XVI LATIN AMERICAN MEETING OF PHOTOCHEMISTRY AND PHOTOBIOLOGY

ELAFOT 2025

2nd LatASP

BOOK OF

ABSTRACTS

From October 27 to 30, 2025

XVI ELAFOT and II LatASP Meeting

Panama City, October 27-30, 2025

Program

	Monday	Tuesday		Wednesday		Thursday	
8:30-9:00		PL3: Michael J. Davies		PL10: Massimo Trotta		PL13: Dario Falcone	
9:00-9:30		PL4: Wenfang Sun		PL11: Manuel Ahumada		PL14: Alessandra Nara de Souza Rastelli	
9:30-10:00		PL5: Virginie Lhiaubet-Vallet		PL12: Luis Larrondo		Coffee break	
10:00-10:30		Coffee break		Coffee break		S11: Photoactive materials for photodynamic therapy applications	S12: Molecular Probes for Sensing and Imaging
10:30-11:00		S2: Photosensitized Processes in Photobiology	S3: Applications of organometallic photochemistry	S6: Photochemical and photocatalytic processes: from semiconductor to protein systems	S7: Photochemical and biomedical applications of nitric oxide donor agents: Recent developments for aPDT and PDT		
11:00-11:30							
11:30-12:00							
12:00-12:30	Registration					Lunch	
12:30-13:00		Lunch		Lunch			
13:00-13:30						Social event (excursion)	
13:30-14:00							
14:00-14:30		PL6: Ryan McCulla		S8: Optogenetics: New Tools for Precise Cell Control			
14:30-15:00		PL7: Xavier Allonas					
15:00-15:30		PL8: Gustavo Pino		S9: Photodynamic Therapy and Photodynamic Inactivation	S10: Time-resolved studies of molecular mechanisms in photochemistry and photobiology		
15:30-16:00		PL9: Mónica C. Gonzalez					
16:00-16:30	Opening ceremony	S4: Singlet oxygen detection and dosimetry	S5: Skin health and sun exposure: from cutaneous pathologies to photoprotection				
16:30-17:00							
17:00-17:30				Awards ceremony			
17:30-18:00	PL1: Sherri McFarland			Poster session (even numbers) (Snack)			
18:00-18:30	PL2: Mauricio Baptista	Poster session (odd numbers) (Snack)					
18:30-19:00	S1: Honoring Eduardo Lissi: A Legacy of Light and Interfaces						
19:00-19:30				LatASP/ELAFOT Assembly			
19:30-20:00							
20:00-20:30	welcome reception					Gala dinner	
20:30-21:00							
21:00-21:30							
21:30-22:00							

PL: Plenary Lecture, S: Symposium

Background

The Latin American Meetings of Photochemistry and Photobiology (ELAFOT) is a biennial event that brings together researchers in photochemistry and photobiology from across Latin America. This event serves as a platform to present innovative scientific advances, share the latest research findings, foster the exchange of ideas, promote collaborations, and strengthen ties between young scientists and established experts in the field.

The history of ELAFOT dates back to August 1982, with the first Latin American Meeting of Photochemistry and Photobiology, organized by Dr. Eduardo Lissi and his team at the University of Santiago, Chile.

In October 2023, during the XV ELAFOT / 1st LatASP Meeting, held in Maresias, São Paulo, Brazil, it was approved that Panama would host the XVI Latin American Meeting of Photochemistry and Photobiology (ELAFOT) and the 2nd Meeting of the Latin American Branch of the American Society for Photobiology (LatASP).

Therefore, this year, both events will be held in Panama City, from October 27 to 30, 2025. This will mark the first time in history that Panama hosts this important scientific gathering.

Panamá

Panama, known as the “bridge of the world, heart of the universe,” is a country of remarkable biodiversity, featuring tropical rainforests, paradisiacal beaches, and lush mountains. Its rich historical legacy, combined with a vibrant cultural heritage, makes it a unique destination, ideal for science, tourism, and culture, offering an unforgettable experience.

Panamá City

Panama City is the perfect host destination. Much more than the country's capital, it is a cosmopolitan metropolis where the modern and the traditional converge. Vibrant and full of contrasts, it offers unique experiences—from biking through its impressive skyline to exploring colonial-era monuments and radiant natural parks.

One of its greatest charms lies in its history, embodied in three cities in one. Panamá Viejo, an archaeological site with the ruins of the first city founded in 1519 and destroyed in 1671 by the pirate Henry Morgan. Casco Antiguo, a colonial gem filled with history, colorful buildings, cobbled streets, and lively nightlife. Both have been declared UNESCO World Heritage Sites. Finally, the city’s modern architecture defines it as one of the most dynamic urban centers in Latin America.

Panamanian gastronomy is as diverse as its architecture. The city offers a rich and high-quality culinary scene, blending flavors and cultural influences that have shaped the country over decades. This gastronomic wealth is reflected in a variety of dishes that surprise and delight both newcomers and seasoned food lovers.

Logo

The logo of the XVI ELAFOT / 2nd LatASP Meeting 2025 represents light as the central element of photochemistry and photobiology. The prism, integrated into the silhouette of the Americas, symbolizes the collective participation of the entire region, united by science and knowledge. The yellow ray highlights Panama, the host country, illuminating its role in this edition. Each color of the spectrum alludes to the various fields of knowledge that converge through these disciplines, enriching the congress experience.

American Society for Photobiology

Founded in 1972 under the leadership of Kendric C. Smith, the American Society for Photobiology (ASP) aims to promote research in photobiology, facilitate the integration of various disciplines within the field, encourage the dissemination of photobiological knowledge, and provide information on the photobiological aspects of national and international issues. Its scope ranges from photochemistry and photomedicine to environmental photobiology and photosynthesis. Through conferences, scientific publications, and training programs, ASP actively promotes the advancement and dissemination of knowledge in the field.

Latin American branch of the American Society for Photobiology

Due to the active participation of research groups from Latin America in the American Society for Photobiology (ASP) and the exponential growth of photochemistry and photobiology research in the region, well-established scientific communities have emerged in countries such as Argentina, Brazil, Chile, Mexico, Panama, and Uruguay. This growth led to the creation of LatASP, the Latin American branch of the ASP. LatASP's objectives include expanding the ASP southward, adopting a Pan-American perspective, with the goal of increasing interaction among research groups across the Americas and fostering new opportunities for collaboration.

Conference Venue

The event will take place at El Domo, the main auditorium of the Harmodio Arias Madrid Campus of the University of Panama. This iconic architectural landmark is surrounded by lush greenery and beautiful gardens. Its futuristic design and striking presence have made it a cultural and architectural reference point in Panama. Located in the heart of Panama City, El Domo hosts international events, exhibitions, conferences, symposia, congresses, and more, making it an ideal venue for XVI ELAFOT and the 2nd LatASP Meeting.

Local Organizing Committee

Dr. José Robinson-Duggon (Coordinador)

• Dr. José Robinson-Duggon (Coordinator) • Dr. Mario L. Miranda • Dr. Edgardo Castro-Pérez • Dr. Janira Jaén • Dr. Carlos Ríos • MSc. Ritzela Lezcano • B.S. Jennifer Otero-González • B.S. Whitney Querini-Sanguillén • Student Rut Urriola • Student Angely Cruz	Universidad de Panamá

Scientific Committee

Coordinators:

- José Robinson Duggon - Universidad de Panamá
- Denis Fuentealba - Pontificia Universidad Católica de Chile
- Andrés Thomas - Universidad Nacional de La Plata
- Mauricio Baptista - Univeridade de São Paulo

Members:

- Josef Wilhelm Baader- Univeridade de São Paulo
- Erick Leite Bastos- Univeridade de São Paulo
- Roberto Santana da Silva- Univeridade de São Paulo
- Thiago Teixeira Tasso- Universidade Federal de Minas Gerais
- Rene Nome- Universidade Estadual de Campinas
- Helena C. Junqueira- Univeridade de São Paulo
- Glaucia Regina Martinez- Universidade Federal do Parana
- Cassius V. Stevani- Univeridade de São Paulo
- Luiza Araújo Gusmão- Univeridade de São Paulo
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- Denis Fuentealba - Pontificia Universidad Católica de Chile
- Andrés Thomas - Universidad Nacional de La Plata
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- Rene Nome- Universidade Estadual de Campinas
- Helena C. Junqueira- Univeridade de São Paulo
- Glaucia Regina Martinez- Universidade Federal do Parana
- Cassius V. Stevani- Univeridade de São Paulo
- Luiza Araújo Gusmão- Univeridade de São Paulo

Plenary Lectures

Plenary Lecture 1. Monday, 17:30 – 18:00
Paraninfo, University of Panama (Central Campus)
Sherri A. McFarland
Title: Light, metal, and medicine: Translating a phototherapeutic concept
The University of Texas at Arlington
Email: sherri.mcfarland@uta.edu

Plenary Lecture 2. Monday, 18:00 – 18:30
Paraninfo, University of Panama (Central Campus)
Mauricio Baptista
Title: Skin under light exposure: from damage mechanisms to adaptive responses
Universidade de São Paulo, Brazil
Email: baptista@iq.usp.br

Plenary Lecture 3. Tuesday, 08:30 – 09:00
Psychology Auditorium – Harmodio Arias Madrid Campus
Michael J. Davies
Title: Singlet oxygen-mediated damage to disulfides and proteins
University of Copenhagen, Denmark
Email: davies@sund.ku.dk

Plenary Lecture 4. Tuesday, 09:00 – 09:30
Psychology Auditorium – Harmodio Arias Madrid Campus
Wenfang Sun
Title: Developing Ir(III) complexes as photosensitizers for phototherapy
The University of Alabama, USA
Email: wsun15@ua.edu

Plenary Lecture 5. Tuesday, 09:30 – 10:00
Psychology Auditorium – Harmodio Arias Madrid Campus
Virginie Lhiaubet-Vallet
Title: Photoreactivity of metabolically generated DNA lesions: the case of etheno adducts
Instituto de Tecnología Química (Universitat Politècnica de València-CSIC), Spain
Email: lvirgini@itq.upv.es

Plenary Lecture 6. Tuesday, 14:00 – 14:30
Auditorium A-107, Research and Graduate Studies Auditorium
Ryan McCulla
Title: The rare single chromophore dual-release photochemistry of sulfoximines and sulfone diimines
Saint Louis University, USA
Email: rmccull2@slu.edu

Plenary Lecture 7. Tuesday, 14:30 – 15:00
Auditorium A-107, Research and Graduate Studies Auditorium

Xavier Allonas
Title: Homo- vs. hetero-FRET in singlet-singlet photosensitization evidenced by photopolymerization experiments
Université de Haute-Alsace, France
Email: xavier.allonas@uha.fr

Plenary Lecture 8. Tuesday, 15:00 – 15:30
Auditorium A-107, Research and Graduate Studies Auditorium
Gustavo Pino
Title: Cold-ion-spectroscopy and excited state dynamics of species of biological interest
Universidad Nacional de Córdoba, Argentina
Email: gpino@unc.edu.ar

Plenary Lecture 9. Tuesday, 15:30 – 16:00
Auditorium A-107, Research and Graduate Studies Auditorium
Mónica C. Gonzalez
Title: Mechanistic insights into solar-driven photocatalysts for sustainable applications
Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Argentina
Email: gonzalez@inifta.unlp.edu.ar, mcgonzalez.quim@gmail.com

Plenary Lecture 10. Wednesday, 08:30 – 09:00
Auditorium A-107, Research and Graduate Studies Auditorium
Massimo Trotta
Title: Beyond Original Purpose: Repurposing Bacterial Photosynthesis
Università di Bari, Italia
Email: massimo.trotta@cnr.it

Plenary Lecture 11. Wednesday, 09:00 – 09:30
Auditorium A-107, Research and Graduate Studies Auditorium
Manuel Ahumada
Title: Carbon dots: Unlocking photochemical and photobiological potential in biological applications
Universidad Mayor, Chile
Email: manuel.ahumada@umayor.cl

Plenary Lecture 12. Wednesday, 09:30 – 10:00
Auditorium A-107, Research and Graduate Studies Auditorium
Luis Larrondo
Title: Optogenetic circuits and optoecology: mapping transcriptional responses and visualizing population dynamics through the eyes of fungi
Pontificia Universidad Católica de Chile, Chile
Email: lflarron@uc.cl, llarrondo@bio.puc.cl

Plenary Lecture 13. Thursday, 08:30 – 09:00
Auditorium A-107, Research and Graduate Studies Auditorium
Dario Falcone
Title: Biocompatible nanosystems under the light: A spectroscopic insight into reverse micelles, vesicles, and other organized systems. Challenges and opportunities toward sustainable chemistry
Universidad Nacional de Río Cuarto, Argentina

Email: rfalcone@exa.unrc.edu.ar

Plenary Lecture 14. Thursday, 09:00 – 09:30
Auditorium A-107, Research and Graduate Studies Auditorium
Alessandra Nara de Souza Rastelli
Title: Antimicrobial photodynamic therapy over oral pathogens: From the bench to the clinical setting
Universidade Estadual Paulista "Júlio de Mesquita Filho" - UNESP, Brazil
Email: alessandra.nara-souza-rastelli@unesp.br

Symposia

Symposium 1. Monday, 18:30 – 19:30
Paraninfo, University of Panama (Central Campus)
Honoring Eduardo Lissi: A Legacy of Light and Interfaces
Chair: Carolina Aliaga (Universidad de Santiago de Chile)
This symposium honors the scientific and human legacy of Prof. Eduardo A. Lissi, one of Latin America's most influential photochemists. His pioneering studies in kinetics, radical chemistry, and interfacial phenomena helped establish the foundations of photochemical research in the region. Beyond his vast scientific output, Prof. Lissi was a mentor of exceptional integrity and generosity, who inspired countless students and colleagues to pursue science with curiosity, collaboration, and humility. The talks gathered in this session celebrate not only his scientific achievements but also the enduring spirit of community he fostered.

18:30-18:40 **Carolina Aliaga** (Universidad de Santiago de Chile)
Introduction to the Symposium
18:40-19:00 **Emilio Alarcón** (University of Ottawa)
Title: Lissi's three magic principles
19:00-19:20 **Manuel Ahumada** (Universidad Mayor)
Title: The answer is "It Depends": Memories of Eduardo Lissi

Symposium 2. Tuesday, 10:30 – 12:30
Auditorium 102 – Faculty of Veterinary Medicine, Harmodio Arias Madrid Campus
Photosensitized Processes in Photobiology
Chairs: Carolina Lorente (Universidad Nacional de La Plata), Susana Nuñez Montoya (Universidad Nacional de Córdoba)

Invited talks
10:30-10:55 **Dennis Fuentealba** (Pontificia Universidad Católica de Chile)
Title: Supramolecular controllable photoactive agents for photodynamic therapy
10:55-11:20 **Carolina Lorente** (Universidad Nacional de La Plata)
Title: Effect of UV-A Radiation on Antioxidant Activity and Cytotoxicity of Vanillin
11:20-11:45 **Camilo I. López-Alarcon** (Pontificia Universidad Católica de Chile)
Title: Tryptophan dimers as biomarkers of protein oxidation: formation, detection, and quantification
11:45-12:10 **Juliana Marioni** (Universidad Nacional de La Plata)
Title: Natural anthraquinones and Photodynamic Therapy: an antifungal strategy against Candida biofilms

Oral Communications
12:10-12:20 **Gricelda Godoy-Ortega** (Universidad Nacional de La Plata)
Title: Pterin–Thymine Adducts as Photosensitizers for Oxidative Damage
12:20-12:30 **Luciano F. Dibona-Villanueva** (Pontificia Universidad Católica de Chile)
Title: Development of Photoactivable Biofungicides: From Laboratory Assessments to Field Tests

Symposium 3. Tuesday, 10:30 – 12:30
Auditorium 103 - Engineering Auditorium – Harmodio Arias Madrid Campus

Applications of organometallic photochemistry
Chairs: Nancy Pizarro (Universidad Andrés Bello), Malcolm D. E. Forbes (Bowling Green State University)

Invited talks

10:30-10:55 **Malcolm D. E. Forbes** (Bowling Green State University)
Title: Influence of topology, architecture, and environment on spin polarization transfer: implications for quantum information science

10:55-11:20 **Nancy Pizarro** (Universidad Andrés Bello)
Title: Photoinduced dual capacity of Re-Mn complexes for singlet oxygen generation and carbon monoxide release

11:20-11:45 **Alan Cabrera C.** (Pontificia Universidad Católica de Chile)
Title: Heteroleptic Copper(I) Complexes type [Cu(dpa)(P,P)]+ as Photoredox Catalyst

11:45-12:10 **Andrés Vega** (Universidad Andrés Bello)
Title: Potential applications of rhenium(I)tricarbonyl molecules with aromatic bridged ligands

Oral Communications

12:10-12:20 **Jesús M. N. Morales** (Universidad Nacional de Santiago del Estero)
Title: Characterization of tyrosine oxidation products generated via the photooxidative quenching reaction of Ru(bpy)32+ by S2O82-

12:20-12:30 **María Paz Herrera Maldonado** (Universidad Tecnológica Metropolitana)
Title: Novel heteroleptic Cu(I)-Dipyridylamine/Diphosphine complexes as active materials in Light-Emitting Electrochemical Cells.

Symposium 4. Tuesday, 16:00 – 18:00
Auditorium 102 – Faculty of Veterinary Medicine, Harmodio Arias Madrid Campus
Singlet oxygen detection and dosimetry
Chairs: Helena C. Junqueira (Univeridade de São Paulo), Steffen Hackbarth (Humboldt-Universität zu Berlin)

Invited talks

16:00-16:25 **Steffen Hackbarth** (Humboldt-Universität zu Berlin)
Title: Optical detection of singlet oxygen in vitro and in vivo – Please stop saying, it would be difficult

16:25-16:50 **Andrés H. Thomas** (Universidad Nacional de La Plata)
Title: Kinetic analysis to evaluate the contribution of type II mechanism in photosensitized oxidations

16:50-17:15 **Fernanda Manso Prado** (Univeridade de São Paulo)
Title: Singlet oxygen in biological systems: mass spectrometry and near-infrared light emission measurements

17:15-17:40 **Ronald Sroka** (Universität München)
Title: Potential of 5-ALA in Neurosurgery – Fluorescence and PDT

Oral Communications

17:40-17:50 **Cristobal A. Mejias Miller** (Universidad de Chile)
Title: Synthesis and characterization of N-ethylpyridin-1-ium-2-pyridones as singlet oxygen releasers in mixed aqueous/acetonitrile media

17:50-18:00 **Helena C. Junqueira (Univeridade de São Paulo)**

Title: Quantifying Singlet Oxygen in Aqueous and Cellular Media Using Time-Resolved NIR Phosphorescence

Symposium 5. Tuesday, 16:00 – 18:00
Auditorium 103 - Engineering Auditorium – Harmodio Arias Madrid Campus
Skin health and sun exposure: from cutaneous pathologies to photoprotection
Chairs: Daniel Gonzalez Maglio (Universidad de Buenos Aires), Glaucia Regina Martinez (Universidade Federal do Parana), Miguel Angel Puertas-Mejía (Universidad de Antioquia), Juan Camilo Mejía-Giraldo (Universidad de Antioquia)

Invited talks

16:00-16:25 **Miguel Angel Puertas-Mejía** (Universidad de Antioquia)
Title: Marine Algae as a Therapeutic and Sustainable Source for Skin Photoprotection Against UV-Induced Damage

16:25-16:50 **Glaucia Regina Martinez** (Universidade Federal do Parana)
Title: Melanoma Cell Responses to Melanogenesis Induction and its consequences

16:50-17:15 **Daniel Gonzalez Maglio** (Universidad de Buenos Aires)
Title: Sunlight-induced modulation of the cutaneous immune response in human tegumentary leishmaniasis.

17:15-17:40 **Juan Camilo Mejía-Giraldo** (Universidad de Antioquia)
Title: Photostability and Photostabilization Approaches for UV Filters: Advancing the Rational Design of Broad-Spectrum (UVA–UVB) Sunscreens

Oral Communications

17:40-17:50 **Pedro Duvan Barrios Mejía** (Universidad del Quindío)
Title: Photochemical properties of Rutin-loaded nanoemulsions

17:50-18:00 **Diego Villamizar** (Universidad Industrial de Santander)

18:00-18:10 **Isabella Canavezzi Matias** (University of São Paulo)
Title: The impact of melanin on melanocyte response to blue light

Symposium 6. Wednesday, 10:30 – 12:30
Auditorium 102 – Faculty of Veterinary Medicine, Harmodio Arias Madrid Campus
Photochemical and photocatalytic processes: from semiconductor to protein systems
Chairs: Claudio D. Borsarelli (Universidad Nacional de Santiago del Estero), Moises Canle (Univerisad de la Coruña)

Invited talks

10:30-10:55 **Moises Canle** (Univerisad de la Coruña)
Title: Heterogeneous Photocatalysis for Environmental Remediation: a Journey from Batch to Continuous Flow Systems

10:55-11:20 **Marcelo H. Gehlen** (University of São Paulo)
Title: Single-Molecule Catalysis in Pd Cross-Coupling Reaction by Fluorescence Microscopy: The Interplay between Experiment and Stochastic Simulation

11:20-11:45 **Giorgia Miolo** (Universita di Padova)
Title: Chemico-physical and biological properties of two monoclonal antibodies, Bevacizumab (Avastin®) and Durvalumab (Imfinzi®) under real-life light doses: a mechanistic approach.

11:45-12:10 **Claudio D. Borsarelli** (Universidad Nacional de Santiago del Estero)
Title: Photosensitized oxidative crosslinking of proteins

Oral Communications

12:10-12:20 **Manuela Saldarriaga Gallego** (Universidad Nacional de Colombia)
Title: Evaluation of the Thermal and Photochemical Stability of Fe_3O_4 Magnetic

12:20-12:30 **Matías A. Carrasco Bozo** (Universidad de Chile)
Title: Phenalenone-functionalized cationic polymers: a versatile platform

Symposium 7. Wednesday, 10:30 – 12:30
Auditorium 103 - Engineering Auditorium – Harmodio Arias Madrid Campus
Photochemical and biomedical applications of nitric oxide donor agents: Recent developments for antimicrobial and cancer therapy
Chairs: Roberto Santana da Silva (Univeridade de São Paulo), Salvo Sortino (Universitá di Catania)

Invited talks

10:30-11:00 **Salvatore Sortino** (University of Catania)
Title: Multifunctional Hyaluronic Acid- and Carbon Dot-Based Conjugates Photoreleasing Nitric Oxide

11:00-11:30 **Amedea Barozzi Seabra** (Federal University of the ABC)
Title: Precision Nanotherapy with Nitric Oxide: Boosting Anti-Cancer Effects and Minimizing Inflammation

11:30-12:00 **Luiz Gonzaga de França Lopes** (Federal University of Ceara)
Title: Controlled NO and HNO Release from Metal Complexes: Chemical and Photochemical Triggers and Biological Effects

12:00-12:30 **Roberto S. Silva** (University of Sao Paulo)
Title: Advancing photodynamic therapy by nitric oxide releasing agent using three-dimensional (3D) biofabricated cancer model

Symposium 8. Wednesday, 14:00 – 15:30
Psychology Auditorium – Harmodio Arias Madrid Campus
Optogenetics: New Tools for Precise Cell Control
Chairs: Alejandra Mussi (Universidad Nacional de Rosario), Matías Zurbriggen (Heinrich-Heine-Universität Düsseldorf)

Invited talks

14:00-14:30 **Matías Zurbriggen** (Heinrich-Heine-Universität Düsseldorf)
Title:

14:30-15:00 **Alejandra Mussi** (Universidad Nacional de Rosario)
Title: Light-modulated Circadian Rhythms in Non-phototrophic Critical Pathogens.

Symposium 9. Wednesday, 15:30 – 17:00
Auditorium 103 - Engineering Auditorium – Harmodio Arias Madrid Campus
Photodynamic Therapy and Photodynamic Inactivation
Chairs: Adriana Casas (Universidad de Buenos Aires), Carlos E. Crespo-Hernández (Case Western Reserve University)

Invited talks

15:30-15:55 **Carlos E. Crespo-Hernández** (Case Western Reserve University)
Title: Development of Biocompatible Multifunctional Agents for Photodynamic Therapy, Cancer Cell Imaging, and Cell Proliferation Inhibition

15:55-16:20 **Mariana B. Spesia** (Universidad Nacional de Río Cuarto)
Title: New strategies for optimizing the photoinactivation of bacteria
16:20-16:45 **Adriana Casas** (Universidad de Buenos Aires)
Title: Theranostic Potential of Aminolevulinic Acid-Derived Porphyrins
16:45-17:10 **Sherri A. McFarland** (The University of Texas at Arlington)
Title: Light-Responsive Metallodrugs: Structure, Excited States, and Biological Function

Oral Communications
17:10-17:20 **Jhohann David Alturo Walteros** (Universidad del Quindío)
Title: Gold Nanoparticle–Polyphenol Conjugates for Dual-Mode Antimicrobial Phototherapy
17:20-17:30 **Jhon Alejandro Arboleda-Murillo** (Universidad del Quindío)
Title: Light-Activated Antimicrobial Films: Structural and Optical Design of Curcumin–Chlorophyllin Alginate Composites.

Symposium 10. Wednesday, 15:30 – 17:00
Auditorium 102 – Faculty of Veterinary Medicine, Harmodio Arias Madrid Campus
Time-resolved studies of molecular mechanisms in photochemistry and photobiology
Chairs: Rene Nome (Universidade Estadual de Campinas), Germán Gunther (Universidad de Chile)

Invited talks
15:30-15:55 **Valentine Vullev** (University of California Riverside)
Title: How Charge-Transfer Dynamics Leads to "Unusual" Photophysics
15:55-16:20 **Igor Alabugin** (Florida State University)
Title: Photoredox Paradox: Uncovering the Roles of Electron Upconversion and Electron Catalysis
16:20-16:45 **Frank Quina** (University of São Paulo)
Title: Probing Complex Systems with Time-Resolved Spectroscopies: From Micelles to the Chromophores of Red Wine
16:45-17:10 **Rene Nome** (Universidade Estadual de Campinas)
Title: Integrating Timescales in Chemistry: concepts, methods, examples

Oral Communications
17:10-17:20 **Analia Young Hwa Cho** (Universidad de Chile)
Title: Photosensitization and Photostability of DAN fluorescent probes
17:20-17:30 **Álvaro Cabrera** (Universidad de Chile)
Title: Design and Synthesis of dicationic styryl dyes for nucleic acid detection enhancing binding through electrostatic interactions

Symposium 11. Thursday, 10:00 – 12:00
Auditorium 103 - Engineering Auditorium – Harmodio Arias Madrid Campus
Photoactive materials for photodynamic therapy applications
Chairs: Thiago Teixeira Tasso (Universidade Federal de Minas Gerais), Luiza Araújo Gusmão (Univeridade de São Paulo), Cristian Camilo Villa Zabala (Universidad del Quindío), Mario Miranda (Universidad de Panamá)

Invited talks
10:00-10:25 **Thiago Teixeira Tasso** (Universidade Federal de Minas Gerais)
Title: Combining carbon dots with porphyrin photosensitizers: a strategy to boost photophysical properties and toxicity against leukemia cells

10:25-10:50 **Luiza Araújo Gusmão** (Univeridade de São Paulo)
Title: Liposomes, Nanoemulsions and Cyclodextrins: Advanced Platforms for Photosensitizers
10:50-11:15 **Cristian Camilo Villa Zabala** (Universidad del Quindío)
Title: Photoactive Materials for Food Preservation
11:15-11:40 **Mario Miranda** (Universidad de Panamá)
Title: Impact of polymeric materials Photochemical redissolution on aquatic matrices

Oral Communications
11:40-11:50 **Juan Fernando Lopez Crespo** (Universidad Nacional de Colombia)
Title: Photostability study on red-emitting carbon dots by PARAFAC Analysis
11:50-12:00 **Cristian Tirapegui Calquin** (Universidad de Chile)
Title: In situ NMR photochemistry of dicationic azobenzenes

Symposium 12. Thursday, 10:30 – 12:30
Auditorium 102 – Faculty of Veterinary Medicine, Harmodio Arias Madrid Campus
Molecular Probes for Sensing and Imaging
Chairs: Carolina Aliaga (Universidad de Santiago de Chile)

Invited talks
10:00-10:25 **Carolina Aliaga** (Universidad de Santiago de Chile)
Title: From Inverted Solvatochromism to Excited-State Dynamics: Triarylpyrimidine Push–Pull Fluorophores as Molecular Probes in Microheterogeneous Media
10:25-10:50 **Alejandro Cortés** (Universidad de Valencia)
Title: Rationalizing the Excited-State Properties and Dynamics of Biphenyl-Based Push-Pull Systems
10:50-11:15 **Moisés Dominguez** (Universidad de Santiago de Chile)
Title: Lessons from the media: guidelines for improving the sensitivity of chromophores
11:15-11:40 **Pablo Rojas** (Universidad de Santiago de Chile)
Title: Detecting different liposomal microenvironments using fluorosolvatochromic dyes.
11:40-12:00 **Germán Gunther** (Universidad de Chile)
Title: Push-Pull fluorescent probes, from Webers' DANs to DAAns

Posters

#	Authors	Abstract title
1	Diego Armando Villamizar-Mantilla, Luis Alberto Nuñez, Elena E. Stashenko & Jorge Luis Fuentes	Erythema protection efficacy of plant derivatives compounds based on narrow-band reflectance spectroscopy data in mice
2	Diego Armando Villamizar-Mantilla, Víctor Alfonso Carrero Pulido, Carina Arciniegas Sierra, Jhon Alexander Suescun Sepúlveda & Jorge Luis Fuentes Lorenzo	Radioresistance, photoprotection, and antigenotoxicity against UVB radiation of the pigmented Kocuria flava strain from Paramo ecosystems in Colombia
3	Fernanda M. Prado, Rafaela O. Nascimento, Marisa H. G. Medeiros, Graziella E. Ronsein, Sayuri Miyamoto, Hermi F. Brito & Paolo Di Mascio	Singlet oxygen in biological systems: mass spectrometry and near-infrared light emission measurements
4	Rocio B. Acosta, Edgardo N. Durantini & Mariana B. Spesia	Effective bacterial inactivation: combination of therapies
5	Verónica E. González, Edgardo N. Durantini & Mariana B. Spesia	Effects of photoinactivation on bacterial resistance and virulence factors
6	Giovanna Coelho Bosso, Luiza Araújo Gusmão, Rogéria Rocha Gonçalves & Antonio Claudio Tedesco	Evaluation of Graphene Quantum Dots in Breast Cancer Cell Line
7	Cristobal Espinoza, Denis Fuentealba & Daniel Guerra	Photophysical and photochemical study of inclusion compounds of indocyanine green with cucurbiturils
8	Álvaro Molina & Daniel Guerra	Photophysical and photochemical study of inclusion compounds of temoporfin with cucurbiturils
9	Lina M. Romero & Denis Fuentealba	Novel supramolecular turn-on/off system for singlet oxygen generation and fluorescence emission using acyclic cucurbituril-type containers

10	André L. Lopes, Thabata V. Ferreira, Fernanda M. Prado, Graziella E. Ronsein, Marisa H. G. Medeiros, Jean Cadet & Paolo Di Mascio	Characterizing the Photodamage Induced by 6-Thioguanine Incorporated Into DNA
11	Sofía Pérez Del Pino, Walter Brown, Daniel Guerra Díaz, Daniel Zúñiga-Núñez, Paula Rivero-Jerez, Daniel Pino, Hilde Harb Buzza & Denis Fuentealba.	Supramolecular prodrug delivery system based on 5-aminolevulinic acid cucurbit[7]uril complex with enhanced fluorescence detection and photodynamic therapy effect for breast cancer
12	Sebastian Crisóstomo-Cáceres, Paula S. Rivero-Jerez & Denis Fuentealba	Supramolecular Modulation of Natural Photosensitizer Aloe Emodin via Acyclic Cucurbituril Complexation: Toward Enhanced PDT Performance
13	Leidy T. Sanchez, Cristian C. Villa & Lina Marcela Agudelo-Laverde	Development of quercetin capped TiO_2 nanoparticles (Que-TiO_2) for the photodegradation of ethylene in food applications.
14	J. Alejandro Arboleda-Murillo, Ana Valentina Luna-Obando, Andrés C. Giraldo-Contreas, Leidy T. Sanchez & Cristian C. Villa.	Photoactive Alginate-Based Films Characterized by Confocal Laser Microscopy and Steady-State Fluorescence
15	Jesuán J. Farías, M. Laura Dántola & Andrés H. Thomas	Photosensitized oxidation of free and peptide tryptophan to N-formylkynurenine
16	Danna Sofia Muñoz-Florez, Diana Blach & Cristian C. Villa	Comparison of the photoinactivation efficiency of chlorophyllin, gallic acid and rose bengal against S. Aureus.
17	Eunice Rios Vasquez, J Alejandro Arboleda-Murillo & Cristian C. Villa	Enhanced ROS Generation by Quercetin-Loaded Nanoemulsions
18	Isabela Canavezzi Matias, Carlos M.V. Palomino & Maurício S. Baptista	Impact of melanin on melanocyte response to blue light
19	Juliana Marioni, Jesús M. N. Morales, Bianca Romero, Tomás I. Gómez, Brenda S. Konigheim, Claudio D. Borsarelli & Susana C. Núñez Montoya	Supramolecular Stabilization of Parietin by a Bio-Inspired Polycation for Photodynamic Applications
20	Jesús M.N. Morales, Cecilia Vera, Lujan Torres & Claudio D. Borsarelli	Characterization and photosensitizing properties of a supramolecular adduct formed between Rose Bengal and BSA crosslinked oligomers
21	Jesús M.N. Morales, Cecilia Vera & Claudio D. Borsarelli	Photosensitized oxidative crosslinnking of bovine serum albumin and the impact on its esterase-like activity

22	Robles J., Cho YHA., Ormazabal-Toledo R. & Gunther G.	Photophysical Characterization of alkyl-amino phenalenone derivatives in homogeneous/ microheterogeneous media and analysis as potential membrane probes
23	Claudia Muñoz-Morcillo, Daniela Arroyo-Ortega, Cristian Hernandez-Sanchez & Juan Camilo Mejía-Giraldo	Synthesis and Evaluation of a Photostable Avobenzone Derivative as a UVA–UVB Photoprotective Ingredient for Sunscreen Formulation
24	María Paz Herrera, Paulina Dreyse, Iván A. González & Alan R. Cabrera	Novel heteroleptic Cu(I)-Dipyridylamine/Diphosphine complexes as active materials in Light-Emitting Electrochemical Cells.
25	Amaro Mejías & Germán Günther	SYNTHESIS AND CHARACTERIZATION OF N-ETHYLPYRIDIN-1-IUM-2-PYRIDONES AS SINGLET OXYGEN RELEASERS IN MIXED AQUEOUS/ACETONITRILE MEDIA.
26	Charis Parramón Jurado, Cecilia Challier, Mariana B. Spesia, Marcela Altamirano & Susana N. Criado	Degradation of topical ophthalmic drugs under simulated oxidative stress conditions
27	Matías Carrasco, Ximena Briones & Germán Günther	Phenalenone-functionalized cationic polymers: a versatile platform
28	Álvaro Cabrera, Germán Günther & Javier Romero	DESIGN AND SYNTHESIS OF DICATIONIC STYRYL DYES FOR NUCLEIC ACID DETECTION ENHANCING BINDING THROUGH ELECTROSTATIC INTERACTIONS
29	Sofía BORASI, E. Taís AGUAYO FRÍAS & Daniel GONZÁLEZ MAGLIO	Development of an in vitro biological test to determine sun protection factor of commercial sunscreens.
30	Ariadna CIROCCO REDIGO, Sofía CONZÓN, E. Taís AGUAYO FRÍAS, Andrea CANELLADA & Daniel GONZÁLEZ MAGLIO	Evaluation of postbiotics and a plant extract for skin active photoprotection: role of Lacticaseibacillus rhamnosus and Smilax campestris on UVB-induced keratinocyte damage
31	Analia. Y.H. Cho & German Gunther	Photosensitization and Photostability of DAN fluorescent probes

32	Pedro Duvan Barrios-Mejia, Leidy T. Sanchez & Cristian C. Villa	Photochemical properties of Rutin-loaded nanoemulsions.
33	Melannie García-Sánchez, Daniel Torres-Mendoza, Mario Miranda, Marcos H. Salazar & José Robinson-Duggon	PHOTOSENSITIZING EFFECT AND BINDING OF TOLUIDINE BLUE ON HUMAN SERUM ALBUMIN
34	Rut Urriola-Mendieta, Angely Cruz, Whitney Querini-Sanguillén, Jennifer Otero-González, Marcos H. Salazar[1], Mario Miranda, Denis Fuentealba, José Robinson-Duggon	PRELIMINARY RESULTS ON THE PHOTOSENSITIZED EFFECTS OF A TOLUIDINE BLUE DERIVATIVE ON SUPEROXIDE DISMUTASE AND CATALASE
35	Jennifer Otero-González, Whitney Querini-Sanguillén, Daniel Torres-Mendoza. Ikhil Yevdayev, Sharon Yunayev, Kamrun Nahar, Barney Yoo, Alexander Greer, Denis Fuentealba, José Robinson-Duggon	Photosulfoxidation of Toluidine Blue O Sensitized by Visible Light
36	Whitney Querini-Sanguillén, Jennifer Otero-González, Melanie García-Sánchez, Daniel Zúñiga-Núñez, German Günther, Mario L. Miranda, Edgardo Castro-Pérez, Carlos Ramos, Denis Fuentealba, and José Robinson-Duggon	Toluidine blue O demethylated photoproducts as type II photosensitizers
37	Manuela Saldarriaga, Juan Fernando López, Juan Bautista López, Carolina Castaño, Cristina Valencia, Donaldo Fabio Mercado & Juliana Palacio.	Evaluation of the Thermal and Photochemical Stability of Fe_3O_4 Magnetic Nanoparticles Functionalized with Methotrexate.
38	Juan F Lopez, Diego Uribe, Esneyder Arias, Gloria Valencia, Adriana Ipiña, Juliana Palacio & Donaldo Mercado.	Photostability study on red-emitting carbon dots by PARAFAC Analysis
39	Gricelda Godoy Ortega, Gemma Rodriguez Muñiz, Virginie Lhiaubet Vallet, Carolina Lorente & Andrés H. Thomas	Pterin–Thymine Adducts as Photosensitizers for Oxidative Damage
40	Bianca Carolina Romero, Juliana Marioni, Tomás Isaac Gómez & Susana Carolina Núñez-Montoya	Reactive oxygen production by a natural anthraquinone and its homodimer on Candida tropicalis biofilm
41	J. Alejandro Arboleda-Murillo, Sergio E. Moya, Eduart Gutierrez-Pineda & Cristian C. Villa4	Light-Activated Antimicrobial Films: Structural and Optical Design of Curcumin–Chlorophyllin Alginate Composites.
42	Jhohann D. Alturo-Walteros, Diana Blach, J. Alejandro Arboleda-Murillo & Cristian C. Villa2	Gold Nanoparticle–Polyphenol Conjugates for Dual-Mode Antimicrobial Phototherapy

43	Carolina Aliaga , Moisés Domínguez, Matías Vidal and Pablo Rojas	Detecting different liposomal microenvironments using fluorosolvatochromic dyes.

Gala Dinner – XVI ELAFOT: Celebrating Light and Science

As part of the official program of the XVI Latin American Meeting on Photochemistry and Photobiology (ELAFOT 2025), a Gala Dinner will be held on October 29 at 8:00 PM at the Hotel Torre de Alba, with a Gala/Formal dress code. This academic and social event is conceived as a space to promote interaction among participants in an atmosphere that reflects the identity of our scientific community.

The evening will bring together researchers, students, and invited speakers from various countries, offering an opportunity to strengthen professional networks, encourage future collaborations, and celebrate the scientific advances that continue to shape the fields of photochemistry and photobiology. In addition to the formal dinner, the event will include artistic and cultural activities, fostering a spirit of exchange, integration, and cooperation. Further details on logistics, transportation, and registration can be found through the corresponding QR codes in the official congress materials.

Tap the link to view the location on Google Maps.

XVI LATIN AMERICAN MEETING OF PHOTOCHEMISTRY AND PHOTOBIOLOGY

ELAFOT 2025

2 LatASP

PLENARY TALKS

ABSTRACTS

Light, Metal, and Medicine: Translating a Phototherapeutic Concept

Sherri A. McFarland[1]

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Photodynamic therapy (PDT) is a special branch of photomedicine that employs a photosensitizer, light, and oxygen to destroy cancer cells with spatiotemporal selectivity. The photosensitizers used for PDT have historically been organic molecules, specifically porphyrins and other tetrapyrrole-related structures. Given the important role of metals in medicine, metallated analogs of these traditional systems (as well as metal complexes of markedly different architectures) have attracted considerable attention in recent years. TLD1433, a metal complex designed in our laboratory, is an example that is also the first ruthenium-based photosensitizer for PDT to advance to clinical trials. This presentation will provide an update on translational activities and outcomes and discuss some of our current research efforts that were shaped by the design and development of TLD1433 as a bladder cancer PDT agent.

Skin under Light Exposure: From Damage Mechanisms to Adaptive Responses

Mauricio S Baptista[1]

[1]*IQUSP*

As our primary environmental interface, the skin navigates the dual nature of solar radiation. This lecture will unravel the skin's photochemical exposome, focusing on the critical balance between damage and adaptation. We will explore how specific wavelengths generate reactive species, disrupt sterol metabolism, and drive the accumulation of secondary and tertiary lipid peroxidation end-products, thereby compromising the skin's redox homeostasis and leading to inflammation, photoaging, and disease. In contrast, we will characterize how beneficial wavelengths, particularly in the red spectrum, induce metabolic reprogramming and systemic survival signaling to enhance resilience and repair, through many intermediates including nitric oxide. By integrating photochemistry and redox biology, this talk will provide a new mechanistic framework for redefining photoprotection and using light for therapeutic benefit.

Singlet oxygen-mediated damage to disulfides and proteins

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Disulfide bonds are critical structural elements in proteins and stabilize folded structures. Modification of these linkages is associated with a loss of structure and function. Previous studies have reported large variations in the rate constants for disulfide bond oxidation by various oxidants due to structural and electronic stabilization of the reaction intermediates.

We hypothesized that singlet oxygen ($^1O_2$), a key intermediate in photo-oxidation reactions would show similar effects, and that this might result in selective oxidation of some protein disulfides, in addition to other targets. Kinetic data for disulfide-mediated $^1O_2$ removal were monitored using the time-resolved 1270 nm phosphorescence of $^1O_2$. SternVolmer plots showed a large variation (~10^3) in the quenching rate constants (2 x 10^7 for the cyclic disulfide □-lipoic acid, to 3.6 x 10^4 $M^{-1}s^{-1}$ for cystamine). Product analysis showed the formation of mono- and di-oxygenated products, with elevated levels detected in D_2O buffers, consistent with solvent effects on $^1O_2$ lifetime. These data are interpreted in terms of a zwitterion intermediate [$–S^+(OO^-)$-S-] which either isomerizes to a thiosulfonate [-$S(O)_2$-S-] or reacts with another parent to give two thiosulfinates [-S(O)-S-], with the variation in quenching rates and product formation are ascribed to stabilization of the zwitterion.

These data indicate that some disulfides are selectively modified, and might have adverse effects on protein structure and function. This has been tested with two large mitochondrial complexes that contain □-lipoic acid bound covalently at lysine residues (lipoyllysines), with these being responsible for complex activity. Alpha-keto glutarate dehydrogenase (KGDH) plays a rate-determining role in the tricarboxylic acid (Krebs) cycle, and pyruvate dehydrogenase (PDC) controls cellular glucose metabolism, by determining whether pyruvate enters the Krebs cycle via conversion to acetyl-coenzyme A. Complex dysfunction has profound impacts on energy metabolism and is linked to metabolic diseases.

Exposure of both KGDH and PDC to $^1O_2$ (generated using Rose Bengal and light) resulted in a loss of enzymatic activity with this being dependent on light exposure, O_2, the presence of Rose Bengal, D_2O and the pre-illumination addition of free lipoic acid and lipoamide; these effects are consistent with $^1O_2$-mediated reactions. Activity loss occurred concurrently with lipoyllysine and sidechain modification (LC-MS peptide mass mapping) and protein aggregation (detected by SDS-PAGE). Peptide mass mapping provided evidence for modification at multiple Met, Trp, His and Tyr residues; (modification extents of 20-50%) and the lipoyllysine sites (6-55% modification). Structure modelling indicated the modifications occur across all the complex subunits, and occurs within functional domains or at multimer interfaces, consistent with damage at multiple sites contributing to the overall loss of activity. These data indicate that both the activity and structure KGDH and PDC are susceptible to $^1O_2$-induced damage, with potential effects on cellular glucose metabolism.

Further information:

1) Gao, Q. et al (2023) The structure of model and peptide disulfides markedly affects their reactivity and products formed with singlet oxygen, Free Radic. Biol. Med., 207, 320-9.
2) Gao, Q. et al (2024) Mapping of oxidative modifications on the alpha-ketoglutarate dehydrogenase complex induced by singlet oxygen: effects on structure and activity, Free Radic. Biol. Med, 224, 723-9.
3) Gao, Q. et al (2025) Inactivation of mitochondrial pyruvate dehydrogenase by singlet oxygen involves lipoic acid oxidation, side-chain modification and structural changes, Free Radic. Biol. Med., 234, 19-33.

Developing Ir(III) Complexes as Photosensitizers for Photodynamic Therapy (PDT) of Cancers and Bacteria

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Photosensitizers (PSs) play a critical role in photodynamic therapy (PDT) for cancers and infectious diseases. However, the drawbacks of the current FDA-approved porphyrin-based PSs for PDT, such as the long cutaneous photosensitivity, weak absorption at its clinical wavelength (630 nm) and virtually no absorption of tissue-penetrating near-infrared (NIR) light, and ineffectiveness in hypoxia, prevent the widespread use of PDT in the clinic. Exploring new PSs to overcome these shortcomings has been a growing area of interest. Transition metal complexes, including the Ir(III) complexes, provide rich and tunable photophysical properties due to the interactions between the metal center and the organic ligands, and can yield high triplet quantum yields because of the metal-induced rapid intersystem crossing (ISC). To exploit the best practice for developing Ir(III) complexes into PSs, my group has designed and synthesized multiple series of mononuclear and dinuclear Ir(III) complexes containing various bidentate and tridentate ligands for anticancer and antimicrobial PDT applications. We aim to develop Ir(III) complexes that exhibit strong NIR absorption and emission in the regions of 730-920 nm for theranostic PDT applications. The photophysical properties of our synthesized complexes, including the UV-Vis-NIR absorption, emission, and transient absorption characteristics, were systematically investigated. Reactive oxygen species generation was studied, and their phototherapeutic effects on melanoma or breast cancer cell lines, and on Gram+ and Gram- bacteria have been evaluated.

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1. Paloma Lizondo-Aranda, Lara Martínez-Fernández, Miguel A. Miranda, Roberto Improta, Thomas Gustavsson, Virginie Lhiaubet-Vallet *J. Phys. Chem. Lett*. **2022**, 13, 251-257
2. Paloma Lizondo-Aranda, Thomas Gustavsson, Lara Martínez-Fernández, Roberto Improta, Virginie Lhiaubet-Vallet. *Chem.Eur. J.* **2024**, 30, e202401835.
3. Paloma Lizondo-Aranda, Gemma M. Rodriguez-Muniz, Miguel A. Miranda, Belinda Heyne, Virginie Lhiaubet-Vallet. *Photochem. Photobiol. Sci.* **2025**, 24, 1–12
4. Laura Francés-Soriano, Gemma M. Rodríguez-Muñiz, Paloma Lizondo-Aranda, Delia Bellezza, María González-Béjar, Virginie Lhiaubet-Vallet. *Nanoscale* 2025, DOI: 10.1039/d5nr01777g

Photoreactivity of metabolically generated DNA lesions: the case of etheno adducts

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The photochemistry of three mutagenic DNA adducts - 3,N^4-etheno-2'-deoxycytidine (εdC), 1,N^2-etheno-2'-deoxyguanosine (εdG), and 1,N^6-etheno-2'-deoxyadenosine (εdA) – will be addressed. In a first stage, the combined experimental/theoretical study of εdC and εdG shows the effect of the extra heterocycle compared to native nucleobases.[1,2] For both compounds, steady-state measurements under neutral conditions reveal a red-shift of the absorption and fluorescence spectra along with an increase of the fluorescence quantum yield. These observations are corroborated by femtosecond fluorescence upconversion experiments showing a substantial increase of the average excited state lifetime. Quantum mechanical calculations rationalize these experimental findings by revealing, for εdC, the presence of a sizeable energy barrier on the emitting $^1\pi\pi^*$ potential energy surface to reach the decay funnel to S_0. A more complex behavior is observed for εdG with the presence of two emissive species associated with two strongly coupled minima inducing a peculiar time-resolved behavior.
Then, the photochemical reactivity of εdA and εdG triggered by two well-known photosensitizers acting by Type I and/or Type II mechanisms, ie. 4-carboxybenzophenone and rose Bengal, will be considered. Steady-state photolysis experiments combined with HPLC and mass spectroscopy measurements show that the photochemical conversion leads to photoproducts that correspond to the repaired nucleosides. In addition, spectroscopic studies point toward a photorepair occurring through both Type I and II mechanisms.[3] With this background and with the goal of shifting the excitation wavelength toward the photobiological window, upconverting nanhohybrids derivatized with a covalently linked rose Bengal (UC@RB) have been developed.[4] The results demonstrate that these nanohybrids acted as a light-harvesting nanozymes that absorb NIR-light and transfer energy to rose Bengal, triggering the photorepair of the DNA purine-derived etheno adducts. These systems allow the use of NIR excitation for deeper and more efficient excitation the photosensitizer, enabling photochemical processes in optically challenging environments such as tissues.

References:

1 Paloma Lizondo-Aranda, Lara Martínez-Fernández, Miguel A. Miranda, Roberto Improta, Thomas Gustavsson, Virginie Lhiaubet-Vallet *J. Phys. Chem. Lett*. **2022**, 13, 251-257

2 Paloma Lizondo-Aranda, Thomas Gustavsson, Lara Martínez-Fernández, Roberto Improta, Virginie Lhiaubet-Vallet. *Chem.Eur. J.* **2024**, 30, e202401835.

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4 Laura Francés-Soriano, Gemma M. Rodríguez-Muñiz, Paloma Lizondo-Aranda, Delia Bellezza, María González-Béjar, Virginie Lhiaubet-Vallet. *Nanoscale* 2025, DOI: 10.1039/d5nr01777g

The rare single chromophore dual-release photochemistry of sulfoximines and sulfone diimines

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Generating two distinct reactive intermediates from a single chromophore is rare in photochemistry. One notable example is the photolysis of dibenzothiophene sulfoximines, which releases both nitrenes and atomic oxygen upon irradiation. This dual release enables localized oxidative stress while nearly simultaneously labeling nearby biomolecules, offering a promising approach to studying oxidative stress in cells.

To investigate this reactivity, we examined several N-aryl dibenzothiophene sulfoximines through product analysis, photophysical measurements, and quantum yield determinations. The electron demand of the N-aryl substituents significantly influenced the quantum yield: electron-withdrawing groups increased dibenzothiophene S-oxide formation, whereas electron-donating groups decreased it. These findings show that modifying the N-substituents can effectively control nitrene production in dibenzothiophene sulfoximines.

Sulfondiimines, a class of organosulfur(VI) compounds and diaza sulfone analogues, have recently attracted interest in medicinal chemistry and drug discovery. Despite their pharmacological potential, their photochemical behavior remains largely unexplored. Their unique reactivity could enable the generation of two different short-lived nitrenes, opening new synthetic pathways. To explore these possibilities, we are currently investigating the dual-release photochemistry of diaryl sulfondiimines and developing predictive models for their reactive intermediates.

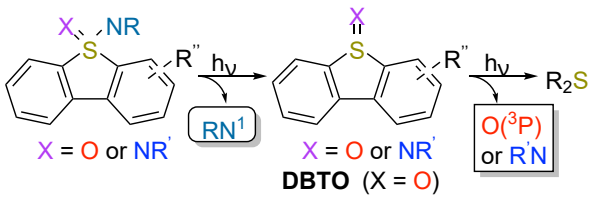

Figure 1. The properties and possibly sequence of photorelease for sulfoximines (X=O) and sulfondiimines (X=NR') can be controlled by properties by changes to R, R', and R''.

Homo- vs. hetero-FRET in singlet-singlet photosensitization evidenced by photopolymerization experiments

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Enhancing the light-absorption efficiency of phosphine oxide photoinitiators remains a central challenge in photopolymerization. In this work, we demonstrate a novel photosensitization mechanism based on singlet–singlet Förster resonance energy transfer (FRET) from fluorescent dyes to phosphine oxides, resulting in a remarkable acceleration of polymerization kinetics—up to sixfold under low-intensity 365 nm irradiation. Comprehensive photophysical and kinetic analyses reveal that the reactivity enhancement arises from hetero-FRET, i.e., non-radiative energy transfer from the excited fluorophore (donor) to the phosphine oxide (acceptor). At higher dye concentrations, additional energy migration among fluorophores (homo-FRET) becomes significant, modulating the overall sensitization efficiency. Incorporating both donor–donor and donor–acceptor interactions into a refined kinetic model quantitatively reproduces the experimental sensitization factors, confirming the coupled contribution of these processes. This study provides the first quantitative evidence that homo-FRET can reinforce hetero-FRET-driven photosensitization in photopolymerization, establishing a new paradigm for understanding and controlling excitation-energy flow in photoinitiating systems. The interplay between homo- and hetero-FRET opens new perspectives for the rational design of advanced photochemical and light-harvesting architectures capable of efficient radical generation under mild UV exposure.

Cold-Ion-Spectroscopy and Excited State Dynamics of Species of Biological Interest

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DNA damage caused by UV and ionizing radiation can lead to genomic instability and carcinogenesis in cases where DNA repair mechanisms fail.[1] Both the ionization of DNA bases and the interaction with metal cations or protons facilitate inter- and intramolecular charge transfer (CT) or proton transfer (PT) processes,[2] which ultimately lead to the formation of non-canonical tautomers of the bases and a consequent point-mutation.[1,2]
The increasing global incidence of skin cancer [1], strongly correlated with cutaneous photodamage, underscores the critical need to develop more effective sunscreens. For this purpose, it is important to achieve a comprehensive understanding of the photophysical and photochemical properties related to the photoprotection activity of model molecules. Organic sunscreen molecules absorb UVA and UVB radiation and undergo ultrafast internal conversion (IC) to the ground state, dissipating the excess energy as vibrational motion and ultimately heat, thus preventing photodamage.
In recent years, our group has studied the effect of the interaction of DNA bases with Ag^+ on their structure, reactivity, electronically excited states properties[3,4] and the formation of $DNA^{\bullet+}$ radical cations,[5,6] at the molecular level. More recently, we have extended these studies to organic sunscreen molecules.
In this talk, I will first present the experimental cold ions spectroscopy set-up that combines mass spectrometry and laser spectroscopies to study cold ions at 10 K in the gas phase and its application to the study of BM-Ag^+ complexes (BM: DNA bases or sunscreens) and their corresponding radical cations.
In the case of the Oxybenzone radical cation an unexpected result was observed reveling an ultrafast process taking place upon excitation at the band origin that is rationalized with the help of ground and excited state theoretical calculations.

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Mechanistic insights into solar-driven photocatalysts for sustainable applications.

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In this talk, I will present our experimental studies on the photocatalytic mechanisms of two different types of solar light activated catalysts: carbon nitrides (CN) and photoactive metal-organic assemblies.

Polymeric melon-type CN nanoparticles were synthesized by thermal treatment of urea and tested for photocatalytic degradation of methyl orange under UV (350 nm) and simulated solar irradiation. Electron spin resonance experiments confirmed the generation of hydroxyl and superoxide radicals, as well as the formation of non-negligible amounts of H_2O_2. The mechanisms leading to these reactive oxygen species and their role in pollutant degradation will be discussed.

In parallel, we developed novel Zr–perylene hybrid nanoparticles (named ZIPER) with strong visible absorption (400–560 nm) and red emission (600–700 nm). Photoluminescence quenching experiments revealed that the excited state of ZIPER behaves as a strong oxidant and a moderate reductant, enabling the reductive dehalogenation of persistent chlorinated pollutants (CCl_4 and CCl_3COOH) and the photocatalytic production of H_2O_2. Due to their repetitive Zr6–perylene structural motifs, ZIPER nanoparticles function as self-assembled arrays of molecular photoredox catalysts.

Our results emphasize that different nanophotocatalysts can follow fundamentally distinct mechanistic routes: CNs behaves as semiconductors with undesired high electron-hole recombination, whereas ZIPER functions as a molecular photoredox array capable of driving reductive transformations in the presence of sacrificial-electron donors. This mechanistic insight is key to guiding the design of more efficient solar-driven photocatalysts.

Beyond Original Purpose: Repurposing Bacterial Photosynthesis

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Bacterial photosynthesis has been thoroughly investigated in the last decades and the overall understanding of the molecular mechanisms of solar light transduction are well understood. There are still some aspects that need further investigation, but the field has matured to the point where applications of bacterial photosynthesis and its components as soft materials to purposes that go beyond the physiological role of this process are now being explored more and more and are becoming real applications in material science.
Several applications to the new promising technologies and some open problems will be presented to illustrate potentiality and limits of the use of bacterial photosynthesis and of the components of the bacterial photosynthetic apparatus in emerging fields.

Project **Adaptive Photochemistry** (PRIN 2022 code n. 20225NSHZ5) funded by MUR – Italian Ministry of University and Research is acknowledged.

Carbon Dots: Unlocking Photochemical and Photobiological Potential in Biological Applications

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Carbon-based nanomaterials have revolutionized various industries, with many applications already on the market. Among them, carbon dots (CDs) have become particularly promising due to their natural luminescence, biocompatibility, and adaptable surface chemistry. Their photoluminescent qualities not only facilitate advanced imaging and sensing methods but also create new opportunities for targeted delivery and phototherapies. Although their popularity is growing in both academic and industrial sectors, key questions remain about their biological interactions, functional capabilities, and safety profiles. This talk will examine how synthesis parameters, such as reagent choice and reaction conditions, greatly influence the physicochemical and biological properties of CDs. It will also review recent progress in their applications within biomedical and agricultural fields, emphasizing their potential to address critical challenges in health and sustainability.

Acknowledgements

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Optogenetic Circuits and Optoecology: mapping transcriptional responses and visualizing population dynamics through the eyes of fungi

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The filamentous fungus Neurospora crassa perceives and responds to light through the White-Collar Complex (WCC), a transcriptional heterodimer containing a LOV (Light-Oxygen-Voltage) domain that senses blue wavelengths. Light absorption triggers a conformational change that promotes dimerization and results in strong, light-intensity dependent transcriptional activation.

We have adopted optogenetic approaches to further delve into Neurospora's light-responses. In doing so, we were able to genetically program 2D-images in this organism. Thus, we can project a photograph onto a Neurospora carrying a luciferase reporter under the control of a light responsive promoter and obtain back a bioluminescent pattern mimicking the original image: a live canvas in which images are genetically processed and reproduced with real-time dynamics. This platform provides a great way to assess transcriptional profiles obtaining (literally!), a picture of gene expression, and also to explore the properties of genetic circuits, circadian systems, and transcriptional (eidetic) memory. We have even developed a cybergenetic platform that allows us to precisely "print" genetic responses through computer-controlled light stimulation.

In addition, we engineered Neurospora-based optogenetic switches for Saccharomyces cerevisiae, enabling robust blue-light–responsive transcriptional systems. In yeast, we can now achieve over 3000-fold induction of gene expression across a wide dynamic range, and by switching the lights on and off, we can control biotechnologically relevant phenotypes such as flocculation. Moreover, by integrating exocrine and optogenetic systems, we have generated complex population dynamics, illustrating how light can function as a potent orthogonal signal to reprogram both individual and collective traits. These approaches have opened the door to studying population behaviors -including the emergence of mutualism- in the emerging field of Optoecology.

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Biocompatible Nanosystems Under the Light: A Spectroscopic Insight into Reverse Micelles, Vesicles, and Other Organized Systems. Challenges and Opportunities toward Sustainable Chemistry

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Supramolecular self-assembled systems represent a dynamic and promising area in modern science and technology. Among these, reverse micelles (RMs) are surfactant aggregates formed in non-polar solvents, where the polar head groups are sequestered in the interior. This structure offers a unique and versatile medium for a wide range of chemical processes, including nanoparticle synthesis and bioorganic reactions. Similarly, vesicles—spherical, self-closed structures formed by amphiphilic molecules—can encapsulate both hydrophilic and lipophilic compounds, broadening their applicability across various fields.

In the pursuit of more environmentally friendly systems, non-traditional components such as ionic liquids (ILs), fatty acid esters, and natural deep eutectic solvents (NADES) have emerged as alternatives to conventional surfactants and organic solvents. ILs, in particular, stand out due to their negligible vapor pressure, excellent chemical and thermal stability, tunable properties, and recyclability—making them attractive candidates for replacing traditional components in organized media.

This presentation will focus on how spectroscopic techniques—including absorption, emission, and light scattering—are employed to characterize the organized systems (RMs and vesicles) formed with these greener components. Key properties such as polarity, electrondonating ability, and viscosity will be discussed. In this context, examples highlighting the incorporation of IL-based surfactants or biocompatible solvents will demonstrate their impact on the interfacial and structural properties of these systems. Applications such as nanoreactors for enzymatic reactions and nanoparticle synthesis will be presented, along with recent findings on IL-based RMs and vesicles. These examples will underscore the versatility and emerging research opportunities surrounding these fascinating supramolecular assemblies.

Antimicrobial Photodynamic Therapy over Oral Pathogens: From the Bench to the Clinical Setting

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Photodynamic therapy (PDT) is a technique that combines a chemical compound or dye known as a photosensitizer with a light source, which can be either visible or invisible, such as lasers and LEDs. When exposed to molecular oxygen, the photosensitizer transitions from its ground state to an excited state, leading to the production of reactive oxygen species (ROS) and singlet oxygen ($^1O_2$). PDT is effective in eliminating unwanted eukaryotic cells, such as cancer cells in the oral cavity, as well as pathogenic microorganisms involved in bacterial, fungal, or parasitic infections. Antimicrobial photodynamic therapy (aPDT) is a technique used in dentistry to control the biofilms associated with various oral conditions, including dental caries, periodontal and periimplant diseases, endodontic issues, simplex herpes, and *Candida* infections. It is also effective for wound healing and treating oral lichen planus. In this way, the purpose of this presentation is to provide an overview of aPDT, including the fundamental concepts, mechanisms, advantages and disadvantages. Additionally, the main findings from our research group will be sharing and discussed, and also some examples of the current clinical applications and protocols for aPDT in dentistry will be presented.

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ABSTRACTS

Supramolecular controllable photoactive agents for photodynamic therapy

Denis Fuentealba[1], José Robinson-Duggon[2], Nory Marino-Ocampo[1,3], Daniel Guerra Díaz[4], Daniel Zuñiga-Nuñez[5], Nancy Pizarro[6], German Gunther[4]

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Photodynamic therapy (PDT) is based on the inactivation of cancer cells or bacteria through the generation of singlet oxygen and other reactive oxygen species (ROS), which readily oxidize proteins, lipids and DNA leading to cell death. One of the strategies used to enhance the generation of ROS and protect the photosensitizers from early decomposition is their complexation with supramolecular host systems.[1] For that purpose, we have previously used cucurbit[*n*]urils (CB[n]s, n = 5, 6, 7, 8, 10), a family of macrocycles that has gained attention in the field of PDT due to their capacity to modify the photochemical properties of photosensitizers in a controlled fashion. Moreover, different CB[*n*] complexes can be used to switch ON or OFF the generation of singlet oxygen.[2,3] More recently, we have investigated the use of acyclic cucurbituril-like containers, which show extraordinary capabilities to control the singlet oxygen.[4,5] Phototoxicity studies in tumoral cell cultures show good potential for the use of these supramolecular containers in PDT.

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Influence of topology, architecture, and environment on spin polarization transfer: implications for quantum information science

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This presentation will feature mostly unpublished results from steady-state and time resolved (CW) electron paramagnetic resonance spectroscopy experiments on stable and transient radicals in unusual environments. The talk will emphasize the breadth of different structures that can be investigated, which include microbubbles, nanocrystals, metal organic frameworks, and vesicles, to learn about structural and physical properties of these systems. Significant attention will be paid to new results on spin probes studies of structured (non-Newtonian) fluids constructed from Aerosil™ nanoparticles in organic solvents, seeking to understand the influence of solventsolvent, solvent-Aerosil, and Aerosil-Aerosil interactions as a function of Aerosil loading, solvent, and temperature. Spin probe measurements in microbubbles reveal orientation effects in the outer layer of these structures for the first time. In nanocrystals we show strong evidence for the presence of radical pair triplet states. The vesicle experiments suggest new directions for small molecule topology in supramolecular systems. New experiments on spin polarization transfer from photoexcited triplet states to stable nitroxide monoradicals and biradicals as potential qubits for quantum information science applications will also be described.

Effect of UV-A Radiation on Antioxidant Activity and Cytotoxicity of Vanillin

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Vanillin (4-hydroxy-3-methoxybenzaldehyde) is widely recognized for its use as a flavoring agent and for its antioxidant properties. However, it remains unclear whether these antioxidant qualities are preserved when vanillin is exposed to electromagnetic radiation. This study aims to evaluate the impact of UV-A radiation on vanillin's antioxidant activity. With this objective, we performed two types of experiments: (*i*) in solution, we evaluated the ability of vanillin to prevent photosensitized damage to biomolecules, and (*ii*) we investigated the in vitro cytotoxicity and phototoxicity of vanillin on HeLa cells:

(i) *Prevention of photosensitized oxidation to biomolecules*: aqueous solutions containing a photosensitizer and a given biomolecule were exposed to UV-A radiation, both in the absence and presence of vanillin. The photochemical reaction was monitored by UV-Vis spectrophotometry, HPLC, fluorescence spectroscopy and Laser Flash Photolysis. The results show that vanillin effectively prevents the degradation of tryptophan and 2'-deoxyguanosine5'-monophosphate. Mechanistic analysis suggests that, in our experimental conditions, vanillin prevents oxidation by facilitating the recovery of the biomolecule radical to its intact form, even though it can deactivate the triplet excited states of the photosensitizer.

Vanillin cytotoxicity and phototoxicity: HeLa cells were incubated with vanillin and either kept in the dark or exposed to UVA radiation. Cytotoxicity, evaluated by the Tukey test, was observed at a high vanillin concentration (0.8 mM), with similar effects whether the cells were exposed to UV-A radiation or kept in the dark. Additionally, reactive oxygen species (ROS) formation was measured using a fluorescent probe based on 2′,7′-dichlorodihydrofluorescein diacetate (DCFH-DA). The results revealed that ROS generation was significantly higher in cells exposed to UV-A radiation in the presence of vanillin compared to cells kept in the dark.

Photoinduced dual capacity of Re-Mn complexes for singlet oxygen generation and carbon monoxide release

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The combined action of singlet oxygen ($^1O_2$) generation and the photoinduced release of carbon monoxide by tricarbonyl metal complexes is a promising synergic treatment against multiresistant bacterial infections.[1] Then, looking for systems that have the dual capacity of acting as photosensitizer and photoCORMs (photoinduced carbon monoxide releaser molecules), in this work, we compare the use of two polydentate ligands (bpm = bipyrimidine; dp = 2,5-bis(1pyrazolyl)pyrazine) that offer the opportunity to accommodate two metal centers exhibiting both capacities, singlet oxygen generation and carbon monoxide releasing properties in a single molecule. The heterobimetallic $[Br(CO)_3Re(bpm)Mn(CO)_3Br]$ and $[Br(CO)_3Re(dp)Mn(CO)_3Br]$ complexes were synthesized and photophysically characterized. In addition, CO-release and $^1O_2$ generation quantum yields were evaluated and compared with values obtained for the monometallic $[Mn(L)(CO)_3Br]$ and $[Re(L)(CO)_3Br]$ complexes.

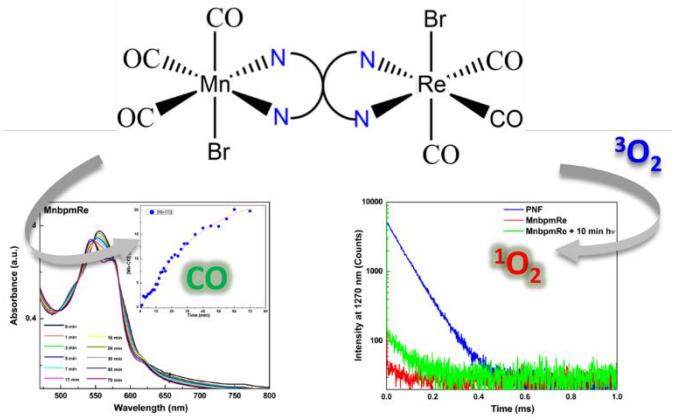

Figure 1. Singlet oxygen ($^1O_2$) generation and carbon monoxide (CO) release upon excitation of $[Br(CO)_3Re(bpm)Mn(CO)_3Br]$.[2]

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Tryptophan dimers as biomarkers of protein oxidation: formation, detection, and quantification

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Oxidation of proteins involves complex mechanisms that produce multiple intermediates and products. Usually, the first step includes the loss of a single electron from the side chain of amino acids, forming secondary radicals (1). These species can react with O_2 to produce oxygenated products (carbonyls, alcohols, hydroperoxides, etc.)(2), or self-react, leading to covalent dimers (3). Di-tyrosine is the most studied species and employed as a biomarker of protein oxidation.

$$\text{Protein-H} + \text{FR}^{\bullet} \rightarrow \text{Protein}^{\bullet} + \text{FRH} \quad (1)$$

$$\text{Proteinl}^{\bullet} + O_2 \rightarrow \text{Protein-}O_2^{\bullet} \rightarrow\rightarrow \text{oxygenated products} \quad (2)$$

$$\text{Protein}^{\bullet} + \text{Protein}^{\bullet} \rightarrow \text{covalent dimers} \quad (3)$$

Tryptophan dimers (di-Trp), generated by self-reactions of tryptophanyl radicals (Trp$^{\bullet}$) have been detected in isolated proteins and biological samples; however, the lack of suitable standards has limited their detection and quantification. In this work, we studied the formation, detection, and quantification of di-Trp species generated by different experimental approaches, involving photochemical, gamma irradiation, and enzyme-mediated systems. **Hypothesis:** one-electron oxidation of tryptophan mediated by photosensitized reactions, gamma irradiation, and processes catalyzed by horseradish peroxidase would lead to high yields of di-Trp, allowing the obtaining of enriched fractions of these species. **Experimental:** aqueous solutions of tryptophan (4 - 30 mM) were illuminated (6 min) in the presence of 103 µM riboflavin using a 450 nm light emission diode (LED, 81.4 W/m^2), exposed to gamma irradiation (4 hr, ^{60}Co, total dose 1 KGy), or incubated with 0.65 µM horseradish peroxidase (HRP) and 500 µM H_2O_2 for 2 min at 25 °C. The resulting solutions were cleaned, di-Trp isolated by semipreparative chromatography, and analyzed by liquid chromatography with mass detection (LC-MS, Triplequad, ABSciex-4500) by selected reaction monitoring (SRM) mode for transitions m/z = 407 to 203 and 407 to 390. **Results:** LC-MS analysis of tryptophan solutions illuminated in the presence of riboflavin (20% O_2), exposed to gamma irradiation or incubated with the HRP/H_2O_2 system, showed the presence of at least 5 peaks ascribed to di- Trp. Interestingly, the pattern of the signals was dependent on the system, highlighting those generated by HRP/H_2O_2. Incubation of tryptophan with HRP/H_2O_2 led to multiple di-Trp isomers detected using m/z 407→203, and m/z 407→390 transitions (with greater yields detected at pH 9.2 than 5.5). The latter contrasts with the riboflavin-mediated photo-oxidation and gamma irradiated tryptophan solutions, where one di-Trp dimer predominated as detected by the m/z 407→203 transition. Docking studies support the formation of di-Trp inside the catalytic site of HRP, and subsequent release, explaining the observed LC-MS pattern by interactions of tryptophan with specific residues of HRP. **Conclusions:** tryptophan dimers were generated by exposure of solutions of free tryptophan to riboflavin-mediated photo-oxidation, gamma irradiation, and the HRP/H_2O_2 system. The obtained data indicate that the HRP/H_2O_2 system is an efficient process, resulting in a specific pattern of di-Trp species, which could be employed for semi-quantitative determination of di-Trp in complex matrices.

Heteroleptic Copper(I) Complexes type [Cu(*dpa*)(*P,P*)]$^{+}$ as Photoredox Catalyst

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A key goal in modern organic synthesis is to create greener methods that avoid toxic reagents and use renewable energy sources. Visible-light photochemistry meets these standards by offering a gentle, selective way to activate organic molecules. Although polypyridyl ruthenium- and iridium-based complexes have set the standard for photocatalysis, their limited availability and high cost prevent large-scale use. In contrast, heteroleptic copper(I) complexes are plentiful, less toxic, and can be easily made from inexpensive starting materials. Their advantageous excited-state lifetimes, combined with simple one-pot syntheses, make them attractive, sustainable options for visible-light-driven reactions.

In this study, we present a family of heteroleptic Cu(I) complexes that pair readily accessible dipyridylamine (dpa) derivatives with commercially available bis-phosphine ligands (Figure 1). Comprehensive spectroscopic and mass spectrometric analyses confirm their structures and show strong metal-to-ligand charge-transfer (MLCT) absorptions in the 300–370 nm range. When excited, the complexes emit between 450 and 520 nm, with quantum yields and excitedstate lifetimes depending on the electronic properties of the *P,P* chelate, and the substituent on the dpa scaffold. Photocatalytic assays demonstrate broad utility: all complexes promote atomtransfer radical addition (ATRA), visible-light-driven decarboxylative couplings, Appel-type halogenations, and bromonitromethylation of styrene with competitive efficiency. The modular, low-cost dpa backbone thus becomes an attractive, sustainable alternative to phenanthroline motifs commonly used in copper photocatalysis, expanding the scope of visible-light-mediated synthesis.

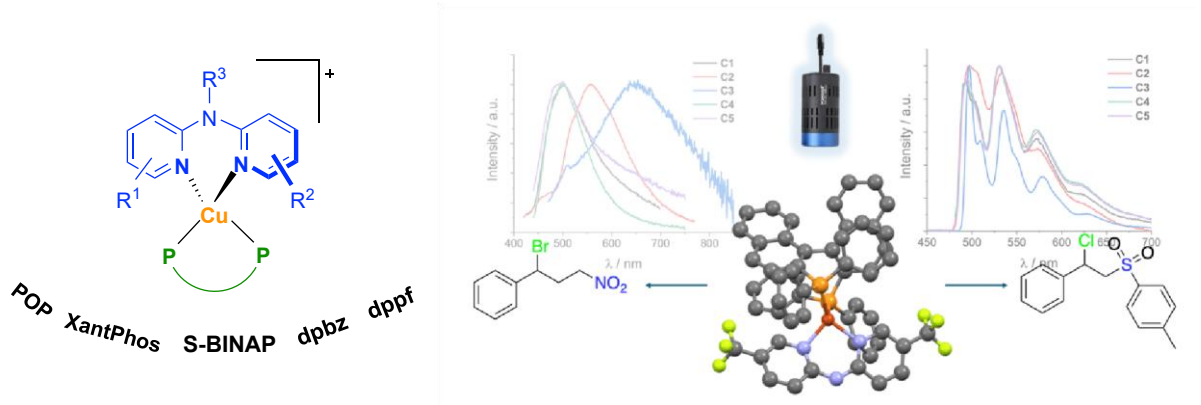

Figure 1. Complexes of the type [Cu(dpa)(*P,P*)]BF_4 and their photocatalytic performance.

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Natural anthraquinones and Photodynamic Therapy: an antifungal strategy against Candida biofilms

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Fungal infections caused by *Candida* species remain a major clinical challenge due to antifungal resistance and their biofilm persistence. Antimicrobial Photodynamic therapy (aPDT), which combines a photosensitizer (PS), light, and molecular oxygen to generate reactive oxygen species (ROS), has emerged as a promising alternative strategy. Our research group has investigated natural anthraquinones (AQ) as antifungal PS, focusing on biofilms and their photobiological mechanisms. We have shown that rubiadin and rubiadin-1-methyl ether, isolated from *Heterophyllaea pustulata* Hook. (Rubiaceae), exhibit significant antibiofilm activity against *Candida tropicalis* under actinic irradiation. Rubiadin, which has two free hydroxyl group at C-1 and 3, was found to be more potent than its O-methylated derivative at C-3 (7.7 µM vs. 58 µM, respetively), highlighting the role of free phenolic substituents in enhancing Type I photoreactivity. Mechanistic assays confirmed that superoxide anion ($O_2^{\bullet -}$) was the main ROS, with a minor contribution from singlet oxygen ($^1O_2$).[1,2]

In a complementary approach, we studied soranjidiol (SOR), a monomeric AQ with two hydroxyl groups, and its dimer 5′5-bisoranjidiol (BISOR). Both compounds reduced biofilm biomass under actinic irradiation, but with different efficiencies. SOR, active at 7.7 µM, produced a moderate reduction of approximately 46%, whereas BISOR, effective at a much lower concentration (1.9 µM), achieved a stronger reduction of about 68%. Quenching assays revealed that SOR involves both Type I and Type II pathways at low concentrations, whereas BISOR acts almost exclusively through a Type I mechanism, suggesting that dimerization enhances electron-transfer processes and $O_2^{\bullet -}$ production.[3]

More recently, we demonstrated that parietin (PTN: 1,8-dihydroxy-3-methoxy-6methyl AQ), a lichen-derived with a methoxy group at C-3 and a hydroxyl at C-7, exerts strong phototoxicity against *C. tropicalis* biofilms, achieving ~4 log reduction in viability at 3.5 µM. Like other AQs, PTN triggered both oxidative and nitrosative stress, as well as antioxidant responses. However, these defenses were insufficient to prevent aPDT-induced biofilm killing.[4]

Taken together, our findings establish that structural variations in AQs—including hydroxylation, methylation, and dimerization—directly influence their photophysical properties and PDT mechanisms. Free hydroxyl groups favor Type I pathways, O-methylation reduces activity, dimerization enhances superoxide generation, and 1,8-dihydroxy arrangement confers singular efficacy. These findings position natural AQs as versatile antifungal photosensitizers, with strong potential for the development of aPDT-based therapeutic strategies against *Candida* biofilms.

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Potential applications of rhenium(I)tricarbonyl molecules with aromatic bridged ligands

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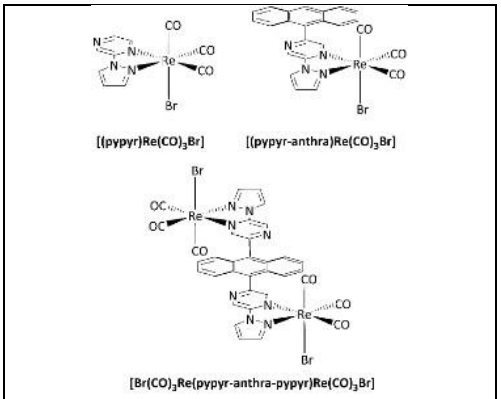
Rhenium(I) diimine tricarbonyl halide molecules have long captured researchers' attention due to their remarkable photophysical properties, ease of preparation, and stability. Among the first studies demonstrating the photocatalytic carbon dioxide reduction activity of a series of **[(bpy)Re^{I}(CO)$_3$X]** (where X = Cl or Br, and bpy = 2,2'-bipyridine) molecules, emission quantum yields of approximately 14% and faradaic efficiencies of 98% were reported. Systematically varying substituents in the 2,2'-bipyridine ligand revealed that carbon dioxide reduction activity linearly depends on the molar absorption coefficients of the molecules. This suggests that ligand structural modifications can optimally enhance catalytic carbon dioxide reduction. Notably, a compound containing the 1,8-bis(2,2′-bipyridin-6-yl)anthracene ligand with two Re^{I}(CO)$_3$Cl moieties exhibited significant photocatalytic carbon dioxide reduction activity for both cis and trans isomers. Additionally, bimetallic compounds outperformed monometallic ones under the same experimental conditions. These findings are attributed to the shorter intermetallic distance in the cis isomer (6.27 Å), enabling cooperative action between both metallic sub-centers, and to the anthracenyl fragment's role as a charge accumulator, facilitating reduction.

In the present work we report the behavior of three ligands based on anthracenyl and pyrazolyl-pyrazine ligands: 2-(*1H*-pyrazol-1-yl)pyrazine (**pypyr**), 2(anthracen-9-yl)-5-(1*H*-pyrazol-1-yl)pyrazine (**pypyranthra**) and 9,10-bis(5-(1*H*-pyrazol-1-yl)pyrazin-2yl)anthracene (**pypyr-anthra-pypyr**) and their respective Re^{I}(CO)$_3$Br complexes: **[(pypyr)Re(CO)$_3$Br]**, **[(pypyr-anthra)Re(CO)$_3$Br]** and **[Br(CO)$_3$Re(pypyr-anthra-pypyr)Re(CO)$_3$Br]** (Scheme 1). We explore their molecular and electronic structure by means of DFT modelling for a complete understanding of the photophysical and electrochemical properties.



Scheme 1. Diagram structure of **[(pypyr)Re(CO)$_3$Br]**, **[(pypyr-anthra)Re(CO)$_3$Br]** and **[Br(CO)$_3$Re(pypyr-anthra-pypyr)Re(CO)$_3$Br]**.

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Optical detection of singlet oxygen in vitro and in vivo – Please stop saying, it would be difficult

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Singlet Oxygen, the long-time denied intermediate and main mediator in the process of photosensitization can be directly observed via its characteristic phosphorescence. This was done for the first time about half a century ago. For many years, it was just a benchmark for the sensitivity of spectroscopic instruments and when the topic moved to *in vivo* detection, it was even claimed that this would be impossible. Still today, a look into recent books or reviews on the detection of singlet oxygen gives the impression, optical detection would be difficult or expensive and other methods like NMR or sensor molecules would be easier and cheaper to perform. The short answer would be: this is simply wrong. Of course, the complete answer is more differentiated.

The presentation will address most technical aspects like detector types as well as optical design and how to get around the typical challenges coming along with biological samples. Finally, a collection of possible setups and their performance, advantages, pit falls and problems will be presented, showing, what is possible nowadays to give evidence, that timeresolved optical detection does not only provide results that are in many cases superior to all other detection methods, but is not that difficult anymore.

Marine Algae as a Therapeutic and Sustainable Source for Skin Photoprotection Against UV-Induced Damage

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Ultraviolet (UV) radiation is a major environmental factor contributing to various skin pathologies, including sunburn, premature aging, and skin cancer. The intensification of UV exposure, driven by ozone layer depletion and the broader impacts of climate change, presents a growing public health concern, particularly for populations exposed to high levels of solar radiation. While the skin possesses natural defense mechanisms such as melanin production and antioxidant enzyme activity, these are often insufficient to counteract the cumulative effects of prolonged UV exposure. This reality underscores the need for safe, effective, and environmentally responsible photoprotective strategies. Marine organisms, particularly macroalgae, have evolved sophisticated protective systems that allow them to thrive in high-UV environments. These include the synthesis of naturally occurring compounds with strong UV-absorbing and antioxidant capabilities. Leveraging such marinederived bioactives offers a promising pathway for developing next-generation skincare products that both shield the skin and align with principles of sustainability.

One of our lines of research focuses on evaluating compounds of marine origin and taking advantage of their ability to neutralize free radicals, which was evaluated by in vitro assays targeting several reactive species commonly implicated in UV-induced oxidative stress. In parallel, their protective effect on lipid structures, critical components of skin cell membranes, was investigated using a complementary model system, a lipid oxidation assay. The compounds showed strong free radical scavenging activity and effectively inhibited oxidative degradation of lipids under stress conditions. Spectroscopic analyses revealed their ability to mitigate key structural changes associated with lipid peroxidation, including the formation of hydroxyl and carbonyl groups, as well as the alteration of aliphatic chains. These effects were especially notable at physiologically relevant concentrations and under conditions that simulate UV-induced damage in skin cells.

The results support the incorporation of marine-derived antioxidants into dermocosmetic formulations as a viable strategy for enhancing skin resilience against UV radiation. Beyond their biological efficacy, such compounds contribute to the sustainable use of marine resources, offering a dual benefit of skin protection and environmental responsibility. This approach complements global efforts toward climate adaptation and public health promotion, in alignment with Sustainable Development Goal 3: Good Health and Well-being.

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Kinetic analysis to evaluate the contribution of type II mechanism in photosensitized oxidations

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Photosensitized reactions are defined as photochemical alterations occurring in one molecular entity as a result of the initial absorption of radiation by another molecular entity called photosensitizer.[1] Photosensitized oxidations are oxygen-dependent processes and play a pivotal role in the generation of skin cancer and other types of photodamage. These reactions are also fundamental to photodynamic therapy developed to kill cells (cancer cell or pathogenic microorganism).

Photosensitized oxidations can take place through type I (generation of radicals) and type II [singlet oxygen($^1O_2$)] mechanisms. Sometimes given a pair photosensitizer-substrate, several mechanisms are thermodynamically feasible and, in this case, both mechanisms will take place simultaneously and therefore compete, the predominant being the faster. In these cases, the principal mechanism is not easy to establish and many times would depend not only on the reactants, but also on the experimental conditions.

In this talk, it is presented a kinetic study of the process of quenching of $^1O_2$ by 2′deoxyguanosine 5′-monophosphate (dGMP), in order to assess the reactivity of this nucleotide toward $^1O_2$. Steady-state near-infrared detection methods were employed to determine the rate constant of $^1O_2$ total quenching (k_t) by dGMP, as well as the rate constant of the chemical reaction between $^1O_2$ and dGMP (k_r), under different pH conditions. Pterins are endogenous photosensitizers that present a profuse and amazing photochemistry and are able to photooxidize biomolecules through both type I and type II mechanisms.[3] Pterin (Ptr) is the parent unsubstituted compound of oxidized pterins and is the model photosensitizer used in these studies.

The oxidation of dGMP photosensitized by Ptr in aqueous solution under UV-A radiation is described. Kinetic analysis of results obtained in steady-state and time-resolved experiments are used to assess the contribution of type I and type II mechanisms under different experimental conditions. This approach is used to analyze photosensitized oxidations.

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Melanoma Cell Responses to Melanogenesis Induction and its consequences

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Anti-melanoma treatments have achieved significant advances; however, they still face major limitations, including low efficacy, high toxicity, and resistance. A distinguishing feature of melanoma, compared to other tumor types, is the presence of melanin—a polymer synthesized in melanocytes through the oxidation of the amino acid L-tyrosine by the enzyme tyrosinase. The presence of melanin and its highly reactive biosynthesis pathway, known as melanogenesis, has been linked to both protective and potentially tumorigenic effects. While melanin protects against UV radiation and reactive oxygen species, its role in promoting DNA damage and impairing repair mechanisms suggests a complex interplay in tumorigenesis and melanoma treatment. One of the major challenges in cancer therapy is the development of resistance by tumor cells, whether in chemotherapy, immunotherapy, or targeted therapy. The proteasome is considered a promising therapeutic target, as it plays a central role in the ubiquitin-proteasome system (UPS), which is responsible for more than 80% of cellular protein degradation. In this study, we aim to investigate two main aspects: (i) the involvement of the melanogenesis pathway in the adaptive capacity of melanoma, specifically its role in the metabolic switch to glycolysis—an important characteristic of advanced tumor cells; and (ii) the response of melanoma cells, with or without melanogenesis stimulation, to treatment with UPS inhibitors. Upon stimulating melanogenesis for 48 hours in B16-F10 murine melanoma cells, we observed a metabolic shift toward glycolysis over oxidative phosphorylation, as measured by oxygen consumption, lactate production, and glucose dependence. In melanogenesis-stimulated B16-F10 cells treated with the UPS inhibitor Bortezomib (BTZ), we observed resistance to the treatment, with reduced proteasome inhibition and attenuated effects on cell viability and apoptosis. Conversely, when inhibiting the ubiquitination process at the E1 enzyme (the first step in ubiquitination) using the compound PYZD-4409, melanogenesis stimulation did not prevent the reduction in the percentage of metabolically active cells, the decrease in cell adhesion, or the induction of apoptosis. These findings suggest that effective therapeutic strategy for melanoma must take in consideration the melanin content. Understanding these intricate relationships could offer novel insights into overcoming tumor resistance and improving treatment outcomes for melanoma patients.

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Singlet oxygen in biological systems: mass spectrometry and near-infrared light emission measurements

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Recent advances in biochemical research have unveiled multiple pathways for generating singlet oxygen ($^1O_2$) and electronically excited species, offering promising applications in therapeutics, while also revealing mechanisms of endogenous oxidative stress and damage [1]. Acting as a signaling molecule, $^1O_2$ induces arterial relaxation and lowers blood pressure. These findings uncover a novel physiological function for $1O_2$ in mammals, linking it to vascular tone regulation under inflammatory conditions [2]. From a biochemical perspective, haloamines derived from amino acids and polyamines were shown to generate $^1O_2$ upon reaction with H_2O_2. Bromamines were especially efficient in this process, supporting the idea that such reactions may serve as an endogenous source of $^1O_2$ in non-illuminated biological systems, especially during eosinophil and neutrophil-driven inflammation [3]. Additionally, studies have shown that neurotransmitters such as dopamine, serotonin, and melatonin can undergo chemiexcitation upon oxidation (e.g., by peroxynitrite). This process forms triplet excited states that transfer energy to DNA, inducing cyclobutane pyrimidine dimers (CPDs) in the absence of light [4]. These findings suggest a novel mechanism of endogenous mutagenesis, with potential implications in inflammation, cancer, and neurodegeneration. Further exploring lipid biochemistry, plasmalogen oxidation by $^1O_2$ was found to produce reactive intermediates like hydroperoxyacetals and dioxetanes. These intermediates can generate triplet carbonyls, additional $^1O_2$, and electrophilic aldehydes, potentially disrupting cell signaling and membrane integrity. This contradicts the traditional view of plasmalogens as antioxidants, revealing a prooxidant role under oxidative conditions [5]. In another study, lipid hydroperoxides were shown to react with the nitronium ion (NO_2^+), a reactive nitrogen species found during inflammation. This reaction yields $1O_2$, confirmed by near-infrared luminescence, suggesting that lipid peroxidation, via nitronium chemistry, contributes significantly to oxidative stress in membranes [6].

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Sunlight-induced modulation of the cutaneous immune response in human tegumentary leishmaniasis.

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Tegumentary leishmaniasis (TL) is a zoonotic disease that affects both the skin and mucous membranes of infected individuals. The etiological agent is an intracellular parasite from the genus *Leishmania*, transmitted through the bite of an infected phlebotomine of the genus *Lutzomyia* (in the Americas). TL is endemic in Latin America, and during the period 20012023, a total of 1.178.436 cases were reported by the Pan American Health Organization, resulting in more than 50.000 cases per year.
The origin and progression of this disease are essentially immunopathological, with the severity of the mucous lesions correlated with the inflammatory hyperreactivity of the immune system. The control of the cutaneous infection (which may cure spontaneously) highly depends on a controlled Th1 immune response, with secretion of adequate amounts of IFN-γ. Ultraviolet radiation (UVR) in sunlight is a well-known inducer of immunomodulation, ranging from an increased local acute inflammatory response to systemic immunosuppression that may persist for weeks. However, the relationship between sunlight exposure and the development, dissemination, and worsening of the leishmania infection has not been studied.
We aim to investigate the role of sunlight exposure in the development of localized cutaneous leishmaniasis, its progression to cutaneous disseminated disease, and ultimately, to the mucocutaneous form.
To this end, we analyzed an *in vitro* model consisting of molecular mediators secreted by sunlight-exposed keratinocytes and their role in the ability of macrophages to respond to a *Leishmania braziliensis* infection. Moreover, we studied serum immune mediators and an indirect sunlight exposure indicator, Vitamin D, and correlated these molecules with the form and severity of the disease in patients with TL. Finally, an epidemiological approach was also employed to compare the incidence of TL according to the geographic location and calculated erythemal UV radiation (from climatic databases).
The results to be presented demonstrate that simulated sunlight exposure modifies the immune response against Leishmania *in vitro*. Moreover, geographical associations between surface UV radiation and the number of TL cases also suggest a possible interaction between sun exposure and the development of the disease. However, the analysis of serum mediators in a small cohort of patients from the Argentine Northwest did not reveal any association.

Potential Potential of 5-ALA in Neurosurgery – Fluorescence and PDT

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Neurosurgery suffered from discrimination of tumor to normal tissue during surgical tissue resection, but also for selective treatment of GBM. The application of photoactive drugs and their use for fluorescence guided resection, optical guided biopsy and photodynamic therapy in neurosurgery could support such requests. Besides the medical needs and boundary conditions, the physics and technical research and developments will be presented. Different clinical aspects of photodynamic therapy (PDT), like treatment planning, treatment and dosimetry protocols, spectral on-line-monitoring (SOM) as well as follow-up evaluation of clinical outcome, are of interest regarding further iPDT developments. Preliminary study results as well as the potential of optical dosimetry concepts based on light-tissue interaction and light-photosensitizer interaction are included summarizing the latest developments in this field.

Photostability and Photostabilization Approaches for UV Filters: Advancing the Rational Design of Broad-Spectrum (UVA–UVB) Sunscreens

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Ultraviolet radiation present in sunlight is a trigger for skin damage and other adverse health effects. To prevent diseases and undesirable effects, cosmetic preparations such as sunscreens are used. However, their formulation and development involve addressing challenges like the photoinstability of certain organic filters. This instability compromises the safety and efficacy of the product. Thus, studying these solutions can lead to sunscreens that effectively fulfill their intended purpose. Through the development of stabilization mechanism, some research has achieved prototypes in which ultraviolet filters maintain their performance after exposure to radiation. This study evaluated the in vitro photoprotective efficacy of formulations combining organic ultraviolet (UV) filters with photostabilizing agents. Using an experimental mixture design, antioxidants (Pentaerythrityl Tetra-di-t-butyl Hydroxyhydrocinnamate, PEG-8 (and) Tocopherol (and) Ascorbyl Palmitate (and) Ascorbic Acid (and) Citric Acid), emollients (Isononyl Isononanoate, Propanediol Dicaprylate, Isopentyldiol, Propylene Glycol), and an optimized blend of organic UV filters (Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine, Butyl Methoxydibenzoylmethane, Ethylhexyl Salicylate, Ethylhexyl Triazone, Polysilicone15, Phenylbenzimidazole Sulfonic Acid) were combined to enhance sunscreen efficacy and photostability.

Multifunctional Hyaluronic Acid- and Carbon Dot-Based Conjugates Photoreleasing Nitric Oxide

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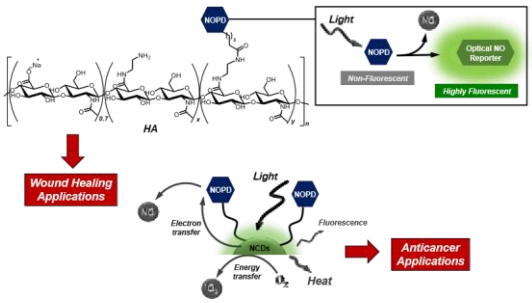
The achievement of nitric oxide (NO) delivery with precise spatiotemporal control is a significant challenge in health care due to the strict dependence of the therapeutic effects of the NO radical on its concentration and generation site.[1] Light-activatable NO precursors, namely NO photodonors (NOPDs), address the above issues since they are stable in the dark and permit in a non-invasive fashion the remote-controlled delivery of NO on demand with great accuracy in space and time.[2,3] Engineering biocompatible materials with NOPDs and their combination with additional imaging, therapeutic and photo-therapeutic components leads to intriguing light-responsive multifunctional constructs exhibiting promising potential for biomedical applications.[4] This contribution reports some recent examples of multifunctional NO photoreleasing materials achieved in our laboratories, integrating suitable NOPD units into hyaluronic acid (HA)[5] and N-doped carbon dots (NCDs) scaffolds.[6,7] We highlight the logical design behind the fabrication of these systems, illustrating the therapeutic potential in wound healing and anticancer applications.



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Heterogeneous Photocatalysis for Environmental Remediation: a Journey from Batch to Continuous Flow Systems

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We have developed a coating technique to produce surfaces that can be used in environmental remediation based on photocatalytic processes. These include film-coated materials (surfaces or pipes) for flow photocatalysis (with or without recirculation) similar to those shown in the Figure below.
The so-devised systems were tested for persistent organic pollutants degradation, enabling its application in custom-designed batch or flow reactors, powered by a sustainable light source (ideally sunlight). Coating was tested with inorganic semiconductors and with semiconductor organic polymers. Batch studies with the catalytic materials in powdered form achieved up to complete (100%) transformation under UV irradiation, and very higher transformation efficiencies under Vis light. Efficiencies are lower, but still very important with the coated surfaces. The experimental data are generally well described by the Langmuir-Hinshelwood kinetic model. High efficiencies are achieved also upon daylight (polychromatic) irradiation. LC/MS analysis of the transformation by-products revealed different pathways depending on factors such as the type of irradiation used, or the surface features of the photocatalytic materials.
A multi-site adsorption model allows explanation of most of the observed kinetic experimental features in this kind of systems.

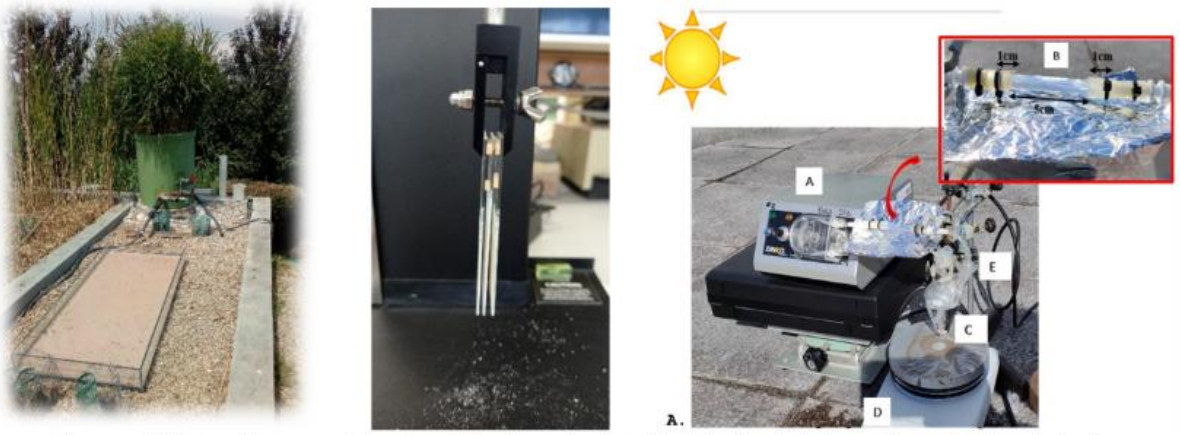

Figure: different types of photocatalyst-coated materials for batch or flow photocatalysis.

Precision Nanotherapy with Nitric Oxide: Boosting Anti-Cancer Effects and Minimizing Inflammation

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Nitric oxide (NO) is an important signaling molecule in the biological system, where it performs a wide range of physiological and pathological functions essential for maintaining homeostasis. NO plays a dual role in cancer, acting as both a pro- and antitumorigenic agent depending on its concentration. While low NO levels may promote tumor growth, higher concentrations can induce cytotoxicity and inhibit metastasis. This complexity has led to the exploration of NO donors and NOS inhibitors as potential therapies. This study presents a novel strategy to enhance the efficacy and selectivity of nanoparticle-based cancer therapy through targeted modulation of intracellular NO signaling. We synthesized cisplatin-loaded zinc oxide nanoparticles (ZnO/CisPt NPs) exhibiting a pH-triggered release profile, delivering significantly higher cisplatin concentrations within the acidic tumor microenvironment. When combined with controlled NO modulation in prostate cancer cells (PC3), this nanoplatform demonstrated markedly improved therapeutic outcomes. Notably, both augmenting NO levels using the NO donor S-nitrosoglutathione (GSNO) and depleting NO via the NOS inhibitor *L*NAME sensitized PC3 cells to ZnO/CisPt NPs. Increased intracellular S-NO levels (indicative of enhanced S-nitrosylation/transnitrosylation processes) correlated with cytotoxic effects and protein function alterations. Conversely, NO depletion reduced NOS expression and regulated pro-inflammatory cytokines. Critically, both modulation directions significantly enhanced the cytotoxic effect of the nanoparticles: chronic low-dose NO treatment induced a 30% greater reduction in PC3 viability and improved the selectivity index compared to normal fibroblasts (FN1). This paradoxical sensitization underscores that altering the intracellular NO balance itself, regardless of direction, is a key mechanism for sensitizing cancer cells to nanotherapy. Our findings demonstrate that precise NO modulation acts synergistically with pH-responsive ZnO/CisPt NPs to amplify tumor cell death while concurrently minimizing tumor-associated inflammation. This dual-action approach—enhancing therapeutic efficacy against prostate cancer and mitigating detrimental inflammation—represents a promising, safer, and more targeted strategy for nanomedicine in oncology, with potential for broader application.

Single-Molecule Catalysis in Pd Cross-Coupling Reaction by Fluorescence Microscopy: The Interplay Between Experiment and Stochastic Simulation

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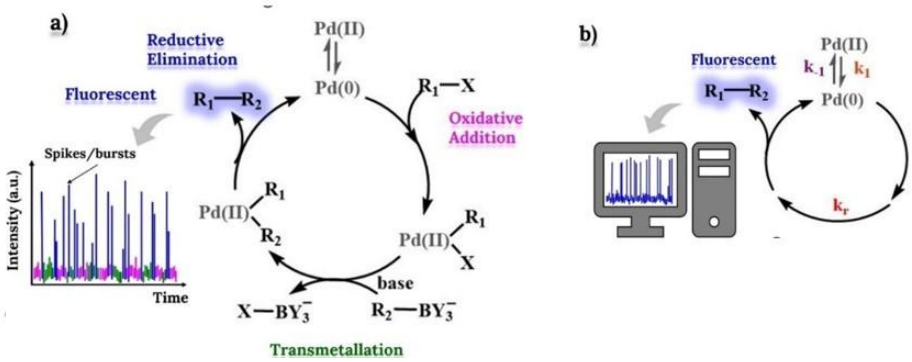
Suzuki-Miyaura cross-coupling reactions using palladium were investigated at single-molecule (SM) level using TIRF microscopy combined with super-resolved optical imaging. Analysis of the SM fluorescence intermittency produced from localized spots provided a direct measure of the catalyst conversion rate (SM-TOF) and thus allowed the calculation of the average number of product molecules generated by a single catalytic center over time. In addition, stochastic simulations study were conducted to validate the statistical method applied to single-molecule data treatment based on the fluctuation threshold analysis. This simulation replicated well the intermittency observed and recovered the SM-TOF values measured in the SM experiments. The higher SM activity observed in zeolite templates with surface bound Pd were explained by the dimer effect and confirmed by simulation.



Controlled NO and HNO Release from Metal Complexes: Chemical and Photochemical Triggers and Biological Effects

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Nitric oxide (NO) and its reduced form, nitroxyl (HNO), play key roles in various physiological processes. Imbalances in their production or distribution are associated with several diseases, including atherosclerosis, hypertension, and angiogenesis-related disorders. Over the past years, our research group has developed a range of metal complexes designed to act as NO and/or HNO donors, either containing coordinated NO or not. These compounds exhibit selective NO and/or HNO release upon activation by different stimuli, such as light irradiation, chemical or electrochemical reduction, and chemical oxidation. The complexes have shown diverse biological activities, including antioxidant effects in ischemia/reperfusion models, antiparasitic activity, vasorelaxant properties, anti-inflammatory effects, and gastroprotective action. In this work, we present the results of several metal complexes activated by chemical and photochemical triggers, highlighting their potential as multifunctional therapeutic platforms.

Chemico-physical and biological properties of two monoclonal antibodies, Bevacizumab (Avastin®) and Durvalumab (Imfinzi®) under real-life light doses: a mechanistic approach.

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Keywords: Bevacizumab; Durvalumab; Photostability; Real-life

INTRODUCTION

Monoclonal antibodies (mAbs) have emerged as a prominent class of protein therapeutics for cancer treatment. However, their protein nature renders them susceptible to various stressors during manufacturing, transportation, storage, handling, and administration [1]. Notably, light exposure can induce chemico-physical changes, particularly when amino acids are located in the complementarity-determining regions (CDRs), potentially compromising efficacy and safety [2,3].

AIMS

This study aimed to evaluate the chemico-physical stability and biological activity of Bevacizumab (Avastin) and Durvalumab (Imfinzi) under light doses mimicking real-life exposure.

RESULTS

Exposure to sunlight doses like those experienced in real-life settings did not alter the conformation of the diluted mAbs. However, light-induced aggregation was observed, with Bevacizumab exhibiting a higher extent of aggregation than Durvalumab. Durvalumab was also evaluated upon induced stress either by direct UVA/UVB exposure or by photosensitization via blue-light excitation of ruthenium(II) tris-bipyridyl dication ($Rubpy^{2+}$)[4].

Liquid chromatography-mass spectrometry (LC-MS) analysis revealed low levels of oxidative damage and deamidation. Chemico-physical modifications affected the target recognition ability of both mAbs (VEGF and PD-L1, respectively). Notably, no significant immunogenic potential was observed in dendritic cells derived from differentiated monocytes.

CONCLUSIONS

The chemico-physical changes induced by real-life light exposure did not significantly impact the overall protein structure of the tested mAbs. Minimal chemical modifications were detected in the CDRs, resulting in a marginal decrease in in vitro target recognition. While aggregation did not induce immunogenicity, it contributed to the decrease in biological activity.

ACKNOWLEDGEMENTS

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Advancing photodynamic therapy by nitric oxide releasing agent using three-dimensional (3D) biofabricated cancer model

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Recently, efforts to find compounds selectively affecting cancer cells while sparing normal ones have grown. Nitric oxide (NO) is critical in physiology and pathology, including cancer. It influences cellular processes like proliferation, apoptosis, and angiogenesis. NO's intricate interaction with cancer cells offers innovative treatment possibilities, but its effects can vary by concentration and site. NO derivative ruthenium complexes, capable of releasing NO upon stimulation, hold promise. These versatile compounds could also enhance Photodynamic Therapy (PDT), a light-activated approach inducing cellular damage. While many photosensitizers show promise, challenges such as low selectivity, high toxicity, and reliance on in vitro models that fail to capture the complexity of primary tumors have limited their successful transition into clinicals. To overcome these challenges, three-dimensional (3D) models are increasingly being used as preclinical platforms to enhance translational research and improve clinical outcomes. In this study, a nitro-ruthenium porphyrin complex, the $\{TPyP[Ru(NO_2)(bpy)_2]_4\}(PF_6)_4$, designated $RuNO_2TPyP$, which releases NO upon irradiation, was investigated for its effects on cancer cells in 2D and in 3D cancer models at increasing complexity, including free-standing spheroids, bioprinted spheroids in hydrogels, and bioprinted patient-derived organoids (PDOs). Spheroids, as the simplest model, demonstrated the compound's effectiveness but required longer incubation and higher irradiation doses compared to 2D culture. Bioprinted spheroids in hydrogels enabled created a more controlled microenvironment, improving spheroid arrangement, irradiation precision, and physiological relevance. Bioprinted PDOs, with controlled size and positioning, provided an advanced platform for evaluating the $RuNO_2TPyP$ complex, yielding promising preliminary results. The findings suggest that this complex has potential for PDT treatment in cancer cell lines, as it exhibits photocytotoxicity at low concentrations without causing cytotoxicity to normal cells. Moreover, treatment of cells with the $RuNO_2TPyP$ followed by light irradiation (4 J cm^{-2}) can induce apoptosis, generate ROS, promote intracellular NO formation, and has anti-migratory effects. Additionally, the complex can modify tumor cell structures and induce photocytotoxicity and apoptosis in 3D culture. These outcomes are attributed to the internalization of the complex and its subsequent activation upon light irradiation, resulting in NO release and singlet oxygen production.

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Photosensitized oxidative crosslinking of bovine serum albumin and the impact on its esterase-like activity

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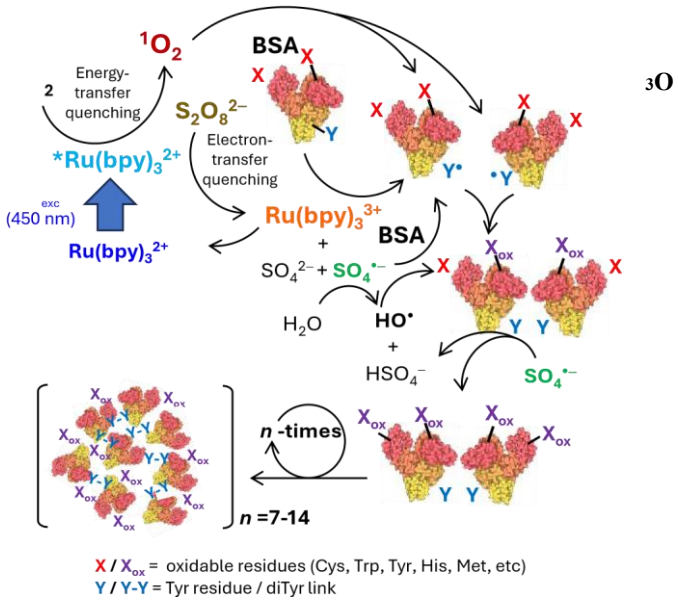
A photosensitized oxidative crosslinking of proteins (POCP) reaction was applied in airsaturated phosphate buffer solutions of bovine serum albumin (BSA) to obtain soluble protein nanoparticles of approximately 100 nm in diameter. A royal blue LED was used as the excitation source for the photosensitizer molecule ruthenium (II) tris(2,2'-bipyridyl) dication, $Ru(bpy)_3^{2+}$, in the presence of the electron acceptor persulfate anion, $S_2O_8^{2-}$. The redox quenching products prompted the formation of side-chain tyrosyl radicals, leading to the formation of dityrosine (Tyr_2), which served as a link in the covalent attachment between proteins. However, the dissolved oxygen competes efficiently with $S_2O_8^{2-}$ to quench the excited photosensitizer, thereby generating singlet molecular oxygen, $^1O_2$, which reacts with electron-rich protein residues, producing an additional oxidative pattern of BSA. Consequently, under air-saturated conditions, the POCP gives rise to a series of oxygen-dependent and independent reactions, resulting in the protein crosslinking with oxidative modifications. The esterase-like activity efficacy of BSA oxidized solely by $^1O_2$ and after the formation of oligomeric protein nanoparticles by POCP was reduced by 51% and 73%, respectively, as compared with that of the native BSA. The combination of the oxidative degradation of key residues in the active sites and steric impediment due to protein oligomerization was found to be associated with this result.



Light-modulated Circadian Rhythms in Non-phototrophic Critical Pathogens

Bárbara E. Perez Mora[1], Rocío Giordano[1], Valentín Permingeat[1], Natalia Arana[1], María Laura Migliori[2], Ramiro E. Rodríguez[3], Diego A. Golombek[4], Ana Rosa Perez[5], María Alejandra Mussi[1]

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Throughout human history, bacterial infections have caused devastating epidemics that shaped human evolution, profoundly impacting societies and medicine. The advent of antibiotics in the last century revolutionized infection control, enabling modern medical advances that extended human lifespan. However, the global emergence of bacteria resistant to most available antibiotics over the past 70 years is pushing towards a new crisis, unless effective alternatives to control these pathogens are urgently developed.
The 2022 Global Burden of Disease study identified *Escherichia coli*, *Staphylococcus aureus*, *Klebsiella pneumoniae*, *Streptococcus pneumoniae*, *Acinetobacter baumannii*, and *Pseudomonas aeruginosa* as the leading causes (73%) of AMR-associated deaths in 2019. These pathogens are part of the 2024 WHO bacterial priority pathogens list and overlap with a distinct group of pathogens, ESKAPEE, known to "escape the action of antibiotics" and cause drug-resistant nosocomial infections.
Our data shows that bacterial critical pathogens such as *A. baumannii* exhibit light-modulated diurnal and circadian rhythms, which shape infection dynamics and antibiotic susceptibility.
In fact, we have recently identified the existence of daily rhythms in *blsA* promoter activity displaying a robust response to light, as well as endogenous circadian rhythms in this microorganism at 23ºC. *blsA* promoter activity can be synchronized to 24-hour blue light-dark cycles, which immediately resynchronizes after a phase shift. Upon release to constant darkness, bacterial populations present free-running oscillations with a period close to 24 hours. Furthermore, our data show that BlsA is involved in synchronization to light-dark cycles. Under constant darkness without previous entrainment, *A. baumannii* is rhythmic but with scattered acrophases, behaving as the *blsA* mutant under light-dark cycles. Interestingly, bacterial antibiotic susceptibility fluctuates rhythmically along the day, as does their ability to cause disease. In fact, our data indicate that there are specific times of the day when these pathogens are more susceptible to antibiotic treatment, and that their internal rhythms condition both their infectivity and infection progress in mice. It should be noted that the bacterial physiological state at the onset of infection is determinant in infection outcome and host fate. These results challenge the current concept of infection and disease and proposes a new angle in antimicrobial treatment: chronotherapy from the pathogen's side. The overall notion is conceptually innovative, as only a few articles describe the existence of circadian rhythms in non-photosynthetic bacteria, but none have investigated their role in bacterial pathogenesis. Implications at the optogenetic level are further discussed.

Development of Biocompatible Multifunctional Agents for Photodynamic Therapy, Cancer Cell Imaging, and Cell Proliferation Inhibition

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Photodynamic therapy (PDT) is a clinically approved, non-invasive cancer treatment that involves administering a photosensitizer (PS) and using light to target the affected area. Currently, the range of photodynamic therapy agents is limited, creating a pressing need for cost-effective, organic photosensitizers that can enhance efficacy through multiple photosensitization mechanisms and serve dual purposes for image-guided PDT.

In this presentation, I will discuss recent advances made by our group in developing biocompatible, all-organic PSs that feature tunable absorption spectra across the visible to nearinfrared (IR) regions of the electromagnetic spectrum. Several of these PSs demonstrate substantial PDT efficacy against human epidermoid carcinoma, melanoma, cervical cancer, and human epithelial cancer cells, regardless of oxygenation status (i.e., under both normoxic and hypoxic conditions), when tested in vitro with a low dose of light. Additionally, they decrease or stop the proliferation of cancer cells and can be activated by two-photon absorption in the near-IR for PDT and bioimaging applications.

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Light-modulated Circadian Rhythms in Non-phototrophic Critical Pathogens

Bárbara E. Perez Mora[1], Rocío Giordano[1], Valentín Permingeat[1], Natalia Arana[1], María Laura Migliori[2], Ramiro E. Rodríguez[3], Diego A. Golombek[4], Ana Rosa Perez[5], María Alejandra Mussi[1]

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Throughout human history, bacterial infections have caused devastating epidemics that shaped human evolution, profoundly impacting societies and medicine. The advent of antibiotics in the last century revolutionized infection control, enabling modern medical advances that extended human lifespan. However, the global emergence of bacteria resistant to most available antibiotics over the past 70 years is pushing towards a new crisis, unless effective alternatives to control these pathogens are urgently developed.
The 2022 Global Burden of Disease study identified *Escherichia coli*, *Staphylococcus aureus*, *Klebsiella pneumoniae*, *Streptococcus pneumoniae*, *Acinetobacter baumannii*, and *Pseudomonas aeruginosa* as the leading causes (73%) of AMR-associated deaths in 2019. These pathogens are part of the 2024 WHO bacterial priority pathogens list and overlap with a distinct group of pathogens, ESKAPEE, known to "escape the action of antibiotics" and cause drug-resistant nosocomial infections.
Our data shows that bacterial critical pathogens such as *A. baumannii* exhibit light-modulated diurnal and circadian rhythms, which shape infection dynamics and antibiotic susceptibility.
In fact, we have recently identified the existence of daily rhythms in *blsA* promoter activity displaying a robust response to light, as well as endogenous circadian rhythms in this microorganism at 23ºC. *blsA* promoter activity can be synchronized to 24-hour blue light-dark cycles, which immediately resynchronizes after a phase shift. Upon release to constant darkness, bacterial populations present free-running oscillations with a period close to 24 hours. Furthermore, our data show that BlsA is involved in synchronization to light-dark cycles. Under constant darkness without previous entrainment, *A. baumannii* is rhythmic but with scattered acrophases, behaving as the *blsA* mutant under light-dark cycles. Interestingly, bacterial antibiotic susceptibility fluctuates rhythmically along the day, as does their ability to cause disease. In fact, our data indicate that there are specific times of the day when these pathogens are more susceptible to antibiotic treatment, and that their internal rhythms condition both their infectivity and infection progress in mice. It should be noted that the bacterial physiological state at the onset of infection is determinant in infection outcome and host fate. These results challenge the current concept of infection and disease and proposes a new angle in antimicrobial treatment: chronotherapy from the pathogen's side. The overall notion is conceptually innovative, as only a few articles describe the existence of circadian rhythms in non-photosynthetic bacteria, but none have investigated their role in bacterial pathogenesis. Implications at the optogenetic level are further discussed.

How Charge-Transfer Dynamics Leads to "Unusual" Photophysics

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The importance of charge transfer (CT) cannot be overstated. CT sustains life on earth and makes our modern ways of living possible.[1] Femtosecond and picosecond CT dynamics governs the optical behavior of molecular and supramolecular species and materials. Transientabsorption spectroscopy, along with time-resolved emission, allows us to decipher the mechanistic features of photoinduced CT processes defining molecular photophysics. For example, balancing the extend of CT character in the singlet excited states of nitroaromatics makes them fluoresce.[2] In complex chromophores with an acceptor-donor-acceptor (A-D-A) or donor-acceptor-donor architecture, CT breaks the quadrupolar symmetry upon photoexcitation. We discovered that a decrease in donor-acceptor electronic coupling enhances the formation of CT states in certain A-D-A conjugates. It leads to simultaneous fluorescence from the donor and acceptor locally excited states along with the CT emission. Tuning this anti-Kashia behavior presents a means for achieving white fluorescence, i.e., emission that spreads through the whole visible spectral region.[3] The ubiquitous nature of dipoles and the strong effects they have on CT warrant a close look at dipolar structures that generate localized electric fields.[4,5] Molecular electrets, possessing ordered electric dipoles, can serve as an indispensable platform for understanding the dynamics of such localized fields. As expected, when the electret macrodipoles are averaged over sub-nanosecond timescales, they show a nice linear dependence on the size of these dipolar structures, reaching magnitudes of 100 and 200 D. Nevertheless, analyzing the dynamics at picosecond resolution shows fluctuation of the molecular dipoles that vary between 50% and 300% of their average values. The electret geometry does not show such drastic variations. Our analysis reveals that the solvent dynamics, via the solvent-generated Onsager reaction fields, is responsible for the enormous picosecond spikes in the dipole magnitude.[6] Further studies show that such dipole fluctuations are universal for condensed media and may explain unusual behavior of gating involving femto- and picosecond CT.[7] Moving to the opposite side of the spectrum from femto- and picosecond timeresolved spectroscopy, we demonstrated the use of microflows for gaining temporal resolution in optical measurements. In microchannels, liquids flowing with small rates of a few microliters per minute can move with speeds of meters per second (depending how small the cross-sections of the channels are). This feature allowed us to develop space-domain time-resolved emission spectroscopy providing sub-millisecond resolution using pressure-driven flows in microfluidic devices.[8] While the impotence of CT is unequivocal, its complexity in condensed media spanning over broad spatial and temporal scales offers a wealth of opportunities for molecular photonics and optoelectronics; and time-resolved spectroscopy provides the indispensable means for exploring them.

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Photoredox Paradox: Uncovering the Roles of Electron Upconversion and Electron Catalysis

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Although photoredox catalysis is complex from a mechanistic point of view, it is also often surprisingly efficient. In fact, the quantum efficiency of a puzzlingly large portion of photoredox reactions exceeds 100% (i.e., the measured quantum yields (QYs) are >1). Hence, these photoredox reactions can be *more* than perfect with respect to photon utilization. In several documented cases, a single absorbed photon can lead to the formation of >100 molecules of the product, behavior known to originate from chain processes.

In this talk, I explore the underlying reasons for this efficiency, identify the nature of common catalytic chains, and highlight the differences between HAT and SET chains. Our goal is to show why chains are *especially* important in photoredox catalysis and where the thermodynamic driving force, that sustains the SET catalytic cycles, comes from. [1, 2]

I demonstrate how the interplay of polar and radical processes can activate hidden catalytic pathways mediated by electron and hole transfer (i.e., electron and hole catalysis). Furthermore, I illustrate how the phenomenon of redox upconversion serves as the thermodynamic precondition for electron and hole catalysis.

After discussing representative mechanistic puzzles, I analyze the most common bond forming steps where redox upconversion is common (and sometimes unavoidable). In particular, we highlight the importance of 2-center-3-electron bonds as a common motif that allows a rational chemical approach to the design of redox upconversion processes

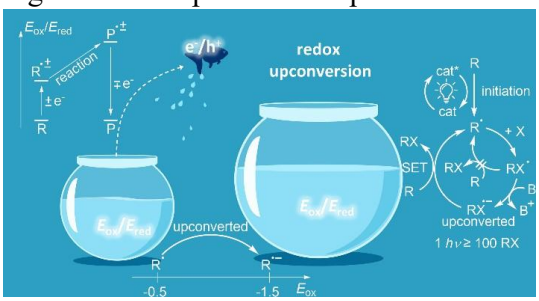

Figure 1. Redox upconversion converts photoredox catalysis into electron catalysis

Funding: NSF support (CHE-2102579)

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New strategies for optimizing the photoinactivation of bacteria

Rocío B. Acosta[1,2], Verónica E. González[1,2], Edgardo Durantini[1,2], Mariana B. Spesia[1,2]

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The growing emergence of bacteria that are resistant to traditional antibiotics highlights the urgent need to develop new antimicrobial strategies. In this context, photodynamic inactivation (PDI) is emerging as a promising phototherapeutic tool.[1] PDI is based on the synergistic interaction of a photosensitizing agent (PS), light, and oxygen, generating reactive oxygen species (ROS) that irreversibly damage microbial cellular components, inducing their death.[2] This study evaluates the antimicrobial potential of the photosensitizer zinc(II) 2,9,16,23tetrakis[4-(*N*-methylpyridyloxy)]phthalocyanine ($ZnPPc^{4+}$) against different strains of *Staphylococcus aureus* and *Escherichia coli*. Its effect on the inactivation of planktonic cells, the modulation of virulence factors, and the ability of bacteria to produce biofilms was investigated, as well as the potential induction of resistance after repeated exposures to PDI. The results demonstrate that $ZnPPc^{4+}$ is highly effective in the photoinactivation of planktonic *S. aureus* at low concentrations and light doses. Interestingly, although PDI with $ZnPPc^{4+}$ effectively eliminated *S. aureus* under the sublethal conditions analyzed, it did not inactivate the activity of virulence factors such as β-hemolysin, lipase, lecithinase, or mannitol fermentation. However, this PS showed significant efficacy in inactivating *S. aureus* biofilms, even at very low concentrations (in the nM range), a crucial finding given the greater resistance of biofilms to treatments.

On the other hand, repeated PDI treatments were performed on *E. coli* using the same photosensitizer, adjusting the parameters to achieve partial inactivation and allow colony survival. After ten PDI cycles, no significant differences were observed in the inactivation of *E. coli*, indicating that repeated sublethal exposure does not induce resistance to subsequent photodynamic treatments. Although some fragmentation was detected in plasmid DNA, the genomic DNA of *E. coli* remained unchanged. In addition, changes in antibiotic susceptibility were observed after repeated photodynamic treatment.

In conclusion, PDI with $ZnPPc^{4+}$ emerges as a promising alternative therapy not only for controlling the reproduction of pathogenic microorganisms and biofilm formation, but also for its ability to not induce resistance to this treatment. This suggests great potential for combating infections, including those associated with biofilms, without the limitations presented by the development of resistance in conventional antibiotic therapies.

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Invited Lecture 31
Wednesday, 16:20-16:45

Probing Complex Systems with Time-Resolved Spectroscopies: From Micelles to the Chromophores of Red Wine

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Time-resolved spectroscopic techniques are powerful tools for investigating fast to ultrafast dynamic processes and otherwise invisible or difficult to measure events in complex chemical systems, as exemplified by examples from our work with surfactant micelles and natural plant pigment analogues. Surfactant micelles are highly dynamic entities. The counterions of ionic detergents exchange at the micellar surface on a ns to ps time scale, the detergent monomers enter and exit the micelles on a □s time scale and the micelles themselves are continuously being formed and breaking up on a ms time scale. Hydrophilic and moderately hydrophobic solutes diffuse in and out of micelles on ns to ms time scales and encounter other solutes or ions within the confines of the micelle on a ns time scale. Time-resolved fluorescence decay measurements employing fluorescent probe-quencher pairs permit studies of the effects of additives on micellar aggregation numbers, on counterion exchange dynamics and selectivity, on the dynamics of entry and exit of surfactant monomers from micelles and on the diffusion of non-ionic solutes into, out of and within micelles. Nanosecond time-resolved laser flash photolysis has been used to detect changes in the affinity of a solute molecule for the micelle upon excitation to the triplet state.

Anthocyanins, the natural pigments responsible for the majority of the red, purple and blue colors of the flowers, fruit and leaves of plants, have a 7-hydroxyflavylium cation chromophoric moiety. In aqueous solution, anthocyanins exhibit a series of very complex pHdependent multiequilibria that occur on time scales that vary from a few seconds up to hours. Anthocyanins are also weak acids (pK_a ca. 4) in the ground state, but become super photoacids in the first excited singlet state (pK_a^* ca. -1) with rates of adiabatic deprotonation on the time scale of ca. 20 ps. Because the excited conjugate base is short-lived (ca. 200 ps), ns laser flash photolysis shifts the position of the ground state acid-base equilibrium in < 1 ns, permitting determination of ground-state protonation/deprotonation dynamics in water and at micelle surfaces. Highly fluorescent synthetic hydroxyflavylium analogues of natural anthocyanins are thus excellent probes of ultrafast excited state proton transfer (ESPT) dynamics in aqueous solution, in mixed aqueous-organic solvents and at the surface of micelles. During the maturation of red wines, the anthocyanins of grapes slowly transform chemically into pyranoanthocyanins, which have a more pH stable color but similar pK_as in the ground state. Synthetic pyranoflavylium cation analogues of pyranoanthocyanins exhibit sub-ns ESPT in the first excited singlet state that has been characterized by ps time-resolved fluorescence combined with TRANES (time-resolved area normalized emission spectra), while the competition between charge transfer and ESPT has been examined by fs pumpprobe spectroscopy. Unlike flavylium cations, for which triplet states have not yet been unambiguously detected, excited triplet states of synthetic pyranoflavylium cations can be readily detected by ns laser flash photolysis and efficiently sensitize singlet oxygen phosphorescence in acetonitrile, making them attractive chromophoric scaffolds for applications in light-harvesting, energy-conversion and photodynamic therapy.

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Theranostic Potential of Aminolevulinic Acid-Derived Porphyrins

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Fluorescence from porphyrins, derived from the application of 5-aminolevulinic acid (ALA), has emerged as a valuable tool in the diagnosis of infections. ALA, a precursor in the heme biosynthesis pathway, leads to the accumulation of porphyrins in tissues with increased metabolic activity, such as infected or abnormal cells. However, ALA-photodiagnosis has been reported only for superficial infected wounds. Therefore, our aim was to investigate the possibility of employing ALA and its lipophilic derivative Hexyl-ALA for the detection of skin and soft tissue infections.

For this purpose, we used a skin and soft tissue model induced after subcutaneous inoculation of *Staphylococcus aureus* in CF1 mice. Porphyrins were visualized by photography after the interposition of a magenta-colored filter, microscopically after cryosectioning of the abscesses, and quantified fluorometrically after chemical extraction.

We topically applied ALA or Hexyl-ALA to the surface of the abscess and monitored porphyrin fluorescence over time. Porphyrin fluorescence remained confined to the subcutaneous tissue and was not visualized from the skin surface when exciting the fluorescence with 365 nm light. However, when the mice were sacrificed, a strong pink fluorescence was observed in the inner layers of the skin, highly confined to the infected area. Since it was not possible to externally detect the fluorescence of porphyrins synthesized from ALA in the treated abscesses, we employed an *in vivo* imaging system (IVIS) Spectrum CT device. The optimal conditions were excitation at 430 nm and emission at 620 nm. Under these conditions, a nonspecific fluorescence was detected in the abscess area.

Interestingly, when mice were infected on both flanks, we visualized fluorescence on the nontopical side, suggesting migration of ALA to the contralateral side. In contrast, fluorescence remained confined to the treated side after Hexyl-ALA application.

After topical application of ALA, the main porphyrin in the abscess was Coproporphyrin III. Following systemic injection of ALA, fluorescence was also confined to the abscesses, mainly due to Protoporphyrin IX fluorescence emitted from eukaryotic cells.

Our findings indicate that ALA is selective for infected tissues (whether bacterial or inflammatory cells), although fluorescence was not visible from the skin surface. Nonetheless, fluorescence derived from porphyrins synthesized from ALA could be useful in fluorescenceguided debridement of infections.

Integrating Timescales in Chemistry: concepts, methods, examples

Rene Nome[1]

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Timescale integration is a simple, well-known concept that is of current interest. From the experimental perspective, one challenge is associated with the tools commonly used to study fast and slow processes at the microscopic level: stroboscopic and asynchronous techniques,respectively. Within this context, the development of suitable methods, as well as their application to specific examples, will open new opportunities for investigation in a broader class of systems. In this talk, we will present results from our group using nano- and bio-materials as case studies, combining experiments and simulations to illustrate the concepts, methods and applications of timescale integration.

Light-Responsive Metallodrugs: Structure, Excited States, and Biological Function

Sherri A. McFarland[1], Wenfang Sun[2], Phoebe Glazer[3]

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Photodynamic therapy (PDT) continues to advance through collaborative innovations in photosensitizer design that expand photoreactivity across the visible spectrum and sustain efficacy under biologically challenging conditions. Building on the translational success of TLD1433—the first ruthenium-based PDT agent to enter clinical trials—our collaborative efforts have focused on developing new classes of Ru(II) complexes that incorporate πconjugated oligothiophene motifs into diverse ligand scaffolds. These systems were designed to modulate charge-transfer character, excited-state lifetime, and redox balance—key factors that dictate photochemical reactivity, reactive oxygen species formation, and hypoxia resilience. Through combined synthetic, photophysical, computational, and biological studies, we demonstrate that tuning conjugation length and metal–ligand coupling yields complexes with strong visible-to-NIR absorption, long-lived triplet states, and light-triggered cytotoxicity under both normoxic and hypoxic conditions. The resulting compounds engage not only classical Type II ($^1O_2$) pathways but alternate and uncharted mechanisms. Together, these findings underscore how coordinated, collaborative research can reveal design principles that link excited-state dynamics to biological outcomes, enabling the creation of metal-based phototherapeutics that perform predictably and effectively in clinically relevant environments.

Combining carbon dots with porphyrin photosensitizers: a strategy to boost photophysical properties and toxicity against leukemia cells

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Recently, efforts to find compounds selectively affecting cancer cells while sparing normal ones have grown. Nitric oxide (NO) is critical in physiology and pathology, including cancer. It influences cellular processes like proliferation, apoptosis, and angiogenesis. NO's intricate interaction with cancer cells offers innovative treatment possibilities, but its effects can vary by concentration and site. NO derivative ruthenium complexes, capable of releasing NO upon stimulation, hold promise. These versatile compounds could also enhance Photodynamic Therapy (PDT), a light-activated approach inducing cellular damage. While many photosensitizers show promise, challenges such as low selectivity, high toxicity, and reliance on in vitro models that fail to capture the complexity of primary tumors have limited their successful transition into clinicals. To overcome these challenges, three-dimensional (3D) models are increasingly being used as preclinical platforms to enhance translational research and improve clinical outcomes. In this study, a nitro-ruthenium porphyrin complex, the $\{TPyP[Ru(NO_2)(bpy)_2]_4\}(PF_6)_4$, designated $RuNO_2TPyP$, which releases NO upon irradiation, was investigated for its effects on cancer cells in 2D and in 3D cancer models at increasing complexity, including free-standing spheroids, bioprinted spheroids in hydrogels, and bioprinted patient-derived organoids (PDOs). Spheroids, as the simplest model, demonstrated the compound's effectiveness but required longer incubation and higher irradiation doses compared to 2D culture. Bioprinted spheroids in hydrogels enabled created a more controlled microenvironment, improving spheroid arrangement, irradiation precision, and physiological relevance. Bioprinted PDOs, with controlled size and positioning, provided an advanced platform for evaluating the $RuNO_2TPyP$ complex, yielding promising preliminary results. The findings suggest that this complex has potential for PDT treatment in cancer cell lines, as it exhibits photocytotoxicity at low concentrations without causing cytotoxicity to normal cells. Moreover, treatment of cells with the $RuNO_2TPyP$ followed by light irradiation (4 J cm^{-2}) can induce apoptosis, generate ROS, promote intracellular NO formation, and has anti-migratory effects. Additionally, the complex can modify tumor cell structures and induce photocytotoxicity and apoptosis in 3D culture. These outcomes are attributed to the internalization of the complex and its subsequent activation upon light irradiation, resulting in NO release and singlet oxygen production.

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From Inverted Solvatochromism to Excited-State Dynamics: Triarylpyrimidine Push–Pull Fluorophores as Molecular Probes in Microheterogeneous Media

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Solvatochromism describes how molecular chromophores respond to environmental polarity, producing characteristic shifts in absorption and emission spectra. Depending on the direction of these shifts, solvatochromism can be classified as positive (bathochromic), negative (hypsochromic), or inverted—the latter involving a transition from positive to negative behavior at a specific "solvatochromic inverse point." While numerous absorption-based examples exist, emissive inverted solvatochromism remains largely unexplored.

Here, we present a family of fluorescent aminocarbonyl derivatives based on 2,4,6triarylpyrimidines (TAPs) functionalized with n-alkyl chains (C_1–C_{12}), designed to probe the interplay between molecular lipophilicity and partitioning in microheterogeneous environments. Among them, three aminocarbonyl derivatives exhibit **emissive inverted solvatochromism**, providing new insight into how polarity gradients within structured media influence excited-state charge redistribution.

Fluorescence experiments in DSPC:Ch (55:45) liposomes, combined with quenching studies using 4-alkanoyloxy-TEMPO radicals (C_2–C_{16}), reveal chain-length–dependent localization and multiple dye populations across the bilayer. Moreover, tuning donor strength and torsional flexibility of N,N-disubstituted amino groups modulates the intramolecular charge-transfer (ICT) dynamics. Quantum-chemical calculations support the presence of twisted ICT (TICT) states that govern fluorescence persistence in different polarity regimes.

Together, spectroscopy and theory provide a unified picture linking solvatochromic inversion, ICT dynamics, and interfacial localization—paving the way for the design of **new polaritysensitive push–pull fluorophores** for sensing and photochemical applications.

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Acknowledgements. The financial support from FONDECYT projects 1240893 (M.D.) and 1240302 (C.A.) are greatly acknowledged.

Liposomes, Nanoemulsions and Cyclodextrins: Advanced Platforms for Photosensitizers

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It is widely acknowledged that PDT faces limitations, including poor solubility, aggregation, low tumor selectivity, and off-target toxicity, which are common issues with most photosensitizers. Nanocarriers like liposomes, nanoemulsions, and cyclodextrin-based systems address these issues by improving stability, bioavailability, and targeted delivery. These platforms enhance therapeutic performance and broaden PDT applications.

Liposomes are versatile vesicles that encapsulate hydrophilic and hydrophobic PSs, reducing aggregation and boosting ROS yield. Their properties can be tailored to extend circulation, utilize the EPR effect, and enable active targeting via surface functionalization. Phthalocyanines, second-generation PSs with strong near-infrared absorption and high photostability, benefit from liposomal encapsulation by enhancing photodynamic efficiency and reducing systemic toxicity. On the other side, n**anoemulsions** offer long-term stability (up to 12 months), high encapsulation efficiency for hydrophobic photosensitizers (PSs), and easy functionalization for theranostic applications. They enhance tissue penetration, biofilm disruption, and co-delivery of agents to overcome limitations in photodynamic therapy (PDT). Our research group has been working extensively on the development of these nanoformulations to improve the performance of organic and inorganic photosensitizers in photodynamic therapy, whether through the production of liposomes for antiviral studies or the production of photoactive nanoemulsions to improve bioavailability and photodynamic performance against tumor cells. Recently, we demonstrated that lipid–polymer nanoemulsions can encapsulate CdTe quantum dots (QDs), reducing cadmium toxicity, improving circulation time, and enabling selective uptake in glioblastoma cells, which enhances their use as fluorescent diagnostic agents and potential PSs in brain tumor PDT. **Cyclodextrins**, cyclic oligosaccharides with hydrophobic cavities, offer another strategy for PS delivery by enhancing solubility and stability while enabling host–guest complex formation. These inclusion complexes can modulate PS pharmacokinetics, prevent self-aggregation, and improve controlled release. When combined with other nanocarriers, cyclodextrins contribute to hybrid delivery systems with synergistic performance.

This symposium will explore how advanced nanoplatforms can overcome key limitations in PDT by enhancing the solubility, stability, and tumor accumulation of photosensitizers, while enabling synergistic combinations with chemotherapy, immunotherapy, and imaging agents. Discussions will highlight theranostic strategies that integrate diagnostic and therapeutic functions within a single nanocarrier, supporting the development of personalized PDT approaches. Emphasis will also be placed on challenges in nanocarrier design, scalability, and regulatory pathways for successful clinical translation.

Keywords: Nanoemulsions, liposomes, cyclodextrins, nanocarriers, theranostics.

Rationalizing the Excited-State Properties and Dynamics of BiphenylBased Push-Pull Systems

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Nitric Among functional molecular architectures, push-pull systems (also known as donor-acceptor systems) stand out for their unique intramolecular charge transfer (ICT) photophysical behavior and controllable excited-state dynamics, which have consequently been the subject of extensive investigation.[1] Herein, by carefully adjusting (1) the **donor moieties**, and (2) **solvent** environment; we present a systematic and comprehensive investigation of the impact of the torsion angle of the *N*,*N*-disubstituted amino moieties on the fluorescence properties of two pull-push systems, 4-[4-(4-***N***,***N***-**dimethylamino**phenyl)phenyl]-2,6-diphenylpyrimidine and 4-[4-(4-***N***,***N***-**diphenylamino**phenyl)phenyl]-2,6-diphenylpyrimidine for both **D1** and **D2**, respectively.[2,3] While a strong deactivation of the fluorescence properties of **D1** is observed as the solvent polarity increases, **D2** retains its emission even in polar solvents such as DMSO (**Figure 1**). Quantum-chemical calculations are entirely consistent with these findings, supporting the existence of a non-emissive twisted geometry (TICT state) for the dihedral angle between the ***N***,***N*-dimethylamino** and the biphenyl moieties in the lowest-energy state of **D1** under highly polar conditions unlike **D2**.[3] Further insight into the ultrafast dynamics reveals multiple conformer-related states, each exhibiting lifetimes strongly modulated by the solvent viscosity and dielectric constant. Additionally, the population of long-lived triplet excited states and the consequent ability to generate singlet oxygen reactive species are demonstrated. Hence, it is only through the combination of steady-state and time-resolved fluorescence spectroscopy, femtosecond and nanosecond transient absorption spectroscopy, and theoretical calculations that we can fully disentangle the complex excited-state relaxation pathways and dynamics in these two push-pull systems. This research contributes to understanding the structure-property relationship and provides avenues for the design of new photosensitizer systems.

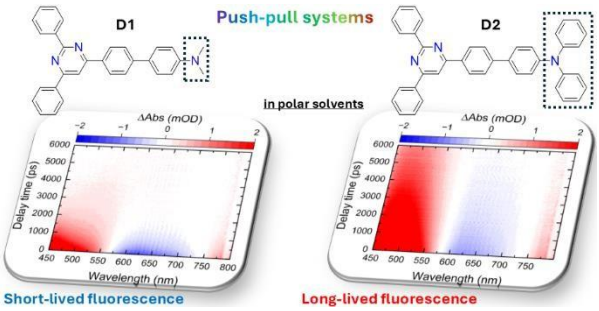

Figure 1. Top: Molecular structures for **D1** (left) and **D2** (right) push-pull systems, where only the amino donor substituents are changed from dimethyl to diphenyl, respectively.

Bottom: Pseudocolor contour plot of transient absorption properties as function of delay time and probe wavelength for **D1** and **D2**, respectively.

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Photoactive Materials for Food Preservation

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Photosensitizers (PSs) play a critical role in photodynamic therapy (PDT) for cancers and infectious diseases. However, the drawbacks of the current FDA-approved porphyrin-based PSs for PDT, such as the long cutaneous photosensitivity, weak absorption at its clinical wavelength (630 nm) and virtually no absorption of tissue-penetrating near-infrared (NIR) light, and ineffectiveness in hypoxia, prevent the widespread use of PDT in the clinic. Exploring new PSs to overcome these shortcomings has been a growing area of interest. Transition metal complexes, including the Ir(III) complexes, provide rich and tunable photophysical properties due to the interactions between the metal center and the organic ligands, and can yield high triplet quantum yields because of the metal-induced rapid intersystem crossing (ISC). To exploit the best practice for developing Ir(III) complexes into PSs, my group has designed and synthesized multiple series of mononuclear and dinuclear Ir(III) complexes containing various bidentate and tridentate ligands for anticancer and antimicrobial PDT applications. We aim to develop Ir(III) complexes that exhibit strong NIR absorption and emission in the regions of 730-920 nm for theranostic PDT applications. The photophysical properties of our synthesized complexes, including the UV-Vis-NIR absorption, emission, and transient absorption characteristics, were systematically investigated. Reactive oxygen species generation was studied, and their phototherapeutic effects on melanoma or breast cancer cell lines, and on Gram+ and Gram- bacteria have been evaluated.

Lessons from the media: guidelines for improving the sensitivity of chromophores

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Solvatochromic dyes function as polarity indicators.[1] The charge-transfer band of these dyes undergoes a shift in response to changes in polarity, and this shift is utilized to gather information about the chemical environment.[2] There are three types of solvatochromic behavior based on the direction of the spectral shift: negative, positive, and inverted (Fig. 1, left). When the polarity of the medium increases, negative solvatochromic dyes undergo hypsochromic shifts, which means that their absorption bands shift towards shorter wavelengths. Conversely, a positive solvatochromic dye undergoes a shift in its absorption band towards longer wavelengths, known as bathochromic shifts. The inverted solvatochromic dyes exhibit a transition from positive to negative behavior at a specific polarity threshold.[3] Solvatochromic dyes can be represented by connecting an electron donor with an electron acceptor through a p-conjugated system. Although various combinations of donor and acceptor moieties have been examined, the specific molecular criteria for a dye to exhibit a particular solvatochromic behavior remain unidentified. In this communication, we discuss various tactics aimed at controlling the type of solvatochromism displayed by push-pull dyes and their extensions to emissive systems.[4]

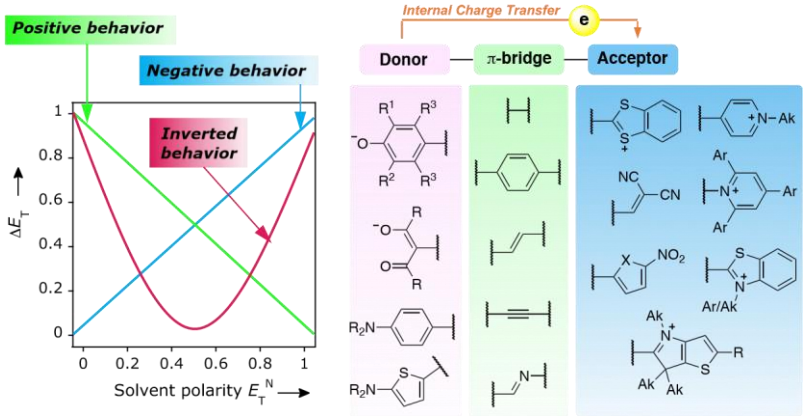

Figure 1. Schematic representation of the three types of solvatochromism and their structures.

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Impact of polymeric materials Photochemical redissolution on aquatic matrices

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Keywords: Plastic, EEMs, PARAFAC, water, environment, DOM.

Plastic materials accumulate in aquatic ecosystems, particularly polymers such as polyethylene terephthalate (PET) and polystyrene (PS), represent a critical environmental issue. Under solar radiation, these materials undergo photodissolution, a process in which polymer chains are fragmented, releasing microplastics, nanoplastics, and dissolved organic matter (DOM). Understanding these mechanisms is essential to evaluate their ecological impacts and their influence on the biogeochemical cycles of carbon. In this current context, excitation–emission matrix fluorescence spectroscopy (EEMs) has emerged as a highly sensitive and non-invasive analytical tool to investigate the products derived from the photochemical degradation of plastics. This technique enables the detection of fluorescent compounds associated with humic-, protein-, and aromatic-like substances. However, the complexity and spectral overlap inherent in aquatic matrices require advanced multivariate data analysis. The Parallel Factor Analysis (PARAFAC) model is applied to decompose EEMs datasets into individual fluorescent components, allowing the identification, quantification, and temporal evolution of the species produced during photodissolution. The combined use of EEMs and PARAFAC enables the tracking of structural and chemical changes in the DOC released from PET and PS, distinguishing polymer-derived fractions from those of natural origin. Moreover, the detection of specific fluorescent signatures provides an effective means to evaluate degradation kinetics, aromaticity, and the bioavailability potential of the dissolved material. In Panama, the application of fluorescence spectroscopy coupled with PARAFAC analysis represents a powerful approach to characterize the photodissolution of plastics and its impacts on aquatic ecosystems. This analytical framework enhances the understanding of carbon transformation processes and supports the development of scientific strategies aimed at mitigating local plastic pollution.

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Detecting different liposomal microenvironments using fluorosolvatochromic dyes

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Keywords: Fluorescence, quenching and microheterogeneous media.

Microheterogeneous systems in biological environments are characterized by the coexistence of multiple phases with varying polarities at the microscopic level, providing diverse microregions to elicit the incorporation of molecules with different lipophilicities. An open question in our research is how the incorporation of *n*-alkyl fragments added to a probe influences its partitioning in these milieux.[1] Previous studies have documented the hydrophobic effects induced by 4-alkanoyloxy-1,1,6,6-tetramethylpiperidinoxyl (TEMPO) radical derivatives in micellar systems and emulsions, revealing localization patterns that prompt a reinterpretation of the polar paradox in microheterogeneous environments.[2,3] In this study we use six fluorescent probes based on 2,4,6-triarylpyrimidine4 (TAP)-derived, functionalized with hydrocarbon chains ranging from 1 to 12 carbon atoms to investigate their localization and orientation in DSPC:Ch (55:45) liposome-based microstructured media. Fluorescence emission and Stern-Volmer constants (Ksv) were measured using TEMPO radical derivatives with chain lengths from 2 to 16 carbons.

Timeresolved fluorescence measurements further revealed the presence of multiple fluorophore populations distributed across the liposome structure, suggesting that radicals with different chain lengths selectively access distinctmicroenvironments.

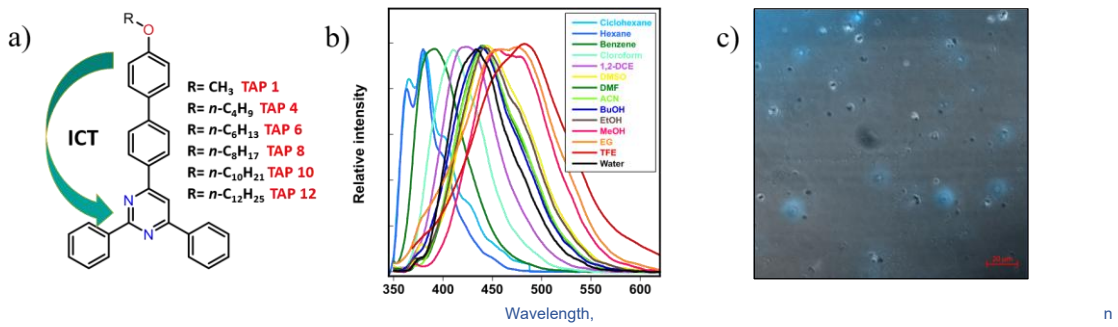

Figure 1. a) Structure of 2,4,6-triarypyrimidine (TAP) derivatives; **b)** Emission spectrum of TAP 6 in pure solvents; **c)** Fluorescence micrograph of TAP 6 probe fluorescence in DSPC:Ch (55:45) liposomes recorded by micrography image (λ exc. = 405 nm)**.**

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Photostability study on red-emitting carbon dots by PARAFAC Analysis

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Carbon dots (CD) are quasi-spherical nanoparticles smaller than 10 nm. They possess high biocompatibility, low toxicity, low manufacturing costs, and other characteristics that have made them the subject of multiple studies and applications. One of these characteristics is their high fluorescence stability (Hai-Li et al., 2023).

In this study, multiemissive CD were synthesized. The different emissive components were separated by PARAFAC analysis. CD suspensions were irradiated with a UV lamp at a maximum wavelength of 367 nm and a full width at half maximum of 16.7 nm for several hours. Modifications in the fluorescence components of the irradiated nanoparticles were observed.

To elucidate the modification and degradation mechanism, irradiation was performed in the multiple components detected in the nanoparticles evidenced a degradation mechanism presence of N_2 to eliminate the presence of oxygen. The behavior and integration of these mediated by a photosensitization pathway.

Key words:
Photostability, carbon dots, Fluorescence

Acknowledgement:
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Push-Pull fluorescent probes, from Webers' DANs to DAAns

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We present several distinct push-pull systems. beginning with CAPRYDAA, an anthracene dye analog of LAURDAN, designed as a molecular probe for investigating membrane dynamics and supra molecular organization. CAPRYDAA features a nine-carbon acyl chain and o diethylamino substitution on the anthracene ring, allowing it to replicate LAURDAN's behavior in lipid membranes.

A key advantage of CAPRYDAA is its red-shifted absorption and emission bands, which retain sensitivity to environmental polarity. lt can be excited using visible light (488 nm). making it more compatible with conventional confocal microscopy, also two-photon loser sources can be employed. Experiments with giant unilamellar vesicles (GUVs) and cells hove demonstrated its ability to distinguish lipid phases and liquid-liquid phase heterogeneity, reinforcing its value as a tool for membrane research.

To further investigate fluorescence quantum yield enhancement and the role of rotamers in membrana emission, we synthesized and characterized the photophysical properties of 3,4dihydrophenanthren-1 (2H)-one and 3,4-dihydroanthracen-1 (2H)-one derivatives, where carbonyl rotation is prevented.

Additionally, we synthesized an amino derivative of phenalenone that exhibits push-pull fluorescent probe characteristics while preserving single/oxygen generation ability. Despite demonstrating a weaker performance compared to DANs, this derivative displayed a hypsochromic shift in response to solvent polarity.

In situ NMR photochemistry of dicationic azobenzenes

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Photoisomerization studies show that dicationic azobenzene derivatives exhibit reversible spectral behavior under cyclic UV and visible-light irradiation. The experimental setup enables irradiation and real-time data acquisition via *in situ* illumination of the samples, particularly during nuclear magnetic resonance (NMR) measurements. This design provides valuable information on the photostationary state (PSS) and photoswitching kinetics, opening new perspectives for the study of molecular switches. In addition, these derivatives can form molecular aggregates at low concentrations that are also reversibly photoactivable, enabling the study of their surface charge and hydrodynamic size. Taking advantage of these features, we are currently developing systems with potential application in light-regulated drug release.

XVI LATIN AMERICAN MEETING OF PHOTOCHEMISTRY AND PHOTOBIOLOGY

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ORAL COMMUNICATION

ABSTRACTS

Pterin–Thymine Adducts as Photosensitizers for Oxidative Damage

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Pterin (Ptr) is the model compound for pterins, heterocyclic aromatic compounds widely distributed in biological systems, known for its efficient photosensitizing properties. Elevated levels of pterins have been detected in the skin of patients with conditions such as vitiligo, making its interaction with biomolecules under UVA irradiation biologically relevant.[1] Under anaerobic and acidic conditions, Ptr reacts with the DNA nucleobase thymine (T) to form covalent photoadducts (T–Ptr). These adducts have been previously reported in free nucleosides, nucleotides, short oligonucleotides, and DNA strands.[2]

In this study, aqueous solutions of Ptr with 2'-deoxythymidine 5'-monophosphate (dTMP) or the oligonucleotide 5'-d(TTTTT)-3' (dT_5) were irradiated with UVA light (350 nm) to generate T–Ptr adducts, which were isolated via HPLC. Spectroscopic characterization confirmed that both adducts retain the absorption and fluorescence properties of free Ptr. Additionally, the dTMP–Ptr adduct was shown to form triplet excited states and to generate singlet oxygen with an efficiency comparable to that of free Ptr.

Furthermore, both dTMP–Ptr and dT_5–Ptr adducts photosensitized the oxidation of biologically relevant targets such as tryptophan and 2'-deoxyguanosine 5'-monophosphate in airequilibrated solutions, achieving efficiencies similar to that of free Ptr. The oxidation mechanisms involved may be of either type I (electron transfer) or type II (energy transfer to oxygen). These results are particularly significant as a photosensitizer bound to the target molecule may cause damage more effectively to the same biomolecule.

It is interesting to explore the potential applications of these adducts as site-specific fluorescent probes or photosensitizers for photodynamic therapy.

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Development of Photoactivable Biofungicides: From Laboratory Assessments to Field Tests Simulation

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The presence of pathogenic fungi in plants and fruits represents a major challenge for global agriculture, causing significant yield losses that can reach up to 20% in developing countries. Although conventional fungicides are commonly used to address this issue, their application is associated with serious drawbacks, such as the accumulation of residues on food, environmental contamination, and resistant fungal strains. A promising alternative is Photodynamic Inactivation (PDI), which uses the cytotoxic effects of reactive oxygen species (ROS), particularly singlet oxygen ($^1O_2$), generated by the activation of a photosensitizer (PS) upon exposure to light. Recent studies have demonstrated that PDI exhibits effective antifungal activity against a variety of phytopathogenic strains [1-2].

In this context, we propose a novel approach combining both PDI and Chitosan through the synthesis of a covalent conjugate between a low molecular weight chitosan and a PS. Here, we present a successful case study involving the development of a photoactivatable biofungicide named BIOSUPRA. This formulation was not only synthesized and validated under laboratory conditions but also scaled up and tested in real agricultural settings, representing a clear example of a technology going from laboratory research to a pre-commercial stage.

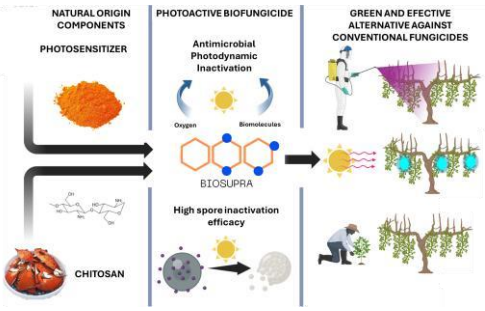

Figure 1. Diagram of the components, mechanism of action and application of the biofungicide BIOSUPRA.

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Novel heteroleptic Cu(I)-Dipyridylamine/Diphosphine complexes as active materials in Light-Emitting Electrochemical Cells

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Increasing interest in functional materials for optoelectronic applications has driven the search for efficient and versatile luminophores. In this context, ionic transition metal complexes (iTMCs) have attracted cosiderable attention in devices like *light-emitting electrochemical cells* (LEECs). Among them, Cu(I) complexes stand out due to their relative abundance and low cost, representing an attractive alternative to the precious metals traditionally employed. However, the development of efficient and sustainable emitters based on copper (I) remains a challenge.

In this work, we report the synthesis and characterization of two novel heteroleptic copper(I) complexes of the type [Cu(*N,N*)(*P,P*)]BF_4, employing *N,N* ligands derived from dipyridylamine and Xantphos as the auxiliary *P,P* ligand (**C1–2**, Figure 1a). Structural characterization was performed using NMR and FT-IR, and for **C1**, via X-ray diffraction analysis. The photophysical and electrochemical properties were evaluated by UV–Vis spectroscopy, emission spectroscopy, cyclic voltammetry, and excited-state lifetime measurements. The complexes exhibited MLCT absorption bands between 300 and 330 nm (Figure 1b) and blue emission in solution at room temperature. In a glassy ethanol/methanol (4:1) matrix at 77 K, the emission showed slight spectral shifts (Figure 1c). Excited-state lifetimes were in the microsecond range. Furthermore, these complexes were used as the active emissive layer in LEEC devices with the configuration ITO/PEDOT:PSS/[Cu(dpa)(Xantphos)]BF_4/Al, exhibiting turn-on voltages of 13 V and maximum emission at 488 nm (Figure 1d).

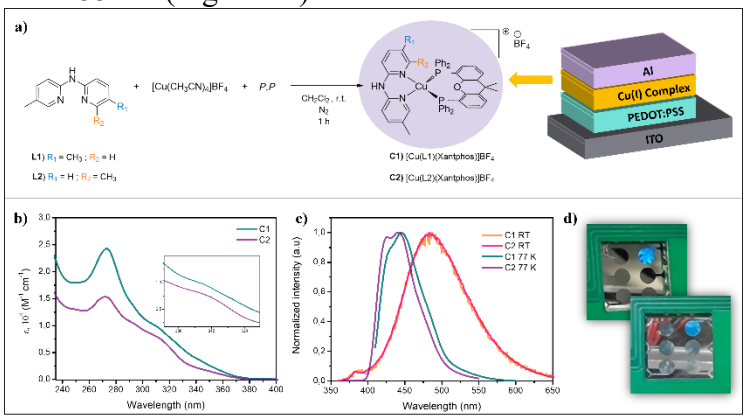

Figure 1. (a) Schematic representation of the synthesis of complexes **C1–2** and the device architectures. (b) Absorption spectra of the complexes in CH_2Cl_2. (c) Emission spectra at room temperature and 77 K in CH_2Cl_2. (d) Fabricated devices: **C1** (top) and **C2** (bottom).

Acknowledgments: The authors acknowledge the support from FONDECYT Regular Projects No. 1210661 and No. 1230199.

SYNTHESIS AND CHARACTERIZATION OF N-ETHYLPYRIDIN-1-IUM-2PYRIDONES AS SINGLET OXYGEN RELEASERS IN MIXED AQUEOUS/ACETONITRILE MEDIA

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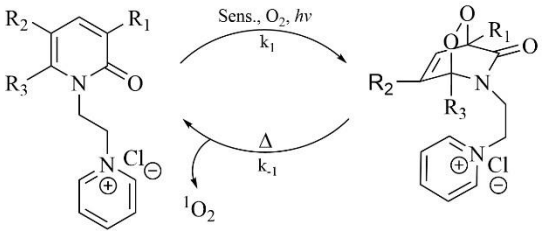
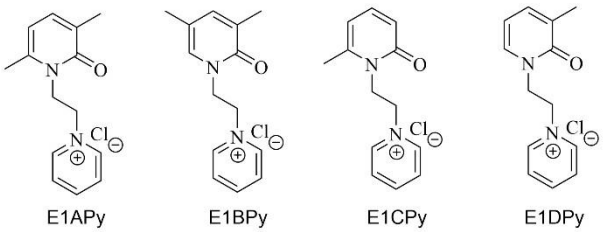
The objective of this study is to synthesize and characterize a series of 2-pyridone-derived endoperoxides. These compounds, based on 2-pyridone scaffold, have been investigated because of their ability to thermally release singlet oxygen (an electronically excited form of molecular oxygen), primarily for medicinal applications in light-independent photodynamic therapy. The ability of these endoperoxides to undergo thermal cycloreversion at relatively low temperatures, efficiently generating singlet oxygen while regenerating the parent 2-pyridone in high yield, positions them as promising candidates for optimizing singlet oxygen generation under dark conditions.

A series of 2-pyridone derivatives featuring various substitution patterns were synthesized, followed by N-alkylations with an ethylpyridinium group. The resulting compounds and their endoperoxides were purified, and spectroscopically characterized.



The rate constants of cycloreversion kk_{-1}, half life $tt_{1/2}$, the retro Diels-Alder % and the yield % of singlet oxygen released were determined by molecular absorption spectrophotometry (UV-Vis). The singlet oxygen yield (%), was determined using diphenylisobenzofuran (DPBF) a highly reactive specie that reacts with the generated singlet oxygen.

All synthesized compounds demonstrated the ability to trap singlet oxygen. Rose Bengal photooxygenation was fast and quantitative, being E1BPy the compound that exhibited the highest singlet oxygen trapping efficiency, whereas E1DPy was the least effective. The endoperoxides formed via sensitization were all capable of undergoing cycloreversion, thereby regenerating the pyridone moiety and releasing singlet oxygen. Notably, E1DPy was the most efficient thermal releaser, with a cycloreversion rate constant of $4.1 * 10^{-5}\ ss^{-1}$ at 30°C and a retro Diels Alder percentage of 72%. Experiments using DPBF confirmed singlet oxygen release from all compounds, with E1DPy inducing the most pronounced decrease in DPBF absorbance.



Photochemical properties of Rutin-loaded nanoemulsions

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Rutin, a natural flavonoid with strong antioxidant and photoprotective properties, suffers from poor aqueous solubility and limited stability, restricting its practical applications. In this study, we developed orange-oil–based nanoemulsions as carriers for rutin and evaluated their photochemical behavior compared to free rutin. The nanoemulsions were prepared using a spontaneous emulsification method, followed by rutin incorporation. Photophysical properties were analyzed through fluorescence spectroscopy, with excitation–emission matrices used to assess shifts in emission maxima (EEM) and changes in intensity. Quantum yield determinations further revealed how the nanoemulsion environment modulated rutin's excitedstate behavior. Results demonstrated that rutin-loaded nanoemulsions exhibited enhanced fluorescence intensity and a blue-shifted emission compared to free rutin in aqueous solution, indicating reduced aggregation and improved stabilization of the chromophore. Quantum yield was significantly higher in the nanoemulsion system, suggesting improved radiative deactivation pathways due to encapsulation. These findings highlight that orange-oil nanoemulsions can act as efficient delivery systems for rutin, enhancing its photochemical stability and optical performance. The study provides new insight into how natural oil-based nanocarriers can optimize the functional properties of flavonoids, paving the way for applications in nutraceuticals, cosmetics, and photoprotection.

Keywords: Nanoemulsions, quantum yield, rutin.

Quantifying Singlet Oxygen in Aqueous and Cellular Media Using Time-Resolved NIR Phosphorescence

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Photoisomerization Singlet oxygen ($^1O_2$, $^1\Delta_g$), the lowest electronically excited state of molecular oxygen, is a highly reactive electrophile with central roles in chemistry, materials science, biology, medicine, and environmental processes. The singlet oxygen quantum yield (Φ_Δ) and lifetime (τ_Δ) are key parameters describing the efficiency of photosensitizer-mediated generation and the persistence of this oxidant across diverse systems. Here, we describe experimental protocols based on the time-resolved detection of $^1O_2$ phosphorescence at ~1270 nm for accurate and reproducible determination of these parameters in both aqueous solutions and cell suspensions. Emphasis is placed on sample preparation and data analysis strategies, with guidance on common pitfalls and troubleshooting. An automated data analysis tool is provided to ensure robustness, minimize user bias, and facilitate cross-laboratory reproducibility. Fundamental theoretical background is included, together with key references intended to welcome newcomers to the field without compromising the hands-on approach of the text. The protocols are validated using well-characterized standard photosensitizers and are extendable to other molecular platforms, nanoparticles, and supramolecular systems.

Evaluation of the Thermal and Photochemical Stability of Fe_3O_4 Magnetic Nanoparticles Functionalized with Methotrexate

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Methotrexate (MTX) is an antineoplastic agent belonging to the pteridine family widely used in chemotherapy due to its ability to inhibit cell proliferation **[1]**, How ever, its therapeutic efficiency presents limitations due to its variable bioavailability (33–77%) **[2]** and high photosensitivity **[3]**, which compromise its clinical effectiveness and stability under different physiological conditions. For this reasons, there is a need to explore new strategies to enhance its performance in biomedical application. In this context, the present study proposes the anchoring of MTX to magnetite nanoparticles (Fe_3O_4) as a strategy to improve cellular uptake, increase chemical stability, and exploit its previously reported photoactive potential of free MTX **[4]**. To achive this, nanoparticles were synthesized via coprecipitation method and subsequently functionalized with MTX through three routes: (i) direct incorporation (Fe_3O_4@MTX), (ii) covalent anchoring using the silane agent APTES (Fe_3O_4@APTES@MTX), and (iii) covalent anchoring via citric acid (Fe_3O_4@CA@MTX). The resulting material were structurally and spectroscopically characterized using UV-Vis, infrared (FTIR), and fluorescence techniques, along with thermogravimetric analysis (TGA) and Z potential measurements to evaluate their composition and surface structure. Additionally, MTX release from the nanoparticles was assessed in aqueous medium, along with their stability under UVA irradiation. The results reveal that the anchoring method affects MTX loading efficiency, drug release profile, and photostability. Notably, Fe_3O_4@MTX nanoparticles incorporated a higher amount of MTX and exhibited a faster release rate compared to Fe_3O_4@APTES@MTX. Consistent with previous reports, free MTX was found to lack photostability under prolonged UVA exposure **[4,5]**. However, the MTX functionalized on the nanoparticles demonstrated improved resistance to photodegradation. Both Fe_3O_4@APTES@MTX and Fe_3O_4@MTX showed greater photostability than free MTX, with Fe_3O_4@MTX being the most stable under irradiation. Collectively, the MTX functionalization method on magnetite nanoparticles markedly influences lixiviation kinetics and photostability. This represents a promising strategy to enhance the therapeutic performance of MTX by enabling more controlled release and improved light stability. Such an approach could have important implications for the development of advanced drug delivery systems in oncological applications.

Acknowledgments
We thank the Human BioScience Laboratory for providing the drug, and the Universidad Nacional de Colombia for financial support through Hermes projects 60864 and 62434. We also acknowledge the ID 584 research seedbed for their support.

Keywords: Methotrexate (MTX); magnetic nanoparticles; magnetite; thermal stability; photostability.

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Phenalenone-functionalized cationic polymers: a versatile platform

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The immobilization of photosensitizers within polymeric matrices offers significant advantages for applications in disinfection, catalysis, and photodynamic therapy. These systems can be tailored to enhance stability, biocompatibility, and responsiveness to external stimuli, while also enabling the controlled deployment or removal of the photosensitizer without compromising the surrounding medium. In this context, the incorporation of derivatives of 1*H*-phenalenone, a stable and highly efficient photosensitizer, into polymeric frameworks is of particular interest.

1*H*-phenalenone is notable for its singlet oxygen quantum yield (Φ_Δ) of unity across various solvents. A compelling derivative is 1-(1-oxo-1H-phenalen-2-yl)pyridinium chloride, commonly referred to as SAPYR. This compound retains a Φ_Δ of unity, exhibits a red-shifted absorption spectrum relative to phenalenone, and is water-soluble. Its cationic nature enhances its suitability for photodynamic bacterial inactivation, as it can disrupt microbial cell walls even in the absence of light. Upon irradiation, the singlet oxygen generated induces cell necrosis, effectively eliminating bacteria without promoting resistance.

This study reports the synthesis and characterization of photosensitizing polymers derived from the functionalization of poly(4-vinylpyridine) with a 2-methylphenalenone halide. Functionalization was investigated at two levels: 1 mol% and 10 mol% phenalenone relative to the polymer. Additionally, the polymer backbone was modified by quaternizing the remaining pyridine groups with 1-bromobutane. To further modulate system polarity, ion exchange was performed to replace bromide ions with tetrafluoroborate.

The resulting polymers exhibited absorption spectra comparable to SAPYR, enabling quantification of functionalization via UV-vis spectroscopy. Results indicated that increased functionalization correlated with reduced photostability. All polymers demonstrated high singlet oxygen generation capacity, with Φ_Δ values approaching 0.8, although slightly below unity. Alkylated and non-alkylated polymers showed similar Φ_Δ values, while ion-exchanged polymers (with tetrafluoroborate counterions) exhibited marginally lower Φ_Δ values.

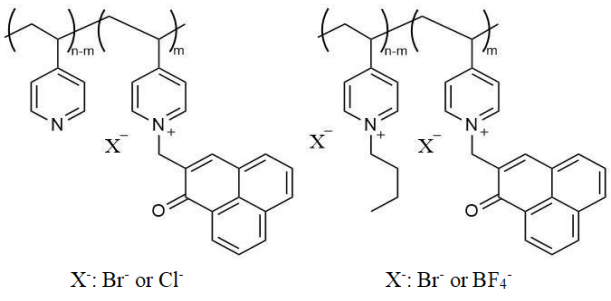

Figure 1. Chemical structures of the investigated systems.

Gold Nanoparticle–Polyphenol Conjugates for Dual-Mode Antimicrobial Phototherapy

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In recent decades, there has been growing interest in the development of new systems and therapies for treating infections that have developed resistance to traditional antibiotics. Among these emerging treatments and materials are nanomaterial-based systems such as gold nanoparticles (AuNPs), which have demonstrated the ability to generate a photothermal effect when irradiated with near-infrared (NIR) light—an effect that can be harnessed for treatments of resistant bacteria. On the other hand, certain naturally derived molecules such as polyphenols, including, curcumin, rutin and quercetin, have shown potential as antimicrobial agents and photosensitizers. In this context, the combination of different materials and bioactive molecules has been proposed as a promising strategy for dual therapy approaches, where conventional antibiotics can be replace with antimicrobial inactivation coupled with methods like photothermal therapy. In this work, we present the study of the ROS generation properties and photothermal activity of three systems curcumin, rutin and quercetin conjugated with gold nanoparticles. Furthermore, we present fluorescence emission spectroscopy studies related to the interaction of the conjugated systems with bovine serum albumin (BSA). Results showed that the three systems are promising agents for dual therapy, as they can produce ROS species when irradiated with blue light, while gold nanoparticles are rapidly heated when irradiated with NIR light. On the other hand, results showed a strong interaction with BSA, which is promising for medical applications.

Keywords: Dual therapy, photoinactivation, polyphenols, nanoparticles.

Light-Activated Antimicrobial Films: Structural and Optical Design of Curcumin–Chlorophyllin Alginate Composites

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The integration of photodynamic antimicrobial strategies into biodegradable packaging materials represents a promising approach to improve food safety while reducing environmental impact. In this study, we developed and characterized photoactive composite films based on sodium alginate reinforced with microcellulose and functionalized with curcumin and chlorophyllin—two natural photosensitizers capable of generating reactive oxygen species (ROS) under visible light. Five formulations (F1–F5) were prepared and systematically analyzed for their structural, mechanical, and optical properties. Atomic force microscopy revealed that films containing chlorophyllin exhibited increased roughness and stiffness, with F5 (highest chlorophyllin content) showing the greatest nanomechanical reinforcement. Confocal laser scanning microscopy confirmed a homogeneous distribution of microcellulose, though heterogeneity increased upon incorporation of the photosensitizers. FTIR spectra indicated no chemical interactions between alginate and the active compounds, while Raman spectroscopy showed distinct bands for chlorophyllin, confirming its presence and stability within the matrix. All films exhibited amorphous structures in X-ray diffraction patterns. UV–Vis analysis demonstrated successful light absorption by curcumin and chlorophyllin, and contact angle measurements indicated enhanced surface hydrophilicity in chlorophyllin-rich films. These results confirm the successful incorporation of natural photosensitizers into alginate–microcellulose matrices without compromising the polymer's structural integrity. The synergistic effect of curcumin and chlorophyllin broadens the light absorption range and enhances the potential for ROS production, positioning these films as strong candidates for next-generation photoactive food packaging systems.

Keywords: Photoactive packaging, food preservation, photodynamic inactivation, biodegradable films.

Novel Photosensitization and Photostability of DAN fluorescent probes

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6-acyl-2-(dimethylamino)naphthalene (DAN) derivatives were first disclosed as environment probes by Weber and Farris in 1979. This family of compounds present an excellent response to surrounding polarity by shifting the emission maxima to red or blue according to the polarity of the environment. LAURDAN, the best-known derivative of this family, is amply used to study membrane phase transitions by tracking its color change through fluorescence microscopy. When inserted into membrane in gel state LAURDAN emits at 440 nm whereas in membrane in disordered state it emits at 480 nm. However, one big drawback of LAURDAN is its rapid photobleaching which makes it usable only with two-photon microscopy techniques. Nevertheless, a detailed description of its degradation pathway is not available. Elucidating this mechanism could afford valuable information to avoid the rapid degradation of this compound and improve its application towards conventional one-photon microscopy techniques. Photobleaching of fluorescent probes is often believed to be triggered from the triplet state and subsequent production of ROS species that chemically inactivate the probe. Thus, we committed to study the photodegradation of DAN probes by characterizing their photoconsumption kinetics, photosensitizing ability and HPLC analysis. New synthetic analogues of DAN probes with restricted rotation were also characterized. These derivatives present a ring constriction at the carbonyl group which eliminates the possible vibrational relaxation pathway that DAN probes may suffer. Results indicate that DAN probes and their constricted analogues can generate singlet oxygen, and the extent is dependent on solvent. The highest quantum yield of singlet oxygen generation was observed in apolar solvents, reaching values near 40%. HPLC analysis indicates that several photoproducts are formed, identifying at least 4 intermediates with lower retention times than the parent probe. Photoconsumption experiments were carried out under oxygen and oxygen-free conditions. Results indicate that photodegradation of restricted analogues involves reaction with oxygen. However, in the case of DAN probes and contrary to common belief, photodegradation was independent of oxygen. In summary, this work provides valuable insights into the mechanistic pathways involved in the inactivation of DAN derivatives.

DESIGN AND SYNTHESIS OF DICATIONIC STYRYL DYES FOR NUCLEIC ACID DETECTION ENHANCING BINDING THROUGH ELECTROSTATIC INTERACTIONS

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Fluorescent dyes derived from styryl structures represent a well-established family of compounds widely employed in the design of molecular probes for biomolecule detection, due to their high sensitivity to environmental changes, accessible synthesis, and the tunability their spectroscopic properties via strategic chemical modifications. Notably, their use in sensing, quantifying, and detecting nucleic acids has gained considerable importance, as they exhibit minimal background fluorescence in solution and markedly enhanced emission upon interaction with structures such as DNA and RNA.

In this study, we report the synthesis of four novel dicationic styryl derivatives bearing a Nmethylpyridinium ring (as the primary cationic moiety) and a 4-methoxyphenyl or N,Ndiethylaminophenyl group, linked via a trans-configured double bond to the 2 or 4 position of the pyridinium ring (see Figure). The diethylamino and methoxy substituents on the phenyl ring were introduced with to modulate the electronic and spectroscopic properties of the dyes. Additionally, the 4-methoxyphenyl and N,N-diethylaminophenyl cores carry alkyl chains with ether linkages, were included to impart a balanced hydrophilic/lipophilic character to each derivative. These chains include a quaternary ammonium group at the terminal position, which serves as the second cationic center.

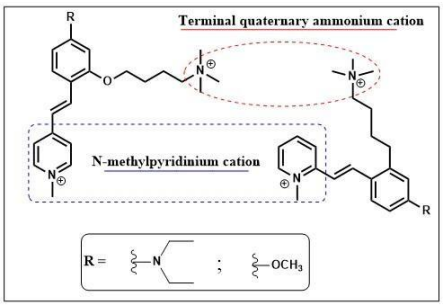

Figure 1: *Chemical structure of studied dicationic styryl derivatives.*

All compounds were synthesized via base-catalyzed Knoevenagel-type condensations, followed by quaternization with trimethylamine, resulting in a second positive charge. Yields ranged from 25% to 67%. The final products exhibit good water solubility and were designed to promote electrostatic interaction with nucleic acids. Spectroscopic characterization included UV-Vis absorption and fluorescence studies. Fluorescence measurements revealed a significant increase in emission intensity (at constant dye concentration) in the presence of single-stranded (ssDNA) and double-stranded (dsDNA) DNA, compared to nucleic acid-free solutions. This enhancement suggests that binding to nucleic acids restricts rotational degrees of freedom, thereby reducing non-radiative decay pathways and enhancing fluorescence.

UV-Vis spectra revealed a bathochromic shift when comparing aqueous media with less polar solvents, indicating sensitivity to the polarity of the surrounding environment. Compounds bearing diethylamino groups absorbed between 465–503 nm, whereas methoxy-substituted analogues absorbed at shorter wavelengths, ranging from 392 to 409 nm. These differences highlight how the nature of the substituent influences electronic delocalization. Furthermore, the observed shift is associated with changes in the fluorophore's environment rather than effects caused by direct binding to nucleic acids.

Photostability study on red-emitting carbon dots by PARAFAC Analysis

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Carbon dots (CD) are quasi-spherical nanoparticles smaller than 10 nm. They possess high biocompatibility, low toxicity, low manufacturing costs, and other characteristics that have made them the subject of multiple studies and applications. One of these characteristics is their high fluorescence stability (Hai-Li et al., 2023).

In this study, multiemissive CD were synthesized. The different emissive components were separated by PARAFAC analysis. CD suspensions were irradiated with a UV lamp at a maximum wavelength of 367 nm and a full width at half maximum of 16.7 nm for several hours. Modifications in the fluorescence components of the irradiated nanoparticles were observed.

To elucidate the modification and degradation mechanism, irradiation was performed in the multiple components detected in the nanoparticles evidenced a degradation mechanism presence of N_2 to eliminate the presence of oxygen. The behavior and integration of these mediated by a photosensitization pathway.

Key words:
Photostability, carbon dots, Fluorescence

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In situ NMR photochemistry of dicationic azobenzenes

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Photoisomerization studies show that dicationic azobenzene derivatives exhibit reversible spectral behavior under cyclic UV and visible-light irradiation. The experimental setup enables irradiation and real-time data acquisition via *in situ* illumination of the samples, particularly during nuclear magnetic resonance (NMR) measurements. This design provides valuable information on the photostationary state (PSS) and photoswitching kinetics, opening new perspectives for the study of molecular switches. In addition, these derivatives can form molecular aggregates at low concentrations that are also reversibly photoactivable, enabling the study of their surface charge and hydrodynamic size. Taking advantage of these features, we are currently developing systems with potential application in light-regulated drug release.

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ABSTRACTS

Theranostic Potential of Aminolevulinic Acid-Derived Porphyrins

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Fluorescence from porphyrins, derived from the application of 5-aminolevulinic acid (ALA), has emerged as a valuable tool in the diagnosis of infections. ALA, a precursor in the heme biosynthesis pathway, leads to the accumulation of porphyrins in tissues with increased metabolic activity, such as infected or abnormal cells. However, ALA-photodiagnosis has been reported only for superficial infected wounds. Therefore, our aim was to investigate the possibility of employing ALA and its lipophilic derivative Hexyl-ALA for the detection of skin and soft tissue infections.

For this purpose, we used a skin and soft tissue model induced after subcutaneous inoculation of *Staphylococcus aureus* in CF1 mice. Porphyrins were visualized by photography after the interposition of a magenta-colored filter, microscopically after cryosectioning of the abscesses, and quantified fluorometrically after chemical extraction.

We topically applied ALA or Hexyl-ALA to the surface of the abscess and monitored porphyrin fluorescence over time. Porphyrin fluorescence remained confined to the subcutaneous tissue and was not visualized from the skin surface when exciting the fluorescence with 365 nm light. However, when the mice were sacrificed, a strong pink fluorescence was observed in the inner layers of the skin, highly confined to the infected area. Since it was not possible to externally detect the fluorescence of porphyrins synthesized from ALA in the treated abscesses, we employed an *in vivo* imaging system (IVIS) Spectrum CT device. The optimal conditions were excitation at 430 nm and emission at 620 nm. Under these conditions, a nonspecific fluorescence was detected in the abscess area.

Interestingly, when mice were infected on both flanks, we visualized fluorescence on the nontopical side, suggesting migration of ALA to the contralateral side. In contrast, fluorescence remained confined to the treated side after Hexyl-ALA application.

After topical application of ALA, the main porphyrin in the abscess was Coproporphyrin III. Following systemic injection of ALA, fluorescence was also confined to the abscesses, mainly due to Protoporphyrin IX fluorescence emitted from eukaryotic cells.

Our findings indicate that ALA is selective for infected tissues (whether bacterial or inflammatory cells), although fluorescence was not visible from the skin surface. Nonetheless, fluorescence derived from porphyrins synthesized from ALA could be useful in fluorescenceguided debridement of infections.

Reactive oxygen production by a natural anthraquinone and its homodimer on *Candida tropicalis* biofilm

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Soranjidiol (SOR) and 5´5-bisoranjidiol (BISOR) are two natural anthraquinones with photosensitizing properties through the Type I (superoxide anion, $O_2^{\bullet-}$) and Type II (singlet molecular oxygen, $^1O_2$) mechanisms, with antibiofilm effect on *Candida tropicalis in vitro* when photostimulated.[1-3] The objective of this work was to establish the photodynamic mechanism mediated by reactive oxygen species.
Both anthraquinones (AQ) were isolated from the genus *Heterophyllaea* Hook f. (Rubiaceae) and identified by their UV spectra and co-chromatography against reference substances and their purity was determined by HPLC (> 93%). Minimum inhibitory concentration (MIC) was determined under light and dark conditions, following CLSI guidelines, against *C. tropicalis* NCPF 3111.[4] A dense biofilm was obtained from the *C. tropicalis* strain after 48 h of growth. The biofilm was exposed to 4 concentrations of each AQ: MIC, MICx2, MICx4 and MICx8; with 100 mM Tiron ($O_2^{\bullet-}$ scavenger) or sodium azide ($^1O_2$ quencher) under darkness and irradiated conditions of 30 min with an actinic lamp (Philips TL/03, λ = 420 nm). Biofilm quantification was performed using the Crystal Violet (CV) staining method and measuring the optical density (OD) at 595 nm.
The photoactive MIC (planktonic cultures) was 1.96 µg/mL for SOR and 0.98 µg/mL foa inforr BISOR, whereas in dark conditions, the MIC was 3.91 and 1.96 µg/mL, respectively. Under irradiation, the higher antibiofilm effect was achieved at 1.96 µg/mL for SOR, producing a 46% reduction (%R); which was completely reversed with Tiron and azide. However, at higher concentrations, its effect was not reversed by the quencher. BISOR produced 68.2% R in the biofilm at 1.96 µg/mL under light conditions; this effect was completely reversed in the presence of Tiron, while it remained unchanged with azide at all active concentrations. In conclusion, SOR primarily acts by a Type I mechanism ($O_2^{\bullet-}$), and at low concentrations also involves a Type II mechanism ($^1O_2$). In contrast, BISOR exerts its photosensitizing effect mainly via a Type I mechanism, being more active than its monomer.

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Marine Algae as a Therapeutic and Sustainable Source for Skin Photoprotection Against UV-Induced Damage

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Ultraviolet (UV) radiation is a major environmental factor contributing to various skin pathologies, including sunburn, premature aging, and skin cancer. The intensification of UV exposure, driven by ozone layer depletion and the broader impacts of climate change, presents a growing public health concern, particularly for populations exposed to high levels of solar radiation. While the skin possesses natural defense mechanisms such as melanin production and antioxidant enzyme activity, these are often insufficient to counteract the cumulative effects of prolonged UV exposure. This reality underscores the need for safe, effective, and environmentally responsible photoprotective strategies. Marine organisms, particularly macroalgae, have evolved sophisticated protective systems that allow them to thrive in high-UV environments. These include the synthesis of naturally occurring compounds with strong UV-absorbing and antioxidant capabilities. Leveraging such marinederived bioactives offers a promising pathway for developing next-generation skincare products that both shield the skin and align with principles of sustainability.

One of our lines of research focuses on evaluating compounds of marine origin and taking advantage of their ability to neutralize free radicals, which was evaluated by in vitro assays targeting several reactive species commonly implicated in UV-induced oxidative stress. In parallel, their protective effect on lipid structures, critical components of skin cell membranes, was investigated using a complementary model system, a lipid oxidation assay. The compounds showed strong free radical scavenging activity and effectively inhibited oxidative degradation of lipids under stress conditions. Spectroscopic analyses revealed their ability to mitigate key structural changes associated with lipid peroxidation, including the formation of hydroxyl and carbonyl groups, as well as the alteration of aliphatic chains. These effects were especially notable at physiologically relevant concentrations and under conditions that simulate UV-induced damage in skin cells.

The results support the incorporation of marine-derived antioxidants into dermocosmetic formulations as a viable strategy for enhancing skin resilience against UV radiation. Beyond their biological efficacy, such compounds contribute to the sustainable use of marine resources, offering a dual benefit of skin protection and environmental responsibility. This approach complements global efforts toward climate adaptation and public health promotion, in alignment with Sustainable Development Goal 3: Good Health and Well-being.

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Combining carbon dots with porphyrin photosensitizers: a strategy to boost photophysical properties and toxicity against leukemia cells

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Recently, efforts to find compounds selectively affecting cancer cells while sparing normal ones have grown. Nitric oxide (NO) is critical in physiology and pathology, including cancer. It influences cellular processes like proliferation, apoptosis, and angiogenesis. NO's intricate interaction with cancer cells offers innovative treatment possibilities, but its effects can vary by concentration and site. NO derivative ruthenium complexes, capable of releasing NO upon stimulation, hold promise. These versatile compounds could also enhance Photodynamic Therapy (PDT), a light-activated approach inducing cellular damage. While many photosensitizers show promise, challenges such as low selectivity, high toxicity, and reliance on in vitro models that fail to capture the complexity of primary tumors have limited their successful transition into clinicals. To overcome these challenges, three-dimensional (3D) models are increasingly being used as preclinical platforms to enhance translational research and improve clinical outcomes. In this study, a nitro-ruthenium porphyrin complex, the $\{TPyP[Ru(NO_2)(bpy)_2]_4\}(PF_6)_4$, designated $RuNO_2TPyP$, which releases NO upon irradiation, was investigated for its effects on cancer cells in 2D and in 3D cancer models at increasing complexity, including free-standing spheroids, bioprinted spheroids in hydrogels, and bioprinted patient-derived organoids (PDOs). Spheroids, as the simplest model, demonstrated the compound's effectiveness but required longer incubation and higher irradiation doses compared to 2D culture. Bioprinted spheroids in hydrogels enabled created a more controlled microenvironment, improving spheroid arrangement, irradiation precision, and physiological relevance. Bioprinted PDOs, with controlled size and positioning, provided an advanced platform for evaluating the $RuNO_2TPyP$ complex, yielding promising preliminary results. The findings suggest that this complex has potential for PDT treatment in cancer cell lines, as it exhibits photocytotoxicity at low concentrations without causing cytotoxicity to normal cells. Moreover, treatment of cells with the $RuNO_2TPyP$ followed by light irradiation (4 J cm^{-2}) can induce apoptosis, generate ROS, promote intracellular NO formation, and has anti-migratory effects. Additionally, the complex can modify tumor cell structures and induce photocytotoxicity and apoptosis in 3D culture. These outcomes are attributed to the internalization of the complex and its subsequent activation upon light irradiation, resulting in NO release and singlet oxygen production.

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Sunlight-induced modulation of the cutaneous immune response in human tegumentary leishmaniasis.

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Tegumentary leishmaniasis (TL) is a zoonotic disease that affects both the skin and mucous membranes of infected individuals. The etiological agent is an intracellular parasite from the genus *Leishmania*, transmitted through the bite of an infected phlebotomine of the genus *Lutzomyia* (in the Americas). TL is endemic in Latin America, and during the period 20012023, a total of 1.178.436 cases were reported by the Pan American Health Organization, resulting in more than 50.000 cases per year.
The origin and progression of this disease are essentially immunopathological, with the severity of the mucous lesions correlated with the inflammatory hyperreactivity of the immune system. The control of the cutaneous infection (which may cure spontaneously) highly depends on a controlled Th1 immune response, with secretion of adequate amounts of IFN-γ. Ultraviolet radiation (UVR) in sunlight is a well-known inducer of immunomodulation, ranging from an increased local acute inflammatory response to systemic immunosuppression that may persist for weeks. However, the relationship between sunlight exposure and the development, dissemination, and worsening of the leishmania infection has not been studied.
We aim to investigate the role of sunlight exposure in the development of localized cutaneous leishmaniasis, its progression to cutaneous disseminated disease, and ultimately, to the mucocutaneous form.
To this end, we analyzed an *in vitro* model consisting of molecular mediators secreted by sunlight-exposed keratinocytes and their role in the ability of macrophages to respond to a *Leishmania braziliensis* infection. Moreover, we studied serum immune mediators and an indirect sunlight exposure indicator, Vitamin D, and correlated these molecules with the form and severity of the disease in patients with TL. Finally, an epidemiological approach was also employed to compare the incidence of TL according to the geographic location and calculated erythemal UV radiation (from climatic databases).
The results to be presented demonstrate that simulated sunlight exposure modifies the immune response against Leishmania *in vitro*. Moreover, geographical associations between surface UV radiation and the number of TL cases also suggest a possible interaction between sun exposure and the development of the disease. However, the analysis of serum mediators in a small cohort of patients from the Argentine Northwest did not reveal any association.

From Inverted Solvatochromism to Excited-State Dynamics: Triarylpyrimidine Push–Pull Fluorophores as Molecular Probes in Microheterogeneous Media

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Solvatochromism describes how molecular chromophores respond to environmental polarity, producing characteristic shifts in absorption and emission spectra. Depending on the direction of these shifts, solvatochromism can be classified as positive (bathochromic), negative (hypsochromic), or inverted—the latter involving a transition from positive to negative behavior at a specific "solvatochromic inverse point." While numerous absorption-based examples exist, emissive inverted solvatochromism remains largely unexplored.

Here, we present a family of fluorescent aminocarbonyl derivatives based on 2,4,6triarylpyrimidines (TAPs) functionalized with n-alkyl chains (C_1–C_{12}), designed to probe the interplay between molecular lipophilicity and partitioning in microheterogeneous environments. Among them, three aminocarbonyl derivatives exhibit **emissive inverted solvatochromism**, providing new insight into how polarity gradients within structured media influence excited-state charge redistribution.

Fluorescence experiments in DSPC:Ch (55:45) liposomes, combined with quenching studies using 4-alkanoyloxy-TEMPO radicals (C_2–C_{16}), reveal chain-length–dependent localization and multiple dye populations across the bilayer. Moreover, tuning donor strength and torsional flexibility of N,N-disubstituted amino groups modulates the intramolecular charge-transfer (ICT) dynamics. Quantum-chemical calculations support the presence of twisted ICT (TICT) states that govern fluorescence persistence in different polarity regimes.

Together, spectroscopy and theory provide a unified picture linking solvatochromic inversion, ICT dynamics, and interfacial localization—paving the way for the design of **new polaritysensitive push–pull fluorophores** for sensing and photochemical applications.

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POSTERS

ABSTRACTS

Erythema protection efficacy of plant derivatives compounds based on narrow-band reflectance spectroscopy data in mice

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Plants are sources of photoprotective compounds that protect human skin against solar injuries. This study investigated the usefulness of a murine model to estimate the erythema protective efficacy (EPE) of natural compounds during prospecting. UVB-induced skin erythema in albino BALB/c mice was measured using a Mexameter MX18 MDD colorimeter. The minimum erythema dose (MED) was determined graphically based on Log_{10} doseerythemal response curves. The EPE values for standard filters (*e.g.,* titanium dioxide or zinc oxide) and promising plant-derived compounds (apigenin, caffeic acid, epigallocatechin gallate (EGCG), kaempferol, and pinocembrin) were computed as the ratio between MED_p in the protected subject skin and MED_u in unprotected subject skin. UVB-induced erythema in female and male mouse skin fits a lineal kinetic function. Erythema varied according to sex and dorsal area studied. The MED values were between 39 and 80 mJ/cm^2; and these values increased linearly with the logarithm of the radiation dose. Plant compounds (apigenin, caffeic acid, EGCG, kaempferol, and pinocembrin) resulted in protection against UVR-induced erythema in mice skin (EPE = 3.4−15.2). The EPE metric in mice resulted valuable for identifying plant compounds potentially useful for human protection.

Radioresistance, photoprotection, and antigenotoxicity against UVB radiation of the pigmented Kocuria flava strain from Paramo ecosystems in Colombia

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Bacteria species belonging to the Actinomycetota phylum produce a variety of secondary metabolites with protective properties. This study investigated resistance, photoprotection, and antigenotoxicity against ultraviolet (UV) radiation in the pigmented *Kocuria flava* strain. Survival to UVB radiation of *the K. flava* strain was determined and compared with that of the *Escherichia coli* and *Deinococcus radiodurans* types. Methanolic extracts obtained from *K. flava* grown in different culture media (e.g., LB − Luria Bertani medium. NB − Nutrient broth medium. RCM − Reinforced Clostridial medium) were evaluated for photoprotection efficacy ($SPF_{spectrophotometric}$) and antigenotoxicity (SOS Chromotest) against UVB radiation. *K. flava* showed radio-resistance (D_{90} = 2708 J/m^2 − $D_{99.99}$ = 3055 J/m^2) higher than in *E. coli*, but lower than D. *radiodurans*, the most radioresistant known bacteria. The yield of *K. flava* pigment extraction varied depending on the culture media used as follows: RCM LB ≈ NB. The *K. flava* methanolic extracts showed high ($SPF_{spectrophotometric}$= 38) photoprotection efficacy; and this activity depended on pigment concentration ($R = 0.67$, $p < 0.05$). Extract antigenotoxicity against UVB radiation resulted in relevant %GI ≥ 30 only at high concentrations; however, photoprotection efficacy and antigenotoxicity activities were highly correlated ($R = 0.93$, $p < 0.05$). Our results shown that the *Kocuria flava* can be a promise as sources of carotenoid pigment useful in cosmetic photoprotection.

Singlet oxygen in biological systems: mass spectrometry and near-infrared light emission measurements

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Recent advances in biochemical research have unveiled multiple pathways for generating singlet oxygen ($^1O_2$) and electronically excited species, offering promising applications in therapeutics, while also revealing mechanisms of endogenous oxidative stress and damage [1]. Acting as a signaling molecule, $^1O_2$ induces arterial relaxation and lowers blood pressure. These findings uncover a novel physiological function for $1O_2$ in mammals, linking it to vascular tone regulation under inflammatory conditions [2]. From a biochemical perspective, haloamines derived from amino acids and polyamines were shown to generate $^1O_2$ upon reaction with H_2O_2. Bromamines were especially efficient in this process, supporting the idea that such reactions may serve as an endogenous source of $^1O_2$ in non-illuminated biological systems, especially during eosinophil and neutrophil-driven inflammation [3]. Additionally, studies have shown that neurotransmitters such as dopamine, serotonin, and melatonin can undergo chemiexcitation upon oxidation (e.g., by peroxynitrite). This process forms triplet excited states that transfer energy to DNA, inducing cyclobutane pyrimidine dimers (CPDs) in the absence of light [4]. These findings suggest a novel mechanism of endogenous mutagenesis, with potential implications in inflammation, cancer, and neurodegeneration. Further exploring lipid biochemistry, plasmalogen oxidation by $^1O_2$ was found to produce reactive intermediates like hydroperoxyacetals and dioxetanes. These intermediates can generate triplet carbonyls, additional $^1O_2$, and electrophilic aldehydes, potentially disrupting cell signaling and membrane integrity. This contradicts the traditional view of plasmalogens as antioxidants, revealing a prooxidant role under oxidative conditions [5]. In another study, lipid hydroperoxides were shown to react with the nitronium ion (NO_2^+), a reactive nitrogen species found during inflammation. This reaction yields $1O_2$, confirmed by near-infrared luminescence, suggesting that lipid peroxidation, via nitronium chemistry, contributes significantly to oxidative stress in membranes [6].

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Effective bacterial inactivation: combination of therapies

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The escalating global challenge of antimicrobial resistance (AMR), leading to the emergence of "superbugs", urgently demands novel therapeutics strategies. This has led to the need to develop new antimicrobial approaches to treat infections caused by these microorganisms.1 Photodynamic inactivation (PDI) is a therapeutic modality that involves the presence of three essential components: a photosensitizing agent (PS), light, and oxygen. None of these components is toxic individually, but together they initiate a series of photochemical reactions that culminate in the generation of reactive oxygen species (ROS), which cause cell death. To enhance the therapeutic effect, PDI can be combined with other drugs or treatments.2 In this study, PDI was joint with conventional antibiotics (ATB) therapy and the enzyme lysozyme (LSZ) to evaluate its effect on Staphylococcus aureus and Escherichia coli.

The ATBs used were cephalexin (CFX) for E. coli and ampicillin (AMP) and rifampicin (RIF) for S. aureus. In addition, 5,10,15,20-tetrakis(4-N,N,N-trimethylammoniumphenyl) porphyrin (TMAP4+) was used as PS. The minimum inhibitory concentration (MIC) and minimum bactericidal concentration (MBC) of ATB, PS, and the combination of both were determined. These are defined as the lowest concentration of antimicrobial necessary to inhibit and eliminate microorganisms, respectively. In the case of S. aureus, treatment with AMP obtained a MIC of 0.0625 μg/ml, while for RIF it was 0.007 μg/ml. On the other hand, for E. coli, the MIC result obtained for CFX was 8 μg/ml. Likewise, the MIC of TMAP4+ obtained for S. aureus was 0.5 □M, while for E. coli it was 32 □M. The MBCs were 16 and 32 □M, respectively. Notably, the combination of both therapies produced a significant decrease in the MIC and the MBC of ATB after 30 minutes of irradiation. This is due to the photodynamic effect produced by PS, as is not observed when cultures are kept in darkness.

Furthermore, we examined the impact of LSZ in conjunction with PDI. The LSZ hydrolyzes the β(1-4) bonds between N-acetylmuramic acid and N-acetylglucosamine, the main components of bacterial peptidoglycan, which is present in greater proportions in the cell walls of Gram-positive bacteria.3 Nevertheless, this enzyme does not affect Gram-negative bacteria, as they have an outer membrane that covers the cell wall and prevents the enzyme from acting. First, it was determined that 0.5 mg/mL was the concentration of LSZ required to observe an effect on the growth curve of S. aureus. Subsequently, the LSZ + PDI combination showed that antibacterial action was enhanced, eliminating S. aureus after 10 minutes of irradiation, unlike when PS was applied individually under the same conditions.

In this way, it is possible to reduce the concentration of the agents required to optimize the antibacterial effect. This ensures the effective elimination of microorganisms, minimizing possible side effects and the development of resistance. Therefore, the combination of therapies allows enhancement the antimicrobial effect of both therapies applied individually through different mechanisms.

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Effects of photoinactivation on bacterial resistance and virulence factors

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The growing emergence of bacteria that are resistant to traditional antibiotics highlights the urgent need to develop new antimicrobial strategies. In this context, photodynamic inactivation (PDI) is emerging as a promising phototherapeutic tool.[1] PDI is based on the synergistic interaction of a photosensitizing agent (PS), light, and oxygen, generating reactive oxygen species (ROS) that irreversibly damage microbial cellular components, inducing their death.[2] This study evaluates the antimicrobial potential of the photosensitizer zinc(II) 2,9,16,23tetrakis[4-(*N*-methylpyridyloxy)]phthalocyanine ($ZnPPc^{4+}$) against different strains of *Staphylococcus aureus* and *Escherichia coli*. Its effect on the inactivation of planktonic cells, the modulation of virulence factors, and the ability of bacteria to produce biofilms was investigated, as well as the potential induction of resistance after repeated exposures to PDI. The results demonstrate that $ZnPPc^{4+}$ is highly effective in the photoinactivation of planktonic *S. aureus* at low concentrations and light doses. Interestingly, although PDI with $ZnPPc^{4+}$ effectively eliminated *S. aureus* under the sublethal conditions analyzed, it did not inactivate the activity of virulence factors such as β-hemolysin, lipase, lecithinase, or mannitol fermentation. However, this PS showed significant efficacy in inactivating *S. aureus* biofilms, even at very low concentrations (in the nM range), a crucial finding given the greater resistance of biofilms to treatments.

On the other hand, repeated PDI treatments were performed on *E. coli* using the same photosensitizer, adjusting the parameters to achieve partial inactivation and allow colony survival. After ten PDI cycles, no significant differences were observed in the inactivation of *E. coli*, indicating that repeated sublethal exposure does not induce resistance to subsequent photodynamic treatments. Although some fragmentation was detected in plasmid DNA, the genomic DNA of *E. coli* remained unchanged. In addition, changes in antibiotic susceptibility were observed after repeated photodynamic treatment.

In conclusion, PDI with $ZnPPc^{4+}$ emerges as a promising alternative therapy not only for controlling the reproduction of pathogenic microorganisms and biofilm formation, but also for its ability to not induce resistance to this treatment. This suggests great potential for combating infections, including those associated with biofilms, without the limitations presented by the development of resistance in conventional antibiotic therapies.

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Evaluation of Graphene Quantum Dots in Breast Cancer Cell Line

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According to the National Cancer Institute, female breast cancer is the most common cancer worldwide, with approximately 2.3 million new cases. In Brazil, between 2023 and 2025, 73,610 cases are expected, corresponding to 66.54 new cases per 100,000 women. Graphene quantum dots (GQDs) are nanoparticles that are used in treatment and diagnosis. This study aimed to evaluate the antiproliferative activity of inorganic nanoparticles such as GQDs in breast cancer cell lines. The GQDs were characterized using UV-Vis spectrophotometry, fluorescence spectroscopy, X-ray diffraction, Fourier transform infrared spectroscopy (FTIR), and Raman spectroscopy. Cytotoxicity was evaluated in a hormone-dependent MCF-7 cell line derived from breast adenocarcinoma and incubated in the dark for 3 h with GQD solution. The results demonstrated that the GQDs were not cytotoxic to MCF-7 cells in the absence of UV light, with cell viability above 90%, even at the highest concentrations tested (250–1000 µg/mL). However, after irradiation with UV light (405 nm), a considerable reduction in cell viability was observed, especially at the lowest concentrations (10–250 µg/mL), where the viability dropped to approximately 50–60%. This difference indicates a phototoxic effect dependent on the presence of UV light, suggesting that the compound itself is not cytotoxic under basal conditions but can be potentially used in photodynamic therapy approaches, exploring its ability to generate a cytotoxic effect under exposure to light.

Photophysical and photochemical study of inclusion compounds of indocyanine green with cucurbiturils

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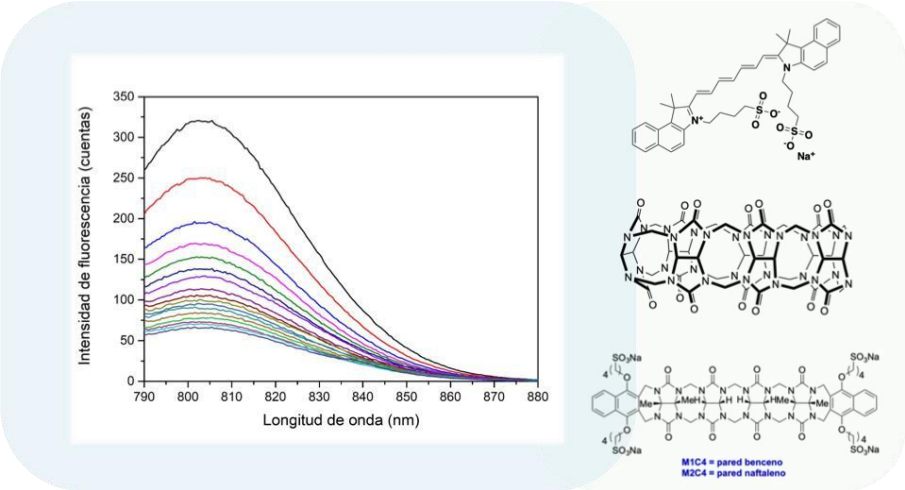
Cancer remains a leading cause of mortality worldwide, and while conventional therapies exist, they often present significant adverse effects for patients. Photodynamic therapy (PDT) offers an attractive alternative, yet improvements in photosensitizer drug properties are crucial for its widespread adoption. This research hypothesizes that the formation of host-guest supramolecular aggregates between photosensitizing drugs and supramolecular matrixes like cucurbiturils and acyclic cucurbiturils will modulate the physicochemical properties of these drugs. This modulation is expected to improve solubility and stability in biological media, disaggregation, specificity, controlled release, and singlet oxygen generation yield, thereby mitigating PDT-associated adverse effects and improving cancer treatment prognoses. The study aims to synthesize inclusion compounds of indocyanine green with cucurbit[7]uril and acyclic containers M1C4 and M2C4. These inclusion compounds will be characterized by determining their association constants, structure, and stoichiometry. Association constants will be determined using UV-Vis and fluorescence spectrophotometric titrations in water to quantify supramolecular interaction strength and study inclusion stoichiometry. Drug and drug complexes photodegradation will be quantified by radiation studies. Singlet oxygen generation and total reactive oxygen species will be determined by bleaching of an aqueous solution of 9,10-Anthracenediyl-bis(methylene)dimalonic acid or tryptophan probes, respectively.



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Photophysical and photochemical study of inclusion compounds of temoporfin with cucurbiturils

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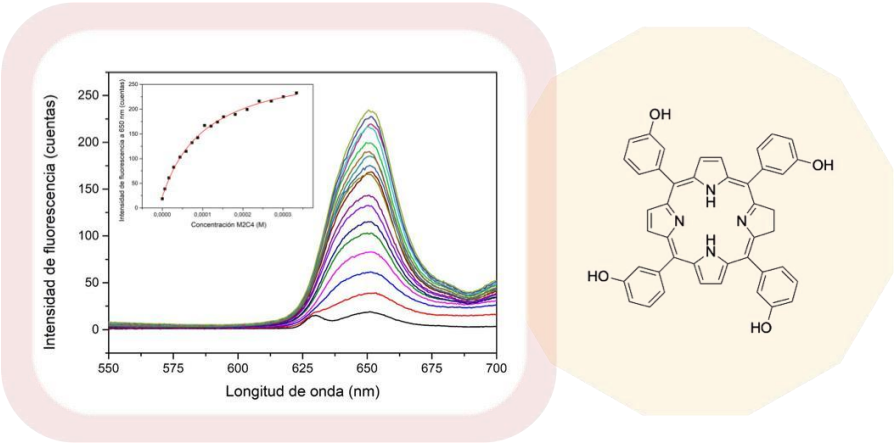
Cancer is one leading cause of death globally, including in Chile. Current treatments have limitations, highlighting the urgent need for safer, more effective, and accessible alternatives. Photodynamic therapy (PDT) offers a promising approach, involving a photosensitizer drug applied to a lesion, followed by light irradiation. This process, in the presence of oxygen, generates cytotoxic species that destroy targeted cells. Despite its potential, PDT faces challenges, primarily due to the low water solubility and aggregation of many photosensitizer drugs. This aggregation reduces the production of the reactive oxygen species crucial for PDT effectiveness. A strategy to overcome these issues is the creation of host-guest inclusion complexes between a photosensitizer and a water-soluble supramolecular matrix. Complex formation can enhance drug solubility, prevent degradation, and disaggregate the drug, boosting its efficiency.

The formation of inclusion complexes between temoporfin (TP), a porphyrinic photosensitizer used in PDT under the name 'Foscan' for advanced cancer processes, and cucurbiturils and acyclic cucurbiturils will modulate the physicochemical properties of this drug. Association constants will be determined using UV-Vis and fluorescence spectrophotometric titrations in water. Drug and drug complexes photodegradation will be quantified by radiation studies. Singlet oxygen generation and total reactive oxygen species will be determined by bleaching of an aqueous solution of 9,10-Anthracenediyl-bis(methylene)dimalonic acid or tryptophan probes, respectively.



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2. Day, S., Pérez, B., Guerra Díaz, D., Mariño-Ocampo, Zúñiga-Núñez, D., Faúndez, M.A., Soto-Arriaza, M., Pizarro, N., Heyne, B., Fuentealba, D. (2024) Supramolecular complex of tetracationic porphyrin with acyclic cucurbituril-like container induces quantitative singlet oxygen generation. Phototoxicity studies in vitro in MCF7 human breast cancer cells. Journal of Photochemistry and Photobiology, A: Chemistry, 449, 115388

Novel supramolecular turn-on/off system for singlet oxygen generation and fluorescence emission using acyclic cucurbituril-type containers

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Acyclic cucurbituril-type containers (ACBs) have demonstrated superior ability to modulate the photophysical and photochemical properties of photosensitizers compared to conventional macrocycles, including cucurbiturils.[1] This advantage is attributed to their open architecture, which facilitates both the interaction of the photosensitizer with the surrounding media and the efficient diffusion of molecular oxygen into the host nanocavity. In this work, we present a supramolecular turn-on/off system that regulates both the fluorescence emission and singlet oxygen ($^1O_2$) generation of the photosensitizer 5,10,15,20-tetrakis(1-methyl-4-pyridinium) porphyrin (TMPyP) through competitive binding between two acyclic containers M1C4 and M2C4. Characterization of the complexes by NMR spectroscopy and isothermal titration calorimetry revealed that, although the ACBs differ only in the nature of their aromatic walls, they exhibit distinct association constants with TMPyP, as well as differentiated thermodynamic contributions, reflecting dominant supramolecular interactions in each system. These differences were also evident in the chemical shift changes observed by NMR. Furthermore, steady-state and time-resolved photophysical studies, along with the direct determination of singlet oxygen quantum yield, confirmed that the supramolecular systems effectively controlled both fluorescence emission and $^1O_2$ generation, enabling the design of an activatable supramolecular platform (Fig. 1.I). The TMPyP@M1C4 complex maintains the photosensitizer in the "off" state; however, upon replacing M1C4 with M2C4, the "on" state is restored, with full recovery of fluorescence (see Fig. 1.II) and efficient $^1O_2$ generation. Owing to their high-water solubility and biocompatibility of these ACBs, these systems hold great potential as theragnostic platforms for applications in photomedicine.

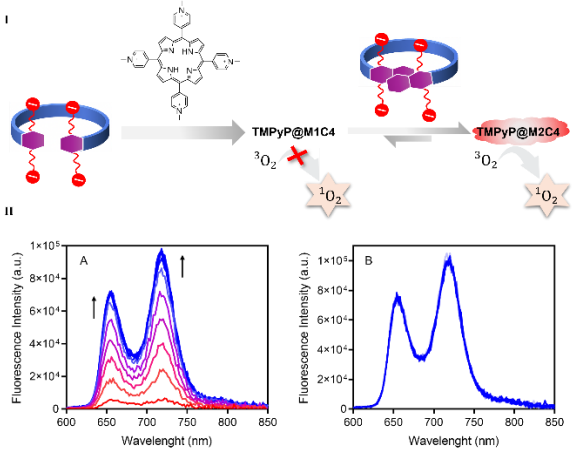

Fig. 1. Schematic of the ACBs-based turn-on/off supramolecular system with TMPyP (I) and (II) fluorescence emission spectra of TMPyP@M1C4 upon addition of 1 µM M2C4 (A) and TMPyP@ M1C4 upon addition of 1

[1] *J. Photochem. Photobiol. A: Chem* 2024, 148, 115388

μM M1C4 (B). [TMPyP] = 5 μM, [M1C4] = [M2C4] = 10 μM, $\lambda_{exc} = 519\ nm$

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Characterizing the Photodamage Induced by 6-Thioguanine Incorporated Into DNA

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Introduction: Singlet molecular oxygen ($^1O_2$) is a reactive oxygen species that, in a biological context, oxidizes biomolecules, such as DNA, lipids and proteins. In DNA, it exclusively targets guanine (Gua) forming the mutagenic lesion 8-oxo-7,8-dihydroguanine (8-oxoGua). This lesion can undergo further oxidation with $^1O_2$, generating secondary products. 6Thioguanine (6-TGua), a guanine analogue used in the treatment of leukemia, autoimmune diseases and transplant patients, absorbs UVA radiation (with a maximum absorption in 340 nm) and acts as a type II photosensitizer, generating singlet oxygen ($^1O_2$). Once incorporated into DNA, 6-TGua can promote *in situ* $^1O_2$ production in skin cells exposed to sunlight, potentially contributing to skin cancer development. **Objective:** This study investigates the role of $^1O_2$ in DNA damage in keratinocytes treated with 6-TGua and exposed to UVA irradiation. **Materials and Methods:** HaCaT keratinocytes were treated with 6-TGua with a dose of 0.25 µM, which leads to an incorporation rate of 0.02% 6-TGua/Gua, consistent with levels measured in the treated patients. Then, cells were exposed to a low dose of UVA of 6 J/cm² using a solar simulator. The DNA damage was assessed by two methods: i) quantification of 8-oxoGua via LC-MS/MS, with an optimized protocol to prevent artifactual oxidation; ii) Alkaline comet assay, to measure strand breaks potentially promoted by the photosensitization *in situ* in DNA. **Results and Discussion:** Our results indicate that the treatment of HaCaT cells with 6-TGua + UVA leads to an increase of 8-oxoGua levels to approximately 34 molecules of 8-oxoGua per 10^6 Gua in DNA (average of three independent experiments). This represents a 3 to 4 times compared to the basal level found in our samples (9 molecules of 8-oxoGua per 10^6 Gua in DNA). Also, preliminary comet assay analysis indicated that this treatment is not sufficient to promote strand breaks immediately after photosensitization. **Conclusion:** These findings support that $^1O_2$ is a major contributor for the formation of 8-oxoGua in the DNA of 6-TGua treated patients exposed to sunlight. However, other photoinduced reactions must also be considered, as the reactivity of Gua towards the $^1O_2$ does not fully explain the development of skin cancer. Further steps involve the quantification of: i) other DNA lesions (pyrimidine dimers and oxidized pyrimidines) by the modified comet assay; and ii) 6-TGua oxidation products, such as guanine-6-sulfinate and guanine-6-sulfonate, by LC-MS/MS. Additionally, experiments in aqueous solution with chemical standards of 6-TGua and its related deoxyribonucleoside (6-TdGuo) were conducted in order to elucidate its reactivity towards $^1O_2$. Altogether, these results contribute to rationalize the complex oxidative damage triggered by the photosensitization of 6-TGua.

Acknowledgements: Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP), CEPID Redoxoma (#2013/07937-8), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Pro-Reitoria de Pesquisa-USP.

Comparison of the photoinactivation efficiency of chlorophyllin, gallic acid and rose bengal against *S. Aureus*

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This study compares the photoinactivation efficiency of three photosensitizers—chlorophyllin (Chi), gallic acid (GA), and rose bengal (RB)—against Staphylococcus aureus under visible light irradiation. Aqueous suspensions of S. aureus (~10^6 CFU/mL) were treated with each compound at optimized concentrations and exposed to red light ($\lambda \approx 630–660$ nm, 30 mW/cm²) for up to 30 minutes. Microbial survival was quantified by plate counting, and results were expressed as log reductions relative to dark controls. RB showed the highest antimicrobial activity,. Remarkably, Chi exhibited a similar photoinactivation profile, thus approaching the performance of RB despite being a food-grade natural derivative. In contrast, GA displayed limited efficacy under the tested conditions, with < 1 log reduction after 30 minutes, likely due to its weaker photosensitizing ability in the red region. These findings highlight chlorophyllin as a promising, safer, and more sustainable alternative to synthetic dyes like rose bengal for photodynamic control of Gram-positive bacteria in food-related applications. The comparable efficiency of Chi to RB under red light irradiation supports its potential integration into active packaging or surface decontamination strategies aimed at enhancing food safety.

Keywords:
Photodynamic inactivation, natural photosensitizers, gram positive bacteria.

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Poster Po12

Supramolecular prodrug delivery system based on 5-aminolevulinic acid cucurbit[7]uril complex with enhanced fluorescence detection and photodynamic therapy effect for breast cancer

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Cancer is one of the leading causes of death worldwide. Due to the significant side effects of current treatments, a promising alternative is photodynamic therapy (PDT). This non-invasive and selective treatment involves applying a photosensitizer (PS), followed by accumulation in the tumor and illumination at a specific wavelength. This process produces reactive oxygen species (ROS), which are responsible of cellular death. [1] The FDA-approved prodrug 5aminolevulinic acid (ALA) serves as a precursor to protoporphyrin IX (PpIX), a very efficient PS. Administering ALA induces PpIX generation intracellularly and its lipophilic derivatives such as ALA methyl ester (ALAm) and ALA hexyl ester (ALAh) are currently undergoing clinical trials. However, its instability in aqueous solutions at physiological pH can lead to decomposition which leads to reduced PpIX generation, limiting their therapeutic efficacy.[2] To address this issue, inclusion complexes between ALA and its derivatives with cucurbit[7]uril (CB[7]) were evaluated in this work. Binding to CB[7] cavity was determined by isothermal titration calorimetry and NMR. Decomposition kinetics of ALA and its derivatives in the presence and absence of CB[7] were studied via absorption spectroscopy. Additionally, 2D and 3D cell culture experiments in breast cancer MCF-7 cells were made to measure cell viability by MTS assay, and to evaluate PpIX generation by fluorescence microscopy, respectively. Additionaly in vivo experiments in CAM model from fertilized chicken eggs showed PpIX generation and accumulation in blood vessels in real-time.

Our results showed an increase in PpIX generation for the ALA@CB[7] and ALAh@CB[7] system, with a consequent increase in cellular death. On the other hand, the opposite effect is observed for the ALAm@CB[7] system. Overall, CB[7] effectively formed inclusion complexes with ALA and its derivatives, enhancing stability in aqueous media at physiological pH for all systems. This enhancement in stability and therapeutic efficacy highlight the potential of CB[7] inclusion complexes in improving PDT outcomes and show a great potential for future application of these compounds in cancer diagnosis.

Acknowledgements: We thank ANID-FONDECYT Regular grants 1251176 and 1241088.

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Supramolecular Modulation of Natural Photosensitizer Aloe Emodin *via* Acyclic Cucurbituril Complexation: Toward Enhanced PDT Performance

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Aloe emodin (AE) is a naturally occurring anthraquinone with diverse pharmacological activities, including antibacterial, anti-inflammatory, antioxidant, and antitumoral effects. Its ability to generate reactive oxygen species upon light irradiation has attracted recent interest for its potential application as a photosensitizer in photodynamic therapy[1]. Although only a limited number of studies have investigated this approach, AE has demonstrated the capacity to induce apoptosis[2] and inhibit tumor growth under blue light activation. Nonetheless, its clinical potential is limited by poor aqueous solubility and reduced photostability, which restricts its use in biological systems and environments involving prolonged light exposure. These limitations underscore the need for strategies to enhance its delivery and photodynamic performance. To improve its stability and modulate its photophysical properties, in this work, AE was encapsulated in the acyclic cucurbituril-type container M2C4. While free AE undergoes marked photodegradation under continuous irradiation, the AE@M2C4 complex exhibits significantly enhanced resistance to photodegradation. This complex was characterized using UV-Vis spectroscopy, fluorescence emission, and time-resolved fluorescence measurements. A 1:1 stoichiometry for the complex was proposed with a binding constant of 3.3×10^5 M^{-1}, as determined by fluorometric titration. Further insights into the structural nature of the inclusion complex were obtained through proton NMR studies.

Complex formation resulted in complete fluorescence quenching, likely due a photo-induced electron transfer from the container to AE. This keeps the photosensitizer in an OFF state. Additionally, controlled release of the photosensitizer was evaluated through competitive displacement using selective agents such as memantine-biotin conjugate[3] or spermidine. These findings, along with ongoing assays in biological systems, will be discussed.

Complex formation resulted in complete fluorescence quenching, likely due a photo-induced electron transfer from the container to AE. This keeps the photosensitizer in an OFF state. Additionally, controlled release of the photosensitizer was evaluated through competitive displacement using selective agents such as memantine-biotin conjugate[3] or spermidine. These findings, along with ongoing assays in biological systems, will be discussed.

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Development of quercetin capped TiO_2 nanoparticles (Que-TiO_2) for the photodegradation of ethylene in food applications.

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Ethylene gas plays a critical role in fruit ripening and senescence, accelerating spoilage during storage and distribution. In this study, we report the synthesis and characterization of quercetincapped titanium dioxide nanoparticles (Que-TiO_2) designed for the photodegradation of ethylene in food preservation systems. A green synthesis approach was employed, leveraging quercetin as both a reducing and capping agent to enhance TiO_2 surface functionality and photocatalytic activity under visible light. The nanoparticles were characterized by dynamic light scattering (DLS), UV-Vis spectroscopy, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and scanning electron microscopy (SEM), confirming nanoscale size, crystalline anatase phase, and successful surface functionalization with quercetin. The photocatalytic performance was evaluated in a model system for ethylene degradation under light irradiation, demonstrating enhanced efficiency compared to bare TiO_2. Application tests on ripe bananas showed a significant delay in ripening and quality loss, confirming the potential of Que-TiO_2 as an active component in smart packaging technologies. This work supports the development of natural antioxidant-modified nanomaterials for sustainable postharvest strategies, offering an effective approach to reduce food loss and extend shelf life.

Keywords:
Photoactive packaging, food preservation, photodynamic inactivation, tropical fruits.

Photoactive Alginate-Based Films Characterized by Confocal Laser Microscopy and Steady-State Fluorescence

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This study investigates alginate-based films functionalized with different natural and synthetic photosensitizers—rose bengal, riboflavin, curcumin, and quercetin—for potential applications in photoactive food packaging. The films were characterized using confocal laser scanning microscopy (CLSM) and steady-state fluorescence spectroscopy to evaluate their structural and optical properties. A Z-stack imaging approach was employed to assess the spatial distribution and homogeneity of the photosensitizers within the film matrix. Additionally, fluorescence recovery after photobleaching (FRAP) experiments were conducted using food simulants A (aqueous) and B (alcoholic) to estimate the diffusion behavior and mobility of the active compounds. Steady-state fluorescence and excitation spectra provided insight into the photophysical stability and excitation profiles of each compound embedded in the alginate matrix. The results revealed significant differences in distribution and diffusion depending on the nature of the photosensitizer, with rose bengal and curcumin showing deeper penetration and stronger fluorescence signals. These findings contribute to the rational design of photoactive packaging systems with controlled release and activation properties. The combined use of CLSM and fluorescence spectroscopy offers a powerful platform for elucidating the behavior of light-responsive compounds in biopolymer films intended for food preservation.

Keywords:
Photoactive packaging, food preservation, photodynamic inactivation, tropical fruits.

Photosensitized oxidation of free and peptide tryptophan to *N*formylkynurenine

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The oxidation of proteins and, in particular, of tryptophan (Trp) residues leads to chemical modifications that can affect structure and function and are related to a series of pathologies triggered by the electromagnetic radiation, such as photoallergy, skin cancer, photoaging, and cataract of the eye lens. UVA radiation (320–400 nm) and visible light can trigger photosensitized reactions.[1] Photosensitization of Trp is important for its reactivity and also because in its degradation generates photosensitizers. This is a case in which products of a photosensitized process can act as photosensitizers themselves, thus amplifying the harmful effects of radiation on biological systems. In this context, perhaps the most important product of the photosensitized oxidation of Trp is *N*-formylkynurenine (NFKyn), which is an efficient photosensitizer able to be excited with UVA radiation.

In this work we studied the photosensitized formation of NFKyn from Trp in different reaction systems.[2] We used two substrates: free Trp and a peptide of nine amino acid residues (S_3GWGS_3, according to the one-letter code for amino acids), Trp (W) being the only oxidizable residue. Two different photosensitizers were employed: Rose Bengal (RB) and pterin (Ptr). The former is intensively used as a type II photosensitizer [acts producing singlet oxygen ($^1O_2$)]. Ptr is the parent compound of oxidized or aromatic pterins and acts mainly through type I mechanisms (generation of radicals). Experimental data were collected in steady photolysis and the irradiated solutions were analyzed by chromatography (HPLC). The oxidation of Trp to NFKyn starts with the reaction of the amino acid with $^1O_2$ to yield an unstable hydroperoxide. If Trp is in a peptide chain, the conversion of this intermediate to NFKyn is fast. In contrast, if the substrate is free Trp, a cyclization, involving the amino group, takes place, leading to the formation of a more stable hydroperoxide (cTrp-OOH). In peptides this reaction is possible only when the Trp residue is the N-terminal amino acid. The intermediate cTrp-OOH undergoes thermal degradation through two competitive pathways: one yields a cyclized alcohol (cTrp-OH) and the other one yields NFKyn. This reaction scheme explains why, given a photosensitizer, the yield of conversion of Trp into NFKyn is lower for free Trp than for Trp residues in a peptide. The thermal degradation of cTrp-OOH is slow at 37 ºC, but is complete in 2 h at 65ºC.

The unstable intermediate cTrp-OOH can also be converted into NFKyn by photosensitization *via* type I mechanism. In Ptr-mediated photosensitization of Trp, cTrpOOH does not accumulate in the solution because is rapidly converted into NFKyn in a type I photooxidation. Therefore, this is a case in which two consecutive photosensitized reactions occur: the first *via* type II mechanism produces cTrp-OOH and the second one oxidizes this intermediate to NFKyn. This compound is the final product since it is thermally stable and it is not significantly oxidized, under the experimental conditions used, either by type I or type II photosensitized mechanisms.

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Comparison of the photoinactivation efficiency of chlorophyllin, gallic acid and rose bengal against *S. Aureus.*

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This study compares the photoinactivation efficiency of three photosensitizers—chlorophyllin (Chi), gallic acid (GA), and rose bengal (RB)—against Staphylococcus aureus under visible light irradiation. Aqueous suspensions of *S. aureus* (~10^6 CFU/mL) were treated with each compound at optimized concentrations and exposed to red light (λ ≈ 630–660 nm, 30 mW/cm²) for up to 30 minutes. Microbial survival was quantified by plate counting, and results were expressed as log reductions relative to dark controls. RB showed the highest antimicrobial activity,. Remarkably, Chi exhibited a similar photoinactivation profile, thus approaching the performance of RB despite being a food-grade natural derivative. In contrast, GA displayed limited efficacy under the tested conditions, with < 1 log reduction after 30 minutes, likely due to its weaker photosensitizing ability in the red region. These findings highlight chlorophyllin as a promising, safer, and more sustainable alternative to synthetic dyes like rose bengal for photodynamic control of Gram-positive bacteria in food-related applications. The comparable efficiency of Chi to RB under red light irradiation supports its potential integration into active packaging or surface decontamination strategies aimed at enhancing food safety.

Keywords:
Photodynamic inactivation, natural photosensitizers, gram positive bacteria.

Enhanced ROS Generation by Quercetin-Loaded Nanoemulsions

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This study evaluates the singlet oxygen ($^1O_2$) generation efficiency of quercetin-loaded nanoemulsions (Q-NEs) formulated with orange oil, compared to free quercetin (Q), under blue light irradiation. Nanoemulsions were prepared via high-energy emulsification and characterized for droplet size, stability, and loading efficiency. ^1O₂ production was assessed using two established probes: 1,3-diphenylisobenzofuran (DPBF) and furfuryl alcohol (FFA). Samples containing Q-NEs or free Q were irradiated with blue light ($\lambda \approx 450$ nm, 30 mW/cm²) for up to 30 minutes, and probe degradation was monitored spectrophotometrically. Q-NEs exhibited significantly faster DPBF bleaching and FFA oxidation than free Q, indicating enhanced singlet oxygen generation upon encapsulation. After 30 minutes of irradiation, QNEs reached markedly higher probe consumption levels, reflecting improved photodynamic efficiency. The superior performance is attributed to the increased solubility, reduced aggregation, and improved molecular dispersion of quercetin within the orange-oil nanoemulsion, which favor efficient interaction with molecular oxygen and energy transfer. These results highlight nanoemulsification as an effective strategy to enhance the photodynamic activity of hydrophobic natural photosensitizers like quercetin, with potential applications in antimicrobial photodynamic therapy and light-driven food preservation technologies.

Keywords:
Photodynamic inactivation, natural photosensitizers, nanoemulsions.

Impact of melanin on melanocyte response to blue light

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Sunlight is composed of ultraviolet (UV), visible, and infrared radiation, each exerting distinct biological effects on the skin [1]. While the harmful effects of UVA and UVB radiation are well documented [2], the effects of visible light—especially high-energy blue light (400–450 nm)—remain poorly understood. Melanin, produced by melanocytes during melanogenesis, is traditionally recognized for its photoprotective role against UV radiation by absorbing and dissipating energy before DNA damage occurs. However, recent studies indicate a paradoxical effect: although protective against UVB, melanin can act as a photosensitizer under visible light, generating reactive oxygen species (ROS) that cause oxidative damage and cellular apoptosis [3,4]. Understanding how melanin modulates the effects of blue light is critical, especially given the increasing prevalence of artificial blue light exposure [5].

In this study, we investigated the impact of blue light (410 nm, 8 J/cm², 5 mW/cm²) on SKMEL-28 melanocytes cells with and without induced melanogenesis. Melanin production was stimulated for 72 hours in DMEM medium supplemented with 0,5mM L-tyrosine and 10mM NH_4Cl, confirmed by morphological analysis and spectrophotometric quantification, which showed an approximately 60% increase in intracellular melanin. Cells were cultured in 96, 48, or 6-well plates, maintained with or without the melanogenic medium, and irradiated in PBS using a Biolambda device (410 nm, 8 J/cm², 5 mW/cm²). A control group was kept in the dark. Cell viability assessed by the MTT assay showed a significant reduction after blue light exposure in both conditions; however, the effect was markedly more pronounced in melanized cells. Irradiation alone decreased metabolic activity in non-induced cells, but the combination with melanogenesis led to the lowest viability, suggesting that melanin intensifies phototoxic damage rather than protecting against it. The clonogenic assay indicated that both melanin induction and blue light reduced the number of colonies formed after 7 days, and their combination almost completely abolished colony formation, demonstrating a severe additive effect. Cell migration assays also revealed delayed or inhibited wound closure 24 hours after irradiation, with melanized cells exhibiting the largest residual wound areas, reflecting impaired motility and survival. Plasma membrane integrity was evaluated using propidium iodide (PI), which penetrates cells with compromised membranes and fluoresces upon binding DNA. Following induction and irradiation, cells were stained with PI and Hoechst and analyzed by fluorescence microscopy. Quantification showed a significant increase in PI-positive cells upon blue light exposure, especially in the irradiated melanized group, which exhibited fluorescence approximately six times higher than the dark control. This suggests that melanin potentiates phototoxicity via ROS-mediated lipid peroxidation and membrane permeabilization. Together, these findings indicate that melanin, rather than providing protection, enhances the cytotoxic effects of blue light in SK-MEL-28 cells.

To further elucidate the underlying mechanisms, we will use the DCFH-DA assay to quantify reactive oxygen species generation. Subsequent steps will include analysis of lipofuscin

accumulation and DNA damage assessment by immunofluorescence, aiming to clarify cellular processes triggered by blue light exposure in the presence or absence of melanin.

Keywords: Melanin; Melanogenesis; Blue light; Phototoxicity; Reactive oxygen species.

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Supramolecular Stabilization of Parietin by a Bio-Inspired Polycation for Photodynamic Applications

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Parietin (PTN, 1,8-dihydroxy-3-methoxy-6-methylanthracene-9,10-dione), a lichenderived anthraquinone, has demonstrated significant potential as a photosensitizer (PS) for antimicrobial photodynamic therapy (aPDT).[1,2] However, its propensity to aggregate in aqueous media compromises its photodynamic efficiency. The objective is to enhance the aqueous solubility and stability of PTN while maintaining its photosensitizing functionality. To this end, this study explores the supramolecular association between PTN and a bio-inspired polycation, composed of each copolymeric unit of four molecules of vinylbenzyltrimethylammonium per vinylbenzylthymine one (P^{4+}).

UV-Vis absorption and fluorescence spectra analyses of 10 □M PTN in hydroalcoholic (5%) solutions at pH = 10-11, where the dianionic form is predominant,[3] revealed a bathochromic shift and bandwidth changes of the absorption band of PTN with increasing concentration of the copolymeric unit P^{4+}. The inflection point in the λ_{max} shift and the peak of bandwidth change occurred near 5 µM of P^{4+}, indicating that this concentration is required to fully electrostatic association of the dianionic PTN per P^{4+} unit in a 2:1 PTN:P^{4+} stoichiometry. The binding isotherm, constructed from steady-state fluorescence anisotropy as a function of P^{4+}concentration, was fitted with the Hill cooperative binding equation, yielding a dissociation constant K_d = 24 µM a Hill coefficient of n = 4, indicating a positively cooperative and multivalent binding process in the formation of the supramolecular adduct.

Preliminary cytotoxicity assays in Vero cells (kidney epithelial cells from *Cercopithecus aethiops*) showed that the PTN:P^{4+} does not induce toxicity under dark conditions, supporting its potential as a biocompatible carrier system. Moreover, by determining the minimum inhibitory concentration (MIC) in *Escherichia coli* under irradiation with three green LEDs (522 nm, 3 W, 30 min), complete photo-inhibition (100%) was observed at a PTN:P^{4+} ratio of 2.5:12.5 µM, compared to 90% relative growth in darkness. Neither PTN or P^{4+} alone showed activity at the same concentrations (pH = 10-11) under to experimental condition (darkness and irradiation), confirming the synergistic photodynamic effect of the complex.

These results suggest that the PTN:P^{4+} complex offers enhanced physicochemical properties and antimicrobial potential, supporting further photobiological evaluation for photodynamic applications.

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Characterization and photosensitizing properties of a supramolecular adduct formed between Rose Bengal and BSA crosslinked oligomers

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Many organic photosensitizers (PS) in a biological environment have been found to bind to macromolecules or cell membranes, depending on their chemical nature. In the case of Rose Bengal (RB), a typical xanthene PS, it has been shown to form 1:1 adducts with serum albumins.[1,2] In this case, the photophysical and photosensitizing properties of RB are modulated by the nanoenvironment of the binding site in the protein.[2] Conversely, under conditions of oxidative stress, proteins undergo chemical modifications, including crosslinking, resulting in the formation of covalently linked oligomeric species. In this context, we evaluated the potential use of supramolecular adducts of RB into soluble crosslinked bovine serum albumin oligomers $(BSA)_n$ as a novel biocompatible nanosized photosensitizer. The $(BSA)_n$ were obtained via the photosensitized oxidative quenching reaction of the excited state of Ru(II)-trisbipyridine cation by the persulfate anion. This process generates side-chain tyrosyl radicals, which leads to the formation of dityrosine interprotein links.[3] The characterization of the oligomeric species was performed by fast performance liquid chromatography (FPLC), SDS-PAGE, and dynamic light scattering (DLS). The binding of RB into the $(BSA)_n$ soluble oligomers of approximately 100 nm of diameter was confirmed through UV-Vis absorption and fluorescence spectroscopies. These analyses revealed the characteristic bathochromic shift of the dye's absorption and emission bands, indicating a less polar environment at the binding site. Additionally, the steady-state fluorescence anisotropy and emission quantum yield of RB in the adduct increased, indicating greater local rigidity upon supramolecular association. The RB:$(BSA)_n$ adduct in air-saturated buffer solution showed a reduced singlet oxygen quantum yield $\Phi_\Delta = 0.4$ but an enhanced photostability under greenlight irradiation (523 ± 20 nm) as compared with RB aqueous with $\Phi_\Delta = 0.8$ but almost with complete photobleaching due to dye self-quenching reactions. Therefore, it was concluded that the RB:$(BSA)_n$ adduct is a soluble supramolecular nanoparticle with remarkable photophysical properties. These properties include high photostability, an enlarged fluorescence quantum yield $\Phi_F = 0.23$, and a good Φ_Δ of 40%. These properties make it a promising candidate for use as a theranostic supramolecular system for cellular imaging and for anticancer or antimicrobial photodynamic therapies.

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Photosensitized oxidative crosslinking of bovine serum albumin and the impact on its esterase-like activity

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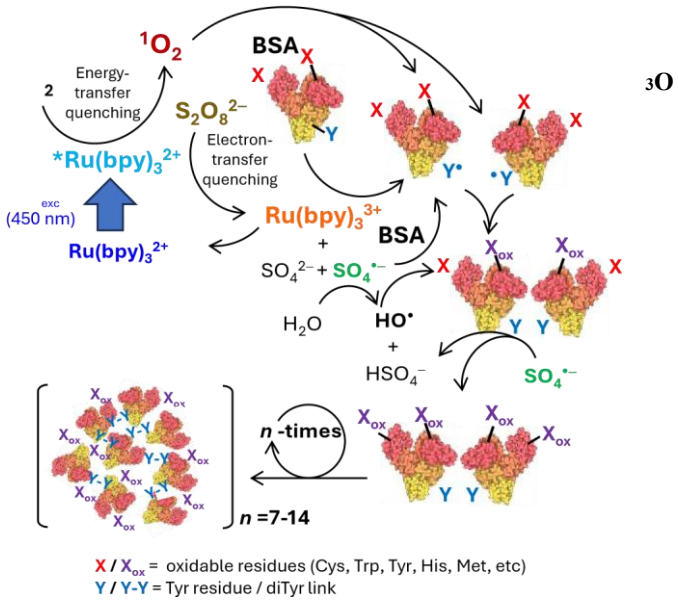
A photosensitized oxidative crosslinking of proteins (POCP) reaction was applied in airsaturated phosphate buffer solutions of bovine serum albumin (BSA) to obtain soluble protein nanoparticles of approximately 100 nm in diameter. A royal blue LED was used as the excitation source for the photosensitizer molecule ruthenium (II) tris(2,2'-bipyridyl) dication, $Ru(bpy)_3^{2+}$, in the presence of the electron acceptor persulfate anion, $S_2O_8^{2-}$. The redox quenching products prompted the formation of side-chain tyrosyl radicals, leading to the formation of dityrosine (Tyr_2), which served as a link in the covalent attachment between proteins. However, the dissolved oxygen competes efficiently with $S_2O_8^{2-}$ to quench the excited photosensitizer, thereby generating singlet molecular oxygen, $^1O_2$, which reacts with electron-rich protein residues, producing an additional oxidative pattern of BSA. Consequently, under air-saturated conditions, the POCP gives rise to a series of oxygen-dependent and independent reactions, resulting in the protein crosslinking with oxidative modifications. The esterase-like activity efficacy of BSA oxidized solely by $^1O_2$ and after the formation of oligomeric protein nanoparticles by POCP was reduced by 51% and 73%, respectively, as compared with that of the native BSA. The combination of the oxidative degradation of key residues in the active sites and steric impediment due to protein oligomerization was found to be associated with this result.



Photophysical characterization of alkyl-amino phenalenone derivatives in homogeneous/microheterogeneous media and their analysis as potential membrane probes

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In this study we investigated and characterized the photophysical behavior of three 9-alkyl amino phenalenone derivatives (6DMAFN, 6MOAFN and 6dodMAFN, see Fig.1) in both homogeneous (nine solvents of different polarities) and micro heterogeneous media (micelles and liposomes).

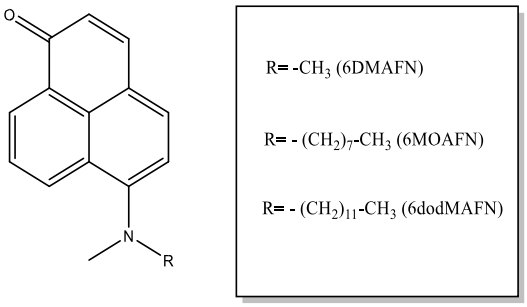

Fig.1 Chemical structure of the three phenalenone derivatives

The solvatochromic properties of all the derivatives were analyzed using Taft – Kamlet linear solvation free energy relationships (LSER). Despite of their push pull design, a blue shift in fluorescence spectra was observed in fluidized micro heterogeneous media for all derivatives. This contrasts with LAURDAN, PRODAN and CAPRYDAA (dyes with similar push pull structure) and most other push pull fluorophores which typically display a red shift under equivalent conditions.

For photophysical characterization absorption and fluorescence spectras were measured and their respective spectral phasors for the 9 solvents were calculated, showing a blue shift as the aliphatic chain's length increases. Singlet oxygen quantum yields were measured in acetonitrile and methanol, fluorescence quantum yields also were measured in water, acetonitrile, chloroform and hexane. The Stokes Shift dependence with the HLB of surfactants composing different micelles was also measured, showing a tendency to decrease the Stokes Shift for more hydrophilic micelles. Free energy of isotopic hydrogen bonds was measured for the three derivatives and LAURDAN, results showed that 6MOAFN was the most sensitive dye to changes in hydrogen bond strength. Finally, all the derivatives (and LAURDAN) were tested as membrane probes in DPPC/POPC liposomes. Fluorescence spectra was measured for different temperatures (from 20°C to 50°C) to fluidize liposome's membranes and then determine the lipidic transition temperature. Spectral phasors were also calculated for each temperature for all the derivatives (against LAURDAN) . Results showed that 6MOAFN again showed the most remarkable performance detecting transition temperatures for different proportions of DPPC/POPC liposomes. The phenalenone derivatives showed a blue shift in their fluorescence spectra for increasing fluidity in membranes, LAURDAN showed a red shift in their fluorescence spectra for increasing fluidity, this behavior discrepancy could be explained by the different location of the phenalenone's core in the bilayer due to it's polarity and geometry (oblate-like structure).

Synthesis and Evaluation of a Photostable Avobenzone Derivative as a UVA–UVB Photoprotective Ingredient for Sunscreen Formulation

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Ultraviolet (UV) radiation is a major public health concern due to its established role in skin photoaging and carcinogenesis. Butyl methoxydibenzoylmethane (BMDM), a widely used UVA filter, is limited by poor photostability. To address this limitation, we synthesized a structural derivative—Avobenzone 2-(9-bromononyl)—and assessed its UV-protective performance and potential use in sunscreen formulations. The derivative was obtained via nucleophilic substitution between BMDM and 1,9-dibromononane. UV absorbance and HPLC analyses were performed over 240 minutes of UV irradiation. Formulations incorporating the compound were prepared and evaluated *in vitro* following ISO 24443 guidelines. The derivative displayed maximum absorption at 262 nm, with lower initial absorbance compared to BMDM, but maintained its activity more consistently over time. HPLC results confirmed reduced photodegradation. Cosmetic formulations containing the derivative showed improved post-irradiation stability, although with lower photoprotective capacity than BMDM. In conclusion, Avobenzone 2-(9-bromononyl) emerges as a promising complementary UVB filter with enhanced photostability. While less potent than BMDM, its incorporation alongside broad-spectrum filters may enable the development of more stable and effective sunscreens.

Novel heteroleptic Cu(I)-Dipyridylamine/Diphosphine complexes as active materials in Light-Emitting Electrochemical Cells

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Increasing interest in functional materials for optoelectronic applications has driven the search for efficient and versatile luminophores. In this context, ionic transition metal complexes (iTMCs) have attracted cosiderable attention in devices like *light-emitting electrochemical cells* (LEECs). Among them, Cu(I) complexes stand out due to their relative abundance and low cost, representing an attractive alternative to the precious metals traditionally employed. However, the development of efficient and sustainable emitters based on copper (I) remains a challenge.

In this work, we report the synthesis and characterization of two novel heteroleptic copper(I) complexes of the type [Cu(*N,N*)(*P,P*)]BF_4, employing *N,N* ligands derived from dipyridylamine and Xantphos as the auxiliary *P,P* ligand (**C1–2**, Figure 1a). Structural characterization was performed using NMR and FT-IR, and for **C1**, via X-ray diffraction analysis. The photophysical and electrochemical properties were evaluated by UV–Vis spectroscopy, emission spectroscopy, cyclic voltammetry, and excited-state lifetime measurements. The complexes exhibited MLCT absorption bands between 300 and 330 nm (Figure 1b) and blue emission in solution at room temperature. In a glassy ethanol/methanol (4:1) matrix at 77 K, the emission showed slight spectral shifts (Figure 1c). Excited-state lifetimes were in the microsecond range. Furthermore, these complexes were used as the active emissive layer in LEEC devices with the configuration ITO/PEDOT:PSS/[Cu(dpa)(Xantphos)]BF_4/Al, exhibiting turn-on voltages of 13 V and maximum emission at 488 nm (Figure 1d).

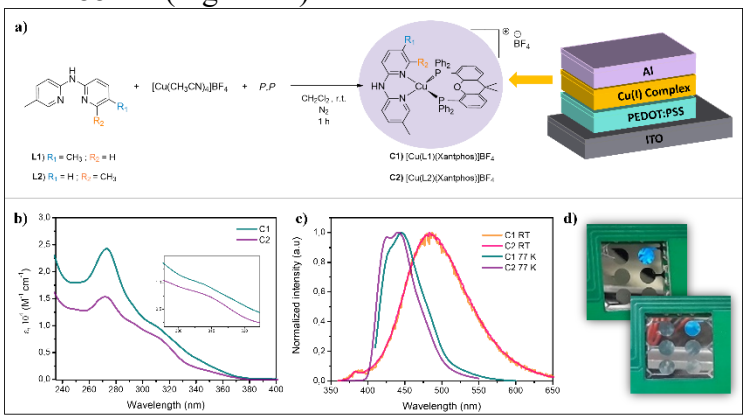

Figure 1. (a) Schematic representation of the synthesis of complexes **C1–2** and the device architectures. (b) Absorption spectra of the complexes in CH_2Cl_2. (c) Emission spectra at room temperature and 77 K in CH_2Cl_2. (d) Fabricated devices: **C1** (top) and **C2** (bottom).

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SYNTHESIS AND CHARACTERIZATION OF N-ETHYLPYRIDIN-1-IUM-2PYRIDONES AS SINGLET OXYGEN RELEASERS IN MIXED AQUEOUS/ACETONITRILE MEDIA

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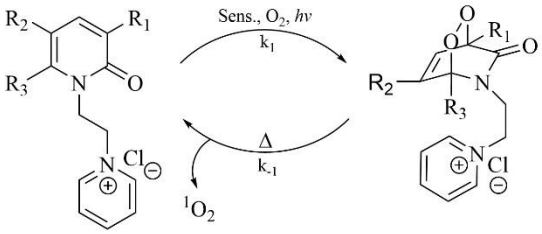
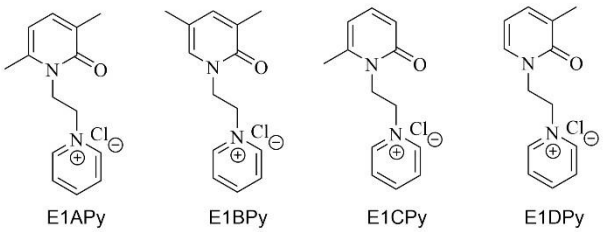
The objective of this study is to synthesize and characterize a series of 2-pyridone-derived endoperoxides. These compounds, based on 2-pyridone scaffold, have been investigated because of their ability to thermally release singlet oxygen (an electronically excited form of molecular oxygen), primarily for medicinal applications in light-independent photodynamic therapy. The ability of these endoperoxides to undergo thermal cycloreversion at relatively low temperatures, efficiently generating singlet oxygen while regenerating the parent 2-pyridone in high yield, positions them as promising candidates for optimizing singlet oxygen generation under dark conditions.

A series of 2-pyridone derivatives featuring various substitution patterns were synthesized, followed by N-alkylations with an ethylpyridinium group. The resulting compounds and their endoperoxides were purified, and spectroscopically characterized.



The rate constants of cycloreversion kk_{-1}, half life $tt_{1/2}$, the retro Diels-Alder % and the yield % of singlet oxygen released were determined by molecular absorption spectrophotometry (UV-Vis). The singlet oxygen yield (%), was determined using diphenylisobenzofuran (DPBF) a highly reactive specie that reacts with the generated singlet oxygen.

All synthesized compounds demonstrated the ability to trap singlet oxygen. Rose Bengal photooxygenation was fast and quantitative, being E1BPy the compound that exhibited the highest singlet oxygen trapping efficiency, whereas E1DPy was the least effective. The endoperoxides formed via sensitization were all capable of undergoing cycloreversion, thereby regenerating the pyridone moiety and releasing singlet oxygen. Notably, E1DPy was the most efficient thermal releaser, with a cycloreversion rate constant of $4.1 * 10^{-5}\ ss^{-1}$ at 30°C and a retro Diels Alder percentage of 72%. Experiments using DPBF confirmed singlet oxygen release from all compounds, with E1DPy inducing the most pronounced decrease in DPBF absorbance.



Degradation of topical ophthalmic drugs under simulated oxidative stress conditions

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In this study In light-exposed organs, reactive oxygen species (ROS) can be generated as byproducts of oxygen metabolism or through photosensitization processes involving natural pigments such as riboflavin. When endogenous antioxidant systems fail, ROS may accumulate excessively, leading to the well-known state of oxidative stress. This imbalance of oxidizing species promotes the development and progression of ocular pathologies such as glaucoma and may alter the therapeutic efficacy of topically administered drugs for its treatment.

In this work, the degradation of three antiglaucoma drugs: dorzolamide (DZ), ethoxzolamide (ET), and brimonidine tartrate (BT), was studied under simulated oxidative stress conditions, using riboflavin (Rf) and rose bengal (RB) as photosensitizers to generate ROS in vitro. Degradation kinetics mediated by singlet oxygen $O_2(^1\Delta g)$ and other ROS were analyzed, as well as the interactions between these drugs and the electronic excited states of Rf.

The results showed that all compounds were susceptible to chemical degradation in the presence of $O_2(^1\Delta g)$, with BT being the most vulnerable, followed by ET and DZ. Nevertheless, the main route of interaction with $O_2(^1\Delta g)$ was through a physical process. Additional oxygen consumption experiments using specific ROS scavengers confirmed the involvement of other ROS, such as superoxide anion, hydrogen peroxide and hydroxyl radical.

Interactions between the drugs and the electronically excited singlet state of Rf ($^1Rf^*$) were negligible compared to other deactivation processes, while quenching of the triplet state by the substrates was slightly competitive with its quenching by molecular oxygen.

Under direct UV irradiation at 266 nm, all three drugs showed the ability to generate $O_2(^1\Delta g)$ and were also capable of self-degradation. DZ degraded rapidly, whereas BT exhibited greater stability under these conditions. These findings provide valuable information on the photochemical stability of these drugs in situations of oxidative stress, as well as their potential impact on the efficacy of ophthalmic topic treatments.

Phenalenone-functionalized cationic polymers: a versatile platform

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The immobilization of photosensitizers within polymeric matrices offers significant advantages for applications in disinfection, catalysis, and photodynamic therapy. These systems can be tailored to enhance stability, biocompatibility, and responsiveness to external stimuli, while also enabling the controlled deployment or removal of the photosensitizer without compromising the surrounding medium. In this context, the incorporation of derivatives of 1*H*-phenalenone, a stable and highly efficient photosensitizer, into polymeric frameworks is of particular interest.

1*H*-phenalenone is notable for its singlet oxygen quantum yield (Φ_Δ) of unity across various solvents. A compelling derivative is 1-(1-oxo-1H-phenalen-2-yl)pyridinium chloride, commonly referred to as SAPYR. This compound retains a Φ_Δ of unity, exhibits a red-shifted absorption spectrum relative to phenalenone, and is water-soluble. Its cationic nature enhances its suitability for photodynamic bacterial inactivation, as it can disrupt microbial cell walls even in the absence of light. Upon irradiation, the singlet oxygen generated induces cell necrosis, effectively eliminating bacteria without promoting resistance.

This study reports the synthesis and characterization of photosensitizing polymers derived from the functionalization of poly(4-vinylpyridine) with a 2-methylphenalenone halide. Functionalization was investigated at two levels: 1 mol% and 10 mol% phenalenone relative to the polymer. Additionally, the polymer backbone was modified by quaternizing the remaining pyridine groups with 1-bromobutane. To further modulate system polarity, ion exchange was performed to replace bromide ions with tetrafluoroborate.

The resulting polymers exhibited absorption spectra comparable to SAPYR, enabling quantification of functionalization via UV-vis spectroscopy. Results indicated that increased functionalization correlated with reduced photostability. All polymers demonstrated high singlet oxygen generation capacity, with Φ_Δ values approaching 0.8, although slightly below unity. Alkylated and non-alkylated polymers showed similar Φ_Δ values, while ion-exchanged polymers (with tetrafluoroborate counterions) exhibited marginally lower Φ_Δ values.

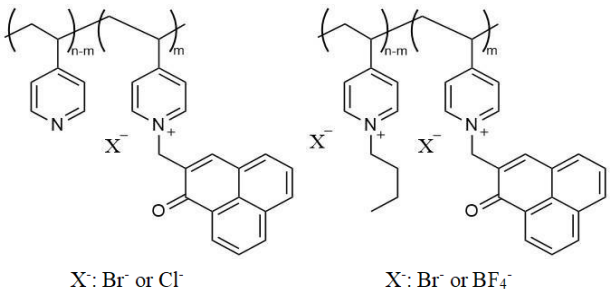

Figure 1. Chemical structures of the investigated systems.

DESIGN AND SYNTHESIS OF DICATIONIC STYRYL DYES FOR NUCLEIC ACID DETECTION ENHANCING BINDING THROUGH ELECTROSTATIC INTERACTIONS

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Fluorescent dyes derived from styryl structures represent a well-established family of compounds widely employed in the design of molecular probes for biomolecule detection, due to their high sensitivity to environmental changes, accessible synthesis, and the tunability their spectroscopic properties via strategic chemical modifications. Notably, their use in sensing, quantifying, and detecting nucleic acids has gained considerable importance, as they exhibit minimal background fluorescence in solution and markedly enhanced emission upon interaction with structures such as DNA and RNA.

In this study, we report the synthesis of four novel dicationic styryl derivatives bearing a Nmethylpyridinium ring (as the primary cationic moiety) and a 4-methoxyphenyl or N,Ndiethylaminophenyl group, linked via a trans-configured double bond to the 2 or 4 position of the pyridinium ring (see Figure). The diethylamino and methoxy substituents on the phenyl ring were introduced with to modulate the electronic and spectroscopic properties of the dyes. Additionally, the 4-methoxyphenyl and N,N-diethylaminophenyl cores carry alkyl chains with ether linkages, were included to impart a balanced hydrophilic/lipophilic character to each derivative. These chains include a quaternary ammonium group at the terminal position, which serves as the second cationic center.

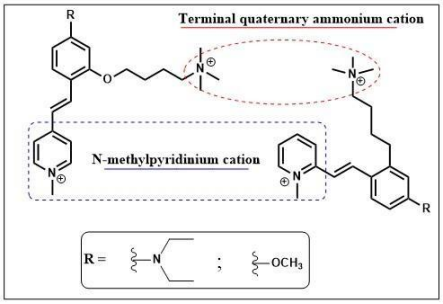

Figure 1: *Chemical structure of studied dicationic styryl derivatives.*

All compounds were synthesized via base-catalyzed Knoevenagel-type condensations, followed by quaternization with trimethylamine, resulting in a second positive charge. Yields ranged from 25% to 67%. The final products exhibit good water solubility and were designed to promote electrostatic interaction with nucleic acids. Spectroscopic characterization included UV-Vis absorption and fluorescence studies. Fluorescence measurements revealed a significant increase in emission intensity (at constant dye concentration) in the presence of single-stranded (ssDNA) and double-stranded (dsDNA) DNA, compared to nucleic acid-free solutions. This enhancement suggests that binding to nucleic acids restricts rotational degrees of freedom, thereby reducing non-radiative decay pathways and enhancing fluorescence.

UV-Vis spectra revealed a bathochromic shift when comparing aqueous media with less polar solvents, indicating sensitivity to the polarity of the surrounding environment. Compounds bearing diethylamino groups absorbed between 465–503 nm, whereas methoxy-substituted analogues absorbed at shorter wavelengths, ranging from 392 to 409 nm. These differences highlight how the nature of the substituent influences electronic delocalization. Furthermore, the observed shift is associated with changes in the fluorophore's environment rather than effects caused by direct binding to nucleic acids.

Development of an *in vitro* biological test to determine sun protection factor of commercial sunscreens.

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INTRODUCTION

Skin cancer incidence has increased worldwide during the last decades, mainly due to cultural changes and an increase in sunlight-derived ultraviolet (UV) surface irradiation. One of the most effective and recommended methods for preventing skin cancer development is the use of sunscreens during outdoor activities. These cosmetic products can effectively block UVB and UVA with varying potency, depending on their formulation. The potency to block UVB radiation is reflected in these products' Sun Protection Factor (SPF).

SPF is determined using an *in vivo* assay, in which human volunteers are exposed to increasing doses of radiation to determine the minimal dose capable of inducing erythema under two conditions: with and without sunscreen protection. The ratio between the two doses is considered the SPF of a given formulation.

OBJECTIVE

We aim to develop an *in vitro* biological test using human keratinocytes to reduce the number of human volunteers exposed to a carcinogenic stimulus such as UVB radiation.

METHODS

A keratinocyte cell line was plated on 96-well plates and exposed to increasing UVB doses (3.6 to 400 mJ/cm2) with and without commercial sunscreens. Two different products (SPF 40 and 15) were applied before exposure. Cells were incubated for 24 hours, and oxidative stress (DCF-DA) and viability (Alamar blue) were determined. A four-parameter sigmoidal curve was fitted for each dataset, and the relationship between lethal dose 50 (LD50) with and without sunscreen was calculated.

RESULTS

Most datasets fitted the sigmoidal curve for viability assays with an R^2 value greater than 0.95 (experiments with a lower fit were discarded). Control and protected curves presented the same maximum, minimum, and slope, allowing for the comparison of LD50 values. Sunscreens effectively increased the LD50 in protected cells; however, the calculated *in vitro* factor was variable and did not correlate with the labeled SPF.

For oxidative stress determination, curves also fit with an $R^2 > 0.95$, but did not show a maximum signal, resulting in incomplete curves. LD50 could not be calculated using the fourparameter sigmoidal curves.

CONCLUSIONS

The viability assessment for the in vitro SPF test needs to be improved to become a viable alternative to the gold standard human SPF assay. A more sensitive assay should be used for evaluating oxidative stress.

A comparison of more commercial products with a broader SPF range is guaranteed to develop this alternative in vitro biological SPF method.

Evaluation of postbiotics and a plant extract for skin active photoprotection: role of Lacticaseibacillus rhamnosus and Smilax campestris on UVB-induced keratinocyte damage

Ariadna CIROCCO REDIGO[1#], Sofía CONZÓN[1#], E. Taís AGUAYO FRÍAS[2,3], Andrea CANELLADA[2,3], Daniel GONZÁLEZ MAGLIO[2,3].

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[#]Both authors contributed equally to this work.

Recent INTRODUCTION. Skin exposure to sunlight promotes acute and chronic detrimental effects on human health. Molecular alterations that occur a few hours after exposure include DNA damage, inflammation, and the accumulation of reactive oxygen species. These molecular changes result in cell death within 18-24 hours. However, some affected cells may survive carrying DNA mutations and can establish skin cancer, which is promoted by UV-induced immunosuppression. To protect skin cells from these effects, several cosmetics have been developed, including filters that block UV radiation from sunlight through different molecular or atomic mechanisms. Over the last few years, the concept of active photoprotection has emerged, and the evaluation and use of plant extracts and enzymes aimed at acting as antioxidants and DNA repair mechanisms have expanded. On the other hand, biotic preparations (probiotics, postbiotics, and prebiotics) used in cosmetics are considered highly attractive but have not been employed in photoprotection, despite their immunomodulatory capabilities.
OBJECTIVES. We aim to evaluate the effectiveness of three preparations of the well-known immunomodulatory probiotic *Lacticaseibacillus rhamnosus (Lr)* and an extract of the antioxidant and anti-inflammatory Argentinean native plant *Smilax campestris (Sc)*.
METHODS. HaCaT cells (immortal human keratinocytes) were exposed to increasing doses of UVB radiation (0-400 mJ/cm2), incubated for 24 hours, and evaluated for viability using Alamar blue. The cells were treated with one of the following preparations: Lr heat-killed, Lr lysate, Lr culture supernatant, Sc aqueous extract (5, 0.5, and 0.05%). The treatments were applied before exposure (photoprotection scheme) or after irradiation (post-solar scheme).
RESULTS. *L. rhamnosus* supernatant presented a protective effect, decreasing cell viability loss when it was applied after irradiation. Heat-killed bacteria and lysate did not show protective effects, and they also increased cell death when used under the photoprotective scheme. On the other hand, *S. campestris* had a slight effect on both photoprotection and postsolar application, but only at lower concentrations.
CONCLUSIONS. The use of probiotic preparations in active photoprotection is not recommended; however, secreted molecules were effective in protecting keratinocytes from cell death after irradiation. The use of *Smilax* in skin photoprotection warrants further study, particularly in exploring the effects of low concentrations of the extracts. The study of the effects of both treatments on post-solar inflammation is guaranteed.

Evaluation of postbiotics and a plant extract for skin active photoprotection: role of Lacticaseibacillus rhamnosus and Smilax campestris on UVB-induced keratinocyte damage

Ariadna CIROCCO REDIGO[1#], Sofía CONZÓN[1#], E. Taís AGUAYO FRÍAS[2,3], Andrea CANELLADA[2,3], Daniel GONZÁLEZ MAGLIO[2,3].

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Novel Photosensitization and Photostability of DAN fluorescent probes

Analia Y.H. Cho[1], Germán Günther[1]

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6-acyl-2-(dimethylamino)naphthalene (DAN) derivatives were first disclosed as environment probes by Weber and Farris in 1979. This family of compounds present an excellent response to surrounding polarity by shifting the emission maxima to red or blue according to the polarity of the environment. LAURDAN, the best-known derivative of this family, is amply used to study membrane phase transitions by tracking its color change through fluorescence microscopy. When inserted into membrane in gel state LAURDAN emits at 440 nm whereas in membrane in disordered state it emits at 480 nm. However, one big drawback of LAURDAN is its rapid photobleaching which makes it usable only with two-photon microscopy techniques. Nevertheless, a detailed description of its degradation pathway is not available. Elucidating this mechanism could afford valuable information to avoid the rapid degradation of this compound and improve its application towards conventional one-photon microscopy techniques. Photobleaching of fluorescent probes is often believed to be triggered from the triplet state and subsequent production of ROS species that chemically inactivate the probe. Thus, we committed to study the photodegradation of DAN probes by characterizing their photoconsumption kinetics, photosensitizing ability and HPLC analysis. New synthetic analogues of DAN probes with restricted rotation were also characterized. These derivatives present a ring constriction at the carbonyl group which eliminates the possible vibrational relaxation pathway that DAN probes may suffer. Results indicate that DAN probes and their constricted analogues can generate singlet oxygen, and the extent is dependent on solvent. The highest quantum yield of singlet oxygen generation was observed in apolar solvents, reaching values near 40%. HPLC analysis indicates that several photoproducts are formed, identifying at least 4 intermediates with lower retention times than the parent probe. Photoconsumption experiments were carried out under oxygen and oxygen-free conditions. Results indicate that photodegradation of restricted analogues involves reaction with oxygen. However, in the case of DAN probes and contrary to common belief, photodegradation was independent of oxygen. In summary, this work provides valuable insights into the mechanistic pathways involved in the inactivation of DAN derivatives.

Photochemical properties of Rutin-loaded nanoemulsions

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Rutin, a natural flavonoid with strong antioxidant and photoprotective properties, suffers from poor aqueous solubility and limited stability, restricting its practical applications. In this study, we developed orange-oil–based nanoemulsions as carriers for rutin and evaluated their photochemical behavior compared to free rutin. The nanoemulsions were prepared using a spontaneous emulsification method, followed by rutin incorporation. Photophysical properties were analyzed through fluorescence spectroscopy, with excitation–emission matrices used to assess shifts in emission maxima (EEM) and changes in intensity. Quantum yield determinations further revealed how the nanoemulsion environment modulated rutin's excitedstate behavior. Results demonstrated that rutin-loaded nanoemulsions exhibited enhanced fluorescence intensity and a blue-shifted emission compared to free rutin in aqueous solution, indicating reduced aggregation and improved stabilization of the chromophore. Quantum yield was significantly higher in the nanoemulsion system, suggesting improved radiative deactivation pathways due to encapsulation. These findings highlight that orange-oil nanoemulsions can act as efficient delivery systems for rutin, enhancing its photochemical stability and optical performance. The study provides new insight into how natural oil-based nanocarriers can optimize the functional properties of flavonoids, paving the way for applications in nutraceuticals, cosmetics, and photoprotection.

Keywords: Nanoemulsions, quantum yield, rutin.

Photosensitizing Effect and Binding of Toluidine Blue on Human Serum Albumin

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Cancer is a chronic disease that represents one of the greatest challenges for medicine today. Photodynamic therapy (PDT) has emerged as a promising strategy in the treatment of this disease, combining the administration of photosensitizers (PS) and light irradiation to generate reactive oxygen species (ROS) that induce the selective death of cancer cells. HSA plays an important role in the distribution of drugs in the circulatory system, so it is crucial to investigate the interaction of photosensitizers with plasma proteins such as human serum albumin (HSA) to understand and improve the efficacy of PDT.

In this investigation, the fluorescent activity of toluidine blue (TBO^+) and derivatives, mono ($d\text{-}TBO^+$) and doubly demethylated ($dd\text{-}TBO^+$), and its association with HSA was explored by steady-state fluorescence in comparison with competing drugs, ibuprofen and warfarin, with PSs. Similarly, supramolecular encapsulation in curcubiturils was performed to evaluate the generation of singlet oxygen.

The results will describe the use of blockers to compare their association with HSA in monitoring tryptophan (Trp-214) corresponding to the binding site in subdomain IIA (Sudlow site I), a comparison of their PLQY and generation of singlet oxygen. The study provides a deeper understanding of the interaction between PSs and HSA in the context of PDT. These results contribute to the development of future research in therapeutic approaches.

PRELIMINARY RESULTS ON THE PHOTOSENSITIZED EFFECTS OF A TOLUIDINE BLUE DERIVATIVE ON SUPEROXIDE DISMUTASE AND CATALASE

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Cancer represents one of the major global health challenges and continues to be the subject of intense scientific research. In the search for more selective and less invasive therapies, photodynamic therapy (PDT) has emerged as a promising therapeutic alternative. This technique is based on the selective irradiation of a photosensitizer (PS), which generates reactive oxygen species (ROS)—particularly singlet oxygen ($^1O_2$)—that trigger specific cell death in tumor tissues. Toluidine Blue (TBO^+) has been widely studied as a PS; however, its efficiency is limited by parallel photooxidative reactions. Its photochemical transformation leads to the derivative dd-TBO^+, which has demonstrated a superior production of singlet oxygen, thereby enhancing the efficacy of PDT.

The use of drug transport vehicles, such as Cucurbit[n]urils (CB[n]), could improve PDT outcomes by forming inclusion complexes that modulate the photophysical and photochemical behavior of photosensitizers. In this study, the photosensitized effects of the inclusion complex between dd-TBO^+ and cucurbiturils (CB[n]) on two key antioxidant enzymes, catalase (CAT) and superoxide dismutase (SOD), were evaluated under photoactivated conditions. The ability of the dd-TBO@CB[n] complex to induce the degradation of both enzymes was confirmed through steady-state fluorescence, where intrinsic tryptophan (Trp) quenching was observed, and polyacrylamide gel electrophoresis, which revealed protein degradation. The results suggest that the supramolecular encapsulation of dd-TBO^+ within cucurbiturils retains its photosensitizing capacity, promoting enzyme photooxidation via ROS generation. These findings highlight the potential of dd-TBO^+@CB[n] complexes as promising systems for controlled PDT applications, encouraging further exploration in supramolecular photochemistry.

Photosulfoxidation of Toluidine Blue O Sensitized by Visible Light

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We report on the formation of toluidine blue O (TBO) sulfoxide by a self-sensitized photooxidation of TBO. Here, the photosulfoxidation process was studied by mass spectrometry (MS) and discussed in the context of photodemethylation processes which both contribute to TBO consumption over time. Analysis of solvent effects with D_2O, H_2O, and CH_3CN along with product yields and MS fragmentation patterns provided mechanistic insight into TBO sulfoxide's formation. The formation of TBO sulfoxide is minor and detectable up to 12% after irradiation of 3h. The photosulfoxidation process is dependent on oxygen wherein instead of a type II (singlet oxygen, $^1O_2$) reaction, a type I reaction involving TBO to reach the TBO sulfoxide is consistent with the results. Density functional theory results point to the formation of the TBO sulfoxide by the oxidation of TBO via transiently formed peroxyl radical or thiadioxirane intermediates. We discover that the TBO photosulfoxidation arises competitively with TBO photodemethylation with the latter leading to formaldehyde formation.

Toluidine blue O demethylated photoproducts as type II photosensitizers

Whitney Querini-Sanguillén[1‡], Jennifer Otero-González[1‡], Melanie García-Sánchez[1‡], Daniel Zúñiga-Núñez[2,3], German Günther[4], Mario L. Miranda[5,6], Edgardo Castro-Pérez[6,7,8], Carlos Ramos[8], Denis Fuentealba[3*], and José Robinson-Duggon[1,6*]

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Toluidine blue O (TBO) is a type I–type II photosensitizer that has shown good efficacy and selectivity in antimicrobial and anticancer photodynamic therapy applications. However, its complex photochemistry with multiple photoproducts hinders its application as a photosensitizer. We have previously described the mechanism for photooxidative demethylation of TBO which in acetonitrile yields two main products: demethylated- TBO (d- TBO) and double- demethylated- TBO (dd- TBO). In the current work, we describe the photophysical properties of these two photoproducts. In acetonitrile and phosphate buffer, demethylation induces an hypsochromic shift in the absorption and fluorescence emission maxima. Fluorescence quantum yields increase slightly for the demethylated photoproducts, in agreement with the lengthening of the fluorescence lifetimes. Triplet excited states lifetimes in the presence of oxygen decreased slightly upon demethylation. However, the singlet oxygen quantum yield increased significantly reaching unity for the dd- TBO photoproduct. These results are interpreted in terms of the competing pathways of TBO photochemistry. For TBO, demethylation is the main pathway for deactivation of the excited state, while for d- TBO, demethylation and singlet oxygen generation are significant. For dd- TBO, singlet oxygen generation is the main deactivation pathway. Overall, TBO demethylated photoproducts demonstrate good potential as candidates for photodynamic therapy applications.

Evaluation of the Thermal and Photochemical Stability of Fe_3O_4 Magnetic Nanoparticles Functionalized with Methotrexate

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Methotrexate (MTX) is an antineoplastic agent belonging to the pteridine family widely used in chemotherapy due to its ability to inhibit cell proliferation **[1]**, How ever, its therapeutic efficiency presents limitations due to its variable bioavailability (33–77%) **[2]** and high photosensitivity **[3]**, which compromise its clinical effectiveness and stability under different physiological conditions. For this reasons, there is a need to explore new strategies to enhance its performance in biomedical application. In this context, the present study proposes the anchoring of MTX to magnetite nanoparticles (Fe_3O_4) as a strategy to improve cellular uptake, increase chemical stability, and exploit its previously reported photoactive potential of free MTX **[4]**. To achive this, nanoparticles were synthesized via coprecipitation method and subsequently functionalized with MTX through three routes: (i) direct incorporation (Fe_3O_4@MTX), (ii) covalent anchoring using the silane agent APTES (Fe_3O_4@APTES@MTX), and (iii) covalent anchoring via citric acid (Fe_3O_4@CA@MTX). The resulting material were structurally and spectroscopically characterized using UV-Vis, infrared (FTIR), and fluorescence techniques, along with thermogravimetric analysis (TGA) and Z potential measurements to evaluate their composition and surface structure. Additionally, MTX release from the nanoparticles was assessed in aqueous medium, along with their stability under UVA irradiation. The results reveal that the anchoring method affects MTX loading efficiency, drug release profile, and photostability. Notably, Fe_3O_4@MTX nanoparticles incorporated a higher amount of MTX and exhibited a faster release rate compared to Fe_3O_4@APTES@MTX. Consistent with previous reports, free MTX was found to lack photostability under prolonged UVA exposure **[4,5]**. However, the MTX functionalized on the nanoparticles demonstrated improved resistance to photodegradation. Both Fe_3O_4@APTES@MTX and Fe_3O_4@MTX showed greater photostability than free MTX, with Fe_3O_4@MTX being the most stable under irradiation. Collectively, the MTX functionalization method on magnetite nanoparticles markedly influences lixiviation kinetics and photostability. This represents a promising strategy to enhance the therapeutic performance of MTX by enabling more controlled release and improved light stability. Such an approach could have important implications for the development of advanced drug delivery systems in oncological applications.

Acknowledgments
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Keywords: Methotrexate (MTX); magnetic nanoparticles; magnetite; thermal stability; photostability.

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Photostability study on red-emitting carbon dots by PARAFAC Analysis

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Carbon dots (CD) are quasi-spherical nanoparticles smaller than 10 nm. They possess high biocompatibility, low toxicity, low manufacturing costs, and other characteristics that have made them the subject of multiple studies and applications. One of these characteristics is their high fluorescence stability (Hai-Li et al., 2023).

In this study, multiemissive CD were synthesized. The different emissive components were separated by PARAFAC analysis. CD suspensions were irradiated with a UV lamp at a maximum wavelength of 367 nm and a full width at half maximum of 16.7 nm for several hours. Modifications in the fluorescence components of the irradiated nanoparticles were observed.

To elucidate the modification and degradation mechanism, irradiation was performed in the multiple components detected in the nanoparticles evidenced a degradation mechanism presence of N_2 to eliminate the presence of oxygen. The behavior and integration of these mediated by a photosensitization pathway.

Key words:
Photostability, carbon dots, Fluorescence

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Pterin–Thymine Adducts as Photosensitizers for Oxidative Damage

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Pterin (Ptr) is the model compound for pterins, heterocyclic aromatic compounds widely distributed in biological systems, known for its efficient photosensitizing properties. Elevated levels of pterins have been detected in the skin of patients with conditions such as vitiligo, making its interaction with biomolecules under UVA irradiation biologically relevant.[1] Under anaerobic and acidic conditions, Ptr reacts with the DNA nucleobase thymine (T) to form covalent photoadducts (T–Ptr). These adducts have been previously reported in free nucleosides, nucleotides, short oligonucleotides, and DNA strands.[2]

In this study, aqueous solutions of Ptr with 2'-deoxythymidine 5'-monophosphate (dTMP) or the oligonucleotide 5'-d(TTTTT)-3' (dT_5) were irradiated with UVA light (350 nm) to generate T–Ptr adducts, which were isolated via HPLC. Spectroscopic characterization confirmed that both adducts retain the absorption and fluorescence properties of free Ptr. Additionally, the dTMP–Ptr adduct was shown to form triplet excited states and to generate singlet oxygen with an efficiency comparable to that of free Ptr.

Furthermore, both dTMP–Ptr and dT_5–Ptr adducts photosensitized the oxidation of biologically relevant targets such as tryptophan and 2'-deoxyguanosine 5'-monophosphate in airequilibrated solutions, achieving efficiencies similar to that of free Ptr. The oxidation mechanisms involved may be of either type I (electron transfer) or type II (energy transfer to oxygen). These results are particularly significant as a photosensitizer bound to the target molecule may cause damage more effectively to the same biomolecule.

It is interesting to explore the potential applications of these adducts as site-specific fluorescent probes or photosensitizers for photodynamic therapy.

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Reactive oxygen production by a natural anthraquinone and its homodimer on *Candida tropicalis* biofilm

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Soranjidiol (SOR) and 5´5-bisoranjidiol (BISOR) are two natural anthraquinones with photosensitizing properties through the Type I (superoxide anion, $O_2^{\bullet-}$) and Type II (singlet molecular oxygen, $^1O_2$) mechanisms, with antibiofilm effect on *Candida tropicalis in vitro* when photostimulated.[1-3] The objective of this work was to establish the photodynamic mechanism mediated by reactive oxygen species.

Both anthraquinones (AQ) were isolated from the genus *Heterophyllaea* Hook f. (Rubiaceae) and identified by their UV spectra and co-chromatography against reference substances and their purity was determined by HPLC (> 93%). Minimum inhibitory concentration (MIC) was determined under light and dark conditions, following CLSI guidelines, against *C. tropicalis* NCPF 3111.[4] A dense biofilm was obtained from the *C. tropicalis* strain after 48 h of growth. The biofilm was exposed to 4 concentrations of each AQ: MIC, MICx2, MICx4 and MICx8; with 100 mM Tiron ($O_2^{\bullet-}$ scavenger) or sodium azide ($^1O_2$ quencher) under darkness and irradiated conditions of 30 min with an actinic lamp (Philips TL/03, λ = 420 nm). Biofilm quantification was performed using the Crystal Violet (CV) staining method and measuring the optical density (OD) at 595 nm.

The photoactive MIC (planktonic cultures) was 1.96 µg/mL for SOR and 0.98 µg/mL foa inforr BISOR, whereas in dark conditions, the MIC was 3.91 and 1.96 µg/mL, respectively. Under irradiation, the higher antibiofilm effect was achieved at 1.96 µg/mL for SOR, producing a 46% reduction (%R); which was completely reversed with Tiron and azide. However, at higher concentrations, its effect was not reversed by the quencher. BISOR produced 68.2% R in the biofilm at 1.96 µg/mL under light conditions; this effect was completely reversed in the presence of Tiron, while it remained unchanged with azide at all active concentrations. In conclusion, SOR primarily acts by a Type I mechanism ($O_2^{\bullet-}$), and at low concentrations also involves a Type II mechanism ($^1O_2$). In contrast, BISOR exerts its photosensitizing effect mainly via a Type I mechanism, being more active than its monomer.

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Light-Activated Antimicrobial Films: Structural and Optical Design of Curcumin–Chlorophyllin Alginate Composites

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The integration of photodynamic antimicrobial strategies into biodegradable packaging materials represents a promising approach to improve food safety while reducing environmental impact. In this study, we developed and characterized photoactive composite films based on sodium alginate reinforced with microcellulose and functionalized with curcumin and chlorophyllin—two natural photosensitizers capable of generating reactive oxygen species (ROS) under visible light. Five formulations (F1–F5) were prepared and systematically analyzed for their structural, mechanical, and optical properties. Atomic force microscopy revealed that films containing chlorophyllin exhibited increased roughness and stiffness, with F5 (highest chlorophyllin content) showing the greatest nanomechanical reinforcement. Confocal laser scanning microscopy confirmed a homogeneous distribution of microcellulose, though heterogeneity increased upon incorporation of the photosensitizers. FTIR spectra indicated no chemical interactions between alginate and the active compounds, while Raman spectroscopy showed distinct bands for chlorophyllin, confirming its presence and stability within the matrix. All films exhibited amorphous structures in X-ray diffraction patterns. UV–Vis analysis demonstrated successful light absorption by curcumin and chlorophyllin, and contact angle measurements indicated enhanced surface hydrophilicity in chlorophyllin-rich films. These results confirm the successful incorporation of natural photosensitizers into alginate–microcellulose matrices without compromising the polymer's structural integrity. The synergistic effect of curcumin and chlorophyllin broadens the light absorption range and enhances the potential for ROS production, positioning these films as strong candidates for next-generation photoactive food packaging systems.

Keywords: Photoactive packaging, food preservation, photodynamic inactivation, biodegradable films.

Gold Nanoparticle–Polyphenol Conjugates for Dual-Mode Antimicrobial Phototherapy

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In recent decades, there has been growing interest in the development of new systems and therapies for treating infections that have developed resistance to traditional antibiotics. Among these emerging treatments and materials are nanomaterial-based systems such as gold nanoparticles (AuNPs), which have demonstrated the ability to generate a photothermal effect when irradiated with near-infrared (NIR) light—an effect that can be harnessed for treatments of resistant bacteria. On the other hand, certain naturally derived molecules such as polyphenols, including, curcumin, rutin and quercetin, have shown potential as antimicrobial agents and photosensitizers. In this context, the combination of different materials and bioactive molecules has been proposed as a promising strategy for dual therapy approaches, where conventional antibiotics can be replace with antimicrobial inactivation coupled with methods like photothermal therapy. In this work, we present the study of the ROS generation properties and photothermal activity of three systems curcumin, rutin and quercetin conjugated with gold nanoparticles. Furthermore, we present fluorescence emission spectroscopy studies related to the interaction of the conjugated systems with bovine serum albumin (BSA). Results showed that the three systems are promising agents for dual therapy, as they can produce ROS species when irradiated with blue light, while gold nanoparticles are rapidly heated when irradiated with NIR light. On the other hand, results showed a strong interaction with BSA, which is promising for medical applications.

Keywords: Dual therapy, photoinactivation, polyphenols, nanoparticles.

Detecting different liposomal microenvironments using fluorosolvatochromic dyes

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Keywords: Fluorescence, quenching and microheterogeneous media.

Microheterogeneous systems in biological environments are characterized by the coexistence of multiple phases with varying polarities at the microscopic level, providing diverse microregions to elicit the incorporation of molecules with different lipophilicities. An open question in our research is how the incorporation of *n*-alkyl fragments added to a probe influences its partitioning in these milieux.[1] Previous studies have documented the hydrophobic effects induced by 4-alkanoyloxy-1,1,6,6-tetramethylpiperidinoxyl (TEMPO) radical derivatives in micellar systems and emulsions, revealing localization patterns that prompt a reinterpretation of the polar paradox in microheterogeneous environments.[2,3] In this study we use six fluorescent probes based on 2,4,6-triarylpyrimidine4 (TAP)-derived, functionalized with hydrocarbon chains ranging from 1 to 12 carbon atoms to investigate their localization and orientation in DSPC:Ch (55:45) liposome-based microstructured media. Fluorescence emission and Stern-Volmer constants (Ksv) were measured using TEMPO radical derivatives with chain lengths from 2 to 16 carbons.

Timeresolved fluorescence measurements further revealed the presence of multiple fluorophore populations distributed across the liposome structure, suggesting that radicals with different chain lengths selectively access distinctmicroenvironments.

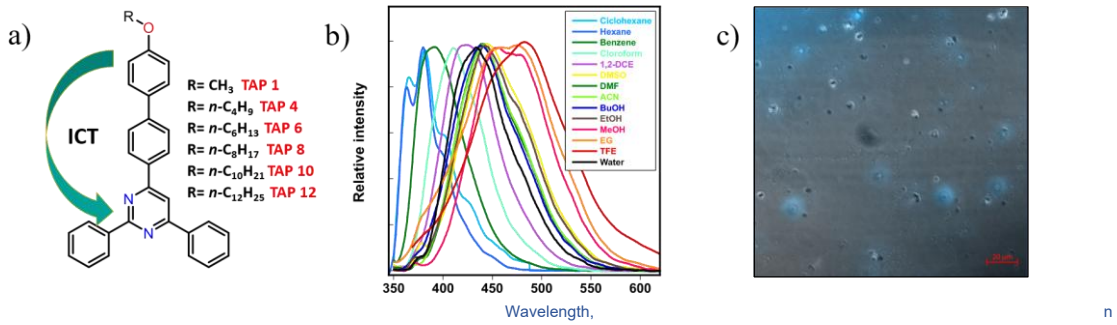

Figure 1. a) Structure of 2,4,6-triarypyrimidine (TAP) derivatives; **b)** Emission spectrum of TAP 6 in pure solvents; **c)** Fluorescence micrograph of TAP 6 probe fluorescence in DSPC:Ch (55:45) liposomes recorded by micrography image (λ exc. = 405 nm)**.**

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