





### **Chemistry For the Future**

International Conference

3-5 July 2024

Via Giuseppe Moruzzi, 13 - 56124 Pisa, Italy cff24unipi@gmail.com

## **BOOK OF ABSTRACTS**





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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









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<sup>\*\*</sup>



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** info@favs.it

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





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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



# SAI VEOLIA

#### IL NOSTRO OBIETTIVO

Fondamentale per noi è porre al centro dei processi decisionali le esigenze e le necessità del cliente al fine di ricercare la migliore soluzione ai suoi problemi. A tal fine forniamo risposte e soluzioni certe in maniera tempestiva grazie all'elevata professionalità delle risorse presenti in azienda, offrendo soluzioni prima che nascano i problemi.

#### COSA FACCIAMO E COME OPERIAMO

Svolgiamo la nostra attività nel settore della depurazione di acque reflue industriali e del trattamento di rifiuti liquidi speciali pericolosi e non pericolosi negli impianti di proprietà di Porto Corsini (Ravenna) e Livorno.

Gli impianti sono di tipo chimico fisico e biologico, con la possibilità di trattamento in continuo o a batch, dotati di tecnologie consolidate che garantiscono un'efficienza di abbattimento del carico organico ed inorganico superiore al 90% e una linea dedicata al trattamento di rifiuti ad elevata concentrazione di metalli. I nostri impianti inoltre sono ubicati in posizione strategica sul territorio, in quanto possiedono lo scarico finale in acque superficiali marine, un vantaggio che consente di poter ritirare rifiuti con elevata salinità.



#### IMPIANTO DI PORTO CORSINI

- Impianto di depurazione reflui industriali e trattamento chimico-fisico e biologico rifiuti liquidi
- Autorizzazione al trattamento di 200.000 tonnellate all'anno di rifiuti pericolosi e non pericolosi
- Scarico diretto in acque superficiali marine (deroga per cloruri e solfati)

Via Baiona 203- 48123 Porto Corsini (RA)



#### IMPIANTO DI LIVORNO

- Impianto di depurazione reflui industriali e trattamento chimico-fisico e biologico rifiuti liquidi
- Autorizzazione al trattamento di 200.000 tonnellate all'anno di rifiuti pericolosi e non pericolosi
- Scarico diretto in acque superficiali marine (deroga per cloruri e solfati)
- Via Leonardo Da Vinci 35/A 57123 Livorno



#### LABORATORI ANALISI

SAI dispone di due laboratori, ubicati presso gli impianti di Porto Corsini e Livorno, dotati di personale qualificato e di strumentazione tecnica all'avanguardia per il controllo analitico sui flussi in ingresso agli impianti, sulle varie sezioni dei trattamenti fino allo scarico finale nel pieno rispetto della normativa nazionale vigente e delle prescrizioni impartite dagli Enti di Controllo.

#### Principali attività dei nostri laboratori

- caratterizzazione preliminare di ciascuna tipologia di rifiuto trattata dagli impianti
- analisi di ciascun rifiuto e refluo conferito
- monitoraggio degli intermedi degli impianti di trattamento
- analisi giornaliera dello scarico in acque superficiali
- analisi dei rifiuti e degli scarichi in acque superficiali come indicato nelle AIA degli impianti
- analisi a supporto della divisione di ricerca e sviluppo

S.A.I. S.r.l. Servizi Ambientali Industriali a socio unico

Società soggetta a direzione e coordinamento di "SARP INDUSTRIES S.A."

#### Sede Legale:

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### I nostri interessi ed attività:

**IBC ENERGY** si occupa dalla sua costituzione nel 2004 di impianti produzione idrogeno su skid, ricerca su forme di alimentazione sostenibili nel settore automotive, realizzazione di HRS, produzione energetica da Biogas e Cogenerazione.

Siamo stati tra i primi membri di H2IT, abbiamo presentato i primi veicoli ad alimentazione mista H2+CNG (Stazione Grecciano 2005, Regione Abruzzo 2007, Roma Magliana Nord 2007).

### Le nostre collaborazioni:

- Incentivi statali ed europei
- Attuazione Decreto Legge 257-16 sulla neutralità dei carburanti sostenibili
- Regola Tecnica di prevenzione 23.10.2018, (Task force normativa)
- Piano di Sviluppo Mobilità Idrogeno e Attuazione PNIEC IPCEI.
- MOU tra FCHJU e Regione Toscana per contributi EU alle regioni
- Consorzio 3emotion contributi Horizon 2020
- Impegni istituzionali
- Automotive bus e stazioni
- Impianti fotovoltaici (FV) per piccola impresa e industriali
- Impianti su pensiline da: 10 kW-500 kW
- Business plan di impianto fv a terra da: 100 kW 1 mW
- Business plan di impianto fv su serra da: 50 kW 1 mW
- Grandi impianti industriali (eolico e solare termodinamico)
- Microcogenerazione civile e industriale
- Le biomasse come fonte di energia
- Progetti case ecologiche a risparmio energetico
- Impianti solari termici combinati
- Celle solari "classiche", celle solari polimeriche, organiche, ibride, a pigmenti, celle solari con nanomateriali
- Libera docenza Università private
- Correlatore Tesi Uni Cattolica

Abbiamo al nostro attivo diverse pubblicazioni scientifiche ed articoli su note testate giornalistiche.



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.

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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 plastic packaging materials. Our products are not only biodegradable and water-soluble but also non-toxic, offering a significant reduction in environmental impact.

Ecopol operates two cutting-edge production facilities to serve our global customer base. In Chiesina Uzzanese, Tuscany, Italy, our purpose-built production campus houses the largest installed base of PVOH blown film capacity in the world, along with the largest PVOH solution cast film line.

In Griffin, Georgia, USA, our newly inaugurated production facility marks a significant expansion of our production capabilities in North America. This facility is designed to meet the growing demand for sustainable products from our global customers and support our mission of providing innovative, high-quality solutions.

Furthermore, our ongoing investment in research and development is a testament to our commitment to innovation and technological advancement.

Our biodegradable films and delivery systems empower leading consumer goods companies to significantly cut carbon emissions and decrease the use of water and virgin plastics in their supply chains. We remain steadfast in our commitment to reducing our carbon footprint by continuously adopting low-impact technologies and production processes.

At the heart of Ecopol's operations is our mission to be the preferred partner for our customers by delivering innovative, high-quality, and value-added delivery systems. We strive to ensure a more sustainable future for our employees, business partners, and communities. Since our inception, Ecopol has been relentless in its pursuit of excellence, consistently delivering superior quality to our customers.

We continually invest in our people, capacity, and capabilities to provide unparalleled service and the highest quality solutions. Ecopol is proud to have built a multicultural and inclusive organization committed to the success and wellbeing of its employees.



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### Il Gruppo Sapio

Il Gruppo Sapio, fondato nel 1922 con sede a Monza, opera nel settore dei gas industriali, medicinali e nell'assistenza domiciliare in Italia, Francia, Germania, Spagna, Slovenia e Turchia.

Con un fatturato di 847 milioni di euro (2023) e 2433 dipendenti (2023), Sapio produce, sviluppa e commercializza gas, tecnologie innovative e servizi integrati che trovano applicazione in ogni settore produttivo, dall'agroalimentare all'ambiente ed energia, dal chimico-farmaceutico all'elettronico, dal meccanico e metallurgico al vetro e cemento.

In campo industriale, oltre ad una serie di acquisizione di nuovi importanti clienti nazionali quali Lavazza, Lamborghini e Ducati, Sapio è tra gli attori principali della transizione energetica ed in particolare dello sviluppo dell'idrogeno quale vettore energetico per la mobilità sostenibile e la grande industria manifatturiera. I progetti finanziati da Pnrr a guida Sapio ammontano ad un totale di circa 60 milioni di euro.

Nel campo della sanità, Sapio Life affianca le strutture sanitarie nella fornitura di gas medicinali e dispositivi medici per ossigenoterapia, ventiloterapia, nutrizione artificiale, telemonitoraggio, medicina del sonno, emodialisi domiciliare assistita, medicazioni avanzate e crioterapia. Negli ultimi anni Sapio Life ha anche realizzato un device digitale per migliorare la comunicazione di pazienti con patologie neurodegenerative ed affette da autismo. Attraverso Life Cure il Gruppo si occupa inoltre di assistenza domiciliare integrata e cure palliative. Sapio è infine presente nel settore delle biotecnologie con un centro di risorse biologiche per la conservazione dei campioni e l'erogazione di servizi di laboratorio e di sequenziamento del DNA a Istituti di ricerca pubblici e privati (ospedali, università, cliniche), aziende biotech e farmaceutiche.

Nell'ultimo decennio Sapio ha avviato un percorso di espansione in Italia e all'estero attraverso una serie di acquisizioni che in 5 anni hanno contribuito a quasi raddoppiare il fatturato. Questo processo di internazionalizzazione e trasformazione è partito nel 2018 con il piano strategico "NexT" - acronimo di *New Extraordinary Transformation* - un programma di crescita sostenibile per ampliare il business e trasformare il modo di pensare, le competenze, il metodo di lavoro di Sapio. Si è trattato di un percorso proseguito nel 2023 con il piano "Inspire", che ha come target principale il superamento del miliardo di fatturato e la creazione di un'unica cultura aziendale di Gruppo.



### **SCIENTIFIC PROGRAM**

### **Chemistry for the Future 2024**

### Wednesday – July 3<sup>rd</sup>

- 13:45 14.30 Registration
- 14:30 14:45 Welcome and Opening

### Session 1\_Chair: Lorenzo Bonaldi and Stefania Volante

- 14:45 15.25 **Prof. Francesco Picchioni** (University of Groningen, Netherlands) *Sustainability and polymers: a 3-D perspective*
- 15:25 15:50 **Alberto Picchi** (DSCM) Sustainable Luminescent Solar Concentrators from chemically recycled poly(methyl methacrylate)
- 15:50 16:15 **Marco Rollo** (DSCM) *Rapid depolymerization of post-consumer PET, PET/Cotton fabrics and polyamide 6,6 by using acidic deep eutectic solvents*
- 16:15 16:40 **Rosaria Lorè** (DSCM) Strategic and green valorization of paper mill wastes within the circular economy framework
- 16:40 17:00 Coffee Break

### Session 2\_Chair: Francesca Nerli and Andrea Giovanelli

17:00 – 17:40	<b>Prof. Valentina Colombo</b> (Università degli Studi di Milano, Italia) - <i>In Situ Insights into adsorption and catalysis in Metal-organic Frameworks</i>
17:40 – 18:05	<b>Elisa Rossi</b> (DSCM) - Utilization and Capture of Carbon Dioxide through a <i>Plastic Waste Upcycling Strategy</i>
18:05 – 18:20	Francesco Criscitiello (Laviosa) – Bentonite: A Brief Review
18:20 – 18:50	<i>Flash Poster Presentations:</i> Amanda Arcidiacono, Leonardo Barlucchi, Elena Betti, Cecilia Campi, Caterina Campinoti, Mariano De Cristofaro, Ludovica Dei
18:50 – 19:30	Poster Session 1 + Happy Hour

### Thursday – July 4<sup>th</sup>

### Session 3\_Chair: Sara Benetti and Matilde Benedettini

9:00 - 9:40	<b>Prof. Antoni RIERA</b> (Institute for Research in Biomedicine, Barcellona, Spain) - Synthesis of biologically active compounds. From chiral amines to protein degraders
9:40 - 10:05	<b>Elisabetta Rosadoni</b> (DSCM) - Direct C-H functionalization of azoles through radical reactions
10:05 – 10:30	<b>Fabiana Cordella</b> (DSCM) - <i>Design and synthesis of new green materials for biomedical applications</i>
10:30 – 10:55	Laura Spagnuolo (DSCM) - Enhancing Biocatalyst Performance: The Potential of Enzyme-Driven Nanostructured Materials
10:55 – 11:20	Coffee Break

### Session 4\_Chair: Ivan Giannì and Piermarco Saraceno

11:20 – 12:00	<b>Prof. Stella Stopkowicz</b> (Saarland University, Saarbrücken, Germania) - Understanding the electronic structure of atoms and molecules in strong magnetic fields and other extreme conditions
12:00 – 12:25	<b>Dario Frassi</b> ( <i>DSCM</i> ) - The interplay between nitro-substitutions and solvent effects in the photoisomerization of spiropyrans
12:25 – 12:55	<i>Flash Poster Presentations:</i> Filippo Giovanni Fabozzi, Arianna Ghelardi, Luca Melega, Serena Reale, Lorenzo Sembranti, Andrea Volpe, Chiara Zappelli
12:55 – 14:30	Lunch Break

### Session 5\_Chair: Alberto Cerchiai and Elena De Gregorio

14:30 – 15:10	<b>Prof. Fernando Pina</b> (Universidade Nova de Lisboa, Caparica, Portugal) - <i>The Triumph of the Blue in Nature and in Anthropocene</i>
15:10 – 15:35	Adele Ferretti (DSCM) - Shedding light on dyes interactions: recipe and environment-dependent effects in ink formulations
15:35 – 16:00	<b>Giulia Caroti</b> (DSCM) - The Role of Proteins in Lipid Oxidation within Paints of Varying Microstructure
16:00 – 16:25	<b>Greta Biale</b> (DSCM) - Microwave-assisted pretreatments coupled to analytical pyrolysis: an efficient approach for the determination of contaminants in environmental samples
16:25 – 16:50	Coffee Break

### Session 6\_Chair: Matilde Benedettini and Vanessa Matteucci

16:50 – 17:15	Zahraalsadat Yousefniayejahromi (DSCM) - Development of an electrochemical biosensor for pathogenic bacteria detection
17:15 – 17:40	<b>Angela Gilda Carota</b> (DSCM) - <i>Low-cost CRISPR/Cas12a-based biosensor</i> for point-of-care application
17:40 – 17:55	Luca Massari (Selene) – Recycle process with deinking phase
17:55 – 18:10	<b>Camillo Cardelli</b> (IPOOL-MOPI) – Applied R&D for green and firesafe polymeric compounds and bitumen compounds
18:10 – 19:00	Poster Session 2

20:00 Social Dinner

### Friday – July 5<sup>th</sup>

### Session 7\_Chair: Patrizia Mazzeo and Alberto Santonocito

9:00 – 9:40	<b>Dr. Danielle Laurencin</b> (Institute Charles Gerhardt Montpellier, Francia) - From isotopic labeling to high-resolution NMR analyses of biomaterials: why focus on oxygen
9:40 – 10:05	<b>Elisa Della Latta</b> (DSCM) - <i>Study of porous materials for gas separation and storage by solid-state NMR</i>
10:05 – 10:30	<b>Andrea Scarperi</b> (DSCM) - In-situ Illumination Solid State NMR approach for the study of photoactive materials
10:30 – 10:55	<b>Michele Pierigé</b> (DSCM) - Study of the Properties of Rubber-Resin Compounds by Solid-State NMR
10:55 – 11:15	Coffee Break

### Session 8\_Chair: Sara Benetti and Marco Bazi

11:15 – 11:55	<b>Prof. Ingo Krossing</b> (University of Freiburg, Germania) - Adventures with Weakly Coordinating Anions: Exploring the Limits of Reactive Cation Chemistry
11:55 – 12:20	<b>Chiara Saviozzi</b> (DSCM) - <i>Tuning the activity of anticancer diiron complexes via derivatization of bridging hydrocarbyl ligands</i>
12:20 – 12:45	<b>Francesca Niccolai</b> (DSCM) - Next-generation polymeric proton-exchange membranes for redox flow batteries
12:45 – 13:15	Closing of the conference and final remarks

### ABSTRACTS

### **ORAL COMMUNICATIONS**

### *In situ* insights into adsorption and catalysis in Metal-Organic Frameworks

### V. COLOMBO<sup>1</sup>

### <sup>1</sup> Dipartimento di Chimica, Università degli Studi di Milano & UdR INSTM Milano valentina.colombo@unimi.it

To develop and optimize novel adsorbents that exhibit selective metal-adsorbate interactions or specific guest adsorption, and to thoroughly characterize their crystal structure, electronic, and oxidation/charge states, it is essential to elucidate the role of coordinatively unsaturated metal centers, specific adsorption sites, and key physical changes upon guest binding. To this aim, the combination of *in situ* and *operando* crystallographic and spectroscopic techniques is becoming essential for understanding the structure-function relationships of metal-organic frameworks (MOFs) demonstrating that a multi technique approach can uncover unprecedented details about the underlying processes.

My research group focuses on understanding the structural changes in long-range order and local environments during adsorption processes and catalysis. We utilize *in situ* X-ray diffraction and *operando* X-ray absorption experiments, or a combination of both. Our work includes synthesizing novel adsorbent MOF materials, rationalizing gate-opening effects and cooperative gas adsorption phenomena, and identifying key active sites during adsorption and catalysis.

In this lecture, I will present our recent findings, achieved through a combination of advanced techniques, including custom-made setups. Key studies to be discussed include: i) *in situ* detectionof specific adsorption sites for CO<sub>2</sub> adsorption under humid conditions; ii) Combined XAS/PXRD experiments to describe the evolution of long-range and local structures during adsorption experiments; iii) in-depth analysis of 'PXRD CO<sub>2</sub> adsorption isotherms', encompassing the retrieval of heat of adsorption and host-guest interactions through ab-initio structure solution and Rietveld methods.

#### **References:**

[1] L. Braglia; F. Tavani; S. Mauri; R. Edla,; D. Krizmancic; A. Tofoni; V. Colombo; P. D'Angelo; P. Torelli J. of Phys. Chem. Lett. 12, 37, 9182 (2021).

[3] A. Tofoni; F. Tavani; M. Vandone; L. Braglia; E. Borfecchia; P. Ghigna; D. Stoian; T. Grell; S. Stolfi; V. Colombo; P. D'Angelo *J. Am. Chem. Soc.* 145, 38, 21040 (2023).

<sup>[2]</sup> R. Vismara; S. Terruzzi; A. Maspero; T. Grell; F. Bossola; A. Sironi; S. Galli; J.A.R.; V. Colombo Adv. Mater. 2209907 (2023).

### Adventures with Weakly Coordinating Anions: Exploring the Limits of Reactive Cation Chemistry.

### I. KROSSING<sup>1</sup>

### <sup>1</sup> University of Freiburg, Albertstr. 21, Freiburg, Germany. krossing@uni-freiburg.de

Weakly Coordinating Anions (WCAs)<sup>[1a]</sup> are a class of chemically robust, large anions that in the best case remain non-interacting with even very reactive cations.<sup>[1b]</sup> We have developed a series of such easily accessible, but almost non-interacting WCAs, the chemistry of which will be described in this lecture.

One part explores the options to stabilize salts of gas phase cations, previously only observed by mass spectrometry, in the condensed phases. Examples provide transition metal carbonyl cations like the  $[M(CO)_n]^+$  metalloradicals (n = 6 for M = Cr, Mo, W; n = 5 for M = Fe and n = 4 forM = Ni) or the first heptacarbonyls  $[M(CO)_7]^+$  (M = Nb, Ta).<sup>[2]</sup>

As part of this endeavour, novel reagents for deelectronation,<sup>[3]</sup> the elemental step of removing an electron from matter, were developed that allowed to push the borders of chemistry to highly positive deelectronation potentials exceeding 2 V vs. Fc<sup>+</sup>/Fc. One needs strategically and dipole maximizing inert, but polar solvents like 1,2-F<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, 1,2,3-F<sub>3</sub>C<sub>6</sub>H<sub>3</sub> or 1,2,3,4-F<sub>4</sub>C<sub>6</sub>H<sub>2</sub> for this purpose. Last, not least this chemical environment made up from WCAs and inert, but polar fluoroarene solvents also allow to study and stabilize a large variety of subvalent Al and Ga complex salts.<sup>[4]</sup> The chemistry of which will be highlighted as well.



Figure 1. The chemical system to introduce *pseudo gas phase conditions*: Inert solvents, very weakly coordinating anions and an example for one of the gas phase ions stabilized by using this system.

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### From isotopic labeling to high-resolution NMR analyses of biomaterials: why focus on oxygen

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Oxygen is everywhere. It is present in the vast majority of molecules and materials, forming covalent, ionic, coordination or hydrogen bonds with neighbouring atoms. Thus, in order to be able to rationalize and optimize the structure and properties of different systems, it is important to finely identify oxygen bonding environments.

With a chemical shift which exceeds 1000 ppm, oxygen-17 NMR spectroscopy appears as ideally suited for this purpose. However, it intrinsically suffers from a very poor sensitivity, the natural abundance of <sup>17</sup>O being only 0.04%. This implies that <sup>17</sup>O-labeling is most-often necessary to perform high resolution analyses. Yet, up until recently, the most-widely used labeling protocols suffered from various drawbacks, including (very) high costs, long reaction times, and/or constraining chemical reactions or experimental set-ups.

In recent years, we have focussed our research on implementing cost-effective and user- friendly <sup>17</sup>O-labeling protocols based on mechanochemistry.<sup>[1]</sup> We have shown that ball-milling (BM) procedures are highly attractive for the <sup>17</sup>O-labeling of a variety of organic and inorganic compounds, using microliter quantities of <sup>17</sup>O-enriched water, and working under ambient temperature and pressure. Here, after exposing the basic principles and possibilities offered by such <sup>17</sup>O-isotopic labeling procedures,<sup>[1-4]</sup> applications to the study of biomaterials will be discussed.<sup>[4-5]</sup>



Figure 1. From <sup>17</sup>O-labeling using ball-milling to high-resolution studies of biomaterials (adapted from [5]).

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### Sustainability and polymers: a 3D perspective

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Our society clearly demands that the development of new or improved (polymeric) products is factually carried out according to well-recognized sustainability principles. For polymeric products this entails, among others, particular attention to three specific topics: the origin of the raw materials (i.e. from renewable sources), the fate of the product after its end-of-life (i.e. possibility for recycling) and the use of green processes along the all lifespan of the product (i.e. from the synthesis until the recycling). In this work we will present our efforts, during the last 20 years, to conveniently combine all these aspects in our research lines. By starting with the synthesis of biobased polymers based on sugars [1] and modification of polysaccharides [2], we will then shiftto the concept of covalently adaptable networks as tool aimed at "cradle-to-cradle" recycling [3-5]. In particular, the use of the Diels Alder reaction between furan and maleimide (Scheme 1), has proven to be an excellent tool for the design of novel self-healing and recyclable materials [5] due to the relatively fast kinetics as well as the relative availability of suitable (biobased) precursors for polymer modification.



Scheme 1. Diels Alder reaction between furan and maleimide

Subsequently, attention will be paid to more recent developments including the possibility of recycling currently used materials such as rubbers [6] and polyolefins. Finally, we will briefly discuss the use of "green solvents" in every step (i.e. from synthesis to recycling) of a polymer lifetime by focusing on the possibilities to use supercritical  $CO_2(scCO_2)$  as processing aid in simpleextraction and during extrusion.

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# Archeological Chemistry. The Triumph of the Blue in Nature and in Anthropocene

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Anthocyanins are the molecules responsible for the reds and blues in angiosperms. While identified by their flavylium cation, anthocyanins are much more than this species, Fig. 1.<sup>1</sup>



Figure 1. Anthocyanins are much more than flavylium cation.

When the evolution of plants, Fig 2A,<sup>2</sup> is compared with the geologic time, Fig. 2B, it can be concluded that the appearance of the blue colour in angiosperms occurred million years after the



first plants exhibiting greens (chlorophyll), yellows and particularly reds (in the form of quinoidal bases) appearing in liverworts (furanoflavylium), mosses and ferns (3-

deoxyanthocyanins), Fig.2B. While furanoflavylium compounds and 3-

deoxyanthocyanins exhibit a colour system with the same chemical species of anthocyanins shown in Fig. 1, their flavylium cations are yellow and quinoidal bases are red. Blue is a colour exclusively achieved by anthocyanins from the anionic quinoidal bases.<sup>1,3</sup>

Figure 2. Tree of the plant's evolution and geologic time scale.

Blue was absent in the first paleolithic cave paintings. Those depictions were made using reds, yellows, and blacks of all hues, but no blue. In addition, blue LEDs and LASERs came later after red and green. It was only at the end of the 20<sup>th</sup> century that genetic engineering was able to create blue flowers adapted to the markets to meet consumer demands. Food and beverage producers continue to look for a natural blue as an alternative to synthetic colorants. Blue remained a second-rate color in the West for a long time. Despite that fact, in many countries blue is now the preferred color.<sup>3</sup>

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# Synthesis of biologically active compounds. From chiral amines to protein degraders

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The development of a new drug is a very complex and difficult process. It starts with the identification of a biological target (very often a protein) whose biological activity needs to be modified. In most occasions, the way to modify its action is based on the inhibition of its enzymatic activity by a small molecule. To find a good inhibitor is a difficult task but, once achieved, it is necessary to develop an efficient and environmentally benign synthetic procedure. On the other hand, many drugs are chiral and need to be prepared in high enantiomeric purity. Asymmetric hydrogenation is perhaps one of the best methodologies for the large-scale preparation of chiral drugs<sup>1</sup>. We will discuss some of the developments done by our group on the asymmetric hydrogenation of chiral amines, key components of many drugs<sup>2</sup>.

In recent years a new pharmacological approach has been developed that might potentially overcome the shortcomings of traditional inhibitors: targeted protein degradation. PROTACs (proteolysis targeting chimeras) are heterobifunctional molecules that hijack the ubiquitin-proteasome system (UPS), native to eukaryotic cells, to induce degradation of a protein of interest (POI)<sup>3</sup>. More generally, PROTACs can be described as bifunctional molecules that induce proximity between two proteins, stabilizing a tertiary complex between a POI, the drug and an effector. We will describe the design, synthesis, and optimization of degraders targeting two important proteins: the p38 MAP Kinase<sup>4</sup> and the oestrogen receptor<sup>5</sup>.



Rivastigmine



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# Assignment of spectra and electronic structure of atoms and molecules in strong magnetic fields

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When atoms or molecules are exposed to strong magnetic fields, their electronic structures change significantly. This can lead to new ways of chemical bonding, alien spectra that bear little to no resemblance to their field-free counterparts and exotic electronic ground states.<sup>1</sup> On Earth, such effects can only be generated in an implicit manner when Coulombic interactions (Rydberg states, quantum dots, nano structures, etc.) are reduced. On strongly magnetized White Dwarf stars, however, they occur naturally. It is easily understood that because of such strong fields, the assignment of observational spectra from these stars crucially needs theoretical predictions. In this talk, recent developments<sup>2-5</sup> in this direction will be presented and the remaining challenges for treating electronic states consistently, the determination of structures, problems with non-Hermitian theories etc., will be discussed.<sup>6</sup>

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### Microwave-assisted pretreatments coupled to analytical pyrolysis: an efficient approach for the determination of contaminants in environmental samples

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One of the most challenging environmental threats of the last years is represented by micro- and nanoplastic pollution. During the past years, microplastics (MPs) have been found in all kinds of environmental compartments and various analytical techniques have been developed and applied for their detection and quantification. Pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) has demonstrated to be a very powerful technique in this research field allowing the analysis not only of micro- and nanoplastics, but also of their degradation products and of non-polymeric organic contaminants associated with MPs. When approaching micro- and nanoplastic analysis, the sample preparation is a crucial procedure that can usually require numerous and time- consuming steps, depending on the matrix of the environmental samples under investigation.

In this work, we developed an analytical approach based on the combination of microwaveassisted pretreatments (extraction [1] and digestion), together with analytical pyrolysis, to simultaneously characterize and quantify various kinds of pollutants, namely MPs, polymer additives (phthalate plasticizers), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and contaminant of emerging concerns (CECs) in environmental and biological matrices. Samples were subjected to microwave-assisted extraction and subsequent pyrolysis at 350 °C for the quantification of phthalates, PAHs, PCBs, and CECs; microwave-assisted digestion and pyrolysis at 600 °C were used for the analysis of microplastics [2].

This newly developed method allowed us to quantify more than 40 compounds in a single chromatographic run with recoveries higher than 84% for most of the analytes.

This method based on microwave-assisted pretreatments and Py-GC-MS represents a fast analytical approach for the detection and quantification of both micro- and nanoplastics and nonpolymeric pollutants associated with them, contributing to the development of efficient strategies that could be employed in environmental monitoring applications.

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# Low-cost CRISPR/Cas12a-based biosensor for point-of-care application

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The clustered regularly interspaced short palindromic repeat loci (CRISPR) and its associated proteins Cas, collectively known as the CRISPR/Cas system, constitute an adaptive immune system present in archea and bacteria to protect the organism from foreign invaders. Due to its programmability and specificity against DNA targets, these endonuclease enzymes are emerging as a powerful tool in biosensing applications<sup>1</sup>. The Cas12a enzyme is mostly used because of its transactivity. The activation of the Cas12a/gRNA complex is triggered by the detection of the target DNA sequence and subsequent cleavage in specific positions (cis-activity), followed by the nonspecific cleavage of ssDNA sequences (trans-activity) (Figure 1). In this work, we present the steps to develop a new class of low-cost CRISPR/Cas12a based electrochemical biosensorsuseful for pathogens detection, especially in low resources settings. We have integrated the CRISPR/Cas12a system into a cost-effective electrode fabricated using inkjet-printed technology with nanoparticlesbased inks printed on a plastic substrate. The biosensor was validated against both Gram-negative E. coli and Gram-positive S. aureus bacteria, and the results compared with those obtained using commercial screen-printed electrodes. DNA targets amplified from various clinically isolated bacteria have been successfully tested and demonstrate the potential of the proposed platform for point-ofcare applications<sup>2</sup>. In line with the goal of developing fully integrated portable biosensor, additional steps were taken in this direction. The lyophilization process of the Cas12a/gRNA complex was optimized, and the previously proposed platform integrated with microfluidic channels and printed NFC antenna for smartphone readout. To further demonstrate the wide versatility of the CRISPR/Cas12a system, non-nucleic acid detection through strand- displacement mechanisms was also performed.



Figure 1. CRISPR/Cas12a system activity mechanism.

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### The Role of Proteins in Lipid Oxidation within Paints of Varying Microstructures

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Lipid oxidation is a complex phenomenon widely investigated in different fields, such as nutrition, biochemistry, biomedicine and cultural heritage.[1] Lipids, being composed of unsaturated triglycerides, react with oxygen leading to the formation of peroxides. Once these are formed, they can undergo different reactions, evolving in two different pathways: oxidative degradation and cross-linking. In cultural heritage, the competition between these two phenomena is really important, because oil paints which are more prone to oxidative degradation can be subjected to several degradation phenomena, while oil paints which have a high level of cross-linking are generally more stable in time. There are several parameters which can influence lipid oxidation in an oil paint – such as paint composition, type of pigment, type of oil, type of oil pre-treatment, and ageing environment conditions. In the literature, there are very few works regarding how proteins can influence lipid oxidation or how lipids influence protein oxidation [2, 3], but nothing is really known of such interaction in the context of paint binders. In this work we aim at investigating the role of proteins in lipid oxidation within paint layers.

This work arises from the necessity of understanding the use of both lipids and proteins in the same paint layers by the Old Masters in the 15<sup>th</sup> century. In this work, different paint formulations were investigated mixing cold pressed linseed oil and egg white with pigment – ultramarine blue and lead white. There are several ways to combine lipid and protein in the same paint layer. In this study, two different painting techniques have been investigated, which feature the same ingredients but different microstructures: tempera grassa and protein coated pigment. Tempera grassa is an emulsion of oil in water, in which the pigment particles are dispersed. In a tempera grassa, oil droplets and pigment particles are dispersed in a continuous porous egg medium: the system is characterised by multiple interfaces: pigment/protein, pigment/oil, oil/protein, oil/air, protein/air. Protein coated pigment is an oil paint in which the pigment particles are coated with a thin layer of proteins; in a protein coated pigment, the oil is in direct contact with oxygen, but the protein layer prevents the interaction of the oil with the pigment particles.

The natural oxygen uptake and the dry to the touch state of the model paints were recorded. The colorimetric changes of model paints were investigated during ageing too.

The oxidation of the binders was monitored with Differential Scanning Calorimetry (DSC) and the mass change due to oxidation was investigated with ThermoGravimetrical Analysis (TGA) underair flow at constant temperature.

Data were compared with those obtained by monitoring the molecular composition of the volatile products of oxidative degradation of model paint layers using solid phase micro-extraction - gas chromatography - mass spectrometry (SPME-GC-MS).

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# Design and synthesis of new green materials for biomedical applications

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The new challenges of modern biomedicine require a molecular approach to rationalize and enhance the properties of new materials for surgical applications or the discovery of new drugs for pharmacological use. A deeper understanding of the relationship between molecular structures and physicochemical properties is crucial. In this respect, two different research lines were followed, focusing respectively on developing cross-linked hydrogels based on hyaluronic acid (HA) and mimetics of natural peptides based on (S)- indoline-2carboxylic acid ((2S)-Ind). As far as HA-based cross-linked materials are concerned, poly(ethylene glycol diglycidyl ether (PEGDE) has been used as a cross-linker in recent years to replace the most commonly used 1,4-butanediol diglycidyl ether for developing new materials for aesthetic medicine.<sup>1,2</sup> The current work aims to extend knowledge of the properties of materials cross-linked with this type of chains, using mono- and polydisperse oligo(ethylene glycol) diglycidyl ether (OEGDE) to deeply investigate the influence of the chain length and polydispersity on the physicochemical, mechanical and rheological properties. Considering the mimetics of natural peptides, the insertion of (2S)- Ind into peptide sequences, a non-natural amino acid with interesting conformational properties, could offer several opportunities for expanding peptide chemical diversity, designing novel bioactive compounds, and probing protein structure-function relationships.<sup>3,4</sup> However, this purpose is challenging because of the low reactivity of (2S)- Ind that we tried to overcome by optimizing the peptide coupling reaction conditions for thesynthesis of hetero-oligomers based on (2S)-Ind and natural amino acids.



Figure 1. General overview on HA cross-linked with OEGDE (A) and (2S)-Ind reactivity limitations (B)

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# Study of porous materials for gas separation and storage by solid-state NMR

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Porous materials have attracted considerable interest given their wide possible applications, such as catalysis, drug delivery and gas storage. The study of these materials' structure and dynamic properties is of particular importance to fully understand their final macroscopic properties. Characterization techniques such as X-ray diffraction (XRD) and absorption spectroscopy are usually employed for the study of Metal-Organic Frameworks (MOFs) and in general Coordination Polymers (CP). However, the structure determination using XRD requires long-range crystallinity, which is not always present. Moreover, diffraction is not suitable for characterizing molecular dynamics or probing guest molecules. In this field, Solid-State NMR (SSNMR) is a powerful technique, being able to study every kind of solid system (crystalline or amorphous) and disclose information on local structure and dynamics on wide spatial and time scales<sup>1,2</sup>; this can be achieved by combining the observation of different nuclei (<sup>13</sup>C, <sup>1</sup>H, <sup>19</sup>F, <sup>17</sup>O, <sup>2</sup>H) with the measurement of different nuclear properties (isotropic chemical shift, chemical shift anisotropy, dipolar interaction and quadrupolar interaction, spin-spin and spin-lattice relaxation times) [2]. Here, we present multi-nuclear and multi-technique SSNMR studies on different classes of porous materials (1D CPs, MOFs, and porous organic polymers). In particular, we will show how NMR canbe a useful probe of the interaction of CO<sub>2</sub> with Ce-based MOFs (F4\_MIL-140A and F4\_UiO-66)<sup>3</sup> and fluorinated aryl ethers porous polymers (FLARE). Cu-based MOFs (HKUST-1)<sup>4</sup> havealso been studied in the presence of a variety of quest molecules by using high-resolution techniques. Furthermore, Hgbased 1D CPs with different topologies have been investigated in the presence of templating solvent molecules<sup>5</sup>, and a characterization of the mobility of guest molecules has been obtained. Moreover, <sup>17</sup>O NMR has been applied to study M<sub>6</sub>-oxoclusters(M=Ti, Zr, Hf, and mixed-metal), inorganic building units of different highly investigated MOFs such as MOF-801 or MOF-808. Indeed, <sup>17</sup>O NMR can be a valuable tool to investigate metal distribution in mixed-metal systems<sup>6</sup>.

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### Shedding light on dyes interactions: recipe and environmentdependent effects in ink formulations

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Over the centuries, the dyes used in ink formulations have been obtained from both natural and animal sources (historical inks), as well as from chemical syntheses (modern inks) [1]. Inks play a crucial role in the conservation of manuscripts and drawings, leading to several preservation challenges such as fading and paper degradation [2]. Thus, the identification of writing inks at molecular level is not only needed to aid restorers in developing effective conservation strategies, but also offers valuable information for improving the readability, dating and authenticating these works [3]-[4]. There is currently a lack of established analytical protocols for examining writing inks, specifically those that allow for the identification of their molecular profiles applying micro- destructive analytical techniques on reference collections subjected to natural or artificial ageing.

In this framework, this study aims to shed light on molecular markers of both dyes/pigments and their ageing products in ink formulations. Thus, both historical (*iron gall* and *logwood inks*) and modern recipes have been selected and used to simulate the degradation processes occurring in manuscripts and drawings. Ageing tests were performed on one side for accessing to degradation products never reported in the literature, and on the other side for modelling the ageing of the selected dyes as a function of the co-presence of additional dyes or of different environmental parameters (relative humidity, light exposure, VOCs in the environment). The investigation was mainly carried out by liquid chromatography coupled to diode array and tandem mass spectrometric detectors (LC-DAD-HRMS), involving several steps for determining optimal analysis conditions for natural and synthetic organic pigments (SOPs). Depending on the analytical questions on the different targets, Raman spectroscopy was also applied to achieve complementary information on organic components or to investigate the inorganic fraction. The developed method was applied to historical case studies.

Our studies devised a methodology that enables the identification of the molecular markers of the organic components in inks by introducing ultra-sensitive chromatographic and mass spectrometric methods in the array of analytical tools available in inks analysis. The outcomes of the project will provide useful information both for authentication and dating purposes, and for studying the light-fading mechanisms to foster the development of specific conservation conditions for manuscripts and drawings.

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# The interplay between nitro-substitutions and solvent effects in the photoisomerization of spiropyrans

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Spiropyrans are a various class of compounds extensively employed in materials science due to their significant photochromic properties. When exposed to UV light, spiropyrans convert into the open, colored form known as merocyanine. Despite their widespread use as molecular switches, the precise mechanism of the photoisomerization reaction remains unclear due to the challenging interpretation of experimental measurements and appears to be highly influenced by the substituents and the surrounding environment.<sup>1</sup> However, to enhance the switcher properties, a thorough understanding of the photochemical mechanism is crucial. For these reasons, we wanted to study the excited-state dynamics of two spiropyrans labeled as BIPS and nitro-BIPS (Figure 1) through "on the fly" surface hopping nonadiabatic dynamics simulations using the FOMO-CI method in a semiempirical AM1 framework.<sup>2,3</sup> Our study involves investigating the modifications of the potential energy surfaces (PESs) of the lowest-lying excited state of BIPS induced by a nitro substitution (nitro-BIPS) and its impact on nonadiabatic dynamics. Additionally, to evaluate the influence of different solvents on the excited-state dynamics of BIPS, we performed simulations in three environments: chloroform, methanol, and ethylene glycol. These findings are then compared with previous simulations performed in a vacuum.<sup>4,5</sup>



Figure 1. Spiropyrans labeled BIPS and nitro-BIPS

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# Strategic and green valorization of paper mill wastes within the circular economy framework

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The urgent global challenges related to energy lack and environmental issue drive the industrial sector to search for innovative solutions for waste resource utilization within a circular economy framework. Among the many difficulties faced by the paper industry, the significant production of waste sludges (Mton/year) stands out, imposing substantial landfill costs and environmental impacts [1]. To address this challenge, the collaborative project with Lucart Company aims to investigate and optimize the valorization of two distinct types of waste sludges: cellulose and inorganic ones. Regarding the first one, the main objective was to convert the cellulose-rich sludge into high-valueadded platforms and biofuels, specifically alkyl levulinates (ALs), through direct alcoholysis of its C6 fraction. According to green chemistry principles, the investigation enhanced AL production efficiency by maximizing substrate concentration and minimizing acid catalyst loadings [2]. On the other hand, regarding the valorization of the inorganic-rich sludge, mainly composed of CaCO<sub>3</sub> with a minor cellulose fiber component, two approaches were pursued: i) integration of the bulk inorganic sludge into biodegradable materials, such as poly(lactic acid) and polycaprolactone, as eco-friendly alternatives to conventional cellulose and mineral fillers [3]. Various preparation methods were explored, including melt-extrusion-compression molding and fused deposition modeling. ii) selective recovery of CaCO<sub>3</sub> through thermochemical processes, including pyrolysis and combustion treatments under mild reaction conditions (400°C). This approach aims to fractionate the inorganic sludge, producing bio-oil/heat energy from the minor cellulose fraction and a solid residue enriched in CaCO<sub>3</sub> [4]. The positive properties exhibited by the solids obtained from the thermal treatments pave the way for recycling them as filler in various materials, including paper, paperboard, polymer, and paint. In conclusion, the valorization of waste resources represents a critical challenge that requires collaboration between industry and academia. This project shows concrete possibilities for the paper industry, offering various valorization methods, at the same time, paying attention to environmental impact and economic feasibility.

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# Next-generation polymeric proton-exchange membranes for redox flow batteries

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Redox flow batteries (RFBs) are considered attractive devices for energy storage.<sup>1</sup> The membrane plays a crucial role in determining both the efficiency and economic feasibility of RFBs.<sup>2</sup> Ideally, it should have high ionic conductivity and selectivity to prevent active species crossover while permitting the passage of supporting electrolyte ions. Moreover, the membrane should be chemically stable, mechanically durable, cost-effective, and capable of withstanding high-power densities. The present work is focused on the design and development of new efficient proton exchange membranes (PEMs) for semi-organic RFBs based on 9,10-anthraquinone-2,6- disulfonic acid disodium salt (AQDS)/bromine (Br<sub>2</sub>) (Figure 1). In particular, our approach for the preparation of polymer membrane precursors consisted in the chemical post-modification of commercially available specialty polymers, namely polyvinylidene fluoride (PVDF) and polyether ether ketone (PEEK). More specifically, PVDF was used as macroinitiator for the grafting of styrene monomer by atom transfer radical polymerization (ATRP). The obtained graft copolymers were then subjected to a sulfonation reaction to incorporate -SO<sub>3</sub>H functional groups on the polystyrene side chains (Figure 1). Different copolymers with tuned mole content of styrene and sulfonated styrene were synthesized and used to prepare PEMs. PEEK was directly subjected to a sulfonation reaction (Figure 1) and used alone or blended with other polymers (PVDF and polyethersulfone (PES)) for the preparation of PEMs. Different degrees of sulfonation were obtained by varying the experimental conditions.

The membranes were extensively characterized to assess their chemical, thermal, mechanical, and electrochemical properties. Selected membranes were also tested in 1W single cell to investigate their electrochemical performance under real operating conditions.



Figure 1. Representation of a semi-organic RFB<sup>3</sup> and chemical structure of the synthesized polymers used for PEM preparation.

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# Sustainable Luminescent Solar Concentrators from chemically recycled poly(methyl methacrylate)

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Poly(methyl methacrylate) (PMMA) is widely used in luminescent solar concentrators (LSCs) as both thin films and slabs. Industrial production of LSCs would significantly increase the amount of polymeric material in the market, raising sustainability concerns. Chemical recycling of PMMA can regenerate high-purity methyl methacrylate (r-MMA) suitable for new polymerization reducing the global warming potential (GWP) by four times and promoting sustainable large-scale fabrication. Devices made from r-MMA exhibit chemical, thermal and mechanical properties comparable to those made from virgin MMA, despite impurities in r-MMA that can reduce LSC lifetimes through photodegradation. Photostability is critical, as UV radiation can degrade organic emitters, reducing efficiency and necessitating replacements, which incur economic and environmental costs. This study investigates push-pull dyes with distorted heptagonal inclusions, Peri2F and Nap2Car,<sup>1</sup> compared to the state-of-the-art emitter Lumogen F Red 305 (LR305)<sup>2</sup> in LSC plates made of chemically recycled PMMA (r-PMMA). The Peri2F/r-PMMA system achieved an ndev of 0.7%, lower than devices with LR305 (1.3%), but demonstrated superior photodegradation resistance. The LSC with 100 ppm of Peri2F experienced no reduction in initial emission intensity after 600 simulated exposure hours, while that of LR305 (400 ppm) was about 4% in half the time, suggesting a forthcoming match between the performance of the two systems over the LSC lifetime.





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## Study of the Properties of Rubber-Resin Compounds by Solid-State NMR

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In the tire industry, resins are vital components because of their roles in curing, reinforcing, and enhancing tackiness. They adjust the rheological behavior of rubber compounds, improving processability and boosting mechanical properties.<sup>1</sup> Resins influence the dynamics of the polymer chain, which in turn affects the viscoelastic behavior and final mechanical properties. This study examines the effects of natural and petroleum-based resins on SBR compounds, with resin content varying from 15 to 45 parts per hundred rubber. To understand the molecular dynamics and structural characteristics of the elastomeric blends as affected by the resins, a combination of Solid-State Nuclear Magnetic Resonance techniques,<sup>2-4</sup> along with dynamic-mechanical, rheometric, calorimetric, and chemical analyses were used. These methods provided an in-depth understanding of the mechanical, thermal, and vulcanization properties and behavior of the elastomeric compounds.



Figure 1. Exemplifying Dynamic Mechanical Analysis data and <sup>13</sup>C solid state NMR spectra.

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## Rapid depolymerization of post-consumer PET, PET/Cotton fabrics and polyamide 6,6 by using acidic deep eutectic solvents

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Chemical recycling offers a practical solution for managing plastic waste composed of polyethylene terephthalate (PET).[1] Lately, deep eutectic solvents have demonstrated intriguing characteristics in the glycolysis and hydrolysis of PET, occasionally even under mild operating conditions.[2,3] In this research, we propose the use of cost-effective and environmentally friendly bifunctional Lewis/Brønsted acidic Deep Eutectic Solvents (LBDESs) containing FeCl<sub>3</sub>·6H<sub>2</sub>O and various acids to depolymerize plastic materials. Specifically, LBDESs composed by methanesulfonic acid and para-toluenesulfonic acid were found to effectively degrade PET with high efficiency under mild conditions (100 °C, 1h), resulting in quantitative yields of high-purity terephthalic acid (TA).[4] When employing weaker Brønsted acids such as acetic acid, similar results were achieved under microwave (MW) irradiation at a higher temperature of 180 °C, even within a shorter reaction time (10 minutes) and in the presence of 10 equivalents of excess water. The addition of excess water is crucial as it facilitates the processing of a significantly larger amount of PET in a single run.[5] LBDESs have also been applied for the selective depolymerization of PET in PET/cotton blends simulating semi-synthetic textiles, varying time and reaction temperature aimed at optimizing and enhancing the highest TA recovery and cellulosic residue. Increasing the severity of the reaction conditions improves PET depolymerization, while leading to partial degradation of the cotton component. The cellulosic residue has been extensively analysed through several different and complementary analytic techniques, including ATR-FTIR, NMR, SEM, XRD, GPC, and elemental analysis, leading to the production of cellulose nanocrystals (CNC) of high quality in significant quantities. Finally, we show the efficiency of LBDESs for the depolymerization of polyamide 6,6 (PA 6,6) to adipic acid which could contribute to a better environmental sustainability in the textile industry, where fabrics PET/PA 6,6 are widely used.



Figure 1. Depolymerization with Lewis/Brønsted acidic Deep Eutectic Solvents.

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### **Direct C-H functionalization of azoles through radical reactions**

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Azoles are key structural cores frequently found in bioactive compounds and organic functional materials such as liquid crystals and fluorescent dyes.[1] Due to their widespread applications, the development of straightforward functional group-tolerant synthetic methods that enable selective heteroaromatic elaboration under mild conditions aroused considerable attention. Generally, procedures for the direct functionalization of azoles require expensive transion metal catalysis, strong bases, long reaction times, inert atmosphere, and expensive materials.[2] These aspects are obviously drawbacks form an environmental and an economic point of view. For this reason, we decided to consider a completely different approach, which is the use radical reactions. Radical reactions offer several advantages in synthetic chemistry due to their unique characteristics. Firstly, they often occur under mild reaction conditions, including ambient temperature and pressure, which can reduce energy consumption and increase safety compared to traditional high-temperature, highpressure reactions. Additionally, radical reactions typically exhibit high functional group tolerance, allowing for the incorporation of diverse functional groups into the final product. Moreover, often radical precursors, such as carboxylic acids or ammines, are available at low cost with a great structural diversity. This versatility enables the synthesis of complex molecules with greater efficiency and flexibility. Anyway, the use of radical reactions is not so common since it is not simple to control the selectivity. So, the aim of this work was the development of protocols for the C-H functionalization of azoles, by a radical approach, that work under mild conditions with easily available reagents and under air atmosphere.



Figure 1. (a) Classical approaches for the C-H functionalization of azoles. (b) This work.

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## Utilization and Capture of Carbon Dioxide through a Plastic Waste Upcycling Strategy

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Because of human activities, two main environmental concerns have raised in the last decades: the increase in atmospheric carbon dioxide concentration and the massive production of plastic waste. While still not widespread, approaches that combine both problems to find a common solution have recently been proposed.<sup>1</sup> Most of these relies on obtaining activated carbons from pyrolysis of plastic waste.

This study addresses the challenge by upcycling polyethylene terephthalate (PET) plastic waste with an innovative approach: the obtainment of a reusable liquid for reversible  $CO_2$  absorption. We started from PET depolymerization *via* ammonium bicarbonate catalysed glycolysis, resulting in the production of bis(hydroxyethyl)terephthalate (BHET) with high purity.<sup>2</sup> During the reaction, the cheap and traceless catalyst decomposes into ammonia, water, and carbon dioxide. Through Density Functional Theory calculations we proved that NH<sub>3</sub> and CO<sub>2</sub> play crucial roles in different steps of the depolymerization mechanism. With subsequent aminolysis of BHET, we obtained a terephthalic diamide that combined with low amounts of an economical and non-toxic diol formed astable homogeneous liquid. This system demonstrated the capacity of absorbing and desorbing CO<sub>2</sub>, thus allowing its classification as *sorbent*. Moreover, it exhibited chemical robustness, being recyclable multiple times (at least 10 absorption-desorption cycles) without performance erosion, achieving an uptake of 38 g<sub>CO2</sub>/kg<sub>sorbent</sub> under 1 atmosphere of the gas. Chemical-physical characterization of the sorbent, performed through differential scanning calorimetry, revealed its classification as a Low-Transition-Temperature Mixture (LTTM), a category of liquids that showcase ideal features for large-scale use, like non-toxicity and easily and cost-effectively productibility.



Figure 1. Plastic waste upcycling into a recyclable LTTM sorbent for CO<sub>2</sub> capture.

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# Tuning the activity of anticancer diiron complexes via derivatization of bridging hydrocarbyl ligands

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Iron is an attractive element for developing drugs alternative to platinum chemotherapeutics, due to its bioavailability, non-toxicity in many forms, and feasible redox chemistry in physiological media. Dinuclear iron(I) complexes featuring carbonyl and cyclopentadienyl ligands are robust, easily available compounds, displaying a wide structural variability that enables the fine-tuning of physicochemical and biochemical properties.<sup>[1]</sup> In particular, cationic complexes with bridging hydrocarbyl ligands (*Figure 1*) are versatile substrates that display desirable features for drug candidates, such as air stability, appreciable solubility in water while maintaining a balanced hydrophilic/lipophilic profile, and robustness in physiological solutions.

Over 70 compounds of types I and II have been screened for their cytotoxicity *in vitro*, with some of them investigated in 3D cell models and also *in vivo*, providing promising results and highlighting structure-activity relationships that encouraged us to design novel structures with optimized activity. The mode of action of the complexes mainly concerns the interference with cell redox processes, via generation of reactive oxygen species (ROS) inside cancer cells.<sup>[2]</sup>

Inspired by the beneficial effect of incorporating sulphur and selenium functions within drug candidates,<sup>[3]</sup> the bridging vinyliminium ligand in **II** has been functionalized with redox-active sulphide and selenide moieties. This synthetic approach takes advantage of the cooperativeeffects provided by the two adjacent iron atoms, enabling reactivity patterns otherwise unavailable on analogous monometallic compounds.



**Figure 1.** Structure of diiron aminocarbyne (I) and vinyliminium (II) complexes. R = alkyl, aryl; R' = alkyl, aryl, pyridinyl, carboxylate, thiophenyl, and others. Functionalization of the vinyliminium bridging ligand with chalcogenide functions (III). E = S, Se; Alk = alkyl.

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# *In-situ* Illumination Solid State NMR approach for the study of photoactive materials

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Over the past decade, research in the fields of photochemistry and photoactive material applications has experienced nearly exponential growth<sup>1,2</sup>. Specifically, one of the most interesting areas involves the development and study of photovoltaic materials, which can interact with sunlight to produce clean and renewable energy. Conjugated polymers and metal halide perovskites, with their exceptional optoelectronic properties, have gained significant attention and are at the forefront of next-generation solar cells. Despite their promising properties, their commercial use is limited by their instability to various environmental factors, including light exposure<sup>3</sup>.

Over the past two decades, Solid-State Nuclear Magnetic Resonance (SSNMR) spectroscopy has gained increasing recognition in the field of chemical physics research, establishing itself as one of the leading techniques for obtaining structural and dynamic information<sup>4</sup>. SSNMR investigations of "operando" materials are currently in an early stage of development and they remain relatively scarce, making this research area highly interesting and full of potential developments. In my doctoral project, I aim to develop SSNMR instrumentation and methods to study the structural and dynamic properties of various promising photovoltaic materials in the absence and presence of *in situ* illumination. Various experimental setups have been explored for both high- and low- field SSNMR experiments as well as Nuclear Quadrupolar Resonance (NQR) spectroscopy.



Figure 1. Instrumentation for High Field (a), Low-Field (b), and NQR (c) in-situ illumination experiments

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## "Enhancing Biocatalyst Performance: The Potential of Enzyme-Driven Nanostructured Materials"

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The study of nanostructured materials reveals a promising avenue for increasing the effectiveness of biocatalysts through immobilization and activation strategies.<sup>1</sup> Among these materials, cellulose nanocrystals (CNCs) emerge as noteworthy candidates, standing out for their sustainability, biodegradability, and substantial surface area, making them optimal for enzyme attachment.<sup>2</sup> The present discussion delves into a mechano-enzymatic methodology for the synthesis of CNCs from cotton linters, followed by the development of antibacterial materials by immobilization of enzymes, particularly lysozyme and lipase, on CNC matrices.<sup>3</sup> These antibacterial attributes have significant relevance to water-dispersible materials, positioning CNC composites as viable solutions for sustainable coatings in the paper and textile industries.<sup>4,5</sup> Beginning with the enzymatic hydrolysis of Avicel using *Aspergillus niger* endoglucanase, a green alternative that produces neutral CNCs, we proceed to explore enzymatic self-assembly, involving chicken egg white lysozyme and Candida rugosa lipase together with carboxyl, neutral or negatively charged sulfated cellulose nanocrystals. Whilst lysozyme displays protective behaviour against *Candida albicans, Aspergillus niger, Staphylococcus aureus*, and *Escherichia coli*, the inclusion of lipase broadens the functional repertoire, elevating the usefulness of biohybrid materials.



Figure 1. Covalent immobilization of lysozyme on nanocellulose

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# Development a novel electrochemical biosensor for bacteria detection

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Healthcare and the food industry face a pressing challenge: rapid detection of pathogenicbacteria. This is crucial due to its substantial fiscal implications and the consequential threat posed to the worldwide healthcare systems. Recent efforts focus on the advancement of pathogen detection methodologies, especially using electrochemical biosensors. The performance of these biosensors is influenced by a vital recognition element to identify specific bacteria. To achieve this goal, this study developed two electrochemical biosensors with different biorecognition elements, such as aptamer [1] and bacteriophage [2] to identify pathogenic bacteria in clinical samples. A screenprinted gold electrode (SPG) was functionalized with P12-55 aptamers to identify E. coli bacteria. Electrochemical impedance spectroscopy (EIS) was used to measure the change in the charge transfer resistance as a consequence of the interaction between aptamer and the pathogenic bacteria. The aptasensor showed a linear response in the presence of *E. coli* within  $7 \times 10^{0} - 7 \times 10^{3}$ CFU/mL with a limit of detection (LOD) of 1.4 CFU/mL (Fig. 1A). Following that, a phage-based sensor was developed with 10<sup>7</sup> PFU Zeno to specifically identify S. aureus with a linear range from 10<sup>1</sup> to 10<sup>4</sup> CFU/mL within 20 minutes with a LOD of 1.2 CFU/mL under physiological conditions (Fig. 1B). Consequently, both biosensors offer a promising approach for quick and accurate detection of bacterial pathogens in biological samples.



**Figure 1**. Electrochemical impedance spectroscopy performed in buffer solution containing K<sub>4</sub>Fe(CN)<sub>6</sub> 5 mM (A) P12-55 aptamer-based biosensors towards *E. coli* (10<sup>o</sup> to 10<sup>6</sup> CFU/mL) in PBS. (B) Zeno phage-sensor to recognize *S.aureus* (10<sup>o</sup> to 10<sup>6</sup> CFU/mL) in PBS

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# Applied R&D for green and fire-safe polymeric and bitumen compounds

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MOPI and IPOOL are engaged in a synergistic collaboration, spearheading advanced research and development projects in the fields of virgin and recycled polymer materials as well as flame retardant technologies. MOPI focuses on formulations and flame retardancy tests for waterproofing bituminous membranes, the recovery of leather production scraps, and the pyrolysis of End-of-Life Tires (ELTs) within bitumen. IPOOL, on the other hand, specializes in flame retardant systems for polymer compounds, with particular attention to Halogen-Free Flame Retardants (HFFR) and PVC in electrical cables, as well as the development of bioplasticizers. Additionally, IPOOL conducts advanced research on polymers for special applications such as TPU, PET, and PA. Through their collaboration, the two companies aim to innovate and enhance the performance and sustainability of polymer materials across various industrial sectors.

## **Bentonite: A Brief Review**

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Bentonite clay is one of the oldest known clays used by humankind since ancient times. Over the past century, researchers have discovered numerous applications for this material due to its unique physical and chemical properties. The properties of bentonite can vary significantly depending on its geographic origin. Bentonite can impart rheological properties to liquid systems and has adsorption capabilities that can be utilized for binding specific molecules in various applications. This study reveals that bentonite clay with a high montmorillonite content has a large surface area, and its functionality can be enhanced by increasing the total surface area of the clay. Due to its high cation exchange capacity, various cations can be incorporated into bentonite. Additionally, if the exchanged cations are organic compounds such as quaternary ammonium salts, it is possible to modulate the interaction between the clay and organic solvents, thereby developingrheology even in those media

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Chemistry for the Future - 2024

## **Recycle process with deinking phase**

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Selene has produced flexible packaging for industrial use for more than 60 years, associating product quality with a sustainable production approach. Selene is specialized in blown extrusion technologies of PE and flexographic printing.

We have made up an industrial plant that enables the valorization of industrial plastic waste and scraps. Thanks to the complex de-inking process, we remove inks and varnishes obtaining an high-quality PE granules. The purpose is the creation of a high-quality secondary raw material that can be reused in our production in high percentages without limiting packaging performances. The regeneration process is divided into 5 stages (grinding, de-inking, rinsing, drying and pelletization).

The central deinking step takes place through a combination of several factors: the intervention of reagents in the water phase, added by a dosing system; the temperature, maintained in the range of 60 degrees centigrade, which facilitates the activation of the reactions; the special mechanical stirring that assists the process through rubbing. Indeed, the choice of the best cationic surfactantin a strongly basic solution has demonstrated a strong penetrating and softening action on the dried varnish layer of current flexographic inks (for both solvent and water-based inks). The entire reaction within the plant is in strongly basic solution due to the controlled addition of NaOH in watersolution.





The plant, which has been operating since 2019, has a water treatment cycle that allows the recovery of reagents, the separation of waste sludge, as well as a water closed cycle.

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## **POSTER COMMUNICATIONS**

## Predicting solvatochromism of carotenoids with Machine Learning

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Solvatochromism is the change in the excitation energies of chromophores induced by an external environment. It occurs in both homogeneous solvents and more complex biological systems, such as proteins. While in both cases the solvatochromic effects report on the surroundings of the chromophore, their interpretation in proteins becomes more complicated not only because of structural effects induced by the protein pocket but also because the protein environment is highly anisotropic<sup>1</sup>. This is particularly evident for highly conjugated and flexible molecules such as carotenoids, whose excitation energy is strongly dependent on both the geometry and the electrostatics of the environment <sup>2</sup>. Here, we introduce a machine learning (ML) strategy trained on quantum mechanics/molecular mechanics (QM/MM) calculations of geometrical and electrochromic contributions to carotenoids' excitation energies <sup>3</sup>. Our ML models aim to reproduced the excitation energy of carotenoids in different environments and to compare solvatochromism in protein and homogeneous solvent. A dimensionality reduction tecnique is also used to analyze the electrostatic potential generated by different environments. Despite the important specifities of the protein, the ML models trained on solvents can faithfully predict excitation energies <sup>4</sup>.



Figure 1. Graphical abstract

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# Biomolecules from the valorization of agri-food by-products for sustainable and active primary packaging (BIO4SUSPACK)

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The aim of BIO4SUSPACK project is the realization, through a proper eco-design, and validation (TRL 6) of new and sustainable flexible packaging solutions for food sector of Emilia Romagna Region (RER) such as fresh chicken meat and DOP Squacquerone cheese, to cite a couple of examples.<sup>1</sup> The research focuses on the activation with antimicrobial biomolecules (i.e. essential oils) available on the market or obtained from agri-food by-products, of pads used in the package of fresh chicken meat. Two flexible films functionalized with cellulose nanocrystals (CNCs), will be also developed. The commercial CNCs and CNCs obtained from food waste have been employed as biobased filler to improve the mechanical and gas barrier properties of the polymeric matrixes.<sup>2</sup>

The polymeric materials were chosen within the family of commercially available biobased, biodegradable in home compost and food-grade polyesters, considering both aliphatic and aromatic ones. From the virgin materials, compression moulded as well as cast extruded films have been prepared and characterized from thermal, mechanical, and surface properties point of view. The tests were repeated on samples refrigerated for 7 days, to estimate the behaviour of the materials in the common shelf-life conditions of the food product, and after loading the commercial CNC fillers. The CNCs were also produced lab-scale by acid hydrolysis<sup>3</sup> starting from purchased commercial microfibrils (MFCs), to have a standard reference for the extraction product from waste biomass (**Figure 1**).





The performances of proposed solutions were compared with those of commercial products purchased by the company involved in the project, to choose the most suitable material for the specific packaging. The developed packaging solutions will contribute to increase safety, shelf life and quality of packaged selected foods. The valorisation of waste and by-products from the agrifood supply chains involved, will also enable the sustainable end-of-life management and the reduction of the environmental impact of the RER industries.

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# Innovative green plastic materials from solution casting of cutin from tomato peels and commercial pectin.

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Tomato processing industry is one of the most important sectors in the Italian productive context. Italian tomato production reached about 6.1 million tons in 2022 (39.8% of total European production)<sup>1</sup>. The total waste amounts to approximately 5-13% by weight of global tomato production also considering the waste from defective tomatoes discarded during processing. Tomato pomace, made up of seeds and peels, represents the main waste from tomato processing. Currently, tomato waste is used as animal feed and/or fertilisers or disposes in landfill<sup>2</sup>. For these reasons, innovative valorisation strategies of tomato waste are currently among the top environmental targets, and alternative uses need to be proposed. Cutin is one of the main components of the cuticular membrane of the tomato peels. Cutin is essentially a hydrophobic bio-polyester made up of esterified hydroxylated and epoxy hydroxylated C16-C18 fatty acids which exhibits excellent barrier properties<sup>3</sup>. Despite its ubiquity in terrestrial plants, cutin is traditionally underutilized as a raw material due to its insolubility<sup>4</sup>. In this work, we investigated the preparation of films through solvent casting, using pectin as a binding agent to overcome the challenges associated with cutin application in filmpackaging [Figure 1]. Pectin is a polysaccharide that can potentially be obtained from tomato peels waste<sup>5</sup>. Different cutin/pectin ratios were investigated in order to evaluate the effect of the cutin addition on the properties of the dried films. The casted films were characterized through multitechnique approaches by using TGA, DSC, spectroscopic techniques (i.e. FT-IR and UV-vis) and stress strain tests as examples with the aim to evaluate the possible application in food packaging and coatings.



Figure 1. Scheme of the solvent casting of pectin-cutin-based films.

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## Nanocellulose decoration with melanin-like materials for water purification membranes

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Water pollutants, such as heavy metal ions, highly concentrated salts, microbes, oils, persistent organic pollutants and emerging contaminants (POPs and ECs), constitute a global threat for health of humans and ecosystems<sup>1</sup>. This scenario becomes even more dramatic in areas with few water resources (e.g. African countries)<sup>2</sup>. Consequently, there is an urgent need to develop new water purification technologies. Cellulose nanomaterials-based membranes are considered cost- effective and efficient, thanks to their biodegradability and high specific surface area that allows great adsorption capacity. Furthermore, surface functionalization with small organic molecules or polymers can provide selectivity towards specific pollutants or enhanced removal efficiency<sup>3</sup>.

This communication describes the decoration of cellulose nanocrystals with eumelanin-like synthons (e. g. 5,6-dimethoxyindole-2-carboxylic acid) or a melanin-like synthetic polymer, polydopamine (PDA), their chemical characterization and the first adsorption tests on the new materials. The choiceof polydopamine and eumelanin building blocks was supported by literature evidences claiming adsorbent behaviour of these materials<sup>4,5,6</sup> and it, also, complied the intent to study structural activity correlations necessary for membranes interactions with pollutants.



nanocellulose decorated with eumelanin-like synthon

nanocellulose decoratad with polydopamine

Figure 1. Strategy for binding of polydopamine (route b) or eumelanin-like synthon (route a) to nanocellulose

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## Quantification of airborne microplastics and related additives in indoor particulate and settled dust collected in a working environment

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The widespread use of synthetic polymers has led to a significant environmental crisis caused by plastic pollution, with microplastics being found in various environments and posing risks to human health and ecosystems. Microplastics in the environment undergo continuous mechanical fragmentation leading to the formation of smaller plastic debris, more prone to be transported by atmospheric agents. The fragments dispersed in the air as particulate could be inhaled by humans, causing potential harm to the respiratory and other systems, posing a particular necessity to study microplastics as an air pollutant. In this study, we tested a combination of analytical pyrolysis, gas chromatography, and mass spectrometry (PY-GC-MS), as well gas and liquid chromatography-mass spectrometry (GC-MS and HPLC-MS/MS, respectively), to identify and quantify both microplastics and their additives in airborne particulate matter and settled dust from air samples collected in a plant where wastes of electric and electronic equipment (WEEE) are treated, and workers are exposed to shredded plastic fragments. We could detect and quantify in PM10 ten distinct synthetic polymers (Figure 1), as well eight classes of polymer additives: phthalate esters, adipates, citrates, sebacates, trimellitates, benzoates, organophosphates, and brominated flame retardants.



**Figure 1**. Py-GC-MS chromatogram obtained from analysis of PM<sub>10</sub> fraction from sampled air, and relative abundance of determined polymers.

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# Valorization of *Posidonia oceanica* balls: from waste to versatile raw material in an integrated biorefinery perspective

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In recent years, the replacement of fossil resources with renewable ones to produce alternative fuelshas received great interest. In this regard, the marine waste Posidonia oceanica balls (POb) is a promising feedstock that accumulates in an uncontrolled manner on Mediterranean beaches, thus causing environmental problem. For this reason, up to now most of POb are conferred in landfills but an integrated chemical conversion of POb into added value products could represent a more sustainable and innovative solution<sup>1</sup>. In this work, according to a biorefinery approach, the exploitation of POb, previously subjected to ethanol extraction, has been developed aiming at the conversion of the cellulose fraction (23.7 wt% of biomass) to n-butyl levulinate (BL), one of the most promising bio-fuel additives for Diesel engines<sup>2</sup>. BL synthesis was conducted under microwave heating, an alternative and more efficient system than the traditional one, using a one- pot alcoholysis approach employing *n*-butanol as the reactant/solvent and sulfuric acid as the homogeneous acid catalyst. The highest BL yield of 54.6 mol% was ascertained working at 180 °C for 30 minutes adopting 5.2 wt% of H2SO2 loading and 14 wt% of biomass loading. Furthermore, due to the recalcitrance demonstrated by POb, the alkaline delignification (AD) with NaOH was performed to increase the biomass reactivity and the highest delignification yield of 40.3 wt% was ascertained under the optimized conditions. Noteworthy, the AD allowed the fractionation of the biomass leading to the production of a polysaccharide enriched residue (PER), a pure acid insoluble lignin and an acid soluble lignin. PER was subjected to alcoholysis reaction, achieving the same BL yield under milder reaction conditions, in particular adopting a lower H2SO2 loading of

2.6 wt%. In conclusion, the biorefinery process proposed in this work not only addresses the urgencyof a sustainable managing of POb, but also offers the opportunity to produce several biobased compounds.

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## A New Class of Ferrabenzenes

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Metallabenzenes have aroused a significant interest due to their potential applications and theoretical considerations regarding their aromaticity<sup>1,2</sup>. While various ruthenabenzenes and osmabenzenes have been reported, including their potential to coordinate a further metal centre, isolated ferrabenzenes remain rare, and reproducible synthetic procedures to access them are still lacking in the literature<sup>3</sup>. Recently, we disclosed a new route to obtain a series of iron-coordinated ferrabenzenes (1), that can be alkylated to yield air-stable cationic derivatives (2). Computational studies were carried out to decipher the reaction mechanism leading to the formation of 1 using DFT and CASSCF. Moreover, the degree of aromaticity of 1 and 2 was assessed by computing the magnetically-induced current density<sup>4</sup> (MICD) and nucleus-independent chemical shifts (NICS)<sup>5</sup>. The in vitro antiproliferative activity of 2 was assessed on a panel of tumoral and nontumoral cell lines, leading to the identification of one specific compound within the series 2 as a promising anticancer drug candidate. The mode of action is attributed to the ability of the compounds to disrupt cell redox homeostasis; correlated with this, spectro-electrochemical studies showed the feasible formation of a reduction product from 1 and an oxidation product from 2.



Figure 1. Overview of experiments conducted on ferrabenzene complexes 1 and 2. R = Me, 4-C<sub>6</sub>H<sub>4</sub>OMe, Naph; R' = Me, Et

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# Comprehensive multianalytical characterization of resinous substances employed as adhesives in archaeological finds

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Resinous substances secreted by trees are often found in archaeological contexts due to their widespread use in ancient times for their sticky, waterproofing, and sealing properties. These substances were used in their natural forms, such as pine and mastic resin, or processed into more refined products like tar and pitch through heat and distillation methods. In particular, birch bark tar was characteristic of Northern Europe, while pine pitch was commonly used in the Mediterranean region<sup>1,2</sup>.

The present work aims to evaluate if the botanical source could affect the chemical composition and the thermal characteristics of the resulting pitch/tar material. To fulfil the objective, we analysed reference pitch/tar samples, prepared using different botanical families or species, using methods based on analytical pyrolysis. A collection of more than 30 tar and pitch was prepared from wood and barks of various deciduous trees (mainly from genus *Betula*) and conifers (mainly from genus *Pinus*). Evolved gas analysis-mass spectrometry and pyrolysis gas chromatography-mass spectrometry (EGA-MS and Py-GC/MS) have proven to be extremely suitable and versatile methods for studying samples from cultural heritage<sup>3</sup>.

By employing these techniques, it was possible to identify the chemical composition and thermal behaviour of pitch and tar derived from different plant sources. The detailed analysis of these materials provided insights into the selection criteria of ancient craftsmen regarding the use of specific resins and their processing techniques. Furthermore, the study emphasizes the importance of botanical sources in determining the functional properties of resinous substances in historical contexts.

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## Sustainable Approaches for Diphenolic Acid Synthesis in Batch and Continuous Reactors

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Diphenolic acid (DPA) is a promising environmentally friendly alternative to bisphenol A for producing epoxy resins and polycarbonate plastics [1]. The conventional synthesis of DPA involves a condensation reaction between phenol (PhOH) and levulinic acid (LA), catalyzed by Brønsted acid catalysts, often mineral ones, which present several drawbacks, such as corrosion and difficulty of recovery/recycling. On this basis, the possibility to use heterogeneous systems, especially those derived from renewable resources, is crucial. In this context, the project PRIN 2020 LEVANTE "LEvulinic acid Valorization through Advanced Novel TEchnologies" aims to synthesize a fully renewable p,p'-DPA in the presence of heterogeneous sustainable biomass- derived catalysts. To achieve this goal, all reaction components, LA, PhOH and the catalyst, should be of renewable origin. LA can be obtained through acid-catalyzed cascade dehydration-rehydration reactions of lignocellulosic biomasses, including waste ones, and PhOH and other phenolic derivatives can be obtained from lignin through thermochemical processes, such as pyrolysis or reductive depolymerization. Lastly, the acid biomass-derived catalyst can be synthesized according to the thermochemical process, already optimized in the LEVANTE project [2]. To realize these objectives, new ad-hoc sulfonated C5- and C6- hydrochar catalysts were prepared through a two-step procedure starting from xylose and glucose (loading of 20 wt%). This process involved an initial hydrothermal carbonization step performed at 220 °C for 5 h, followed by a sulfonation functionalization. Once the catalysts were synthesized, they were properly characterized and tested in the synthesis of p,p'-DPA, adopting both batch and continuous reactors, investigating the effects of the main reaction parameters for the selective production of the target isomer. Using the batch system, after a reaction optimization, p,p'-DPA yields about 20 mol% were achieved, paving the way for its fully renewable synthesis. Simultaneously, a Life Cycle Assessment analysis was carried out to compare the environmental impacts of the newly developed DPA preparation with the conventional chemical route in the presence of mineral acids.

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## Multipotent Precursors as Immobilization Strategy for Conjugated Polymers with Complementary Electronic Properties

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Indubitably, conjugated polymers played a significant role in the rise of organic electronics in the pastdecades, contributing dramatically to the development of technologies such as OLEDs, OPVs, and flexible electronics. The success of these materials, which comprise a fully conjugated backbone where the carbons are all sp2 hybridized and electron wavefunctions can span several units, is to be ascribed to the combination of appealing semiconducting and redox properties with their high processability in solution processes precluded to silicon. However, their inherently flat structure and tendency to form aggregates, can lower their solubility, resulting in complex issues during device fabrication or even the synthesis of high-molecular weight well-characterized materials. At the same time, addition of solubilizing side chains can make the materials too soluble, complicating the device design when steps with orthogonal processes are necessary.

To avoid these limitations and investigate new fabrication possibilities, we are developing a novel approach based on solution-processable polymeric precursors that can be employed for the immobilization of high-molecular conjugated polymers characterized by different structures and properties. In particular, during this presentation, I will introduce the concept of highly-processable polymeric precursors as a solution to prepare high-molecular weight conjugated polymers with the absence of solubilizing chains and discuss an example of two different semiconducting materials characterized by complementary electronic properties but originating from the same precursor. Notably, such transformations are achieved by different chemical treatments, which can also be applied orthogonally and on the solid state, thus generating different phases on a single substrate. We characterized the systems proposed and show several examples of how this methodology can be applied for the fabrication of OFETs, redox polymers, and multicolored electrochromic displays.

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# How Machine Learning enhances simulation of energy transfer in Light-harvesting Complex II

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In plant photosynthesis, the harvesting of solar energy is made possible by aggregates of pigmentsembedded in specialized membrane proteins, called light-harvesting complexes (LHCs)<sup>1</sup>. Specific interactions with the protein and electronic couplings with other chromophores alter the optical properties of individual pigments, and light absorption in the aggregate is followed by a cascade of energy transfer processes. Because of the complex nature of LHCs, the simulation of such excited state dynamics is challenging and requires expensive multiscale methods<sup>2</sup> to estimate all the involved parameters. Structural disorder adds on top, requiring calculations to be repeated over many configurations of the system. Machine learning (ML) can represent a valuable alternative to traditional approaches in the simulation of the energy transfer events. Here, we show that a ML strategy<sup>3</sup> can be applied to estimate excitonic quantities of LHCII of higher plants with accuracy comparable to standard multiscale methods, with the advantage of an extremely higher speed which allows wide sampling of the configurational space of the system when coupled to molecular dynamics. The resulting estimated parameters are robust and allow simulation of the excited state dynamics which closely reproduces the experimental one, as demonstrated by comparison to transient absorption<sup>4,5</sup>. New insights on the most relevant pathways and associated characteristic times are achieved through this integrated model.



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## Distribution of Polyunsaturated Fatty Acids in Dried Blood Spots of Heart Failure Patients

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Heart failure (HF) is a complex clinical syndrome resulting from a structural and/or functional abnormality of the heart, which fails to pump effectively to ensure an adequate supply of blood and oxygen to the body [1]. There is no cure for heart failure and the diagnosis is usually complex. However, a correct therapy and a healthy lifestyle can extend the life expectancy of HF patients.

Dysfunction of cardiac mitochondria is a hallmark of HF and a leading cause of oxidative stress, which in turn causes myocardial tissue damage and inflammation thus contributing to HF progression. Monitoring markers of oxidative stress and inflammation can provide insights into disease progression. An example of such markers includes polyunsaturated fatty acids (PUFAs) and their derivatives, oxylipins. The analysis of oxylipins and PUFAs in minimally invasive biological specimens, e.g. oral fluid and dried blood spots (DBSs), can be extremely useful in elucidating their biological activity [2].

Here, a very powerful analytical platform, based on micro-extraction by packed sorbent (MEPS) coupled to liquid chromatography-tandem mass spectrometry (UHPLC-ESI-MS/MS), was fully developed, and validated for the targeted profiling of fifty-two oxylipins and four PUFAs in DBSs [3]. The protocol was successfully employed in a pilot study on a cohort of HF and healthy control subjects (n=100) during the cardiopulmonary exercise testing (CPET) to evaluate metabolic derangements during effort.

The statistical analysis suggested the occurrence of significant differences in PUFA levels between HF subjects and controls. HF population showed generally lower levels of omega-3 PUFA than controls, in line with the "malnutrition-inflammation complex syndrome" [4]. Arachidonic acid (AA) significantly (p <0.05) differed between HF patients with preserved, HFpEF, and reduced, HFrEF, ventricular ejection fraction at rest (LVEF), highlighting a different bioavailability of this circulating omega-6 PUFA. AA levels significantly (p<0.01) decreased during the exercise only in HFpEF population, thus suggesting distinctive changes in myocardial uptake and utilization of energy substrates. A lipid rearrangement typical of the HF was clearly evidenced from these results.

This work provides a solid foundation for further research in the world of PUFAs and their application as diagnostic and prognostic markers for the Heart Failure disease.

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## A biophysical study on the interaction of tetrapyridyl metal complexes with relevant nucleic acid molecules

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Metal compounds form an attractive class of ligands for a variety of nucleic acids. Platinum complexes have been studied since the discovery of cisplatin, which is known to produce DNA damage and cell apoptosis. Due to the many similarities between Pt(II) and Pd(II), there is interest in studying Pd(II) complexes as potential anticancer drugs. Given the much faster hydrolysis of Pd(II) complexes with respect to the Pt(II) analogues, there is the need for a very strong nitrogen ligand, able to ensure the reaching of its biological target.<sup>1,2</sup> Compounds with tetradentate ligands obviate this rapid hydrolysis reaction. Another series of metal complexes that have a similar coordination structure to Pt(II) complexes are the Au(III) ones. They generally suffer from stabilization issues, due to their tendency to be easily reduced to Au(I) or Au(0) particles, making the choice of the ligands particularly relevant. Differently from DNA-focused Pt(II) species, Au(III) complexes often preferentially bind proteins.<sup>3</sup>

Here, we present five metal complexes of Pt(II), Pd(II) and Au(III) bearing aminopyridyl-2,2'bipyridine tetradentate ligands and possessing a quasi-planar geometry. These compounds were challenged with different types of nucleic acid molecules. Natural double-stranded DNA, poly(rA)poly(rU) and poly(rA)2poly(rU) RNAs, DNA G-quadruplexes and a RNA four-way junction (RNA-4WJ) are all considered in our studies. These systems are analysed using different techniques and approaches (spectrophotometric and fluorometric titrations, melting assays, viscosity tests and mass spectrometry). Interestingly, the analysed metal complexes seem to react better with RNAs with respect to DNA, even in the triplex form. As for the binding with the RNA- 4WJ, one Pd(II) and the Au(III) complexes seem to be the species able to bind RNA at the junction. In fact, they show binding features which appear only in the presence of RNA-4WJ and not for its duplex counterpart.

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## Development and characterization of new contrast agents for imaging technology called spectral photon counting computed tomography (SPCCT)

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Spectral photon-counting computed tomography (SPCCT) is a recent imaging technique that has significant potential for clinical applications. One of the key advantages of SPCCT is its ability to detect x-ray photons based on their energy, which allows for the simultaneous quantification of multiple contrast agents<sup>1</sup>. Our study focused on evaluating the contrast- enhancing properties of Pt(II), Pt(IV), Re(III), Ir(IV), W(II), Au(III), and Gd(III) as potential contrast agents. Among these, Au(III), Gd(III), and W(II) exhibited better attenuation.Furthermore, we investigated the potential of heterogenous mixtures. The results showed that reverse micelles (PLGA/PEG)<sup>2</sup> loaded with W(II), Au(III), and Gd (III) salts exhibited similar trends observed for homogeneous metal complexes. We also conducted in-vitro experiments on U-87 type cells that yielded positive results, although limited to a feasibility study.

In conclusion, our study provides valuable insights into the contrast capabilities of differentelements and their potential for use as contrast agents in SPCTT imaging. These findings could aid to pave the way for the development of more effective and efficient contrast agentsfor clinical imaging applications<sup>3</sup>.





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# Synthesis and characterization of new gold(I) NHC complexes containing fluorescent probes as potential anticancer agents

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The need to find new antitumor agents with improved pharmacological profiles compared to the platinum complexes currently in use has led to the study of various metal complexes with different mechanisms of action. Gold-based complexes, especially, have been gaining the interest of researchers due to their activity at the mitochondrial level.<sup>1,2</sup> However, it is crucial to fully comprehendthe mechanism of action and biological activity of these complexes in order to design more potent antitumor complexes. Therefore, a series of N-heterocyclic carbene gold(I) complexes bearing anthracene and BODIPY fluorescent probes were synthesized to be studied in cellular uptake and biodistribution evaluations, employing confocal microscopy, and for target protein identification via electrophoresis.



Figure 1 panel of complexes synthesized for this work

Various attempts were made for the synthesis of the BODIPY bis-carbene with no results. The synthesized compounds were characterized through 1H, 13C NMR, and elemental analysis. The structure of the anthracenyl monocarbene was also confirmed by X-ray crystallography. All the synthesized complexes resulted stable in DMSO for 48 h at 25 °C but unstable in PBS buffer under the same conditions. HSA interaction studies through UV-Vis absorption spectroscopy showed signsof interaction between the BODIPY monocarbene and the protein. Cellular uptake on A2780 ovariancancer cells studies using FACS cytofluorimetry highlighted strong cellular uptake of all compounds. The cytotoxic activity of the complexes was evaluated on the same cell line, showing goodantimicrobial activity of the anthracenyl carbenes which demonstrated higher activity in cisplatin- resistant cells rather than in sensitive ones. The cytotoxicity of the BODIPY complex was not possible to evaluate due to its low solubility.

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## A novel strategy for syngas production through the oxygasification of pulp and paper mill sludge

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Pulp and paper mill sludge (PPMS) is the main organic residual generated from the wastewater treatments of the pulp and paper industry. It is generally divided into primary sludge, characterised by cellulosic-rich fibre and ash, and secondary sludge, primarily composed of organic matter with a high microbial content. Due to the huge production of the paper-making industry, around 400 million wet tons of PPMS are produced annually [1]. Nowadays, the management and disposal of PPMS are landfilling and/or incineration, incurring economic, environmental and social costs. The present work concerns the use of the gasification process as a promising valorisation method of primary and secondary PPMS, with the goal of the production of syngas. The syngas obtained by gasification is generally composed by CO, CO2, H2 and CH4, and it is commonly used as feedstock for the synthesis of key molecules within the chemical industry, such as methanol and hydrocarbons, or for plant energy recovery (heat or electricity generation) [2]. The composition of PPMS depends on several factors [3], however, due to the biological activity of secondary PPMS, only primary PPMS has been characterised, highlighting a total amount of 70 wt% of CaCO3 and 25 wt% of cellulosic fibre. The experimental activity has mainly focused on an oxy-gasification strategy. Initially, fir pellets were used as a benchmark, followed by experimentation with a blend of PPMS and wood pellets in a 1:4 wt/wt ratio. The gasification attempts have been conducted in a downdraft fixed bed reactor (≈100 KwTH) by adopting a mixture of O2/H2O as a gasifying agent. Notably, the co-gasification with both primary and secondary PPMS resulted in obtaining nitrogen- free syngas characterized by a high H2 content (40 mol%) and CO (21 mol%). However, only the syngas composition derived from primary PPMS has shown to be stable over time, displaying high values (≈80%) of Cold Gas Efficiency (CGE), which is an indicator of gasification effectiveness. Finally, the characterization of the side products, such as ash and tar (condensable hydrocarbon and aromatic molecules) has been also performed. In particular, FT-IR analysis revealed that the primary PPMS ash predominantly consisted of CaO. In conclusion, this work proposes the integrated valorization of PPMS through gasification, leading to a promising syngas composition for energy recovery and a high CaO content in gasification ash primary PPMS, which opened up possible strategies for its recovery and recycling.

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## Two-photon excitable ligands: a new step for in vivo imaging

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The development of new fluorescent probes is one of the cornerstones of real-time imaging, as well as a fundamental tool for cell biology and the study of tissue physiopathology<sup>1</sup>. Research in this relatively well-explored field has experienced a renaissance following efforts devoted to the development of bioorthogonal chemistry methodologies, which can add functionalities to biomolecules with minimal disruption to the biological system of interest<sup>2</sup>. Numerous probes have been created over time, with their structures designed to be sensitive to one or more specific parameters of interest, such as pH, halide concentration, calcium, and redox potentials and many more. In this context, it is interesting to exploit the unique properties of lanthanides, particularly their long lived excited-state lifetimes, to createprobes ameneable to time-gating microscopy<sup>3</sup>. This type of microscopy allows the visualization of molecules with longer fluorescence lifetimes. which makes it very promisingfor analyzing samples characterized by strong background noise, such as histological preparations. Furthermore, it is possible to design the fluorophore to be excitable by two-photon excitation, allowing the use of low energy excitating light, which is less harmful and suitable for potential in vivo imaging applications. Our efforts have been directed towards this goal: the design and creation of biomolecular lanthanide-based probes suitable for two-photon excitation based on the structure of dipicolinic acid<sup>4</sup>, and the bioconjugation of modelproteins with these fluorophores.



Figure 1. Designed, synthesized, and compared systems

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## Preliminary Studies on Using Atomic Oxygen for Cleaning Silk

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Silk is a protein fiber secreted by the Bombyx mori L. juvenile worm, historically used to produce precious textiles. As a cultural heritage material, it is subject to degradation and presents several challenges in the cleaning process with traditional methods due to its fragile nature. This study is part of the Green Atmospheric Plasma-Generated Monoatomic Oxygen Technology for Restorationof the Works of Art (MOXY) project, which aims to develop a new non-contact method to clean delicate surfaces using a cold plasma of atomic oxygen (AO) that can convert carbon-based contaminants into volatile species. Currently, the AO technology is still in development, with its application limited to small areas. Given that silk is a delicate and valuable material that is not widelyused in large quantities, it serves as an ideal candidate for cleaning with AO.

To investigate the effect of AO, a preliminary set of tests was conducted on mock-ups of both undyed silk threads, as well as Rhodamine B (RhB) and Carminic Acid (CA)-dyed silk threads. AO action involves a radical pathway, similar to the one triggered by light. Moreover, RhB is a direct dye, whereas CA is a mordant dye that uses alum, which can influence its reactivity with AO. For this reason, the two dyes were selected for their different photostabilities: low for RhB and high for CA. The threads were treated using AO in conditions tuned in other preliminary tests and did notshow any visible degradation to either the fibre or the dyes. The thermostability of the samples wasanalysed using Evolved Gas Analysis coupled with Mass Spectrometry (EGA-MS). Even though the Total Ion Thermogram (TIT) curves did not show any differences in the profile, when extracting 4- hydroxybenzene (m/z 138), a known degradation product for wool and silk [1], it is possible to see that AO causes an increase in the relative intensity of this ion, indicating the degradation of the fibre.No measurable differences were detected between the undyed and dyed samples, as expected fromEGA-MS analysis. These analyses were performed a few days after the treatment, but monitoring the long-term effects of AO on silk is necessary to assess this cleaning technique. Further investigations are being planned to study the potential long-term effects of atomic oxygen by artificially aging both untreated and treated samples.



**Figure 1**. Extracted ion thermograms for the fragment with m/z 138 obtained by EGA-MS analysis for treated and untreated samples for undyed silk (top), RhB-dyed silk (left) and CA-dyed silk (right). Each curve has been normalized for the weight of samples.

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# Electro-oxidative nitroso-Diels-Alder reaction for the regioselective functionalization of dihydropyridines

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The nitroso Diels-Alder (nDA) reaction represents a powerful tool in organic synthesis as it promotes the simultaneous formation of a  $C \square N$  and  $C \square O$  bond with complete regio- and stereoselectivity. Theestablished mechanism requires the *in situ* generation of the short-lived acyl nitroso (dienophile), which is further trapped by the 1.3-diene.[1] An essential condition is therefore the use of a stoichiometric amount of strong chemical oxidants (COx), polluting and toxic reagents typically used to access the desired reactive species, often leading to substrate decomposition in presence of oxidation-sensitive heterocycles (Figure 1, A).[2] Pyridines and dihydropyridines are privileged scaffolds in drug discovery.[3] These dienes can be promptly functionalized also via nDA, giving rise to key intermediates for the regioselective synthesis of diverse biologically active compounds (Figure 1, B).[4, 5] With the aim of targeting greener and sustainable procedures.[6] we report an electro- oxidative nDA protocol which replaces the toxic COx's with electric current. promoting a selective and viable methodology for the functionalization of pyridine and dihydropyridine moieties (Figure 1,C). Preliminary results highlight the potential of electrochemistry to reduce the formation of undesired oxidative side-reactions and product decomposition, thanks to a fine tuning of reaction parameters. Future efforts will converge to elucidate the key mechanistic insights along with the application to the regio- and stereoselective synthesis of biologically active compounds.



### Figure 1

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## Electrospinning of Microbial Polyhydroxyalkanoates for the Development of Naringenin-Loaded Microfibrous Meshes

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Polyhydroxyalkanoates (PHA) are aliphatic polyesters produced by microorganisms under carbon source excess and limiting nitrogen availability [1]. Although being biocompatible, these biopolymers possess low thermal stability and poor melt processing properties, limiting their biomedical applications. The electrospinning technique is suitable to fabricate non-woven micro/nanofiber meshes simulating the structure and function of the native extracellular matrix for advanced tissue engineering applications [2]. In this study, blends of poly(3-hydroxybutyrate-*co*-3- hydroxyvalerate) (PHBV) or poly(3-hydroxyvalerate-*co*-3-hydroexanoate) (PHBHHx) with poly(D,L- lactide-*co*-glycolide) (PLGA) were employed for the fabrication of electrospun microfibrous meshes loaded with the flavonoid naringenin (Nar) (1% wt) in order to exploit its anti-inflammatory activity. Scanning electron microscopy (SEM) analysis demonstrated that the optimized meshes were constituted by fibres with a diameter in the range  $1.2-2.0 \mu m$ , without the presence of structural defects (e.g., beads). The developed electrospun meshes showed an *in vitro* Nar release kinetics characterized by an initial burst phase with around 90% or 70% of the loaded drug released in the first 24h in the case of PHBV/PLGA or PHBHHx/PLA meshes, respectively. The *in vitro* degradation behavior of the electrospun fibres was investigated for 3 months by means of SEM, mass loss measurement, GPC,

and <sup>1</sup>H-NMR. The results showed that the degradation rate of PLGA was higher than those of PHBV and PHBHHx. 2,2-diphenyl-1-picrylhydrazyl (DPPH) assay revealed that Nar loading endowed electrospun meshes with antioxidant activity.



Figure 1. Scheme of electrospinning process for naringenin (Nar)-loaded meshes fabrication.

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## From giant reed to carotenoids: development and optimisation of an innovative cascade process

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Giant reed is a perennial herbaceous plant that can grow in all temperate zones, it does not require pesticides and it needs limited irrigation. Moreover, it is characterised by a high biomass productivity, soil bioremediation capacity and a high polysaccharides content (60 wt%) which can be valorised [1]. On this basis, in this work, this biomass was pretreated with a solvothermal process using an aqueous imidazole solution to remove the lignin fraction, making the solid residue enriched in polysaccharides and more reactive towards the subsequent saccharification step based on the enzymatic catalysis. The pretreated solids were hydrolysed with the commercial enzymatic mixture Cellic<sup>®</sup> CTec 3 HS to obtain glucose and xylose which were converted to carotenoids by the commercial and safe yeast Rhodosporidium toruloides [2]. Carotenoids are valuable molecules used in various fields, including the food industry, human health and semiconductor technology [3]. The efficiency of the pretreatment process was affected by several parameters, such as imidazole concentration, reaction time, temperature and initial biomass loading, all of them investigated in this work. Regarding the saccharification step, the effect of enzyme and biomass loadings was studied. Under the optimised pretreatment conditions (22 wt% imidazole solution, 140 °C, 3 h, 9 wt% initial biomass loading), lignin removal of 41.3 wt% was obtained. Lignin was recovered through precipitation by acidifying of the liquid phase, obtaining an average recovery of 95 wt% of pure lignin suitable for subsequent characterisations and exploitation strategies. Under the optimised enzymatic hydrolysis conditions (50 °C, 96 h, 45 FPU/g glucan, 10 wt% initial substrate loading), the glucose yield achieved for the optimised pretreated residue was 99 mol%, whereas the xylose yield was 82 mol%. The monosaccharides fermentation process was also optimised by studying the C/N ratio (20, 40, 60 g/g) in the formulation of the culture medium and the time of the inoculum (48, 72 h). Under the optimised conditions (C/N 60 g/g, inoculum time of 72 h) the cellular carotenoid content of 12.8 mg/g of dry cell weight was obtained from the fermentation of the biomass hydrolysate. Finally, this work also focused on the study of different downstream approaches for the cell lysis and recovery/purification of carotenoids by comparing different methods based on ultrasounds, ball milling or DMSO treatment of cells coupled with hexane or acetone extraction. Separation of carotenoids was performed by silica gel column utilising the mobile phase of hexane/acetone 98.5/1.5 v/v%. The spent yeast obtained from the extraction step contained approximately 5 wt% of total nitrogen, making it suitable for further valorisation as a nitrogen source in fermentation processes or as a feedstock for the production of nitrogen-rich activated carbons by catalytic pyrolysis.

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## LIG-based electrochemical platform for gas sensor fabrication

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Laser-induced graphene (LIG) is a form of graphene produced by exposing carbon-rich precursors to laser irradiation. During this process, the precursor (typically a polymer, but also wood or paper) is converted into a porous graphene structure. The laser heat causes localized pyrolysis of the material, breaking down the molecular structure and rearranging the carbon atoms into graphene [1]. Despite LIG being employed in many applications, such as flexible electronics and bio-sensors [2], its application in the field of gas sensors is relatively unexplored. In this work, we present a novel LIG-based electrochemical platform for gas sensor fabrication. A CO<sub>2</sub> laser (30W, 10.6  $\mu$ m, Trotec) was used to fabricate conductive tracks on a polyimide film, respectively the working (WE) and reference (RE) electrodes of the sensors. Before the fabrication of the WE, a small amount of sensitive material (Pd/C, ZnO and WO<sub>3</sub>) was placed onto the film, to incorporate the material into the LIG porous structure (Figure 1,a).

A conductive polymer was placed in contact with the two tracks, creating cheap and easy-tofabricate solid-state sensors. The LIG was characterized using IR and electrical conductivity measurements. A lab-made 3D case was printed, which allows both the electrical contact and the measurement of the potential difference between the two electrodes (Figure 1,b).

Finally, the sensors were exposed to known concentrations of various analytes. The most interestingsensors proved to be those functionalised with Pd/ C and WO3. In particular, the Pd/C-LIG sensor was able to detect instantly H2 (Figure 1,c), while WO3-LIG sensor can detect selectively amines (NH3 over N(CH3)3).



Figure 1. (a) LIG sensor, (b) 3D render of sensor case, (c) exposure to H<sub>2</sub>.

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## Bioprinting of gelatin methacryloyl-based bioinks for *in vitro* ovarian cancer modelling

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Ovarian cancer is the most lethal gynaecological cancer due to several factors: (i) asymptomatic nature, (ii) resistance to treatments, and (iii) multiple recurrences after treatment [1]. Reliable *in vitro* models that faithfully mimic the complexity of the ovarian tumour microenvironment are urgently needed to develop more effective therapies [2]. In this context, bioprinting has emerged as an advanced approach for fabricating complex cancer tissue engineering constructs. The aim of this study is the bioprinting of gelatin derivatives for the development of *in vitro* ovarian cancer models. Indeed, gelatin can be made susceptible to photocrosslinking into a hydrogel stable in physiological conditions through a direct reaction with methacrylic anhydride [3]. For this purpose, two gelatin methacryloyl (GeIMA) synthesis protocols were developed under different pH conditions, which resulted in a different degree of methacrylation, as shown by <sup>1</sup>H-NMR spectroscopy analysis. The extrusion printing and photocrosslinking parameters of the two developed GeIMA formulations were optimized, producing stable scaffolds under physiological conditions. Ongoing studies are aimed at

printing bioinks containing human ovarian cancer cells to directly encapsulate them into a crosslinkedGelMA matrix hydrogel.



Figure 1. GeIMA synthesis and bioprinting of *in vitro* ovarian cancer models.

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## Four component relativistic calculations at reduced cost: a Cholesky decomposition implementation

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Including relativistic effects<sup>1</sup> in the computational description is paramount when dealing with molecules containing heavy-metal atoms. Such effects can be divided into scalar relativistic and spinorbit effects. The former have a large impact on the overall energy, while the latter are responsible for fine effects on the electronic states. In this contribution, we pursue a computationally efficient but rigorous description of scalar relativistic effects by adopting the four- component spin- free Dirac-Coulomb Hamiltonian<sup>2</sup> in combination with Coupled-Cluster with single and double excitations (CCSD)<sup>3</sup> as an electronic structure method. A four-component treatment introduces a major computational bottleneck, because the 4-component structure of the wave function leads to asizeably larger number of two-electron integrals that need to be computed and processed when compared with the non-relativistic case. The additional two-electron integrals are not only affecting all computationally intensive step of a quantum chemistry calculation, but are also per se expensiveto compute. However, they are numerically smaller than the non-relativistic integrals, which makes them an ideal problem for rank reducing techniques. In this contribution, we apply the Cholesky Decomposition (CD)<sup>4</sup> to the spin-free, relativistic two-electron integrals to accelerate the computation. We present an efficient, two-step<sup>5</sup> implementation of the CD, and discuss possible approximations that can be adopted when selecting the Cholesky basis, and in particular, the neglect of pivots stemming from the small component integrals. Using the CD has several advantages: it reduces the cost of computing the integrals themselves, accelerates the SCF and integral transformation computations, which further become trivially parallelizable, and, due to the effective compression of the two-electron integral tensor achieved by the technique, allow for an efficient MO implementation of the CCSD treatment that is not memory limited. This is particularly attractive, as it allows to use the same machinery used for non-relativistic CD-CCSD calculations, making thus it possible to perform the correlation calculation, which is the most expensive overall computational step, at no additional computational cost with respect to the non-relativistic counterpart. Various numerical experiments are presented to show in detail the possibilities and performance of the CD-SFDC-CCSD implementation.

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## PERICARD: a targeted Plasmatic pEptidomic profile foR monitoring CARdiovascular Diseases

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Cardiovascular diseases (CVDs) are a group of heart and blood vessels disorders including heart failure, thromboembolism, coronary artery disease, and chronic kidney disease<sup>[1]</sup>. They currently stand as the leading cause of global mortality because of their challenging diagnosis and their non-specific symptoms<sup>[2]</sup>. Current diagnostic strategies rely on assessing risk factors and dosing biomarkers i.e., protein and peptide levels in human plasma, by using commercial immunoassays. However, the approaches are typically employed when symptoms are already present. Moreover, the analysis of CVDs biomarkers can be hampered by the high cross-reactivity with structurally similar species<sup>[3]</sup>.

Here we present, an ultra-high performance liquid chromatography-electrospray ionizationtandem mass spectrometry (UHPLC-ESI-MS/MS) method to determine targeted plasma peptidomics overcoming immunoassay limitations. The importance of a reliable plasma sample pre-treatment procedure for the determination of low-abundant (unit-tenths of pg/mL) intact peptides (such as endothelins, fibrinopeptides, guanylins, urotensins) is discussed. Additionally, strategies to mitigate the potential risks, such as secondary adsorption phenomena and peptide degradation have been also investigated.

Microextraction by packed sorbent (MEPS) technique has been tested as an alternative procedure for sample pre-treatment and analyte pre-concentration. Finally, the suitability of this methodology will be established for the analysis of human plasma from patients affect by CVDs.

PERICARD seeks to meet the need for an efficient, high-throughput tool for early identification of at-risk individuals. Its potential applications such as diagnosis, prognosis, prediction of disease recurrence, and therapeutic monitoring, may pave the way in the management of CVDs.

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### Synthesis, characterization and biological applications of peptoid-based metal chelators

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Chelation therapy refers to the administration of a chemical agent, called chelator, to remove toxic exogenoeus metals from the body. It is used as well to reduce levels of essential metals in cases of overload disorders that are linked to various pathologies.<sup>1</sup> There is a constant need for the development of new chelators as the number of molecules suitable for chelation therapies is still limited, and many suffer from important side effects due to their poor selectivity and depletion of essential metals. Peptoids represent a promising platform for biomedical applications because of their modular design that allows for easy incorporation of a variety of structural elements and functional groups through simple synthetic processes.<sup>2</sup> Several examples of peptoid-based metal ligands bearing aromatic mojeties indicate the potential application of peptoids as metal chelators.<sup>3</sup> This project aims at the synthesis of selective chiral oligopeptoid chelators derived from natural amino acids that are promising biocompatible molecules. The first step involves the development of a modular, divergent and free-protecting group solution synthetic strategy for the synthesis of highly functionalizable --oligopeptoids based on L-homoserine lactone. To optimize this synthetic process, the submonomeric approach was tested for the synthesis of monomeric and dimeric 
-peptoids. Additionally, some chromophores were conjugated to L-homoserine lactone through classical peptide coupling reactions to obtain model molecules for testing their potential chelation properties by ECD titration with different metal ions. Ring-opening reactions with different nucleophiles were performed to achieve divergent post-modification of the sidechains of the obtained molecules. Subsequently, complexation studies on these final compounds were carried out using NMR and ECD titrations with various metal ions. Future steps will involve transposing the optimized solution synthetic strategy to solid-phase synthesis to create a combinatorial library of supported peptoids. After identifying a set of chelating peptoids among those supported on resin through ICP-OES analysis with multi-element solutions, an in-depth characterization of selective metal/chelate couples will be performed using multiple techniques, such as NMR analysis, chiroptical analysis and ITC analysis, to determine stoichiometries and association constants.



Figure 1. Modular, divergent and free-protecting group solid-phase and solution synthetic strategy

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## DAM4CO<sub>2</sub> project: Synthesis and Characterization of Metal-Organic Frameworks for CO<sub>2</sub> Separation

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"Double Active Membranes for a sustainable CO<sub>2</sub> cycle" (**DAM4CO<sub>2</sub>**) is a European project that proposes an innovative and integrated membrane technology aimed at fostering a sustainable CO<sub>2</sub> cycle through a net-zero emissions carbon capture and utilization process. In this framework, a novel double active membrane technology made up of a durable and highly selective gas separation layer and a photocatalytic layer able to simultaneously combine in one pot the reverse water gas shift and Fischer-Tropsch reactions to obtain C4+ molecules as renewable fuels will be developed. At any stage of the process, attention will be paid to using non-critical raw materials.

The gas separation layer is a mixed matrix membrane made up of a porous polymeric material in which metal-organic frameworks (MOFs) are dispersed as fillers. MOFs are a class of crystalline and porous coordination polymers built by metal ions or clusters and organic linkers. Due to their structural and functional tunability, MOFs are of great interest for applications in CO<sub>2</sub> separation.<sup>1</sup>

In this work, we present the synthesis and characterization of four different MOFs: Catrimesate,<sup>2</sup> Ca-squarate,<sup>3</sup> Zr-squarate,<sup>4</sup> and Zn/K-citrate<sup>5</sup> (UTSA-16). These MOFs are based on notenvironmentally hazardous and commercially available organic ligands, and metals classified as non-critical raw materials by the European Commission. The syntheses were carried out in either aqueous or hydroalcoholic solutions and in mild conditions (T < 100 °C). Each material was characterized through powder X-ray diffraction, scanning electron microscopy, thermogravimetric analysis, and solid-state nuclear magnetic resonance spectroscopy. These MOFs will be shared with project partners for further characterization of their gas sorption properties and, ultimately, preparation for mixed-matrix membranes, whose gas separation performance will also be evaluated.

#### Acknowledgment

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### 15<sup>th</sup> Century Paint Microstructure

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The objective of this study was to characterize the microstructure of 15<sup>th</sup> century paints based on drying oils and proteinaceous media prepared using different formulations and preparation methods. Until the end of the 14<sup>th</sup> century Italian artists used egg as the prevalent binding media for their paints, which are classified as egg tempera. In 15th century these artists started experimenting with siccative oils in addition to the traditional binder. This led to the introduction of mixed media paintingtechniques such as tempera grassa, which consist in an emulsion of protein binder and oil, and oil paint with protein-coated pigments, which is an oil paint where the pigment particles have previouslybeen coated with a layer of proteins. [1][2]

Previous studies showed that mixed media paints have widely different wet behaviours and drying characteristics based on preparation method and composition, leading to the hypothesis that the microstructure of the paints could be a driving factor in these differences.[1][2]

The objective of our study was to characterize the microstructure of paints based on drying oils and proteinaceous media prepared using different formulations and preparation methods.

To this aim, modern replicas of tempera grassa and protein coated pigment (oil paint with protein coated pigment particles: pcp) paints were produced, as well as oil and tempera paints as control samples. These replicas were produced using known amounts of ultramarine blue, as pigment, and egg white and linseed oil, as binders. Proteins were labelled with a luminescent tag by functionalizing egg white with 5-(4,4,4-trifluoro-3-oxobutanoyl)thiolane-2-sulfonyl chloride, acting as the luminescence sensitizer, and Europium.[3] The drying oil, instead, was treated with Neuro-DiO, a readily available fluorescent dye.

These paints were applied as a thin layer onto glass slide and left to dry until set to the touch. The resulting samples were observed using a confocal laser scanning microscope equipped with an Airyscan detector and a scanning electron microscope.

Combining the results of the two techniques, it was possible to fully appreciate the differences in themicrostructures and to comprehensively characterize them.

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A comparative study of the adsorption of an organic compound such as methylene blue was carried out using biochars derived from local waste in Morocco as argan cake (AC) and olive cake (OC). The biochars were prepared at three different pyrolysis temperatures of 600, 700, and 800 °C to investigate the effect of pyrolysis temperature on the properties of the biochar's and also on their adsorption capacity towards methylene blue (MB). Pyrolysis was performed in a muffle furnace at 600, 700, and 800 °C with a heating rate of 2 °C/min. Proximate, TGA-DTG, CHNS-O, XRF, FTIR, SEM-EDX, BET, and XRD analyses were used to characterize the materials for physicochemical, structural, and thermal properties. Results showed that biochar yield, decreased with increasing pyrolysis temperature for both feedstocks. However, ash content, fixed carbon, thermal stability, carbon content, pH, electrical conductivity (EC), and specific surface area (SSA) of biochar increased with increasing pyrolysis temperature. Fourier-transform infrared spectroscopy (FTIR) analysis showed that the surface of the biochar was rich with hydroxyl, phenolic, carbonyl and aliphatic groups. SEM scanning revealed a porous structure for olive cake biochar. In batch adsorption studies, the biochars were used to remove MB from aqueous solutions, showing that adsorption capacity increased with pyrolysis temperature for both biomasses. MB adsorption capacity was used as an indicator of biochar quality. In addition, the three biochars prepared from olive cake (BOC600, BOC700, and BOC800) showed higher ability to remove MB from aqueous solutions compared to biochars prepared from argan cake (BAC600, BAC700, and BAC800).

## Design of Organic Building Blocks for the On-Surface Synthesis of Conjugated 2D-Covalent Organic Frameworks

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Conjugated Single Layered Two-Dimensional Covalent Organic Frameworks are molecularly thin highly ordered macromolecules that extend into the second dimension and promise to be the next generation systems for electronics and photonics.<sup>[1]</sup> Formation of such organic nanomaterials is challenging as their synthesis requires the use of dynamic reactions to induce self-correction processes within their architecture, leading to highly extended covalent nanostructures. Achieving the single layer necessitates 2D confinement through interfacial synthesis, either at the solid-liquid, solid-air or liquid-liquid interface. The study emphasizes the critical role of the organic building blocks supramolecular pre-organization at the interface for effective 2D-polymerization. By employing HOPG as surface, formation of honeycomb π-conjugated vinylene-linked (C=C) single layer covalent organic frameworks via an optimized dynamic Knoevenagel polycondensation was studied.<sup>[2,3]</sup> In particular, we show that benzene-core building blocks form rather stable hydrogen- bonded supramolecular nanoporous structures, while the use of the triazine-core building blocks enables the 2D-polymerization even at room temperature without the use of any base or catalyst. Visualization of the 2D-Polymers formed was carried out by Scanning Tunneling Microscopy (STM) at the solidliquid interface (HOPG/octanoic acid) complemented by molecular modelling calculations. Furthermore, the electronic properties of these frameworks were characterized using Scanning Tunneling Spectroscopy (STS), highlighting their potential in the fields of electronics and photonics.



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## Eco-friendly refinement of N,N Dialkyl-2-arylindol-3ylglyoxylamides synthesis

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The transition to more sustainable chemistry synthesis is imperative for achieving the European Union's goal of carbon neutrality by 2050, as outlined in the European Green Deal. A major concern in synthetic chemistry is the extensive use of solvents, which are predominantly petroleum-derived, volatile, and pose significant risks to safety and health. To address these challenges, researchers are exploring new solvents as safer and more environmentally friendly alternatives. The pharmaceutical industry heavily relies on solvents, and so it is necessary a selection of greener solvents for the synthesis of active pharmaceutical ingredients (APIs). It is also fundamental to develop new synthetic pathways that minimize energy consumption and waste generation, while also facilitating sustainable work-up processes. An interesting class of APIs, N,N Dialkyl-2-arylindol-3-ylglyoxylamides (figure 1), targets the translocator protein (TSPO), which is implicated in various diseases. However, the conventional synthesis [1] of these compounds involves hazardous solvents like diethyl ether and requires chromatographic purification. In our research, we identified the critical factors affecting this synthesis and focused on substituting traditional solvents with safer and more sustainable alternatives. Additionally, we optimized the synthesis to minimize waste generation and streamline the work-up process.



Figure 1 Structure of N,N-Dialkyl-2-arylindol-3-ylglyoxylamides

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## Eu(III)-TTA Metal Complexes For The Fluorescent Labelling Of Cyclodextrin-Nanosponges (CyD-NSs)

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Cyclodextrin nanosponges (CyD-NSs) have numerous fields of application ranging from drug delivery to the purification of environmental pollutants [1]. This project focuses on the fluorescent labeling of CyD-NSs supramolecular systems for the delivery of nucleic acids into cells. These systems are composed of  $\beta$ -cyclodextrin ( $\beta$ -CyD) units linked together by carbonate bridges, and within the cavities, adamantane derivatives with positively charged functional groups are included. This forms a polycationic system capable of interacting with nucleic acids and neutralizing their positive charge to facilitate their entry into cells. The fluorescent labelling of these systems was conducted by including into some of the nanosponge cavities adamantane derivatives conjugated to TTA (thenoyltrifluoroacetone), a diketonate capable of coordinating Eu(III) and stimulating its emission at 614 nm (Fig.1). The excited-state lifetimes of Eu(III) are much longer compared to those of organic fluorescent molecules present within the cellular environment, such as aromatic residues of proteins and coenzymes. This spectroscopic characteristic allows for the tracking of these delivery systems using time-gated fluorescence microscopy, thereby eliminating the background autofluorescence of the cells.

Within the scope of this project, a synthesis strategy for a TTA-adamantane derivative was developed, and its inclusion within  $\beta$ -cyclodextrin and complexation with Eu(III) ions was studied. Inclusion studies were conducted using UV-Vis absorption spectroscopy and NMR experiments (DOSY and ROESY), while complexation studies with Eu(III) were conducted using spectrofluorimetry.



Figure 1. Fluorescent labelling of nucleic acid CyD-NSs carrier system

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# Analytical pyrolysis to characterize lignins obtained by microwave-assisted eutectic solvent extraction and fractional precipitation

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Lignin-first biomass fractionation methods using innovative strategies are now of great interest thanks to the potential valorization of lignin into materials, industrial building blocks, and lignin-based polymers. After extraction, lignin is usually isolated by precipitation with water. Fractional precipitation can be used to narrow the lignin polydispersity and increase its suitability for numerous applications [1]. Eutectic solvents (ES) are sustainable, economic, and safe solvents that can extract and solubilize lignin under mild conditions. A detailed characterization of ES-lignins is necessary to determine its suitability for different valorization strategies. Analytical pyrolysis- based techniques can provide a variety of information on ES-lignins [2], but very little information is available in the literature on this topic. In addition, no result is available on the properties of ES- lignins obtained with fractional precipitation. In this study, we extracted lignin from four different substrates (fir, oak, giant reed, Neptune grass) using ES and microwave-assisted heating. Fractional precipitation of the extracts was then performed, and the fractions were characterized by analytical pyrolysis coupled to GC-MS and evolved gas analysis by mass spectrometry. Semi- quantitative parameters were calculated from the experimental results to evaluate the efficiency of the extraction method, and the properties of the resulting lignins. This study highlights the ability of analytical pyrolysis-based techniques in providing in-depth information on isolated lignins, and provides a first report of the fractional antisolvent precipitation of ES-lignin.



Figure 1. Extraction procedure and Py-GC/MS profiles of extracted DES lignins.

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## Comparison of dynamics and structure of polymorphs by solid-state NMR: the case of Leflunomide

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Active pharmaceutical ingredients (APIs) in solid formulations are influenced by their chemical and physical properties in the solid-state, impacting crucial characteristics like solubility and stability<sup>1</sup>. Polymorphism, the ability of a compound to exist in multiple solid forms, significantly affects these properties<sup>2</sup>. Leflunomide, a Disease Modifying Antirheumatic Drug (DMARD) primarily used for rheumatoid arthritis<sup>3</sup>, exhibits two known polymorphs, Form  $\alpha$  and Form  $\beta^{4,5}$ . While their structures are confirmed<sup>4,5</sup>, dynamic insights remain unexplored. Here, we utilize solid-state Nuclear Magnetic Resonance spectroscopy (ssNMR) to characterize the structural and dynamic aspects of leflunomide polymorphs<sup>6</sup>. High-resolution spectra of various nuclei (<sup>1</sup>H, <sup>19</sup>F, <sup>13</sup>C and <sup>15</sup>N) allow for the differentiation of the two forms, confirmation of their structural properties, and provide further insights into their intermolecular environment. The measurement and analysis of spin-lattice relaxation times allowed the quantitative characterization of internal motions to be obtained in terms of activation energies and correlation times. This comprehensive study enhances our understanding of leflunomide polymorphs and underscores the utility of ssNMR in pharmaceutical research.



**Figure 1**. <sup>1</sup>H (a), <sup>19</sup>F (b), <sup>15</sup>N (c) and <sup>13</sup>C (d) MAS spectra of the two different polymorphs of the active ingredient Leflunomide,  $\alpha$  and  $\beta$  with signal assignment.

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The drug targeting and delivery (DTD) strategy employs specific ligands or molecules adept at identifying overexpressed biomarkers on the surface of cancer cells [1]. This approach enhances the selectivity of therapeutic agents and reduces adverse effects. Through this methodology, drugs, upon binding to these biomarkers, are internalized into cells and released into the cytoplasm. Peptides, as vectors for DTD, are extensively investigated and utilized due to their versatility and efficacy in overcoming barriers such as poor cell permeability, an historical challenge in the therapeutic use of metallodrugs [2,3]. The selected peptide sequences were obtained by solid- phase microwave-assisted synthesis (MW-SPPS) and analyzed through RP-UHPLC-MS. These studies were conducted at the BIOCIS Laboratory of the CY Cergy University, in Paris. New Pt(II) complexes were synthesized and characterized, by using <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectroscopy as well as elemental analysis at the Department of Chemistry and Industrial Chemistry, in Pisa. With the aim of evaluating the potential of bioconjugates as targeted anticancer agents, these metal complexes have been linked to the peptide chains. Coupling attempts were conducted in both solidphase and solution.

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## Pd(II)-indenyl complexes bearing N-heterocyclic carbene ligands do bind nucleic acids: mechanistic tests and DNA/RNA comparison

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The use of metal complexes as anticancer drugs became a priority sector of research since the discovery in 1965 of the cytotoxic properties of cis-platinum. Many compounds based on platinumand other metals have been synthesized since then in search of better-performing drugs. In this regard, palladium, a transition metal belonging to the same group as platinum, represents a promising candidate for new anti-tumour drugs [1]. Indenyl and allyl palladate complexes bearing N-heterocyclic carbene ligands were synthesised using a mechanochemical process; they showed excellent cytotoxicity towards ovarian cancer cell lines, anticancer activity in high-grade serous ovarian cancer (HGSOC), and inhibition of the antioxidant enzyme thioredoxin reductase (TrxR) [2]. Here, we studied the reactivity of one of these species, the indenyl palladium complex called IP-2 (Figure 1).

We have analysed the interaction between IP-2 and nucleic acids (natural DNA and synthetic RNA) using mainly spectrophotometric and spectrofluorimetric experiments. We will discuss the results and comment on possible selectivity, strength and binding type. These studies enable us to gain mechanistic information on the mode of action of this class of palladium metal complexes.



Figure 1 – The indenyl Pd(II) complexstudied in this work

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## Comparative study of cytotoxic auranofin analogues: impact of phosphine, arsine, and stibine ligands on the biological activity

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Since the discovery of the cytotoxic properties of auranofin, a growing interest within the bioinorganic community has emerged to develop more effective gold-based compounds that could overcome thewell-known drawbacks of Pt-based complexes.<sup>1-2</sup> The aim of this project was to conduct a comprehensive investigation into the synthesis, characterization, and reactivity of three linear gold(I) compounds [Aul(LPh3)]. The nature of the ligand was modified by moving down among some elements of group 15, i.e. phosphorus, arsenic and antimony, obtaining the three complexes [Aul(PPh3)], [Au(AsPh3)I], and [Aul(SbPh3)]. A pivotal aspect of the study involved examining the impact of these strategic ligand modifications on different coordination bond strengths and, hence, to a different reactivity of the entire molecule. The structures were solved through XRD and the reactivity behaviour towards selected biomolecules was investigated through a multi-technique approach involving NMR, HR-MS and IR. Moreover, the biological activities were comparatively analysed through classical methodologies. The reactivity against some aminoacids as a mimic for the thioredoxin reductase was investigated through NMR and IR spectroscopy. All the compounds rapidly formed stable adducts. The reactivity was also evaluated with some biologically relevant proteins (HSA, hCA I and SOD). In the case of compound [Aul(PPh<sub>3</sub>)], HSA formed stable adducts with the reactive fragment [Au(PPh3)]<sup>+</sup> while compounds [Au(AsPh3)I] and [Aul(SbPh3)] only showed protein metalation with a nude Au atom. This behaviour was perfectly in agreement with the decreasing bond strengths of Au with P, As and Sb. The evaluation of the biological activity of the complexes was carried out on A2780 S/R and SKOV-3 ovarian cancer cells, in comparison to the parent compound auranofin and cisplatin as reference. Compound [Aul(PPh3)] emerged as the most potent, with IC50 values lower than cisplatin, showing also good selectivity on cancer cells and important effect on the TrxR inhibition. The interaction studies provided insights into the potential mechanisms of action, shedding light on the specific interactions that underlie the complexes' cytotoxic effects. Despite no synergistic effects were highlighted, [Aul(PPh3)] stood out as a potential anticancer molecule.



**Figure 1**. The three complexes [Aul(LPh<sub>3</sub>)] synthesized and analysed in this project.

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## **3D Printed Surgical Anti-Adhesive Chitosan Membranes Incorporating Eugenol-Ioaded Polymeric Nanoparticles**

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Postoperative adhesions have a considerable impact on human health and are a frequently encountered problem in patients after surgery. Clinical complications can range from pain to more delicate situations in which further surgery is required to remove the scar tissue formed. To facilitate tissue separation following surgery, several techniques have been developed in recent decades that rely on the use of biocompatible, in some cases biodegradable, polymeric membranes implanted at the level of the surgical incision to prevent tissue adhesion and ensure clean margins<sup>1</sup>.

In this project, chitosan was used to fabricate polymeric membranes loaded with poly(lactic-*co*glycolic acid) (PLGA) nanoparticles (NPs) encapsulating eugenol, an active ingredient known for its antioxidant, antimicrobial, antiviral, antifungal, and anti-inflammatory activities. In particular, its bioactivity can be exploited for the prevention and treatment of numerous post-surgical complications (Fig. 1). NPs were prepared by nanoprecipitation of an acetone solution of PLGA and eugenol into an aqueous phase, using chitosan as a surfactant, given its amphiphilic nature. The membranes were fabricated using Computer-Aided Wet-Spinning (CAWS), an additive manufacturing technique based on the extrusion and layer-upon-layer deposition of a polymeric solution into a coagulation bath<sup>2</sup>. *In vitro* biological characterization studies demonstrated the cytocompatibility of the developed NPs and hydrogels using the murine fibroblast cell line Balb/3T3 *clone* A31. Nevertheless, cells did not adhere to the polymeric surface, proving the anti-adhesive properties of the developed membranes.



Figure 1. Schematic representation of chitosan exploitation to develop surgical anti-adhesive membranes

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## Iodine as Propellant in Electric Thrusters: Development of a FeedingSystem and Hollow Cathode

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In electric propulsion for space applications, the exploration of alternative propellants has gained significant importance due to limited resource availability and economic considerations.

This challenge has led researchers to investigate several possible candidates, with iodine emerging as a promising choice [1] due to its favourable chemical and physical properties for propulsive performance [2], as well its lower cost and simpler storage conditions compared to xenon [3]. However, iodine corrosive nature presents a disadvantage, as it reacts highly with many common materials used in the aerospace field [4] [5], exposing materials to harsh conditions. The development of an iodine hollow cathode derives from the lack of positive results in long-term tests with this propellant. The designed cathode is capable of sustaining a discharge current in the range of 1-3 A to an external anode. To study and investigate the interaction between iodine and the insert after testing, the cathode has an LaB6 emitter composed of two halves. The overall cathode architecture is made of graphite tube and keeper, ceramic insulators, and an in-house heater, made of refractory metal wire wrapped. This cathode is fueled by an innovative iodine feeding system that stores, sublimates, and controls the mass flow rate of iodine with reduced heating power consumption. The prototype includes a sublimation assembly, where the temperature is used to regulate the pressure within the iodine tank, a normally closed ON-OFF valve, and a thermal throttle to perform the fine control of the mass flow rate. Prior to conducting tests with iodine, the cathode was tested with argon to verify the proper functioning of the system. The iodine tests can be subdivided into different phases: short (<1h) and long (>6h) functional tests for initial material characterization, an implementation of the design and endurance tests. After tests, the components undergo chemical analysis techniques, such as SEM-EDS to characterize cathode materials. The objective of this research is to demonstrate the effectiveness of using alternative propellants in electric propulsion systems, particularly in hollow cathodes, and to identify potential issues revealed during the tests, such as material selection and functional characterization of the cathode.

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### Filter-aided sample preparation protocol to investigate urinary proteome in heart failure patients

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Heart failure (HF) poses a substantial public health and socioeconomic burden<sup>1</sup>. Its multifaceted nature renders it difficult to identify specific features contributing to the syndrome's pathophysiology through a single biomarker analysis. While blood is commonly employed in biomarker discovery for cardiovascular diseases (CVD)<sup>2</sup>, urine presents a feasible alternative due to its ease of collection. Proteins secreted from multiple organs during certain pathological conditions can enter the bloodstream and subsequently be filtered across the kidneys into the urine<sup>3</sup>. Therefore, a comprehensive urinary proteomics analysis may elucidate changes associated with systemic diseases- underlying kidney diseases and various other systemic disorders, including CVD. However, most of these studies have focused on identifying the urinary proteomics.

In this work, urine samples (n=71) were collected during a follow-up visit from patients suffering from HF (n=56), and patients at risk of developing HF due to comorbidities (i.e., hypertension, obesity, diabetes (n=15)) were considered as controls. A total of 546 urinary proteins were identified in both HF and control groups using filter-aided sample preparation protocol (FASP) followed by nanoLC-MS/MS analysis and label-free quantification. Interestingly, proteins originating from filtered plasma were also identified, including serum amyloid P-component, beta-2- microglobulin, insulin-like growth factor-binding proteins, and complement-related proteins. The results of our study revealed significant differences in several proteins between individuals with HF and control, reflecting proteomic changes induced by the pathological state. The most prominent alteration identified was the dysregulation in complement and coagulation cascades. An abnormal complement activation has been shown to exacerbate systemic inflammation and tissue damage in HF patients. The KEGG pathway analysis revealed 54 distinct pathways exhibiting differential expression in HF. The complement and lysosomal pathways were the most significantly upregulated in HF patients, emphasizing the involvement of cellular processes and the immune system. Additionally, most upregulated pathways were related to metabolism, including carbon metabolism, amino acid biosynthesis, and glycolysis.

My results highlighted the potential of monitoring urinary proteomes in HF patients. Furthermore, future applications of urinary HF proteomics could be pivotal in elucidating the pathophysiology of HF, including its subtypes (HFpEF and HFrEF), in a non-invasive manner.

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### Quantum-Cutting Ytterbium-Doped Perovskite: synthesis, characterization, and prospects in solar energy conversion technologies

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Metal Halide Perovskites are currently under the spotlight as some of the most promising materials of the 21st century, due to the ease with which they can be synthesized as well as their tunable optical properties. Coupling CsPbX<sub>3</sub> (X = Br, Cl or Br/Cl) to lanthanides is a promising way to realize UV-to-NIR downconversion, which paves the way for many applications, from optoelectronics to photovoltaics.<sup>1,2</sup>

In this contribution, we report the study of Yb<sup>3+</sup>: CsPbCl<sub>3</sub> cubic nanocrystals obtained by hot injection synthesis, characterized by optical spectroscopy, TEM, XRD, and compared to undoped CsPbX<sub>3</sub> (X = Br, Cl and Br/Cl).<sup>1,3</sup> Ytterbium ions occupy some of the lead reticular positions: these punctual defects and lead vacancies modify the band edge structure of the hosting lattice, introducing electronic states within the band gap. The peculiarity of Yb<sup>3+</sup> doping is the effect termed *quantum cutting*, in which photons absorbed at the perovskite bandgap are re-emitted through the f-ftransitions of Yb<sup>3+</sup>, leading to the emission of two NIR photons per absorbed photon. Driven by punctual defects, this outstanding process can exhibit luminescence yields reaching over 190% in the near IR. (Figure 1).



**Figure 1**. Absorption (blue) and emission (red) spectra of Yb<sup>3+</sup>: CsPbCl<sub>3</sub>. The inset depicts the proposed quantum-cutting mechanism. [1]

As the NIR window is the spectral region in which silicon-based photovoltaic modules show high efficiency, embedding Yb<sup>3+</sup>: CsPbCl<sub>3</sub> NCs in PMMA thin films, allowed us to study their optical characteristics inside a polymeric matrix, which is useful for a further application in fully transparent solar concentrators (LSCs).

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## Exploring Intramolecular Proton Transfer Dynamics with Machine Learning Multiscale Simulations

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Proton transfer has a pivotal role in numerous processes occurring at both ground and excitedstatelevels. Our focus lies on the 3-hydroxyflavone molecule, a fluorescent probe employed in the study of membranes and intermembrane proteins<sup>1</sup>. This molecule serves as a model system for studying excited-state intramolecular proton transfer (ESIPT). Such process enables the interconversion between the normal (N) and the tautomeric (T) form (Figure 1), each exhibiting distinct fluorescenceproperties. Experimental investigations have revealed that this ESIPT reaction is highly sensitive to the environment conditions: in the presence of hydrogen-bond forming solvents, fluorescence emanates from both N and T forms, whereas in non-hydrogen bond forming solvents, only the T formexhibits fluorescence<sup>2</sup>.

Here we propose a machine-learning (ML) based approach to study the dynamics of these systemson the ground and excited-state potential energy surfaces. Our ML model is designed to predict energies and forces within a quantum mechanics/molecular mechanics (QM/MM) electrostatic embedding framework. We coupled this model with a molecular dynamics code to investigate the ESIPT reaction in two different solvents. Since this algorithm is considerably fast, we were able to investigate both the fast and slow components of ESIPT. Our ML/MM simulations accurately distinguish between hydrogen-bonding and non-hydrogen-bonding solvents, effectively replicating the environmental effects on proton transfer dynamics in agreement with both *ab-initio* simulations<sup>3</sup> and experimental data<sup>4</sup>.



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## Implementation of Coupled Cluster analytical gradients based on the Cholesky decomposition of ERIs

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In recent years, rank-reducing techniques have seen a surge of interest by the quantumchemistry 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 (ERIs) tensor<sup>1</sup>, 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, makingit possible to manipulate it without recomputing or reading the integrals from disk, but also affords astrict control over the accuracy of their representation, since the approximation error is bound to belower 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<sup>2-4</sup>. We present an efficient and parallelized implementation of CD, using a two-step algorithm<sup>5</sup> that can fully exploit Abelian point- group symmetry<sup>6</sup> 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 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 and CCSD(T) levels. The capabilities of our new implementation are tested on a range of systems, for which we compute the energies and molecular structures.

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## Natural materials Development from Collagen-based Wastes: ArtDECOW

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The ARTDECOW project envisages the molecular characterization of leather waste as a preliminary step to support the development of novel eco-friendly collagen extraction methods based on the use of green solvents - deep eutectic solvents / natural deep eutectic solvents (DES/NADES) in combination with microwave energy irradiation. This approach would allow us the exploitation of collagen, providing molecular guidelines for the engineering of versatile, highly performing new collagen-based biomaterials (CBBM).

Several crust leather samples treated in tannery with different tanning agents were analysed by ATR-FTIR and by evolved gas analysis coupled with mass spectrometry (EGA-MS). The leather was treated with the following tanning agents: chromium, zeolite, triazine salt (F90), vegetal, oxazolidine, phosphonium salt and synthetic phenolic.

Fourier transform infrared spectroscopy (FT-IR) is a well-established technique to analyse the secondary structure of polypeptides and proteins<sup>1</sup> and it can be a useful approach to investigate the leather collagen structure at the molecular level. The spectrum of collagen has four characteristic IR absorption bands, namely amide A, B, I and II<sup>2</sup>. Each leather sample was analysed in triplicate and the spectra were processed through principal component analysis (PCA) in the 1800-900 cm<sup>-1</sup> region (fingerprint region) in order to verify if there are characteristic bands which can be used to identify the tanning process. Moreover, the amide I band was subject to peak fitting, to investigate the secondary structure of collagen.

EGA-MS gives information on the thermal stability of the sample but also on the chemical composition of the organic materials in a sample, enabling for some degree of estimation of the molecular structure of the material. This technique can therefore be used to evaluate the impact of the tanning agents on the thermal stability of collagen, and to evaluate the degree of crosslinking <sup>3</sup>. EGA-MS allowed us to evidence as metal-free tanned leather presents more complex thermograms characterized by evolved compounds released in a wider range of temperature when



compared to chromium tanned leather.

The poster presents the results obtained with the combined use of FTIR and EGA-MS to elucidate the chemical structure of the leather samples tanned with different agents.

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# Screening of oleaginous yeasts for the valorization of sewage scum polysaccharides through the production of Single Cell Oil

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Among renewable energy sources, biodiesel is one of the most promising bio-fuels in the transportation sector. Biodiesel is composed of long-chain alkyl esters of fatty acids (FAMEs), which can be obtained from various renewable raw materials, mainly from oilseed crops. Recently, microbial lipids, namely single cell oils (SCOs), have received great interest as feedstocks for biodiesel production, due to the advantages given by their use over the vegetable oils, including the overcoming of the concerns about the competition with the food supply chain [1] and the seasonality of crops. Among the oleaginous microorganisms, yeasts are the most promising lipid- accumulating microbes due to their ability of growing faster, independently from environmental conditions, and utilizing a wide range of carbon sources. Moreover, the economic and ecological feasibility of the veast lipids production process can be enhanced by using low-cost raw materials [2], for examples sewage scum (SS), a special waste obtained from urban wastewater treatment plants. SS is composed of a polysaccharide fraction [3], which can be used as potential source of fermentable sugars for the bioaccumulation of lipids, and a lipidic fraction, which can be directly used for transesterification reaction to produce FAMEs. The aim of this work was to identify an efficient commercial oleaginous yeast strain able to utilize glucose and xylose contained into the SS enzymatic hydrolysate to produce SCOs. The species Cryptococcus curvatus, Rhodosporidium toruloides and Trichosporon oleaginosus were compared in terms of microbial growth and lipid accumulation and productivity. Considering the estimated concentration of the main monosaccharides present in the undetoxified SS hydrolysate, the screening of the three different oleaginous yeasts was carried out using an equivalent synthetic medium containing glucose and xylose as carbon source. In addition, optimal C/N ratio, pH, type and concentration of micronutrients were formulated for each yeast to ensure its best performance. After fermentation, standard acidic cell lysis and liquid-to-liquid extraction of SCO were carried out. Triglycerides were subjected to hydrolysis and esterification reactions, yielding FAMEs, whose profile was characterized. Finally, the main outputs of the bioprocess were calculated for the three selected yeasts, such as cellular lipid content and productivity. The results indicated T. oleaginosus as the best oleaginous yeast, due to its high lipid cell content (55 wt%) and productivity (71 (mg/L)/h): this species will be subsequently tested on the real hydrolysate obtained from SS.

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## Tuning of the CO<sub>2</sub> adsorption mechanism in flexible F4\_MIL-140A(Ce) by ligand engineering

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Flexibility in crystalline solid-state porous systems represents an intriguing feature exhibited only by a limited class of materials. In metal-organic frameworks (MOFs), the backbone's ability to respond dynamically to external stimuli (i.e., temperature, pressure, gas adsorption) is a remarkable aspect that enables the engineering of cutting-edge materials in the field of gas storage and separation.<sup>1</sup> Recently, some of us have discovered a flexible microporous MOF named F4\_MIL-140A(Ce), made of 1D inorganic units of cerium-oxide connected by tetrafluorinated terephthalic acid as organic linker. This MOF exhibits a non-hysteretic CO<sub>2</sub> step-shaped adsorption isotherm below 1 bar attributed to a cooperative CO<sub>2</sub> adsorption, involving a concerted linker rotation upon CO<sub>2</sub> adsorption. This behaviour leads to an outstanding CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub> selectivity making this material appealing for real-life application in post-combustion capture and biogas upgrading.<sup>2</sup>

In our effort to address the role played by the fluorine atoms on the CO<sub>2</sub>-induced concerted ring rotation in F4\_MIL-140A(Ce), we examined the framework's response to CO<sub>2</sub> adsorption by progressively removing fluorine atoms from the linker. This was achieved by a ligand engineering approach targeting the MIL-140A architecture, employing terephthalic acid with different fluorination degree. Therefore, we synthesised a

series of isoreticular Fx MIL-140A(Ce), by both an



Figure 1. Ligand engineering in F4\_MIL-140A(Ce)

acetonitrile solvothermal procedure and a milder methanol/water mixed solvent approach. Powder X-Ray diffraction revealed that highly crystalline  $Fx_MIL-140A(Ce)$  can be obtained under solvothermal conditions, whereas the milder synthetic route led to less crystalline materials, often favouring the formation of the competitive UiO-66 phase with certain linkers. To complement diffraction data with short-range structural insights, we employed multinuclear solid-state nuclear magnetic resonance spectroscopy, while in situ infrared spectroscopy using CO as a Lewis basic probe was used to investigate the Ce Lewis acidic nature, tuned by the different electron withdrawing character of the linkers. By measuring  $CO_2$  adsorption isotherms, no  $CO_2$  step-shaped adsorption isotherms were observed upon removing fluorine atoms from the linker. This suggests that the  $CO_2$  induced ring rotation is highly sensitive to the fluorination degree of the linker and even the removal of one fluorine atom is enough to switch off the cooperative rotation mechanism. We believe that the knowledge resulting from this study might help to guide the design of advanced materials sharing the same operating principle and to rationalize their adsorption applications.

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## Microplastics in agricultural soils and underground water

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Plastic in all forms is ubiquitous in daily life because of the durability and the low costs, although the high production of this products leads, coupled with a low recycling rate, to the production of tons of plastic waste that end up in landfills and in the environment.<sup>[1]</sup> The use of plastic mulch in agriculture has increased in recent decades but, despite the benefits of this technique, it largely contributes to the pollution of agricultural soils.<sup>[2]</sup> The purpose of the bilateral Italy-China project ENCOMPASS is to develop appropriate sampling and analytical procedures to identify and quantify microplastics (MPs, fragments smaller than 1 mm<sup>[3]</sup>) in agricultural soils and underground waters collected in an intensely cultivated area south of the Massaciuccoli Lake (LU). To do so two different procedures will be applied:

- Mass-based and polymer-specific quantification of the MPs by the PISA procedure [4]
- Particle-based counting of individual MPs separated by the environmental matrix by flotation using high density salt solutions (NaCl or NaBr, and sodium polytungstate) followed by further purification and µ-FTIR analysis



Figure 1. PISA procedure workflow <sup>[4]</sup>

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## Emerging pollutants in seawater: the interaction between the brown alga *Ascophyllum Nodosum* and four antibiotics

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Since the discovery of penicillin in 1929, antibiotics had a crucial role in the evolution of medicine and agriculture. Thanks to them, life conditions became better and life expectancy longer. However, the large use of antibiotics caused their increased concentration in the environment, especially in water. Antibiotics misuse, in addition to antibiotic resistance, has the major consequence of pollution <sup>[1],[2]</sup>. These long-lasting molecules are difficult to remove and different kind of techniques have been studied for their removal, including physical, chemical, and biological methods. Biological methods are promising because they are cheaper than the others and more eco-friendly thanks to the fact that they use bio-organisms already living in the polluted area. Algae are the best choice for this role because they are ecological indicators and bio accumulators. Also, algae have a short growth cycle, a fast stress-response mechanism and, most importantly, don't need additional energy for removing pollutants. Although the firsts experiments about removing pollutants by algae were conducted in the '50s, only recently the interest in these organisms has widely increased <sup>[3]</sup>.

In this study, we tested the possible interaction between a seawater brown alga, the Ascophyllum Nodosum (Figure 1), and four different antibiotics: Chloramphenicol, Dimetridazole, Metronidazole and Nitrofurantoin. In the first phase of studies presented here (a future one will be endowed with GC-MS analyses), the experimental data were obtained by UV-Vis spectrophotometry, focusing on both active and passive interactions.



Figure 1. a) fresh Ascophyllum Nodosum b) UV-Vis spectra of the water of the aquarium with Nitrofurantoin and fresh algae at different days (from 1st day to 8th day – from darker to lighter colour)

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### Assessment of in-situ Conservation Measures on Archaeological Wooden Artifacts: Insights from the StAr JPI-CH Project

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This work explores the importance of in-situ conservation for archaeological artifacts, a method endorsed by UNESCO for its efficacy in preserving cultural heritage artefacts<sup>1</sup>. The European StAr project (Development of Storage and Assessment methods suited for organic Archaeological artefacts) focuses on preserving organic archaeological materials, such as wood and leather, in a wet state especially in the period immediately following the excavation- a period noted for its heightened complexity and difficulty. The project aims to mitigate the risk of cracks, structural collapses due to degradation, and the loss of crucial information pertaining to the artifact. The Biskupin site in Poland serves as an example of *in-situ* conservation, where wooden materials are preserved underwater or buried.

Chemical characterization by Py-GC/MS, EGA-MS, and X-ray diffraction (XRD), have been used to evaluate changes in the composition of wood, alteration in hemicellulose and lignin fractions, as well as alterations in the crystallinity of cellulose in the artefacts. The samples were collected under two different circumstances. The first excavation campaign, spanning 2003-2008, revealed well preserved polysaccharides and lignin in most analysed fragments. However, some of them showed an unusually high polysaccharide content, similar to fresh, undegraded wood. Additionally, these samples also show a low crystallinity index, when compared to the reference woods. This apparent discrepancy may derive from the specific environmental conditions in which the finds were found. The subsequent campaign in 2022, resulted in significant degradation of the polysaccharide component in most fragments, with percentages below 15% (in sound wood 70%). Observations included depolymerization and/or oxidation of hemicellulose, along with lignin oxidation and side chain lignin alteration. Pine wood samples exhibited slightly better preservation compared to other wooden species studied .

The findings point to substantial oxidative degradation suffered by the wooden artifacts following the second campaign. Indeed, fragments collected during the latter campaign exhibited significantlyhigher levels of oxidation than those from the former. The wooden finds preserved *insitu* are susceptible to altering their conservation status due to several factors: i) repeated extractions and re-immersions due to the monitoring activities; ii) ongoing climate change characterized by prolonged periods of drought, and iii) agricultural activity, particularly the use of chemical fertilizers and herbicides.

Consequently, fluctuations in water levels and contamination with nitrogen and phosphorus-based products pose collective threats to the preservation level of the archaeological wooden artifacts. Despite advanced degradation, the Biskupin fragments are only partially oxidized. Musealization of the artifacts would still be feasible using consolidating materials. However, it would be advisable to suspend extraction and re-immersion operations, which can facilitate degradation and oxidation. Alternatively, developing remote monitoring systems based on sensors could assess environmental conditions and artifact status continuously without invasive interventions.

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## Cruising Towards Sustainability: Unraveling the Fate of Biodegradable Plastics in Real Marine Environments

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The proliferation of plastic items has revolutionized entire sectors of industry and society but has also triggered a serious global environmental problem [1]. Currently, there is a growing interest in the use of biodegradable plastics as potential solutions. However, crucial questions remain open regarding their actual degradability, impact on biogeochemical cycles and ecosystems, and effects of biodegradation products. This interest represents a significant step towards environmental sustainability, and requires further in-depth research [2]. The described study aimed to evaluate the degradation/aging processes of biodegradable plastics in a real marine environment, comparing them with conventional plastics. Granules of different polyolefins (HDPE, PP) and biodegradable polyesters (PLA, PBAT) were examined, after a continuous immersion in the sea for specific periods (Figure 1). Samples were periodically collected after 19 and 24 months of immersion. This was the first experiment of this type carried out in the Mediterranean Sea, as reported by De Monte et al. [3]. Analyses, conducted through various analytical techniques including SEM, ATR-FTIR, DSC, TGA, EGA-MS, Py-GC-MS, and GPC, provided a deeper understanding of the effects of the physicalchemical parameters measured in the sea and/or the temperature of the degradation/aging phenomena, and stability of the plastic granules. Significantly, the studied biodegradable plastics showed signs of degradation/aging primarily on the surface of the granules, highlighting the fact that they require a considerable amount of time to be completely degraded, unlike the faster degradation observed in industrial composting conditions. On the other hand, HDPE and PP granules showed few significant variations, except for some signs of mechanical degradation on the surface. Further research is needed to assess the environmental impact of degradation residues released into the marine environment, in order to contribute to a better understanding and management of plastic waste.



**Figure 1**. a) Geographical location of the station used to submerge the samples. b) Timeline depicting the periods when the samples were collected (the collecting time of the analyzed samples is highlighted).

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## Exploring curing kinetic, thermodynamic and molecular features of industrial oil paint formulations

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Metal-based driers play a key role in the curing of modern oil paints, as they reduce the drying time of oils to an acceptable time. Driers performances have been mainly studied in simplified systems [1-2] and on a short-term time scale by investigating the sole kinetic of autoxidation. However, long-term effects of driers on the molecular features of the polymeric fraction and the mechanical properties of the final film are also important [3,4]. The present work aims to study, for the first time, the effect of selected metal-based driers on a realistic oil paint formulation in terms of drying time, curing kinetic and thermodynamic, molecular features and mechanical properties of the final paint film. A methodological approach implemented in our previous research articles was applied [5,6] and further expanded. Six realistic oil paints with the same composition in terms of pigment, oil, and additives (beeswax and calcium carbonate) and different metal-based driers were produced and supplied by Golden Artist Colors, Inc. Driers based on calcium, zirconium, cobalt, a combination of cobalt and calcium and a combination of cobalt and manganese were selected for examination. The curing process was monitored for different ageing times and the features of the final paint layers were analysed after 3 years of natural ageing.

The main effect of the investigated driers was observed on the curing kinetic. Ca and Zr based driers only slightly reduce the drying time respect to the drier-free paint. Co containing paints dry extremely much faster with respect to other formulations. The combination of Co and Ca further reduces the drying time. The addition of Mn to Co increases the drying time with respect to Co alone. A different mechanism of the secondary driers (Ca and Mn) in combination with Co were highlighted. Ca further catalyses peroxide formation and decomposition, differently Mn catalyses only the peroxide formation step.

The use of driers in paint formulations does not appear to significantly alter the molecular features of the paint film, which are primarily determined by the composition of the oil and pigment. Although driers have an impact on curing kinetics, their effects primarily impact the short-term behaviour of the paints. The study of the long-term effects on the chemical composition and physical properties of the paint layers appears very limited. Thanks to a vast array of techniques, it was possible to detect a slight increase in the cross-linked density of the formulations with Co, Co/Ca and Co/Mn driers. An increased polarity of the surface was found for the Co-containing formulations. All driers, including those classified as secondary driers (Ca and Zr alone), slightly increase stiffness, ultimate stress and toughness of paint layers.

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## Oxaliplatin-based Pt(IV) complexes functionalised with monohaloacetate ligands as potential anticancer prodrugs

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Pt(IV) complexes are considered valuable prodrugs due to their electronic and structural properties. They show greater stability and higher inertness towards ligand substitution compared to Pt(II) complexes, reducing the risk of side effects. Pt(IV) complexes are activated through reduction, releasing the axial ligands and the corresponding active Pt(II) species. Activation preferentially occurs in cancer cells, where the environment is more reducing, ensuring greater selectivity. Additionally, the ability to bind bioactive molecules as axial ligands enables Pt(IV) compounds to show dual action [1].

In light of this, six oxaliplatin-based Pt(IV) complexes mono- and di-functionalised with monohaloacetate (MAA) ligands in axial position were successfully synthesized. Monofluoroacetate (MFA) and monochloroacetate (MCA) were selected for their ability to target mitochondria inhibiting the Krebs cycle, while monobromoacetate (MBA) was chosen for its ability to induce double-strand DNA breaks [2,3]. To better understand the potential behaviour of the complexes in a physiological environment, some chemical properties such as solubility and stability in aqueous solution, lipophilicity, and reduction kinetics, were primarily evaluated using <sup>1</sup>H NMR and UV-Vis spectroscopy. The complexes functionalised with MFA show good chemical properties and, in addition, a significant increase in cytotoxic activity under hypoxic conditions when incubated in a concentration of 10  $\mu$ M. This makes them suitable as a prodrug and grants them potential selectivity towards cancer cells.



Figure 1. Molecular structures of di-MFA (a) and mono-MFA.

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## Exploring Trikafta Therapy Effects on Exhaled Breath Molecules by Comprehensive GCxGC-Q-TOF

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Background: The introduction of Trikafta therapy has significantly improved the quality of life for individuals affected by cystic fibrosis (FDA approved in late 2019). [1] We investigated the possible effects of Trikafta therapy on exhaled breath chemical composition which may allow to obtain clinically relevant information about disease and treatment progression directly from the breath samples.

Methods: Mixed breath samples were collected at the University Children's Hospital Zurich from 19 patients (12-18 years) in 2L handmade Nalophan bags. An aliquot (250 mL) of breath was transferred at 50 mL/min into sorbent tubes (packed with 250 mg of Tenax GR 60/80 mesh) [2] and then analysed with thermal desorption unit (TD) coupled with a comprehensive two-dimensional gas chromatography (GCxGC) connected to a quadrupole time-of-flight mass spectrometer (Q-TOF). [3]

Results: We could tentatively identify 166 molecules which were significantly increased for the breath vs. room samples. We investigated the differences in breath chemical composition during Trikafta therapy (ANOVA with post-hoc t-test with p-value < 0.01) which resulted in 25 significantly different compounds (12 endogenous, 3 unknowns, 10 anthropogenic). The endogenous breath volatiles were mainly related to energy metabolism and often lipid peroxidation (Figure 1).

Conclusion: We can report significant differences in exhaled breath molecules after Trikafta therapy.





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### Synthesis of multicomponent fluorinated MOFs as CO<sub>2</sub> adsorbents

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The Paris Agreement has long-term goal of limiting the temperature increase to 2 °C above preindustrial levels, and net-zero emissions in the second half of this century. The world is seeking deep reductions in emissions, for this the development of efficient and cost-effective CO2 separation technologies is imperative.<sup>[1]</sup> In this context, an appealing candidate for a real life application in carbon capture is F4\_MIL-140A(Ce), an ultramicroporous metal-organic framework (MOF) based on Ce(IV) and tetrafluoroterephthalic acid as organic linker. This system exhibits a non-hysteretic step-shaped CO2 adsorption isotherm below 1 bar, due to a phase transition occurring upon CO2 adsorption, whose origin is attributed to a cooperative CO2 mechanism that involves the concerted rotation of fluorinated aromatic rings.<sup>[2],[3]</sup> Isoreticular MOFs based on linkers with lower fluorination degree and Zr as the metal do not display this cooperative mechanism, suggesting that there is a peculiar synergy between metal and linker in F4\_MIL-140A(Ce).

In this work, we investigated the influence of the fluorination of ligands and the nature of the metal on the step-shaped adsorption isotherm of mixed-component analogues of F4\_MIL-140A(Ce)(Figure 1). To this end, we report new synthetic methods to obtain novel mixed-linker F4:Fx\_MIL- 140A(Ce) (where x = 3, 2, 1, 0) and mixed-metal F4\_MIL\_140A(Ce/Zr) MOFs. Mixed-linker MOFs were obtained by means of both methanol/water mixed solvent and pure water solvent approach: the latter allowed cleaner, phase-pure and higher crystalline materials to be obtained. Many syntheticand post-synthetic approaches were tried to obtain mixed-metal F4\_MIL\_140A(Ce/Zr) MOFs, the most promising being an acetonitrile-based solvothermal synthesis, that is still being optimized. EachMOF was characterized by Powder X-Ray Diffraction, the F4/Fx ligand ratio was determined by <sup>1</sup>H and <sup>19</sup>F liquid-state nuclear magnetic resonance upon MOF digestion, while the Ce/Zr amount in mixed-metal MOFs was confirmed by Energy-dispersive X-ray spectroscopy. CO2 adsorption experiments are planned to investigate the existence of a cooperative mechanism in mixed-component MOFs.



Figure 1. Ligands and metals used in this work

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## Use of Alcohol Dehydrogenases as efficient biocatalysts for the enantioselective reduction of prochiral ketones

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Nowadays, more than 50% of drugs on the market are chiral molecules. Therefore, the ability to obtain pure enantiomers with innovative strategies has become crucial for pharmaceutical industry.<sup>[1]</sup> In this context, biocatalysis is recognized as a mature and widely used technology for asymmetric synthesis, based on the exquisite chemo-, regio- and enantioselectivity of enzymes.

Chiral alcohols are key intermediates of multiple Active Pharmaceutical Ingredients (APIs) of drug candidates and biocatalytic methods for their syntyhesis have attracted special attention. Among the different classes of enzymes, alcohol dehydrogenases (ADHs) have a strong synthetic potential enabling the enantioselective reduction of prochiral ketones to the corresponding alcohol on preparative scale under mild reaction conditions .<sup>[2]</sup>

In this work, three commercially available ADHs enzymes were immobilized on different silicabased supports and used in the reduction of acetophenone derivatives **1a-c** (**Figure 1**).<sup>[3]</sup> The carriers were chosen for their cost-effectiveness, versatility, and thermo-mechanical stability under different reaction conditions.<sup>[4]</sup>





The activity and selectivity of the immobilized samples were compared to those of the corresponding soluble enzymes. In most cases, the chiral alcohols **2a-c** were obtained with good to high conversions and excellent enantioselectivities (ee>99%). The best performing biocatalyst was employed for the optimization of the synthesis of an important intermediate and for the reusability studies in a flow system. Five consecutive reaction cycles were run in predominantly organic medium at 30°C and led to the complete conversion of the substrate and the recovery of the enantiopure alcohol *via* simple solvent evaporation. These results may be of practical interest for the development of a sustainable approach for a large scale production of chiral alcohols.

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## Structure, dynamics and water status in a polyketone-based anion exchange membrane for electrochemical applications: a solid state NMR study

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In recent years, research has focused on developing new strategies and technologies to produce greener and more sustainable materials and energy resources, driven by the climate and energy crisis. Among these, green hydrogen represents one of the most interesting materials, with applications in the domestic, industrial and automotive sectors. One promising technology for producing green hydrogen relies on the electrolysis of water using anion exchange membranes (AEMs).<sup>[1]</sup> AEM are typically based on polymer backbones with charged groups, whose chemical structure can be adjusted to enhance and optimize the membrane's performance, efficiency, and characteristics. The final properties of the membrane are also closely linked to the structural and dynamic properties of the polymer network at both the molecular and supramolecular levels. Another crucial aspect is the state of water and its degree of interaction with the polymer network, which determines the formation of the so-called ionic channels. Investigating these properties is essential to understand the mechanism of ion transport within these membranes.

In the present work, we characterized the structural and dynamic properties of AEMs for water electrolyzers based on low molecular weight polyketone (PK) by means of solid state NMR spectroscopy (SSNMR). The membranes were functionalized through a Paal-Knorr reaction with a diamine, which was quaternized with alkyliodides. Dialkyliodides were employed as crosslinking agents. Various (di)alkyliodides, including (1,4-di)iodobutane, were studied to explore their effect on the properties of the AEMs. Different alkyliodide/dialkyliodide ratios were also probed.<sup>[2], [3]</sup> <sup>1</sup>H and <sup>13</sup>C high-resolution SSNMR spectra provided information on the structural properties of the polymer network and the degree of functionalization. Variable temperature <sup>1</sup>H T<sub>1</sub> relaxation times revealed insights into the dynamics of the polymer chains and functional groups, as well as sample homogeneity on the nanometer scale. Additionally, <sup>2</sup>H spectra of water in membranes hydrated with deuterium oxide were analyzed to study water dynamics and interaction with the polymer matrix, varying both the membrane composition and water content.

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# First-principles simulations of CP29 unveil the effect of mutations on light harvesting

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Natural light harvesting is exceptionally efficient thanks to the optimal arrangement of pigments within light-harvesting complexes (LHCs). To understand the design principles underlying energy transport in LHCs, ultrafast spectroscopy is often complemented by mutational studies that introduce perturbations to the excitonic structure of the natural complexes. However, such studies may fall short of identifying all excitation energy transfer (EET) pathways and their change upon mutation.

Here we show that a synergistic combination of first-principles calculations [1] and ultrafast spectroscopy can give unprecedented insight into the EET pathways occurring within LHCs. We measure the transient absorption spectra of the minor CP29 complex of plants [2] and of two mutants [3], systematically mapping the kinetic components seen in experiments to the simulated exciton dynamics. Our combined strategy shows that EET in CP29 is surprisingly robust to the changes in the exciton states induced by mutations, explaining the versatility of plant LHCs.



Figure 1. CP29 and mutants. (a) Representation of the Chls embedded in the protein scaffold. (b) Calculated EET rates.

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# Thermoresponsive unimer micelles of amphiphilic fluorinated copolymers for encapsulation of hydrophobic drugs

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The concept of single-chain nanoparticles (SCNPs) has recently emerged as a new class of functional polymeric nanomaterials from the idea of replicating the folded structure of natural macromolecules, that can provide complex functions related to their three-dimensional arrangement.<sup>[1]</sup> Within this vast field fall the so-called unimer micelles, obtained from the spontaneous folding via solvophobic interactions of a single amphiphilic polymer chain when dissolved in a selective solvent, typically water.<sup>[2,3]</sup> Amphiphilic copolymers were prepared through of poly(ethylene glycol) methyl ether methacrylate (PEGMA) copolymerization and perfluorohexylethyl acrylate (FA) by ARGET-ATRP, allowing control over structural parameters of final product. The ability of copolymers to self-assemble in solution was investigated through dynamic light scattering (DLS) and DOSY NMR technique, highlighting the presence of small nanoassemblies with hydrodynamic diameter  $D_h = 7 - 15$  nm. DLS measurement carried out above a critical temperature, identified as the cloud point temperature ( $T_{Cp}$ ) by light transmittance measurements, showed multi-chain assemblies with much larger D<sub>h</sub>, showing a LCST-type thermoresponsive transition fully and sharply reversible. The potential use of unimer micelles for the encapsulation of highly hydrophobic drug, such as Combretastatin A-4 (CA-4), an anticancer drug, was investigated. The drug was encapsulated with a very high efficiency (91–95%) with a polymer/drug ratio of 19/1 and released from the micelles with a slower rate in comparison to the free system. Cytotoxicity tests demonstrated effectiveness against two different cell lines, similar to non-encapsulated CA-4. Additionally, covalent attachment of a fluorescent comonomer allowed the copolymer to be used as fluorescent probes, enabling visualization of cellular internalization in a human pancreatic cell line.

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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 researchersled by Gotch and Sargent introduced a parameter with the objective of assessing the adequacy of dialysis: Kt/V<sup>1</sup>. 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 indialysate 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 the indoalinine derivative 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 sensor fabricated using different amount of enzyme

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### Evaluating the impact of atomic oxygen surface cleaning on oil paint

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In the conservation of cultural heritage surface, cleaning constitutes one of the most critical and frequently performed procedures. Historical approaches include "dry" methods, involving mechanical removal of dirt, and "wet" methods, which use water and solvents to eliminate contaminants. However, solvents can be toxic, surfaces can be sensitive to mechanical action or water and process control can be challenging in certain cases.

To address these challenges and promote green methodologies, the MOXY project was initiated. It aims to develop a non-contact cleaning technique for cultural heritage objects using atomic oxygen (AO) cold plasma, which allows for non-liquid, non-thermal treatment<sup>1</sup>. Atomic oxygen is highly reactive with a short lifetime of a few milliseconds, likely leading to the oxidation of organic contaminants and the production of volatile byproducts. However, before applying this method to historical artifacts, it is crucial to understand how AO affects the underlying substrate material and to compare its effectiveness with more established cleaning methods. In the frame of this work experiments were focused on oil paints. The oxidation of oil is a well-studied process involving radical chain reactions<sup>2</sup>. By comprehending the potential outcomes of such chemical interactions and employing analytical methodologies, we can qualitatively and quantitatively assess the effects of AO treatment on the substrate.

To this end, experiment was carried out on a number of fresh and aged simplified mock-up models of handmade oil paint. Subsequently, treated and untreated areas were analyzed to detect changes in the chemical composition of the binder, using EGA-MS for characterization of the binder polymeric structure, SPME GC-MS for investigation of the volatile organic compounds evolved from samples, and DSC for evaluation of radical activity. Finally, ATR-FTIR was employed to study the surface of the samples. Results presented in this poster display the initial analytical data and form a foundation for further research into the applicability of this technology for actual art objects.

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# Sustainable energy storage: hazelnut shell-biochar as electrode material for supercapacitors

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The imperative need to move away from fossil fuels is intensifying the exploration of alternative energy sources and storage solutions. Integrating electrochemical energy devices, such as batteries, supercapacitors (SCs) and fuel cells with existing forms of energy is essential to achieve a sustainable energy landscape. SCs have attracted great interest, because of their high-power density, long lifetime and fast charging capability. SCs can be classified into two main types on the basis of their charge storage mechanisms: electric double-layer capacitors (EDLCs) and pseudocapacitors. Furthermore, it is possible to integrate the two operating mechanisms to develop devices which are known as hybrid supercapacitors (HSCs). EDLCs store energy through doublelayer charges on electrode surfaces and their efficiency relies on enhancing electrode surface properties, commonly employing carbon-based materials, like activated carbon (AC), carbon nanotubes and graphene, due to their cost-effectiveness, high conductivity and large surface area [1]. In this context, biomass emerges as a promising resource for electrode production by generating carbon chars through thermal processes. On the other hand, pseudocapacitors store energy via rapid reversible redox reactions, employing different metal oxides, such as RuO2, IrO2, Fe3O4 and CuO. In particular, CuO is potentially attractive, due to its high theoretical pseudocapacitance and good conductivity. Therefore, the development of composite materials containing CuO represents a promising solution for the fabrication of new electrode materials with high performance and stability [1].

In this work, new biochars were prepared starting from the waste biomass hazelnut shells and testedas new electrode materials for EDLCs. Specifically, three ACs were synthesized by chemical activation, using KOH as the activating agent, with the precursor/KOH weight ratio of 1/4, working at 600 °C for 1 hour, under N2 flow, with the heating rate of 10 °C/min [2]. The first AC was obtained from the raw biomass (HS-AC), the second one from the hydrochar originating from hydrothermal carbonization (HTC) (HTC-HS-AC) of the starting biomass [3], and the last one from the pyrochar obtained after pyrolysis post-treatment of the same hydrochar (PYRO-HS-AC). Moreover, the char obtained at the end of the two-step treatment of HTC and pyrolysis (without the final activation pyrolysis step, PYRO-HTC) was also tested. The electrochemical behaviour of the obtained biochars were investigated through cyclic voltammetry and galvanostatic charge- discharge measurements in different aqueous electrolyte solutions, showing promising performances as functional materials to be implemented in EDLCs electrodes fabrication. In addition, regarding HSCs, the CuO doping procedure was performed on the three ACs, previously activated via pyrolysis with KOH [4]. For this purpose, each AC was impregnated with a solution of the copper (II) acetate salt, causing the in-situ precipitation of copper (II) hydroxide by adding NaOH (at controlled pH), followed by the calcination of the solid product. Physico-chemical and electrochemical characterizations of the synthesized CuO doped chars are in progress to rightly assess structure-application correlation.

### Acknowledgements

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# Preparation, physicochemical characterization and applications of a Cobalt-based Deep Eutectic Solvent

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Deep eutectic solvents (DESs) are a novel class of liquid mixtures characterized by a significant lowering of their melting points compared to those of their neat constituents, usually compounds classifiable as Hydrogen Bond Donor (HBD) and Hydrogen Bond Acceptor (HBA) species<sup>1</sup>. These materials are potentially "designer" solvents<sup>2</sup>. promising exhibiting tunable physicochemical properties as a function of the nature and ratio of their components<sup>3</sup>. Unfortunately, achieving this "tunability" remains challenging due to the many difficulties associated with developing predictive models for DES physicochemical properties<sup>4</sup>. These difficulties arise from two factors: the inherent complexities in describing DESs through computational simulations<sup>5</sup>, as well as the absence of a comprehensive dataset of their physicochemical properties necessary for empirically derived predictive models<sup>6</sup>.

Our research aims to bridge this informational gap by carrying out a systematic evaluation of DES physicochemical properties and how these change as a function of the identity of their constituents. In this work, we report the physicochemical characterization of a DES having Choline Chloride as HBA and Cobalt Chloride Hexahydrate as HBD. Cobalt-based DESs were prepared by simply mixing the precursors in different molar ratios and heating them at 70°C for 30 min (Figure 1), obtaining a



**Figure 1:** Preparation of DES by mixing Choline Chloride (white) and Cobalt Chloride Hexahydrate (pink) with a molar ratio of 1:1. The formation of a new liquid phase can be observed at the interface.

homogeneous deep blue liquid. Physicochemical properties such as thermal stability, viscosity, electrical conductivity, density and electrochemical window were characterized across a wide rangeof temperatures and compositions. The recovery of the metal from these mixtures was also investigated by electrowinning, resulting in the deposition of a layer of metallic Co having purity as high as 94%.

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## Investigating the Behavior of Azurite in Different Paint Systems

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Azurite, a basic copper carbonate (Cu<sub>3</sub>(OH)<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub>), is a natural pigment derived from grinding the mineral azurite. This pigment has been used since Egypt's Fourth Dynasty and gained significant popularity throughout the European Middle Ages as the primary blue pigment in paintings. Azurite was predominantly used with proteinaceous media, such as egg yolk or animal glue, also when drying oils replaced proteinaceous media as the most popular paint binder. The use of azurite in oil paint introduces several issues, such as its tendency to promote a shift to a greenish hue and the accumulation of the oil in the paint surface <sup>[1]</sup>. It is reported that the Cu catalyses the autoxidation of polyunsaturated glycerides, deactivating the antioxidants naturally present in the oil, thus leading to a fast curing process <sup>[2]</sup>. A few studies have examined the behaviour of azurite with drying oils, noting the formation of metal soaps as the paint layer ages. However, most of these studies focus on the optical properties of these systems, which vary according to the relative amounts of binder, and on changes in Cu coordination <sup>[2,3]</sup>.

The aim of this work is to understand the chemistry of the oil binder in azurite paint layers, investigating how copper and the formation of metal soaps affect the curing behaviour of the paints and the overall characteristics of the resulting paints. For this work, model paints with azurite and linseed oil were prepared. Furthermore, mixed media model paints were prepared combining oil with proteinaceous media Two distinct methods of paint preparation were used: tempera grassa and protein coated pigment (PCP). The former is made by adding oil to fresh egg yolk tempera to create an oil-in-water emulsion, while the latter is made by first preparing an egg white tempera, letting it dry and subsequently grinding it with oil, to disperse the protein coated pigment particles in the oil binder <sup>[4, 5]</sup>.

The initial phase of my research was conducted at the LAMS laboratory in Paris, where I used ATR-FTIR to examine the changes of the main functional groups upon curing. This technique enabled the monitoring of the isomerization of double bonds in fatty acid chains and the formation of oxidised moieties <sup>[6]</sup>. Additionally, NMR-MOUSE Relaxometry was employed to observe the evolution of the T<sub>2</sub> (transverse relaxation time) value, which decreases as the oil cures due to the reduced mobility of protons in the forming cross-linked network. Further analysis will be carried out in Pisa, based on the combined use of mass spectrometric and thermoanalytical techniques.

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## Synthesis and characterization of tungsten citrate complexes as potential contrast Agents in SPCCT

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Spectral photon-counting computed tomography (SPCCT) is an emerging imaging technique holding a notable potential in the field of medical diagnostics. With respect to conventional CT, SPCCT has the ability to differentiate and quantify X-ray photons by their energy, providing elemental identification through their distinct K-edge absorption<sup>[1]</sup>. Considering the novelty of the technique, the development of tailored contrast agents is necessary to exploit its full diagnostic potential. Following a screening study on various 5d metal-based easily available compounds, tungsten displayed the best attenuation profile and emerged as a promising candidate for the synthesis of customized contrast generating materials<sup>[2]</sup>.

The coordination chemistry of tungsten(VI) with the biologically-relevant ligand citric acid was investigated, in order to obtain aqueous soluble and stable derivatives. An extensive screening of experimental parameters (pH, stoichiometry, temperature, time) allowed to identify milder synthetic conditions and improved purification procedures with respect to the literature<sup>[3]</sup>, affording mono- and dimeric citratotungstates in high yields. The characterization of these complexes has been carried out using IR-ATR, UV-Vis, multinuclear NMR, mass spectroscopy, elemental analysis and molar conductivity analyses, while DFT calculations allowed to rationalize the possible formation of isomers. High water-solubility and stability of the complexes in biological media pave the way for further *in vitro* and potentially *in vivo* biological studies.



Figure 1. Example of dinuclear tungsten citrate complex to be employed as potential contrast agent in SPCCT.

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## **Bentonite in Our Daily Life**

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Laviosa Chimica Mineraria is a leading global company in the research, extraction, processing, and marketing of bentonite. The unique structure and chemical composition of this mineral are responsible for its diverse chemical and physical properties, making it a vital component in many aspects of our daily lives. Bentonite is used across various industrial sectors, including paints, composites and nanocomposites, waterproofing technologies, civil engineering, drilling and tunneling, cat litter, foundry, detergents, cosmetics, animal feed, beverages, water treatment, and more. This work provides a brief overview of the main applications of this naturally occurring material.

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## BIO-based FR plasticiser and natural FR minerals for low smoke, low acidity, no dripping, flame retardant PVC

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New design of cables and new compounds have been developed to comply with new standards and to get the best classification B2ca d0 s1, due to the introduction of the Construction Production Regulation (CPR).

Positive competition between PVC and HFFR compounds became even more compelling, moving up the FR performances of these families of raw materials.

Even PVC, considered by many to be a mature and traditional material, has accepted the challenge of the new regulations and has evolved towards levels of fire safety never achieved before. In this paper, the recent developments in terms of PVC formulations suitable for safe and competitive cables are described. New raw materials have been successfully developed and introduced into market to help PVC in this challenge.

## **Recycle process with deinking phase**

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Selene has produced flexible packaging for industrial use for more than 60 years, associating product quality with a sustainable production approach. Selene is specialized in blown extrusion technologies of PE and flexographic printing.

We have made up an industrial plant that enables the valorization of industrial plastic waste and scraps. Thanks to the complex de-inking process, we remove inks and varnishes obtaining an high-quality PE granules. The purpose is the creation of a high-quality secondary raw material that can be reused in our production in high percentages without limiting packaging performances. The regeneration process is divided into 5 stages (grinding, de-inking, rinsing, drying and pelletization).

The central deinking step takes place through a combination of several factors: the intervention of reagents in the water phase, added by a dosing system; the temperature, maintained in the range of 60 degrees centigrade, which facilitates the activation of the reactions; the special mechanical stirring that assists the process through rubbing. Indeed, the choice of the best cationic surfactant in a strongly basic solution has demonstrated a strong penetrating and softening action on the dried varnish layer of current flexographic inks (for both solvent and water-based inks). The entire reaction within the plant is in strongly basic solution due to the controlled addition of NaOH in water solution.



The plant, which has been operating since 2019, has a water treatment cycle that allows the recovery of reagents, the separation of waste sludge, as well as a water closed cycle.

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# Controlled thermolysis of End-of-life tires in bitumen, used as fluxing oil

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Bitumen is a non-renewable raw material obtained as a crude oil distillation residue. Due to its waterproofing and adhesive properties, bitumen is currently recognized as among the most eligible materials in highway paving technologies. However, neat bitumen has a limited performance temperature range because it is brittle in a cold environment and softens readily in a warm environment [1]. In addition, there is a continuous increase in traffic speed and load, which reduces the life of asphalt pavements. These led to the use of polymer-modified binders to improve the performance of asphalt binders in terms of rutting resistance and fatigue cracking [2]. Performance enhancement is achieved when "phase inversion" is obtained [3]. This phenomenon marks the transition from a bituminous continuous phase to a polymeric continuous phase in which the overall mechanical properties of the Polymer Modify Asphalt (PMA) markedly reflect those of the polymer. A further problem related to the growing number of road vehicles is the generation of millions of End-Of Tyres (ELT) every year. In fact, they represent a significant portion of waste destined for landfills. Due to their chemical composition, they are extremely resistant to environmental degradation phenomena with a potential long-term permanence. Among the different solutions to recycle waste rubber from ELT, the coupling of waste rubber and bituminous binder has proved very profitable since the first applications [4]. These include the Terminal Blend (TB) method for thermodegradation ELTs into bitumen. The work aimed to demonstrate the importance of oils as compatibilizers of bitumen/polymer blends. Oils of different natures (vegetable, mineral, synthetic) were selected and compared with recycled oil from the degradation of ELT. In general, it has been observed that the oil reduces the weight percentage of polymer to be added to the bitumen to achieve phase inversion.



Scheme of the thermodegradation reaction of ELT (top) and fluorescence microscopy of Bitumen+Oil, at different wt. % of added polymer: a) 15% (bituminous continuous phase), b) 25%, and c) 30% (polymeric continuous phase) (bottom).

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