox (550 W/m$^2$ (280-800 nm); 60 – 90°C; RH 50 %)

**References:**
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# First-principles picture of energy transfer in plant Photosystem II

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Photosystem II (PSII) is a protein supercomplex, found in thylakoid membranes of plants and algae, responsible for the photon-to-chemical energy conversion that initiates photosynthesis (1). PSII has the extraordinary ability to balance between efficient light-harvesting and photoprotection functions, so that photosynthetic organisms can thrive under continuously changing light conditions. Such a complex activity is strictly connected to its modular architecture, composed of a highly conserved core, hosting the reaction center, and an apparatus of peripheral antennas, which absorb photons and efficiently transfer the excitation to the reaction centers. In the last decades, fluorescence experiments have allowed investigating typical timescales of energy transfer along the supercomplex (2). However, the spatial dimension of such processes has long remained elusive due to the lack of suitable experimental and computational techniques: this has prevented a full understanding of the underlying evolutionary strategies for efficient light-harvesting and photoprotection at the molecular level. In recent years, the publication of novel cryoEM PSII structures (3) has stimulated new attempts to build structure-based models of PSII, but most of them have employed parameters fitted or computed on isolated proteins (4), since the complexity of the system and the limited accuracy of the structures remain a challenge for *ab initio* calculations. In this contribution, we show a new protocol, combining structure refinement and QM/MM excitonic calculations, able to fully characterize the energy landscape, visualize the flow of excitation and estimate exciton migration times in PSII, entirely from first principles. Moreover, by connecting excitation quenchers to the EET network, we could also simulate photoprotective mechanisms. By bridging mechanistic knowledge on quenching in single antenna complexes (5) with the overall picture of energy transfer in PSII, we were able to propose design principles for efficient energy quenching in PSII which question the simplistic idea of a hard switch between light-harvesting and photoprotection.

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# Naringenin Loading into Polymeric Nanoparticles and 3D Printed Hydrogels for Wound Healing

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Naringenin (Nar) is a natural flavonoid, predominantly found in citrus fruits, such as grapefruit (*Citrus paradisi*) and orange (*Citrus sinensis*), widely recognized for its antioxidant, anti-inflammatory, antimicrobial, and anticancer properties. Despite its promising therapeutic potential, Nar suffers from low bioavailability due to its poor water solubility, limiting its clinical applications. To address this limitation, encapsulation into polymeric nanoparticles (NPs) has emerged as an effective strategy to enhance the solubility and stability of Nar, as well as to enable its controlled release [1]. In this project, poly(lactic-*co*-glycolic acid) (PLGA) NPs were developed to encapsulate Nar via nanoprecipitation, using Pluronic F-127 as a stabilizer in an aqueous coagulation bath. The optimized NPs colloidal suspension exhibited a mean particle size of around 240 nm and a polydispersity index of 0.2 determined by dynamic light scattering, as well as an encapsulation efficiency of 74% obtained by UV-Vis spectroscopy. *In vitro* studies revealed a cumulative release in phosphate-buffered saline at 37 °C of 56% of the loaded Nar within the first 24 h and a slow release in the following days. Subsequently, these NPs were embedded into 3D printed hydrogels composed of a blend between chitosan and poly(vinyl alcohol) (PVA) and investigated as dressings for skin repair [2]. The hydrogels were fabricated using computer-aided wet-spinning, a manufacturing technique based on the extrusion of a polymeric mixture directly into a non-solvent bath (ethanol) to obtain 3D scaffolds with a controlled porosity [3]. UV-Vis spectroscopy analysis showed that the encapsulation efficiency of the hydrogels ranges between 58 and 83% depending on the post-processing treatment. This protocol has also been realised without NPs, by loading Nar directly into the blend, as a reference drug-loaded system. These results show that the integration of NPs into 3D printed hydrogels is a promising approach to designing bioactive dressings for wound healing.

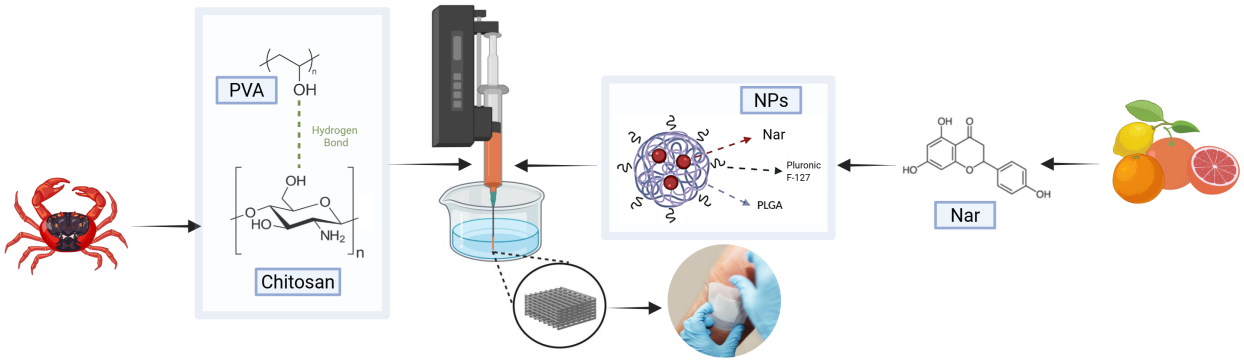

**Figure 1**. Scheme of the production of Nar-loaded PLGA NPs and their incorporation into 3D printed hydrogels for wound healing

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# Sticky stories: chemical investigation on multi-component adhesives in archaeology

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Resinous materials, such as resins, pitches, and tars, have been extensively utilized by humans throughout history thanks to their numerous properties. In particular, their application as adhesive, represented a decisive development in the evolutionary history of early hominins, with evidence of hafting technologies dating back to Palaeolithic. In addition, during time their properties have been deployed to fit every new technological challenge. For this reason, their composition evolved during time, and additives such as beeswaxes, vegetable oils and inorganics may have been added [1-3]. In this optic it is crucial to study their composition, but also their peculiar properties, as this could provide valuable insights for their preservation.

For that aim, different mock-up mixtures were prepared and analysed with Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR) in order to highlight their compositional differences. The rapidity of this technique makes it ideal for monitoring the aging process of such materials. In addition, to study how the coexistence of the adhesive and additives could affect the thermal behaviour, and, in this sense, the chemical properties of the resulting materials, both Thermogravimetric Analysis (TGA) and Evolved Gas Analysis-Mass Spectrometry (EGA-MS) were performed. By employing these techniques, it was possible to identify the chemical composition and thermal behaviour of the materials, providing insights into their aging processes.

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# Highly cytotoxic gold(I) complexes with anthracenyl moiety on the phosphine ligand

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Auranofin (AF), introduced in 1985 for the clinical treatment of rheumatoid arthritis, also showed promising cytotoxic properties against some selected cancer cell lines [1]. Since then, extensive studies have explored the possible applications of gold complexes as anticancer agents [2].

In this context, three new gold(I) complexes (Figure 1) (named FDAu-X, where X = Cl, Br, I) with an anthracenyl and a phosphine ligand were proposed. The anthracenyl moiety, besides strengthening some possible nucleic acid interactions, is thought to be a fluorescent probe for possible future confocal microscopy measurements. The two phenyls could enhance the lipophilicity of the complex and so its cellular uptake. The halogen ligand was thought to be an exchange moiety to release the active positively charged compound FDAu+.

The synthesis and characterisation of the three gold complexes have been performed, and their solubility and stability in physiological-like conditions have been evaluated. The antiproliferative activity on different cancer cell lines and one normal cell line highlighted the high toxicity of this family of compounds, with $IC_{50}$ values in the micromolar order in just 24 h. Interestingly, all the complexes can overcome cisplatin resistance mechanisms in ovarian cancer cells.

Finally, to understand possible mechanisms of action, the interaction with natural DNA and one type of protein overexpressed in cancer, like Cathepsin B, was also investigated. Further experiments are ongoing, implementing a fourth complex which presents the thiosugar of AF as a ligand in place of the halogen to hopefully enhance water solubility and to mimic the pharmacokinetics of AF.

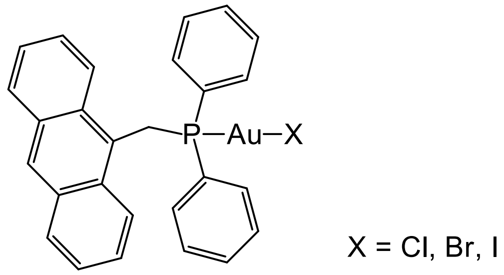

**Figure 1**. Molecular structure of diphenyl-(anthracen-9-ylmethyl)phosphine-Au-X where X=Cl, Br, I.

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# Urolithin A-loaded polymeric nanoparticles for the treatment of Alzheimer's disease

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Urolithin A (Uro-A) is a natural compound, obtained from the metabolism of ellagitannins and ellagic acid by the gut microbiota. Pomegranates, berries, and nuts are the primary sources of these polyphenols. Uro-A has a neuroprotective effect, as it helps to reduce oxidative stress and inflammation in neuronal cells [1]. This evidence suggests that Uro-A could play a significant role in managing neurodegenerative diseases (e.g., Alzheimer's) and improving overall brain health [2]. In this work, poly(lactic-*co*-glycolic acid) (PLGA) nanoparticles (NPs) loaded with Uro-A have been developed using the nanoprecipitation technique (Figure 1). Several formulations of NPs were prepared by varying the concentration of PLGA and Pluronic F-127 used as surfactant. The optimised formulation was selected by analysing the diameter and polydispersity index of the NPs by dynamic light scattering, as well as their encapsulation efficiency and loading by UV-Vis spectroscopy. FTIR-ATR spectroscopy analysis confirmed the presence of all components in the NPs and differential scanning calorimetry analysis suggested a strong interaction between PLGA and the surfactant. Moreover, NMR spectroscopy analysis suggested that Uro-A was deeply incapsulated in the core of the NPs, ensuring physical protection of the active ingredient from degradation pathways. NPs were characterized by a constant release rate of Uro-A *in vitro*, with a cumulative drug release of 31% after 8 days. Ongoing studies are aimed at verifying the ability of NPs loaded with Uro-A to exert a neuroprotective action on the SH-SY5Y neuroblastoma cell line, which is used as an *in vitro* model of Alzheimer's disease.

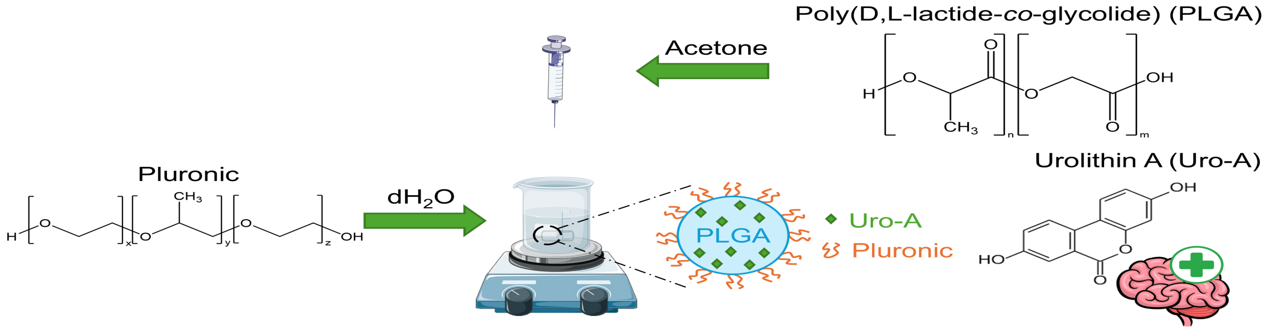

**Figure 1**. Schematic representation of the nanoprecipitation technique.

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# From Monomer to Crystal: A Computational Protocol for the Optical Properties and Photo-induced Dynamics of Pentacene

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The field of organic optoelectronics is rapidly advancing, driven by technologies such as organic photovoltaics (OPVs) and field-effect transistors (OFETs), which enable light-to-charge conversion and current modulation in semiconductors, respectively. Molecular arrangement and electronic interactions critically influence charge generation and transport efficiency. Pentacene has long been a key material in this field due to its high crystallinity and charge mobility [1].

Simulating its optical and photoinduced electronic properties remains challenging because of the complex coupling between localized and charge-transfer states and vibrational motion. To address this, we present a hierarchical computational protocol aimed at minimizing phenomenological modelling. The approach begins with the monomer, extends to multimers, and ultimately to the crystal, identifying justified approximations at each step to balance efficiency and accuracy.

The protocol relies on various diabatization techniques and hierarchical vibronic Hamiltonians to define effective coordinates. We first compute the vibronic spectrum of the monomer and interactions in dimers. These results—couplings and mode gradients—are used to parametrize a vibronic Hamiltonian for a larger crystal supercell. Simulated linearly polarized absorption spectra agree well with experiments [2], revealing exciton anisotropy and character.

Finally, this Hamiltonian is applied in quantum dynamical simulations (ML-MCTDH, [3]) to explore femtosecond-scale photoinduced dynamics, involving many vibrational degrees of freedom and a dense manifold of excited states.

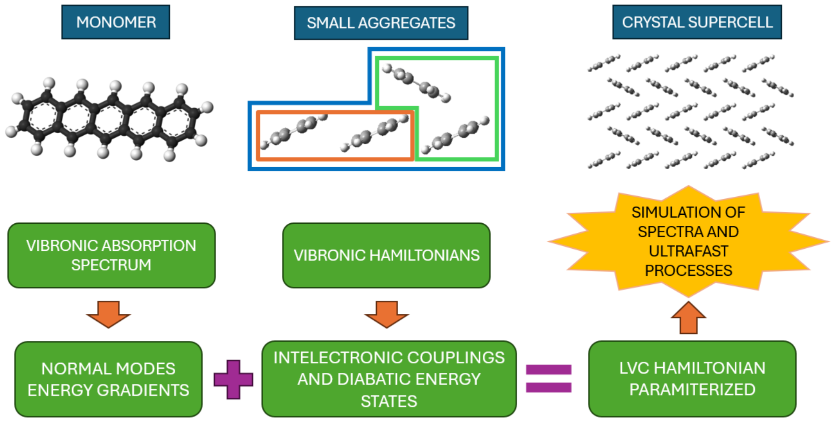

**Figure 1**. Workflow of the computational protocol proposed

**References:**
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# Understanding the Ageing of Plastics in Art and Design: A Thermoanalytical Approach

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The first half of the 20th century witnessed the industrial-scale production of synthetic polymers such as polyurethanes (PU) and cellulose acetate (CA), which quickly found application in different compartments including arts and design, appealing to artists' interest in novel materials and modern aesthetics. However, these revolutionary and widespread polymers are found to undergo degradation reactions, such as *hydrolysis, deacetylation*, and *photo-oxidation*, all of which compromise their mechanical properties and durability, challenging their preservation [1,2]. To support conservation and restoration efforts of plastic artistic and design objects, a systematic study of reference materials, both unaged and artificially aged, is pivotal. This can help to better understand the composition of synthetic polymers and investigate the degradation pathways involved in the ageing processes of plastic-based artistic objects. In this context, the PERSPECTIVE (PolymEr Research Studies for PreventivE Conservation Through non invasIVe analytical strategiEs) project is pioneering a new approach in conservation science by developing non-invasive, multimodal techniques building on robust analytical methods. Within the framework of the project, this work focuses on the application of thermoanalytical techniques to provide a comprehensive molecular characterization of plastic items formulations, including polymers, plasticizers and additives. Micro-destructive methods including analytical pyrolysis coupled to gas-chromatography/mass spectrometry (Py-GC/MS) and evolved gas analysis coupled to mass spectrometry (EGA-MS) were applied for investigating reference CA and PU materials, both unaged and artificially aged. EGA-MS results obtained in the analysis of unaged and aged PU mock-ups, treated either with a consolidant solution or with a consolidant and solution light stabilizer, show a distinct thermal behaviour for each material, allowing the identification of the isocyanate and polyether fractions of the polymer, along with those of the light stabilizer and/or consolidant in the treated ones. Differences in the thermal degradation temperatures due to ageing are also visible comparing the aged and unaged samples. On the other hand, EGA-MS results of CA mock-ups, though not showing statistically significant changes in the thermal behaviour among progressively aged samples, prove that the different pigments (i.e., green PG7 and yellow PY215) used in the plastic formulation do not influence their thermal stability, and reveal the presence of diethyl phthalate (DEP) as a plasticizer. Double shot Py-GC/MS conditions (i.e., temperature and thermodesorption time) were tentatively optimized to investigate plasticizer and polymer pyrolysis products separately, but did not allow the quantitative evaluation of DEP. Hence, as future perspective, a high performance liquid chromatography (HPLC) based method will be implemented to quantitatively determine DEP in CA samples.

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# Tetraphenylethylene derivatives: characterization and nucleic acids binding properties of two new molecules of this interesting class of compounds

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In the fight against cancer, the use of targeted drugs has proven promising in recent decades, in addition to radiotherapy and chemotherapy.[1] Such targeted small molecules are often designed to interact with nucleic acids, such as DNAs and RNAs, both through covalent bonds with nitrogenous bases or through non-covalent interactions, leading to cell death. Recently, G-quadruplex and *i*-motif structures are found in telomeres and promoters of genes leading to oncogenesis and have emerged as promising anticancer targets.[2],[3] In this frame, the tetraphenylethylene (TPE) core is an interesting moiety, containing four benzene rings, for binding to these non-canonical nucleic acid structures. With regards to TPE photophysical properties, TPE-derived ligands exhibit increased fluorescence upon aggregation/motion restriction according to a phenomenon called aggregation induced emission (AIE), that can be applied for sensing and imaging of biomolecules.[4]

In this study, we investigated the interaction between nucleic acids and two TPE derivatives: N1-(2-(bis(2-((3-aminopropyl)amino)ethyl)amino)ethyl)-N3-(4-(1,2,2-triphenylvinyl) benzyl)propane-1,3-diamine (**TPE-TAL**) and N1-(3-aminopropyl)-N4-(3-((3-(1,2,2-triphenylvinyl)benzyl)amino)propyl) butane-1,4-diamine (**TPE-spermine**) (Figure 1). In the first phase, we characterized the acid-base behavior of the two ligands by potentiometry, UV-vis and fluorescence emission experiments. In the second phase, we studied the interaction between these ligands and nucleic acid structures, ranging from natural DNA and synthetic RNA polynucleotides to G-quadruplexes and *i*-motifs.

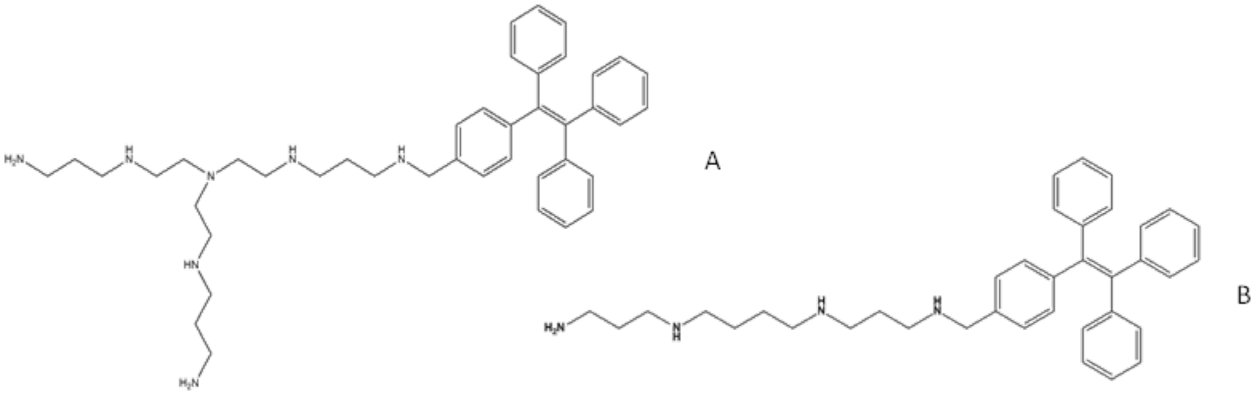

**Figure 1**. Molecular structures of TPE-TAL (A) and TPE-spermine (B)

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# Revealing the degradation mechanisms of historical logwood and iron gall logwood inks (19th-20th century)

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From the 19th to the 20th century, iron gall inks have been widely used for their ability to produce chromatic black. However, their presence in manuscripts and drawings have caused numerous conservation issues [1], such as fading and corrosion of paper supports and pen nibs [2],[3]. For this reason, the 19th century called for the creation of new non-corrosive ink formulations, thus leading to the introduction on to the market of logwood-based inks [3]. Moreover, despite logwood inks were inexpensive, their lack of permanence made them unsuitable for official documents [4]. To date, ageing processes involving the organic component of historical inks have been never or seldom investigated, preventing us to fully understand the conservation issues associated with inked artworks [5].

The goal of this work is to characterize the main degradation mechanisms that involve logwood´s molecular markers in historical ink formulations. To achieve this, historical logwood and iron gall-logwood ink recipes have been selected and replicated in the laboratory. For each formulation, a model ink has been prepared following the same historical recipe, using analytical standards (i.e., hematoxylin and gallic acid) instead of the natural raw material. Then, the inks obtained were cast on Whatman filter paper to prepare a series of mock-ups, which were also subjected to ageing by exposure to natural indoor light. Our investigation is mainly carried out through colorimetric and liquid chromatographic techniques ((HPLC-DAD, HPLC-ESI-Q-ToF), which enable us to monitor the changes in ink's colours molecular profiles in function of ageing.

The preliminary results show that already after one month of natural light ageing significant changes of the investigated formulations can be highlighted. On the one side, the colorimetric analysis has detected changes in all colorimetric coordinates (L*, a* and b*). We determined as general trend a decrease in the L* and a* coordinates (i.e., desaturation), as well as an increase in b* (i.e., yellowing) of the ink mock-ups. On the other side, the chromatographic analyses (HPLC-DAD e HPLC-ESI-Q-ToF) showed differences in the molecular profiles between freshly cast and aged inks, by allowing us to detect novel degradation markers. The identification and study of these compounds in historical formulations and ink models could help in explain the main degradation mechanisms involved in ageing processes, thus supporting conservation efforts and providing a suitable database for ink's identification in historical manuscripts.

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# $CO_2$ adsorption in metal-organic framework-based matrix membranes: a multi-technique approach

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Mixed-matrix membranes (MMMs) constitute a class of very promising materials for $CO_2$ capture since they combine the easy processability, flexibility, low cost, and good permselectivity of the polymeric matrix with the advantageous adsorption properties of metal-organic frameworks (MOFs) [1,2]. In the framework of the DAM4$CO_2$ project, MMMs for $CO_2$ capture are developed by exploiting polymers of intrinsic microporosity (PIMs) and MOFs based on non-critical metals and non-environmentally hazardous organic linkers and characterized using a multi-technique approach to shed light on physico-chemical properties and on $CO_2$ adsorption capacity and mechanism.

Here, results are shown on two MMMs prepared using PIM-1 and two different MOFs, i.e., UTSA-280 (calcium squarate, $Ca(C_4O_4)(H_2O)$) and UTSA-16 (zinc citrate, $K_2Zn_3(C_6H_4O_8)_2$), showing promising $CO_2$ adsorption properties [3,4]. $CO_2$ adsorption and separation properties from other gases ($N_2$, $CH_4$, $O_2$, $H_2$, He) were determined in comparison with the parent materials. Improved selectivity and enhanced $CO_2$ adsorption were found in the MMMs with respect to the neat polymer membrane. Structural properties of MOFs, polymer, and MMMs were investigated by X-ray diffraction, scanning electron microscopy, and solid-state NMR spectroscopy. Moreover, solid-state NMR gave insight into interactions between $CO_2$ and MMM materials at the atomic level and allowed the investigation of $CO_2$ reorientation dynamics in the MMMs in comparison with their parent materials.

This study has received funding from the European Union's Horizon Europe research and innovation programme, European Innovation Council and SMEs Executive Agency (EISMEA), under grant agreement No 101115488, project "DAM4$CO_2$".

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# Salivary peptide profiling as a novel approach for cardiovascular disease monitoring

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Cardiovascular diseases (CVDs) remain the leading cause of mortality worldwide and represent a complex group of disorders affecting the heart and blood vessels [1]. Despite significant advances in understanding molecular pathways involved in CVDs, current diagnostic tools, such as imaging studies and routine laboratory tests, fail to predict nearly 50% of cardiovascular events. Peptides, due to their key roles in vascular homeostasis and their rapid diffusion into biological fluids, are emerging as promising biomarkers for CVD diagnosis and monitoring [2].

The present work introduces an innovative, simplified, patient-friendly and non-invasive protocol for the quantification of cardiovascularly active peptides (e.g., Endothelins, Natriuretic Peptides, Fibrinopeptides, Vasopressin) in human saliva.

The method is based on a top-down peptidomics approach based on micro-extraction by packed sorbent (MEPS) for selective analyte enrichment, followed by ultra-high-performance liquid chromatography coupled with electrospray ionization tandem mass spectrometry (UHPLC-ESI-MS/MS) for accurate and reliable peptide profiling.

In collaboration with the Department of Clinical and Experimental Medicine at the University of Pisa, a pilot study is currently underway to investigate correlations between salivary peptide expression and clinical variables.

This novel methodology offers a practical and accessible tool for the early detection and longitudinal monitoring of CVD-associated biochemical alterations, potentially improving risk stratification and supporting personalised patient care.

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# Probing Host–Guest Interactions in FLARE Membranes via Solid-State NMR Spectroscopy

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The rise of $CO_2$ emissions presents a major environmental challenge. In this frame, carbon capture and storage (CCS) is widely recognized as a key strategy to reduce $CO_2$ emissions and mitigate climate change [1]. Polymer-based membranes technology offers a promising, energy-efficient alternative to conventional energy-intensive separation methods like cryogenic distillation and absorption, commonly used in industry [2,3]. However, their application is limited by the trade-off between permeability and selectivity (described by the Robeson upper bound), along with aging and plasticization effects that reduce separation performances [5]. The incorporation of rigid bulky triptycene groups can enhance the overall fractional free volume (FFV) of the material, improving separation performances and mitigating these detrimental effects.

In this work, we present a solid-state NMR study of a triptycene-containing fluorinated aryl ether (FLARE) polymeric film [6] and its interaction with $CO_2$. Solid-state NMR is a well-established tool for investigating porous materials and their interaction with guest molecules [7], disclosing information on structural and dynamic properties. Especially, the study of dynamics of both the host and guest molecules can provide insights into the host-guest interaction [8,9].

We measured spin-lattice relaxation times ($T_1$) of $^{19}F$ and $^{1}H$ nuclei of the polymer as a function of temperature and Larmor frequency, before and after $CO_2$ adsorption, to assess the effects of $CO_2$ adsorption on the dynamics of the host.

To directly probe the behavior of $CO_2$, we recorded static and high-resolution spectra (*i.e.* under magic angle spinning). $^{13}C$ $CO_2$ static spectra are dominated by the anisotropic part of the chemical shift interaction (chemical shift anisotropy – CSA), which is modulated by molecular motions giving information on the geometry and rate of these motions [10]. Additionally, variable temperature $^{13}C$ $T_1$ of $^{13}CO_2$ provided insights into reorientational motions and self-diffusion of adsorbed $CO_2$ [10].

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# CPL Photoscopy: Circularly Polarized Luminescence Detected by Chromaticity Differences

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Circularly polarized luminescence (CPL) is attracting growing interest for a wide range of applications,[1] spanning from materials with advanced optical properties[2,3] to innovative imaging techniques.[4] The traditional approach to CPL consists of measuring the emission intensity difference between the left and right polarizations of light and usually requires spectral separation through colour filters or a monochromator. However, in the last few years many efforts were undertaken to make CPL detection cheaper and easier.[5,6]

In this work, we show the possibility of extracting CPL information from the chromaticity values of a couple of snapshots of the emitted light taken under different polarizations when a CPL spectrum contains at least two bands with different polarizations. This concept paves the way for a novel approach to CPL measurements, based on chromaticity difference rather than intensity difference. This technique requires cheap instrumentation, as it can be performed with an entry-level camera, offers complementary features with respect to the traditional methods and could potentially be applied to CPL imaging.

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# Black soldier fly eumelanin: purification and chemical characterization

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Melanins are the most widely distributed pigments in nature, exhibiting a range of physicochemical and biological properties, including UV radiation protection, energy harvesting, and radical scavenging[1]. Based on their precursors, which determine their structural features, melanins are classified into several types, with eumelanin being the most prominent. Eumelanins originate from the oxidative polymerization of 5,6-dihydroxyindole (DHI) and 5,6-dihydroxyindole-2-carboxylic acid (DHICA)[2]. The extraction of eumelanin from natural sources has enabled notable advancements in materials science and engineering, although only a few examples are reported in the literature[3–5] due to challenges associated with extraction and purification methods, which are often inconsistent. Beyond fungi and cephalopod inks, insect exoskeletons have emerged as a valuable source of eumelanin. A recent patent by Insectta[6] describes a method for extracting high-purity eumelanin from black soldier fly cuticles[7], supporting the growth of the insect farming industry[8,9]. In this study, we present a method for extracting eumelanin from black soldier fly samples, yielding two fractions: one soluble in an organic phase and the other in an aqueous phase. These fractions were analyzed and characterized by attenuated total reflectance- Fourier transform infrared (ATR-FTIR), UV-visible and $^{31}$P-nuclear magnetic resonance ($^{31}$P-NMR) spectroscopies, as well as field emission scanning electron microscopy (FE-SEM). The results confirm the presence of DHICA in the complex melanin structure, addressing and refuting ongoing debate regarding its occurrence in this class of melanin.

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# Thermo-Oxidative Degradation of Cotton Treated with Flame Retardants: Insights from Solid-State NMR and EPR

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Cotton is naturally flammable, posing a serious risk in the event of a fire, especially when used in indoor furnishings. Its fire resistance can be improved with flame-retardant treatments. Among emerging bio-based solutions, polyamidoamines (PAAs) derived from natural α-amino acids stand out as sustainable, effective, and smoke-free alternatives [1]. This study explores the degradation of cotton treated with PAAs under fire-like conditions. Since combustion is a fast and complex process, controlled thermos-oxidation was used to simulate it, allowing the characterization of intermediate products. To date, no detailed mechanism has been reported for the thermo-oxidation of cotton in the presence of PAAs. To gain insight into this process, $^{1}H$ and $^{13}C$ solid-state NMR and EPR spectroscopies were employed to analyze the char residues of cotton treated with PAAs derived from glycine and cystine, as well as the residues of the chars from pure PAAs. The combined use of these spectroscopies suggests that the PAAs form a protective layer inaccessible to oxygen which effectively shifts the thermal degradation pathway of the impregnated cotton towards a pyrolysis-like process. As an example, Fig. 1 shows that pyrolyzed cotton and cotton impregnated with the PAA and thermo-oxidized exhibit similar spectra, which are markedly different from that of thermo-oxidized pure cotton.

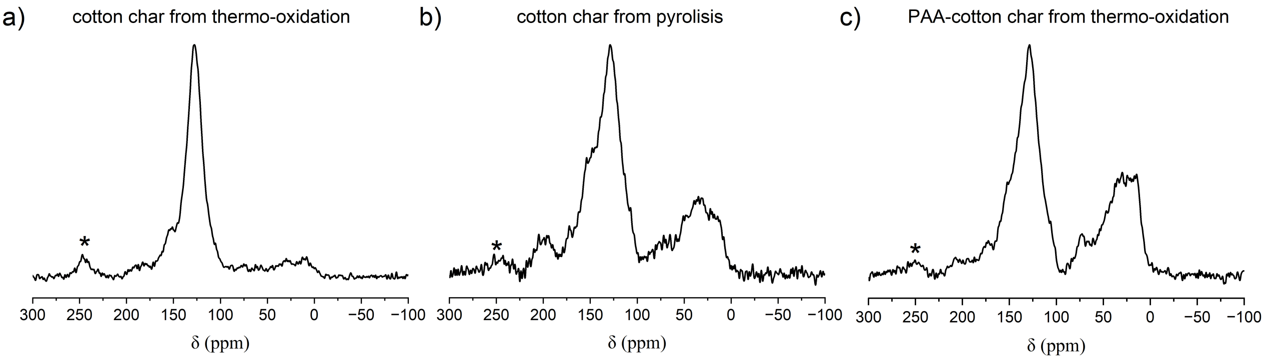

**Figure 1**. $^{1}H$-$^{13}C$ cross-polarization MAS NMR spectra for: a) pure cotton and c) cotton impregnated with a cystine-based PAA, both thermo-oxidized at 350 °C, and b) char from pure cotton pyrolyzed at 350 °C. Spinning sidebands are marked with asterisks.

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# Novel chiral cobalt(II) complexes exhibiting remarkable VCD signal enhancement

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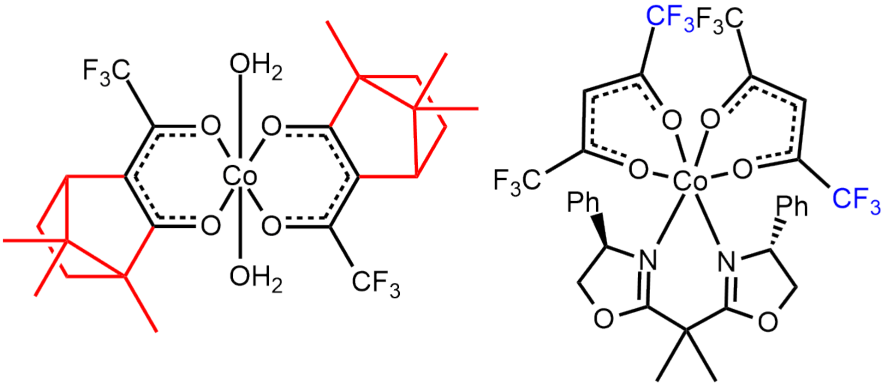
The study of transition metal complexes offers numerous and significant examples of chirality-based applications.[1][2] Specifically, chiral complexes based on $Co^{II}$, $Co^{III}$, $Ni^{II}$, $Cu^{II}$, and $Ln^{III}$ (where Ln refers to a lanthanide metal) can show a variety of circular dichroism bands, often accompanied by amplification of vibrational circular dichroism (VCD) signals.[3] In this work, new bis- and tris-chelate cobalt(II) complexes were synthesized. Bis-chelates complexes (**1**) contain two chiral β-diketone ligands - (+)/(-)-3-(trifluoroacetyl)camphor. Neutral tris-chelates (**2**) are based on two achiral β-diketone ligands and one chiral bisoxazoline ligand - (R,R)/(S,S)-2,2′-isopropylidenebis(4-phenyl-2-oxazoline). All compounds were isolated and then characterized by elemental analysis, solid-state IR spectroscopy, circular dichroism spectroscopy (ECD and VCD), and single-crystal X-ray diffraction when possible. The bis-chelates (**1**) exhibited exceptionally strong VCD signals due to aggregation phenomena, with g-factors of the order of $10^{-2}$. The neutral tris-chelates (**2**), showed remarkable VCD signal amplification in solution, with g-factors comparable to those observed for **1** in gel or microcrystalline form. The observed VCD is unprecedented, as no comparable amplification intensities have been reported for metal complexes or isolated molecules.[4]



**1a** **2a**

***Figure 4.*** *Examples of the structure of the synthesized complexes.*

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# A Sustainable Chemical Recycling Approach for Complex Plastic Waste

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Plastic packaging is among the main applications of plastics, with multilayer materials widely employed in the food industry and fast-moving consumer goods. However, they are difficult to recycle, as they are chemically heterogeneous as composed of polymers with different chemical and physical properties. [1]

In this context, we propose a chemical recycling process for complex polymer matrices: the process begins with a preliminary delamination step in formic acid (75 °C, 1 h), which selectively solubilizes polyamides and polyurethane adhesives, followed by a density-based separation between PET and polyolefins.[3] The isolated polymers were subsequently subjected to dedicated processes:

- PET was treated with an iron-based bifunctional Lewis/Brønsted acidic Deep Eutectic Solvent (LBDES), or using a NaOH/EtOH/$H_2O$ mixture. The latter is particularly promising because it enables direct treatment of mixed PET and polyolefin waste without prior delamination;
- the recovered polyamides (nylon 6,6 and nylon 6) were also depolymerized via acidic hydrolysis in HCl (140 °C, 4 h), with quantitative conversion, allowing recovery of the corresponding monomers: adipic acid and 6-aminohexanoic acid hydrochloride;
- for the recovered mixture of polyolefins, namely polyethylene and polypropylene, oleic acid and ethyl oleate demonstrated the ability to selectively dissolve polyethylene at 100 °C, with a maximum solubility of 0.04 g/ml. In this perspective, efforts are being made to recover high-oleic fatty acids from exhausted cooking oils, thus valorising a waste by-product as a green solvent for the recovery of polyolefins.

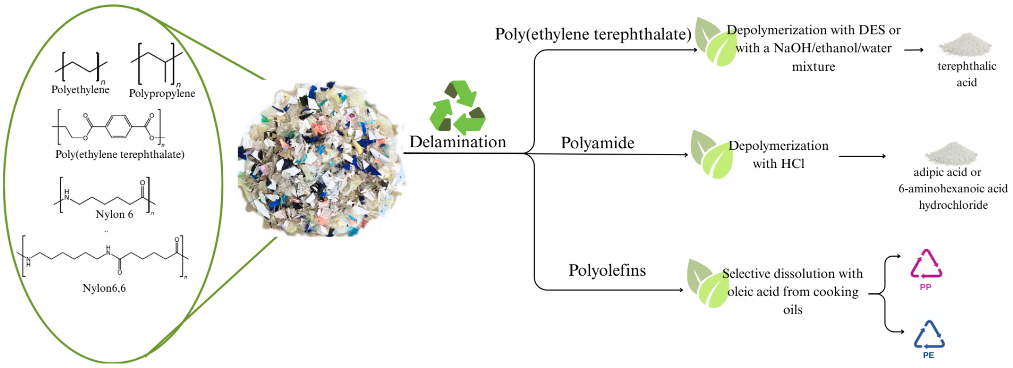

**Figure 1**. Chemical recycling process of complex plastic matrices.

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