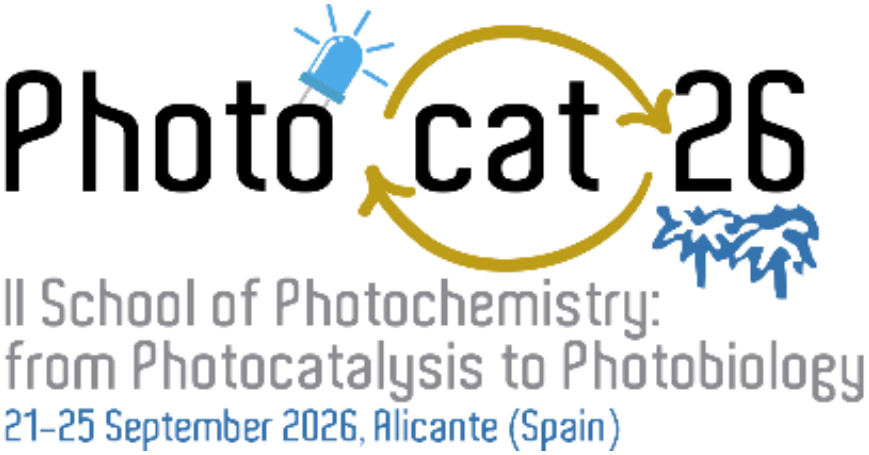
Photocat26

II International School of Photochemistry: from Photocatalysis to Photobiology

September 21st -25th 2026
Alicante (Spain)

BOOK OF ABSTRACTS



CONTENTS

1. INTRODUCTION

Photocat26: II International School of Photochemistry: from Photocatalysis to Photobiology

PHOTOCAT26 is the second edition of an international advanced training school aimed at PhD students, postdoctoral researchers, and early-career scientists working in sustainability-related fields such as photochemistry and biocatalysis, both in academic and industrial contexts.

Building on the success of the inaugural edition held in Padova, Italy, which gathered over 200 participants and featured 15 lectures by world-renowned scientists, PHOTOCAT26 continues to promote interaction between academia and industry by strengthening a European network for advanced training in sustainable chemistry. This biennial and itinerant series takes place at venues associated with the Scientific Committee members, fostering a pan-European perspective on sustainability in chemical research.

This edition, PHOTOCAT26, will be hosted in Alicante, Spain, and will further help bridge the gap between academic research and industrial applications by training a new generation of researchers in green chemistry, utilizing sustainable resources such as sunlight and biocatalysts. The international scope and biennial format of the event will support the sustainable growth of the regional chemical ecosystem, with significant impact at national and European levels. Additionally, the European network established through these editions will encourage collaborative projects and facilitate mobility for young researchers involved.

The Local Organizing Committee

2. COMMITTEES

2.1 SCIENTIFIC COMMITTEE

Irene Bosque
University of Alicante, Spain

Olalla Vázquez
Philipps University Marburg, Germany

Luca Dell'Amico
University of Padova, Italy

Bartholomäus Pieber
Institute of Science and Technology Austria (ISTA), Austria

2.2. LOCAL ORGANIZING COMMITTEE

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2.3. INTERNATIONAL ADVISORY BOARD

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3. CONFERENCE VENUE

3.1. Location: Aulario II – Universidad de Alicante

Carretera de San Vicente del Raspeig, s/n
03690 San Vicente del Raspeig, Alicante (ES)

3.2. About the University of Alicante (UA)

The **University of Alicante** is delighted to welcome you and to host this conference, which provides a valuable opportunity for dialogue, knowledge exchange and interaction among researchers, professionals and students.

Located in an open, dynamic and international Mediterranean environment, the University of Alicante is firmly committed to the generation and transfer of knowledge, excellence in education, research and innovation, as well as to its responsibility and commitment to society.

Although the University of Alicante is a relatively young institution in its modern form, its academic roots in the province of Alicante go back much further. Its historical predecessor can be traced to the **University of Orihuela**, whose origins date back to the 16th century. The project began in **1546**, received papal recognition in **1569**, began teaching in **1610**, and eventually closed in **1808**.

The direct origins of the present-day University of Alicante can be traced to the **University Studies Center (CEU)** in Alicante, inaugurated in **1968**. This institution laid the foundations for the future university and enabled the city to re-establish stable higher education. Later, during the **1975–76 academic year**, the University of Valencia established the faculties of **Arts and Humanities** and **Sciences** in Alicante, incorporating the CEU's existing departments as part of the transition towards university independence.

The official creation of the **University of Alicante** came with **Law 29/1979, of October 30**, which initially assigned it the faculties of **Sciences** and **Arts and Humanities**, together with the university schools of **Business Studies** and **Teacher Training for Basic General Education (EGB)**, which had previously been affiliated with the University of Valencia. The new university also incorporated new faculties, including **Medicine**, **Law**, and **Economics and Business Administration**, as well as the **University School of Nursing**.

The story of the University of Alicante is also closely connected to the unique place where the campus was built. The university was established on the site of a former **light-aircraft hangar**, giving the campus an unusual connection with the history of aviation and with the transformation of the surrounding landscape. One of the most distinctive reminders of this past is the **former control tower**, which has been preserved and still retains its original name. Today, the tower is one of the landmark buildings of the campus, standing as a visible reminder of the site's previous life.

The former hangar has also acquired a new role within the university. Rather than disappearing completely, it has been transformed into a **small green refuge within the campus**, providing a space where traces of the site's industrial and aviation past coexist with vegetation and the contemporary university environment. In this way, the campus itself tells part of the University's story: a place where the past has not simply been replaced, but incorporated into a new academic, scientific and social environment.

In **1985**, the University approved its **first Statutes**, consolidating its institutional identity and organizational structure. During the **1980s and 1990s**, the University experienced a period of rapid expansion, with the construction and opening of key facilities, including the faculties of **Law** and **Sciences**, the **University Hall of Residence**, the **Lecture Halls**, the **General Library**, the

Rectorate, and numerous new teaching and research facilities. In **1991**, the **Alicante Higher Polytechnic School**, which had previously been dependent on the Polytechnic University of Valencia, was incorporated into the University of Alicante, significantly strengthening its technical and engineering profile.

This history reflects an institution that has continuously evolved in response to the educational, scientific and social needs of its environment. From its historical academic roots to its development as a modern, international university, the University of Alicante has built a strong community dedicated to education, research, innovation and the transfer of knowledge. Its campus itself embodies this evolution, bringing together historical traces of its former identity with the spaces devoted today to teaching, research, collaboration and innovation.

Hosting this event at our University offers an excellent opportunity to share experiences, establish new collaborations and work together to address the scientific and societal challenges of our time. We hope that your stay in Alicante and on our campus will also contribute to creating academic and personal connections that will continue beyond the conference itself.

This welcome is particularly meaningful as it coincides with the celebration of the **50th anniversary of the Faculty of Sciences of the University of Alicante**. For five decades, the Faculty of Sciences has played a fundamental role in educating generations of professionals, promoting scientific research and contributing to the transfer of knowledge to society.

Celebrating fifty years of history also means recognising the commitment and dedication of all those who have contributed to building this academic community: faculty members, researchers, technical staff, students, and administrative and support staff. It is a celebration of half a century of science, education, innovation and social commitment, which has helped establish the Faculty of Sciences as a key centre for scientific knowledge within our University and its wider environment.

This anniversary is also an opportunity to look towards the future. The challenges facing science and society today require collaboration across disciplines, institutions and borders. Universities have a central role to play in generating knowledge, fostering critical thinking and preparing future generations to respond to these challenges. Conferences such as this one provide an important space in which these goals can become a reality through dialogue, cooperation and the exchange of ideas.

We hope that this conference will be a rewarding scientific and academic experience and that Alicante and the University of Alicante will provide an inspiring environment for discussion, collaboration and the generation of new ideas.

We warmly welcome you to the University of Alicante and wish you a successful and enjoyable conference.

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For further information about the University of Alicante, please visit:

https://www.ua.es/

3.3 About Alicante

There are cities that you visit, and there are cities that stay with you. **Alicante is both.**

Set between the Mediterranean Sea and the mountains, Alicante offers a unique combination of history, culture, gastronomy and an unmistakable Mediterranean way of life. Its spectacular coastline, mild climate and vibrant urban atmosphere make it a natural meeting point for people from all over the world.

At the heart of the city stands **Santa Bárbara Castle**, rising above Mount Benacantil and overlooking the bay. From its historic walls, Alicante reveals itself as a city shaped by centuries of encounters between cultures and civilizations. At street level, the historic quarter invites visitors to wander through narrow streets and colourful façades before reaching the iconic **Explanada de España**, where more than six million marble tiles create one of the city's most recognisable landscapes.

And then there is the sea. Alicante makes the Mediterranean remarkably accessible: from the city centre, the sandy shores of **Postiguet Beach** are just a few steps away. The waterfront becomes a natural extension of the city — a place to walk, meet, relax and enjoy the light that has made the Costa Blanca famous.

But Alicante is more than sun and beaches. It is a city with a strong cultural identity and a rich gastronomic tradition. Rice dishes, local products, tapas and traditional specialities are part of an everyday culture in which eating is also a way of sharing. Museums, archaeological heritage, festivals and contemporary cultural spaces add further dimensions to the city, making Alicante a destination where the past and the present continuously interact.

For conference participants, this combination creates a particularly attractive setting. Alicante is a city designed not only for **meeting and exchanging ideas**, but also for discovering, connecting and enjoying. A morning of scientific discussion can lead to an afternoon by the sea; a formal meeting can continue over a Mediterranean dinner; and a conference programme can become an opportunity to experience a city whose greatest asset is perhaps its ability to make people feel at home.

Alicante therefore offers more than a destination for a congress. **It offers a Mediterranean state of mind: open, welcoming, curious and connected.**

3.4. How to Get to UA

Alicante Turismo

Once you arrive at Alicante Airport or the Train Station, follow the signs to baggage claim/ground transportation.

From the Airport

There are primarily two ways to get from the Airport to the University of Alicante: Taxi or Bus and Tram (Rail).

- Taxi: You can get to the University of Alicante within 20 minutes by taxi; the cost is approximately 20 € (depending on traffic).
- Taxi Location & Information: Taxis will line up outside of both Arrivals and Departures. Radio Taxi Elche operates the official Alicante Airport taxis and can be identified by the green strip and coat of arms of Elche. Contact: +34 965 42 77 77. Operating hours: 09:00 to 01:00.
- Bus: There is a single bus stop for all lines at the second level (Departures) of the main terminal. Bus Line C6 runs from the Airport to downtown Alicante every 20 minutes (night service hourly from 00:00 to 05:00). It stops at Luceros and Mercado TRAM Stations, which connect to lines 1, 2, 3, and 4. Line 2 to *San Vicente* takes you directly to the University.

From the Train Station

- Taxi: Travel time is about 20 minutes to the University, at a cost of approx. 15€.
- Taxi Location & Information: Taxis wait outside the station. Company: *Radio Taxi Alicante*. Contact: +34 965 25 25 11.
- Public transport: Use Bus Line 24 or Tram Line 2.

4. GENERAL INFORMATION

Language
All lectures are in English. There will be no facilities for simultaneous translation.

4.1. Internet

The conference venue will have open-access wireless networks available for all conference participants.
Remember that the electric current in Spain is 220V and plugs are two-pin continental sizes.

4.2. Communication certificates

Attendance certificates, as well as certificates for oral and poster presentations, can be downloaded from the conference website (user area) once the congress has ended.

4.3. Advice to presenters

- ***Oral Presenters***

Duration

Plenary Lecture (PL): 60 min (50 min + 10 min Q&A)

Invited Lectures (IL): 30 min (25 min + 5 min Q&A)

Oral Communications (OC): 15 min (12 min + 3 min Q&A)

Information

- ✓ Presentations must be prepared in either **PowerPoint 2016/2019/2021/365**. Presenters are advised to use standard Office fonts and embed videos in the slides.
- ✓ Please bring your widescreen slides in either **PowerPoint or PDF** form on a flash drive well in advance and before your presentation day.
- ✓ There will be a chair in the room to introduce each presenter, moderate the Q&A for each talk and ensure you keep to the time.
- ✓ Please arrive at least **15 minutes earlier** to your session.

- ***Poster Presenters***

The poster format is: Size A0 Portrait (841mm wide × 1189 mm high)

Information

- ✓ Your poster board will be numbered by the **ID** of your contribution from the Conference Program.
- ✓ Poster(s) should be readable at a distance of at least 1 meter.
- ✓ Information on the day and time of your poster session is available in the Conference Program, but your poster will be displayed during the three days of the conference. Please make sure you attach your poster to the correct board.
- ✓ Materials to pin up your poster will be available.
- ✓ You will be expected to **print and bring** your poster with you to the conference. Printing will not be available at the conference.
- ✓ The poster should be place the first day of the conference (20th) and removed after Poster sesion 2 (Wednesday 23rd).

5. CONFERENCE OFFICE

The Conference Area will be located on the ground floor of the Aulario II building (conference venue). Outside the lecture theatre, in the central access area, the Conference Office will be permanently established next to the Hospitality Desk. Sponsors stands will be located on the 1st floor.

Meeting Room

17-20 Sept: RoomA2/E04
21 Sept (9-12 h): RoomA2/A21B
21 Sept (from 12 h): Room A2/E04
22 Sept: Room A2/E04
23 Sept (9-13 h): RoomA2/D01
23 Sept (from 14 h): Room A2/E04
24-25 Sept: Room A2/E04

From the Conference Office room:

- You may access the Club Social II building, where work lunches will take place.
- Make coffee breaks, although they could also be carried out on the 1st floor, depending on the availability.
- Access the 1st floor where the poster sessions will take place

6. SCIENTIFIC PROGRAM

6.1. Reduced Program

	Mon 21	Tue 22	Wed 23	Thu 24	Fri 25
9:30		9:30-10:30 PL3 Olga García Mancheño	9:30-10:30 PL6 Geraldine Masson	9:30-10:30 PL9 Marcos Suero	
10:00					10:00-11:00 PL12 Luke D. Lavis
10:30		10:30-11:30 OC 1-4	10:30-11:00 IL2 Johannes M. Wahl	10:30-11:30 OC 11-14	
11:00			11:00-11:30 OC 7-8		11:00 -12:00 PL13 Corey Stephenson
11:30		11:30-12:00 Coffee Break	11:30-12:00 Coffee Break	11:30-12:00 Coffee Break	
12:00		12:00-1:00 pm PL4 Grace Han	12:00-1:00 pm PL7 Mariola Tortosa	12:00-1:00 pm PL10 David Nicewicz	12:00 -12:30 Coffee Break
12:30					12:30-1 pm Sponsors
13:00		1:00-1:30 IL1 Leyre Marzo	1:00-1:30 IL3 Anastasios Polyzos	1:00-1:30 IL4 Marcio Weber Paixao	1 pm-1:30 pm Awards and final remarks
13:30		1:30 pm-3 pm Lunch	1:30 pm-3 pm Lunch	1:30 pm-3 pm Lunch	
14:00	2-3:30 pm Registration				Suggested: visit ERN stands at UA
14:30					
15:00		3 pm-4 pm PL5 Alexander Breder	3 pm-4 pm PL8 Ming Joo (MJ)Koh	3 pm-4 pm OC 15-18	
15:30	3:30-4 pm Op. Ceremony				
16:00	4 pm - 5 pm PL1 Thorsten Bach	4 pm-4:30 pm OC 5-6	4 pm-4:30 pm OC 9-10	4:00 pm-5:00 pm PL11 María Luisa Marín	
16:30		4:30 pm - 6 pm Coffee break + Poster session 1	4:30 pm - 6 pm Coffee break + Poster session 2		
17:00	5 pm -6 pm PL2 Henry Dube			4:45 -5 pm Coffee Break	
17:30					
18:00	6:30 pm - 8 pm Get-together cocktail	Guided activity: Beach Volleyball	Guided activity: Visit to Alicante city		
18:30					
19:00					
19:30					
20:00					
20:30				8:30 pm - 00:30 am Social dinner and party	
21:00					
21:30					
22:00					

6.2. Full program

Monday, 21/09/2026

Aulario II – Salón de Actos

14:00 – 15:30 Registration

15:30 – 16:00 Opening Ceremony

Chairperson: Irene Bosque

Wiley-sponsored session: Advanced Synthesis & Catalysis, Advanced Science, and Advanced Chemical Engineering

16:00 – 17:00 **PL1. Thorsten Bach** (TUM Munich, Germany)

17:00 – 18:00 **PL2. Henry Dube** (Friedrich Alexander University, Germany)

The Museum of the University of Alicante (MUA)

18:30-20:00 Get-together Cocktail

Tuesday, 22/09/2026

Aulario II – Salón de Actos

Chairperson: Alejandro Baeza

9:30 – 10:30 **PL3. Olga García Mancheño** (Rostock University, Germany)

10:30 – 10:45 **OC1. Vid Kermelj**.

Nickel-Catalyzed C(sp³)–H Arylation of *N,N*-Dialkyl Enaminones via Blue-Light-Driven Direct Hydrogen Atom Transfer.

10:45 – 11:00 **OC2. Chiara Antenucci**.

Synthesis of Amino-2,3-Dihydrofurans by Radical–Polar Crossover Visible-Light Photoredox Ring Expansion of α-Ketoaziridines.

11:00 – 11:15 **OC3. Kenta Tanaka**.

Redox-potential-controlled Thioxanthylium Organophotoredox Catalysis

11:15 – 11:30 **OC4. Francisco Juliá-Hernández**.

Earth-Abundant Metal Photodecarboxylation for Radical Fluoroalkylations

11:30 – 12:00 *Coffee break*

Chairperson: Bartholomäus Pieber

12:00 – 13:00 **PL4. Grace Han** (University of California, Santa Barbara, USA)

13:00 – 13:30 **IL1. Leyre Marzo** (Universidad Autónoma de Madrid UAM, Spain)

13:30 – 15:00 *Lunch (Club Social I)*

Chairperson: David Guijarro

15:00 – 16:00 **PL5. Alexander Breder** (Universität Regensburg, Germany)

16:00 – 16:15 **OC5. Valeska Viereckt.**

Triazole substitution turns cyanine dyes into viable probes for straightforward three-colour bacterial cell tracking.

16:15 – 16:30 **OC6. Sara Cuadros.**

Dual-role Iron Species in Photoelectrocatalytic Radical Trifluoromethylation with Trifluoroacetates.

16:30 – 18:00 *Coffee break* + **Poster Session 1** (**P1 – P45**)

18:00 – 20:30 Guided activity: Beach Volleyball or Walk by the Beach

Wednesday, 23/09/2026

Aulario II – Salón de Actos

Chairperson: Francisco Alonso

9:30 – 10:30 **PL6. Geraldine Masson** (CNRS Paris, France)

10:30 – 11:00 **IL2. Johannes M. Wahl** (Johannes Gutenberg-Universität Mainz, Germany)

11:00 – 11:15 **OC7. Mauro Mato Gómez.**

Learning from and Teaching Nature with Light.

11:15 – 11:30 **OC8. Nayan Saha.**

A de novo Approach to 3-Azabicyclo[3.1.1]heptanes via the Synergistic Combination of Odd-Alternant Photocatalysis and Orthogonal Lewis Acid Activation.

11:30 – 12:00 *Coffee break*

Chairperson: Albert Guijarro

12:00 – 13:00 **PL7. Mariola Tortosa** (Universidad Autónoma de Madrid, Spain)

13:00 – 13:30 **IL3. Anastasios Polyzos** (University of Melbourne, Australia)

13:30 – 15:00 *Lunch (Club Social I)*

Chairperson: Luca Dell'Amico

15:00 – 16:00 **PL8. Ming Joo (MJ)Koh** (National University of Singapore, Singapore)

16:00 – 16:15 **OC9. Manuel Plaza Martínez.**

New photochemical reactions for C(alkenyl)-S bond formation.

16:15 – 16:30 **OC10. Elena Cassera.**

Aldehydes as CO-releasing molecules: in-situ and ex-situ Giese reactions and palladium-catalyzed aminocarbonylations.

.

16:30 – 18:00 *Coffee break* + **Poster Session 2** (**P46 – P83**)

18:00 – 20:30 Guided activity: Visit to Alicante city

Thursday, 24/09/2026

Aulario II – Salón de Actos

Chairperson: Gabriela Guillena Townley

9:30 – 10:30 **PL9. Marcos G. Suero** (ICIQ Tarragona, Spain)

10:30 – 10:45 **OC11. Felicity Draper.**

Surpassing Photon Limits in Earth-Abundant Photoredox Catalysis.

10:45 – 11:00 **OC12. Fabio Juliá**.

Ferrioxalate Photocatalysis.

11:00 – 11:15 **OC13. Giulio Goti**.

Radical Approaches to Saturated Analogues of Aryl C−Glycosides.

11:15 – 11:30 **OC14. Aniket Kumar Srivastawa**.

Mechanophotochemistry: Lighting up EDA complexes in the Solid-State.

11:30 – 12:00 *Coffee break*

Chairperson: Isidro M. Pastor

12:00 – 13:00 **PL10. David Nicewicz** (Nanyang Technological University (NTU), Singapore).

13:00 – 13:30 **IL4. Marcio Weber Paixao** (Federal University of São Carlos, Brazil)

13:30 – 15:00 *Lunch (Club Social I)*

Chairperson: Olalla Vázquez

15:00 – 15:15 **OC15. Jorge García-Lacuna**.

Diasteroselective Radical hydroalkylatins of cyclopropenes enabled by EDA complexes.

15:15 – 15:30 **OC16. Ian MacKenzie.**

Predictive Control over Photocatalytic Properties in Improved Pyrylium Photocatalysts.

15:30 – 15:45 **OC17. Giuseppe Zuccarello**.

Enantioselective Hydrogen Atom Relay via Non-covalent Catalyst Assembly.

15:45 – 16:00 **OC18**. **Hugo Salazar.**

Atomic-level engineering of carbon nitride via heteroatom doping for solar-driven hydrogen peroxide production.

16:00 – 17:0 **PL11. María Luisa Marín** (Universitat Politècnica de València, Spain)

17:00 – 17:15 *Coffee break*

20:30 – 00:30 Social Dinner

Friday, 25/09/2026

Aulario II – Salón de Actos

Chairperson: Jose C. Gonzalez-Gomez

10:00 – 11:00 **PL12. Luke D. Lavis** (HHMI Janelia Research Campus, USA)

11:00 – 12:00 **PL13. Corey R. J. Stephenson** (University of British Columbia, Vancouver, Canada)

12:00 – 12:300 *Coffee break*

Chairperson: Irene Bosque

12:30 – 13:00 **Sponsors and Editors**

13:00 – 13:30 *Awards and final remarks*

13:30 – 14:30 Suggested activity: Visit 'European Research Night' stands at UA.

7. Plenary Lectures

PL1.

Catalytic Photochemical Deracemization Reactions

Thorsten Bach

(TUM Munich, Germany)

PL2.

Photoresponsive tools for constructing and steering synthetic and biological molecular machines

Henry Dube

(Friedrich Alexander University, Germany)

PL3.

Photocatalysis Unleashed: From (Hetero)cycle Construction to Molecular Fine-Tuning

Olga García Mancheño

(Rostock University, Germany)

PL4.

Photoswitches for energy storage and release: new molecular transformations and aromaticity control

Grace Han

(University of California, Santa Barbara, USA)

PL5.

The Principle of σ-Bond Quantum Poling

Alexander Breder

(Universität Regensburg, Germany)

PL6.

From Photocatalyst Design to Selective Synthetic Transformations

Geraldine Masson

(CNRS Paris, France)

PL7.

Shining light to prepare sp3-rich building blocks

Mariola Tortosa

(Universidad Autónoma de Madrid, Spain)

PL8.

Simplifying Synthesis through Photochemical Editing

Ming Joo (MJ)Koh

(National University of Singapore, Singapore)

PL9.

Catalytic carbyne transfer in organic synthesis

Marcos G. Suero

(ICIQ Tarragona, Spain)

PL10.

Photochemical-Driven Natural Product Synthesis

David Nicewicz

(Nanyang Technological University (NTU), Singapore).

PL11.

Supported Photocatalysts for Environmentally Relevant Photoredox Applications

María Luisa Marín
(Universitat Politècnica de València, Spain)

PL12.

Illuminating biological processes using chemistry

Luke Lavis
(HHMI Janelia Research Campus, USA)

PL13.

Photoredox Catalysis and the Rise of Programmable Radical Chemistry

Corey R. J. Stephenson
(University of British Columbia, Vancouver, Canada)

PL1: Catalytic Photochemical Deracemization Reactions

Thorsten Bach

Technical University of Munich, School of Natural Sciences, Germany

Photochemistry enables an access to reaction pathways that are not viable in conventional transformations. The talk will revolve around the conversion of a racemic mixture to a single enantiomer in a catalytic photochemical deracemization reaction. In an ideal scenario, quantitative yields of enantiomerically pure (>95:5 enantiomeric ratio) compounds can be achieved in a single operation.

The entropically disfavored and thermally impossible process is driven by light energy. The reactions are catalyzed by a single photocatalyst which either acts by energy transfer or by a reversible hydrogen atom transfer. Product classes which have been successfully deracemized by energy transfer include chiral allenes, olefins and cyclopropanes. A reversible hydrogen atom transfer was found to facilitate the deracemization of hydantoins, 3-oxindoles, N-carboxyanhydrides, 2,5-diketopiperazines, aza-1-isoindolinones and chromanes. Possible applications, the underlying mechanistic considerations, and ongoing work on the topic will be presented.

PL2: Photoresponsive tools for constructing and steering synthetic and biological molecular machines

Henry Dube

FAU Erlangen-Nürnberg, Department of Chemistry and Pharmacy. Germany

In this talk a central question of nanotechnolgoy will be addressed: How can one miniaturize mechanical processes and how can related molecular processes in biology be controlled from the outside? To this end, conceptual ideas spanning synthetic organic and photochemistry as well as chemical biology will be explored while rediscovering the colorful chemistry of the late 19th and early 20th century. The journey will lead us from molecular photoswitches to synthetic molecular machine building to photopharmacology. Applicability in synergistic polymeric and smart display materials as well as for regulation of kinases and the proteasome will showcase the unique capabilities instilled by commanding molecular-resolved light-matter interactions.

PL3: Photocatalysis Unleashed: From (Hetero)cycle Construction to Molecular Fine-Tuning

Olga García Mancheño

Leibniz Institut for Catalysis, Rostock University, Germany

In recent years, visible-light mediated photocatalysis has emerged as a powerful synthetic tool for the construction and modification of organic molecules in a simple, selective and more sustainable manner.[1] Moreover, it allows for unlocking new reactivities by moving from classical polar chemistry to radical processes. However, the in-sequence combination of both types of chemistries provides the potential to design and perform even more elaborated transformations, for which polar-radical and radical-polar crossover reactions are gaining increasing attention.[2]

Another important direction in modern photocatalysis relies on the design of novel photosensitizers aiming at accessing uncovered chemical space and reactivities. In this regard, the acridinium-based photoredox catalysts have attracted a vast interest, especially due to their great structural variety combined with their easy fine-tuning, providing new possibilities for the generation of reactive intermediates.[3]

In this lecture, our recent advancements in the use of radical-polar crossover strategies for the construction of (hetero)cycles either by formal cyclization or ring-opening/expansion reactions will be presented.[4] Complementarily, site selective benzylic and late-stage functionalization with acridinium-based organic photocatalysts,[5] as well as direct hydrogen atom transfer (d-HAT) catalysts based on un precedented N-centered amidyl radicals from zwitterionic amidate-acridinium species capable of alkane C-H bond functionalization[6] will be covered.

References

[1] a) Narayanam, J. M. R.; Stephenson, C. R. J. Chem. Soc. Rev. 2011, 40, 102; b) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. Chem. Rev. 2013, 113, 5322; c) Pitre, S. P.; Overman, L. E. Chem. Rev. 2022, 122, 1717.

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PL4: Photoswitches for energy storage and release: new molecular transformations and aromaticity control

Grace Han

University of California, Santa Barbara, USA

Molecular solar thermal (MOST) energy storage relies on molecular photoswitches that isomerize to a metastable state, storing chemical energy in strained bonds. This energy is later released as heat upon triggering, as the molecule returns to its original, lower energy isomer. Our research focuses on designing new photoswitch structures that efficiently absorb light, store large quantities of energy in the metastable state, retain that energy over long timescales from days to years, and release it efficiently on demand. One of our recent discoveries shows that light-induced dearomatization is an effective strategy for enhancing energy storage density, with molecules now exceeding 1.6 MJ/kg, surpassing the specific energy of Li-ion batteries. Notably, our latest compounds release enough heat upon triggering (i.e., catalysis) to boil water, demonstrating the practical magnitude of the stored energy. In this talk, I will describe how these molecular transformations occur and how structural modifications can be used to tune the optical, thermal, and physical properties of these systems.

PL5: The Principle of σ-Bond Quantum Poling

Alexander Breder

University of Regensburg, Germany

The unimolecular fission of covalent σ-bonds constitutes an integral elementary step in countless chemical transformations, including SN1-, E1-, and intramolecular rearrangement reactions. The decisive factors governing the equal or unequal electron redistribution during the cleavage of σ-bonds, that is, homolytic vs. heterolytic bond cleavage, are the electronic state from which a given substrate is about to fragment and the nature of the medium in which the bond fission is taking place.[1,2] Regarding the unimolecular heterolysis, this circumstance has a decisive influence on whether a given bond constitution is even amenable to ionic fission. More concretely, if a σ-bond consists of two identical constituents, that is, a symmetric σ-bond, its unimolecular fission from its ground or chemically most relevant excited states, that is, S1 and T1 according to Kasha's rule, can only occur homolytically, irrespective of whether the bond activation occurred thermally or photochemically.[3]

This fundamental mechanistic constraint has taken symmetric σ-bonds categorically out of the focus of method-oriented investigations centering on unimolecular heterolysis. Yet, at the same time, this state of affairs offers an invaluable opportunity for the development of bond activation principles that are entirely complementary to conventional protocols. One such auspicious example is the quantum poling of symmetric and homopolar σ-bonds.[4] Concretely, this activation principle includes the initial thermal homolysis of a given bond, furnishing a quantum-entangled radical pair – i.e., a geminate pair of spin-correlated doublets with global singlet multiplicity. Photoexcitation of one of the pair members results in a stimulated doublet-doublet electron transfer (SDET), giving access even to constitutionally identical ion pairs. As will be detailed, the quantum poling of symmetric/homopolar σ-bonds has far-reaching implications for chemical synthesis, catalysis, and related disciplines.

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PL6: From Photocatalyst Design to Selective Synthetic Transformations

Geraldine Masson

Institut de Chimie des Substances Naturelles (ICSN), CNRS UPR 2301, Université Paris-Saclay, France

Visible-light photoredox catalysis provides powerful opportunities for redox transformations under mild conditions;[1] however, improving the efficiency and sustainability of photocatalytic processes remains an important challenge.[1b] With these objectives in mind, I will present our work on Ru-based photocatalysts immobilized on functionalized detonation nanodiamonds as efficient and recyclable heterogeneous systems,[2a] followed by the development of metal-free molecular heptazines for challenging oxidative transformations.[2b,c]

Beyond photocatalyst design, new synthetic approaches based on light activation will be presented, including a photocatalyst-free decarboxylative borylation providing access to aminoboron derivatives.[3] The challenge of stereocontrol will be illustrated by stereoselective Truce–Smiles rearrangements, in which readily available chiral auxiliaries enable selective aryl migration.[4]

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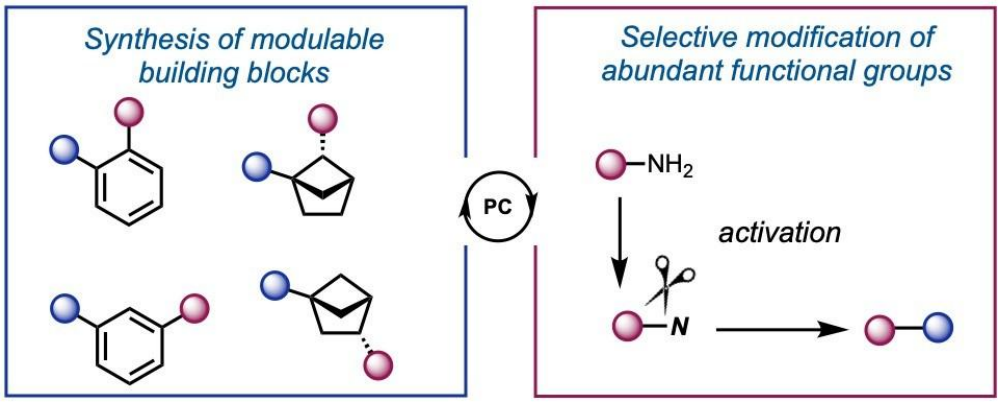
PL7: Shining light to prepare sp3-rich building blocks

Mariola Tortosa

Universidad Autonoma de Madrid, Spain

Photocatalysis is at the core of modern synthetic chemistry and has become increasingly important for the pharmaceutical industry. As the pharmaceutical industry is shifting from compounds with a strong sp2 character to libraries of compounds with enlarged three-dimensionality, the need to develop photocatalytic methods to provide compounds with an increased sp3 character becomes apparent. In our group, we have recently focused on the development of catalytic transformations for the preparation of sp3-rich building blocks, providing tools for the synthesis of benzene bioisosteres and selective carbon-nitrogen bond cleavage. These methods have allowed us to prepare a broad variety of useful synthetic intermediates, with special emphasis on the synthesis of functionalized strained-rings.[1] Some of these transformations will be presented in this talk.



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PL8: Simplifying Synthesis through Photochemical Editing

Ming Joo Koh

National University of Singapore. Singapore

The vast majority of physiologically active molecules contain at least a heterocycle within their skeletons, and the structure of the ring typically dictates its function. On the other hand, approximately one-fifth of all natural products are glycosylated, and the carbohydrates associated with these compounds are often essential for their biological activity. Despite past advances made in the field, the conventional synthetic logic of sugars and heterocycles still relies on extensive functional group interconversions, redox manipulations and protecting group chemistry, leading to problems such as lengthy synthetic routes, limited scope and excessive waste generation. Therefore, there is compelling demand to devise new synthetic approaches that address these challenges. In this talk, we will describe our recent efforts in the development of photochemical peripheral and skeletal editing strategies to streamline access to biologically important glycosides and heterocyclic pharmacophores.

PL9: Catalytic carbyne transfer in organic synthesis

Marcos García Suero

Institute of Chemical Research of Catalonia (ICIQ), Spain

The art of organic synthesis and reaction discovery relies on logic-guided thought processes that often involve hypovalent carbon reactive species and their corresponding stabilized equivalent forms. However, not all of the possible carbon reactive intermediates and their reactivity rules have attracted the same attention by the synthetic community. This is mainly because of the perception of the lack of synthetic utility and importantly, because of the challenges associated with controlling its extreme reactivity and lack of efficient sources. In this presentation, I will show how the catalytic generation of conceptually-novel carbyne equivalents, enabled the discovery of new carbon reactivity towards C–H and C–C bonds. The photocatalytic or metal activation of tailored sources revealed new reactivity rules at carbon that have been under-appreciated, not only in the design and discovery of new chemical reactions, but also in their use to build molecular complexity through unexplored disconnection approaches via skeletal editing and late-stage functionalizations of complex molecular architectures.

PL10: Photochemical-Driven Natural Product Synthesis

David Nicewicz

Nanyang Technological University (NTU), Singapore

Photochemical methods have emerged as versatile platforms for rapid molecular assembly and structural diversification, with recent advances in photoredox catalysis greatly expanding the synthetic repertoire available to chemists.[1,2] Herein, we present a photochemically driven strategy for natural product synthesis that exploits radical reactivity to access architecturally complex frameworks. Through an iterative sequence enabled by visible-light activation, we achieved the synthesis of three stemoamide alkaloids in the shortest routes reported to date, combining mild reaction conditions with operational simplicity and novel bond-forming tactics.[3] Central to this approach is the dual oxidative and reductive manifold of an acridinium photoredox catalyst, which mediates a polar radical crossover cycloaddition to construct a densely substituted tetrahydrofuran motif. The resulting butyrolactone intermediate subsequently undergoes a second radical polar crossover cyclization, furnishing a distinctive oxaspirocyclic butenolide scaffold. A late-stage heteroarene transmutation then provides a common intermediate from which the three target alkaloids are accessed. These concise syntheses underscore the synthetic potential of iterative photochemical transformations, illustrating how unconventional retrosynthetic logic can enable efficient access to complex natural products while highlighting an emerging paradigm in synthetic design.

This work was supported by a grant from the U.S. National Institute of General Medical Sciences (R35 GM136330)

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PL11: Supported Photocatalysts for Environmentally Relevant Photoredox Applications

Maria Luisa Marin

Instituto de Tecnologia Quimica (ITQ, CSIC-UPV), Valencia, Spain

Antimicrobial resistance is a major global health threat, underscoring the need for alternative disinfection strategies. In this context, antimicrobial photodynamic inactivation represents a promising approach for controlling pathogenic microorganisms. Moreover, water contamination, including microplastics and recalcitrant organic compounds, is also a critical concern. Meanwhile, the transition towards sustainable energy requires efficient green hydrogen production.

This work presents a portfolio of supported photocatalytic platforms designed to address these interconnected challenges. Hybrid photocatalytic materials based on Rose Bengal-functionalized supports, including glass wool and polyamide fabrics, subsequently decorated with cationic chains, exhibit synergistic antimicrobial effects. These systems efficiently inactivate Gram-positive and Gram-negative bacteria, as well as viruses such as adenovirus rAd5. Detailed photophysical studies revealed that, in addition to the well-established Type II photosensitization mechanism, electron-transfer processes contribute substantially to the antimicrobial activity of Rose Bengal.[1] Advanced TiO2-based materials supported on glass wool and incorporating SiO_2@TiO_2 core@shell structures also show outstanding performance, achieving rapid and complete mineralization of pollutants under continuous-flow conditions without catalyst leaching. These results demonstrate their strong industrial potential for wastewater treatment.[2] The same platforms enable photocatalytic wastewater photoreforming for H_2 production, particularly after decoration with Pd nanoparticles.[3]

Overall, the integration of inorganic and organic photocatalysts into robust, reusable, and scalable platforms demonstrates the potential of photocatalysis to contribute simultaneously to public health protection, sustainable water treatment, the clean-energy transition, and the circular economy.

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PL12: Illuminating biological processes using chemistry

Luke Lavis

Janelia Research Campus, HHMI, Virginia, USA

Fluorescence microscopy has transformed our understanding of cellular processes, but progress is limited by the brightness and photostability of available fluorescent labels. Over the past 15+ years, our laboratory has developed a comprehensive synthetic toolkit that fundamentally changed how small-molecule fluorophores are designed and accessed by the scientific community. Our key breakthrough was the discovery that incorporation of four-membered azetidine rings into fluorophores dramatically enhances both quantum efficiency and photostability.[1] Building on this foundation, we developed the Janelia Fluor® (JF) platform, creating an optimized palette of dyes that spans the visible spectrum with exceptional brightness and photostability.[2] We also elucidated key structure–activity relationships that enable rational design of fluorogenic and bioavailable dyes. These advances enabled us to pioneer chemigenetic indicators—hybrid small-molecule:protein sensors that combine the brightness of chemical dyes with the genetic specificity of fluorescent proteins—as well as develop deuterated rhodamines for enhanced photostability, spontaneously blinking fluorophores for super-resolution microscopy, and bespoke dyes tailored for specific biological applications. Recognizing that scientific tools only matter if scientists can access them, we established Open Chemistry—a unique initiative that has distributed aliquots of fluorescent dyes to thousands of scientists in 40 countries, representing over $250,000,000 in value to the community. This open approach has democratized access to cutting-edge fluorophores and accelerated discoveries across biology and medicine. Our portfolio of enhanced fluorophores now enables advanced microscopy experiments from single-molecule tracking in individual cells to population-scale voltage imaging in vivo, allowing scientists to fully harness the power of imaging in biological research.

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PL13: Photoredox Catalysis and the Rise of Programmable Radical Chemistry

Corey Stephenson

University of British Columbia, Vancouver, Canada.

Visible-light photoredox catalysis has transformed the way synthetic chemists generate and control reactive open-shell intermediates. More than simply providing mild access to free radicals, photocatalysis offers a means to couple photon absorption with selective single-electron transfer, allowing radical intermediates to be generated from otherwise stable precursors under precisely defined conditions. This ability to control when, where, and from what precursor a radical is formed has helped move radical chemistry from a collection of highly useful but often specialized transformations toward a broadly programmable strategy for reaction design.

This lecture will describe our efforts to develop that concept, from the design and mechanistic interrogation of photocatalytic radical reactions to their application in increasingly complex molecular settings. Particular emphasis will be placed on how understanding the elementary steps that govern radical generation, reactivity, and selectivity can be used to uncover new modes of bond construction and to expand the range of chemical space accessible using visible light.

I will also describe our recent development of an ultra-high-throughput platform for conducting photocatalytic reactions in nanoliter-scale droplets. By combining massive reaction miniaturization with rapid direct analysis, this approach allows hundreds to thousands of photocatalytic experiments to be interrogated with minimal material. These capabilities point toward a future in which photocatalytic reaction development moves beyond testing individual transformations toward the systematic exploration—and ultimately prediction—of radical reactivity.

8. Invited Lectures

IL1.

From Triplet State to C–C Bond: Photophysical and Synthetic Dimensions of Acyl Azolium Salts

Leyre Marzo

(Universidad Autónoma de Madrid UAM, Spain)

IL2.

From Fluorine-Promoted to Fluorine-Enabled Photochemistry

Johannes M. Wahl

(Johannes Gutenberg-Universität Mainz, Germany)

IL3.

Multiphoton Photoredox Strategies for the Generation of Reactive Intermediates

Anastasios Polyzos

(University of Melbourne, Australia)

IL4.

Photochemical Strategies for the Synthesis and Modification of Bio-Relevant Molecules

Marcio Weber Paixao

(Federal University of São Carlos, Brazil)

IL1: From Triplet State to C–C Bond: Photophysical and Synthetic Dimensions of Acyl Azolium Salts

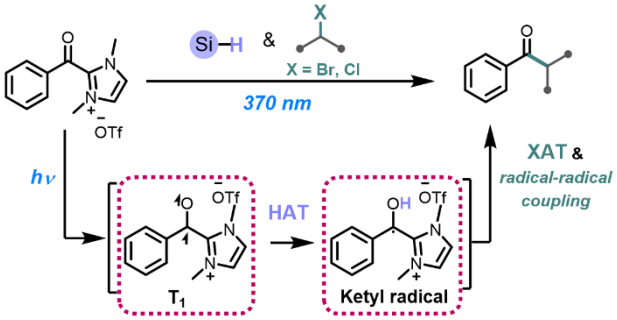
Leyre Marzo

Organic Chemistry Department (Módulo 1), and Institute for Advanced Research in Chemical Sciences (IAdChem), Universidad Autónoma de Madrid, Spain

Subject area: Photocatalytic organic transformations
Keywords: Acyl azolium salts; Photochemistry; Acylation; Alkyl halides

N-Heterocyclic carbenes (NHC) are prevalent structures largely employed as ligands in organometallic chemistry or as organocatalysts,[1] opening the door to the development of countless useful transformations. Nevertheless, a completely new type of reactivity has been achieved under photochemical or photocatalytic conditions.[2] Acyl azolium salts have been recently described as good HAT mediators in their excited state[3] — similarly to diaryl ketones— and good acylating reagents,[4] with the beneficial property of enabling incorporation of the acyl residue into the final molecule. Nevertheless, despite significant synthetic efforts in the field, the knowledge and understanding of the key reactive intermediates — especially through spectroscopic investigations — remained elusive.

In this work[5] we present a photochemical study of the reactivity of acyl azolium salts that comprises the detection and characterization of the triplet excited state and of the decisive ketyl radical intermediate. Moreover, this mechanistic insight allowed us the development of an alternative method based on a silane-mediated tandem HAT/XAT activation strategy that enables not only the acylation of alkyl bromides, but also the acylation of the more challenging alkyl chlorides. The method has proven to be efficient regardless of the electronic properties of the acyl azolium or the substituents present in the alkyl halide. Furthermore, its robustness has been proven through the functionalization of natural product derivatives either as acyl azolium or alkyl bromide derivatives.



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IL2: From Fluorine-Promoted to Fluorine-Enabled Photochemistry

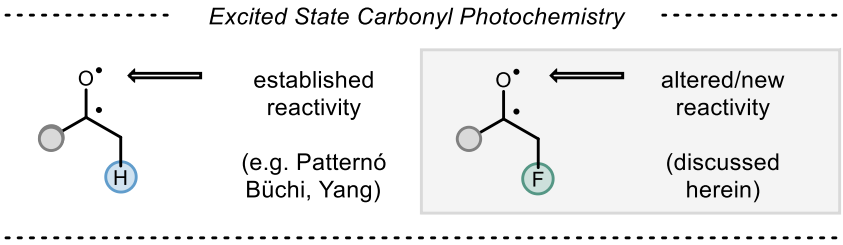
Johannes M. Wahl

Johannes Gutenberg-Universität, Duesbergweg 10-14, 55128 Mainz, Germany

Subject area: Photocatalytic organic transformations

Fluorine is ubiquitous in medicinal chemistry, agrochemicals, and advanced materials,1 yet its influence on the photochemistry of carbonyl compounds remains surprisingly underexplored.2 In particular, α-fluoroketones have received little attention despite the rich photochemistry of their non-fluorinated counterparts.3

In this talk, I will show how fluorine fundamentally changes the excited-state behavior of carbonyl compounds and how these changes can be exploited to control reaction outcomes and eventually divert from established pathways. I will further highlight how these initial results can be leveraged for building up molecular complexity.4 Potential applications in molecular solar thermal (MOST) energy storage5 and in the development of new photoclick chemistry will be highlighted.6 Overall, these studies demonstrate that fluorination can be used as a strategic tool to reshape excited-state reactivity and expand the synthetic and functional potential of photochemistry.



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IL3: Multiphoton Photoredox Strategies for the Generation of Reactive Intermediates

Anastasios Polyzos

School of Chemistry, The University of Melbourne, Australia

Subject area: Photocatalytic organic transformations

Keywords: multiphoton, photoredox, radical-polar crossover, radical anion

The reductive activation of organic molecules through single electron transfer (SET) is routinely deployed in diverse synthetic settings. Within the context of catalytic approaches enabling the controlled one-electron reduction of common functional groups or inert bonds, photoredox catalysis provides an intuitive strategy to furnish potent SET reductants that activate challenging substrates and generate potent reactive intermediates. Thus far, photoredox methods remain scarce due to the highly negative reduction potentials of many organic substrates (< -2.0 V) which fall beyond the scope of conventional photoredox catalysts. Multiphoton excitation catalysis is an emerging strategy to overcome the thermodynamic limitations of visible light photoredox catalysis. Our group recently disclosed a method for the in-situ generation of a high energy photoreductant from the readily available iridium photocatalyst via a two-photon tandem photoredox cycle[1] and more recently, with cyanoarene donor-acceptor organophotocatalysis.[2] This approach has successfully engaged unactivated organohalides and olefins to generate acyl radicals, and olefinic radical anions respectively. These reactive intermediates are primed for new C-C[3] coupling reactions, showcasing the ability of common photoredox catalysts to yield potent excited-state electron donors via multiphoton excitation. The discovery and application of these catalytic reductive protocols to strategic reaction development, and target synthesis will be discussed.

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IL4: Photochemical Strategies for the Synthesis and Modification of Bio-Relevant Molecules

Marcio Weber Paixao

Federal Univeristy of São Carlos. Brazil

The design of new chemical strategies for the construction and modification of structurally complex and biologically relevant molecular architectures is of significant interest across different fields of chemistry. In this context, visible-light-driven photochemical methodologies, by enabling the controlled generation of highly reactive open-shell intermediates, can provide access to unconventional bond-forming processes, complementary retrosynthetic disconnections, and reaction pathways that are difficult to achieve through conventional two-electron chemistry.[1]

In this lecture, we will present our recent efforts toward the development of photochemical methodologies for the synthesis and diversification of bio-relevant molecules. Particular emphasis will be placed on the synthesis of non-canonical amino acids and their derivatives, the construction and functionalization of heterocyclic scaffolds, and the late-stage modification of structurally complex molecules. This will include site-selective metallaphotoredox functionalization of peptides on solid support and emerging approaches for the selective modification of carbohydrate-containing molecules.[2] Together, these studies highlight the versatility of visible-light photochemistry for both the construction of molecular complexity and the selective modification of biologically relevant structures.

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9. Oral Communications

OC1. Vid Kermelj. Nickel-Catalyzed C(sp^3)–H Arylation of *N,N*-Dialkyl Enaminones via Blue-Light-Driven Direct Hydrogen Atom Transfer.

OC2. Chiara Antenucci. Synthesis of Amino-2,3-Dihydrofurans by Radical–Polar Crossover Visible-Light Photoredox Ring Expansion of α-Ketoaziridines.

OC3. Kenta Tanaka. Redox-potential-controlled Thioxanthylium Organophotoredox Catalysis

OC4. Francisco Juliá-Hernández. Earth-Abundant Metal Photodecarboxylation for Radical Fluoroalkylations

OC5. Valeska Viereckt. Triazole substitution turns cyanine dyes into viable probes for straightforward three-colour bacterial cell tracking.

OC6. Sara Cuadros. Dual-role Iron Species in Photoelectrocatalytic Radical Trifluoromethylation with Trifluoroacetates.

OC7. Mauro Mato Gómez. Learning from and Teaching Nature with Light.

OC8. Nayan Saha. A de novo Approach to 3-Azabicyclo[3.1.1]heptanes via the Synergistic Combination of Odd-Alternant Photocatalysis and Orthogonal Lewis Acid Activation.

OC9. Manuel Plaza Martínez. New photochemical reactions for C(alkenyl)-S bond formation.

OC10. Elena Cassera. Aldehydes as CO-releasing molecules: in-situ and ex-situ Giese reactions and palladium-catalyzed aminocarbonylations.

OC11. Felicity Draper. Surpassing Photon Limits in Earth-Abundant Photoredox Catalysis.

OC12. Fabio Juliá. Ferrioxalate Photocatalysis.

OC13. Giulio Goti. Radical Approaches to Saturated Analogues of Aryl C−Glycosides.

OC14. Aniket Kumar Srivastawa. Mechanophotochemistry: Lighting up EDA complexes in the Solid-State.

OC15. Jorge García-Lacuna. Diasteroselective Radical hydroalkylatins of cyclopropenes enabled by EDA complexes.

OC16. Ian MacKenzie. Predictive Control over Photocatalytic Properties in Improved Pyrylium Photocatalysts.

OC17. Giuseppe Zuccarello. Enantioselective Hydrogen Atom Relay via Non-covalent Catalyst Assembly.

OC18. **Hugo Salazar.** Atomic-level engineering of carbon nitride via heteroatom doping for solar-driven hydrogen peroxide production.

OC1: Nickel-Catalyzed C(sp³)-H Arylation of N,N-Dialkyl Enaminones via Blue-Light-Driven Direct Hydrogen Atom Transfer

Vid Kermelj (1), Aljaž Flis (1), Helena Brodnik (1), Tilen Zorko (1), Bogdan Štefane (1), Jurij Svete (1), Uroš Grošelj (1)

(1) Faculty of Chemistry and Chemical Technology, University of Ljubljana, Večna pot 113, 1000 Ljubljana, Slovenia

Subject area: Photocatalytic organic transformations

Keywords: enaminones, direct hydrogen atom transfer (d-HAT), C(sp³)-H (hetero)arylation, metallaphotoredox, nickel catalysis

Herein, we report, to the best of our knowledge, the first example of a blue-light-driven direct hydrogen atom transfer (d-HAT) metallaphotoredox cross-coupling.[1,2] Transformations were performed using a novel photocatalyst, 1,8-dimethoxyanthraquinone (DMAQ). X-ray diffraction (XRD) analysis revealed an unusual out-of-plane orientation of its 9-carbonyl group, presumably arising from electronic strain between the carbonyl oxygen and the lone pairs of the adjacent methoxy substituents. Density functional theory (DFT) calculations further suggest that this distortion is relieved upon the HAT process, restoring molecular planarity. While numerous photochemical transformations targeting the enaminone double bond have been reported,[3] activation of the *N*-alkyl moiety remains rare and has thus far been limited to aerobic conditions.[4,5] We harnessed the HAT reactivity of DMAQ for the *α-N* C(*sp³*)-H activation of *N*,*N*-dialkyl enaminones, which were in turn cross-coupled with (hetero)aryl bromides. Thorough reaction optimization identified DMAQ as the optimal catalyst, demonstrated the necessity of rigorously anhydrous conditions, and revealed that the reaction proceeds most efficiently at higher concentrations and elevated temperatures. A broad range of enaminones and electrophile coupling partners proved compatible under the optimized conditions. Mechanistic investigations, including Hammett correlation studies and hydrogen isotope effect measurements using a model Giese addition reaction, provide strong evidence that the transformation proceeds via a direct hydrogen atom transfer mechanism. Furthermore, subsequent work-up of the cross-coupling products enabled the direct synthesis of *N*-alkyl aminomethylated derivatives from (hetero)aryl bromides.

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OC2: Synthesis of Amino-2,3-Dihydrofurans by Radical-Polar Crossover Visible-Light Photoredox Ring Expansion of α-Ketoaziridines

Chiara Antenucci (1), Vittoria Martini, Olga García Mancheño (1)

(1) Leibniz Institute for Catalysis, Rostock, Germany

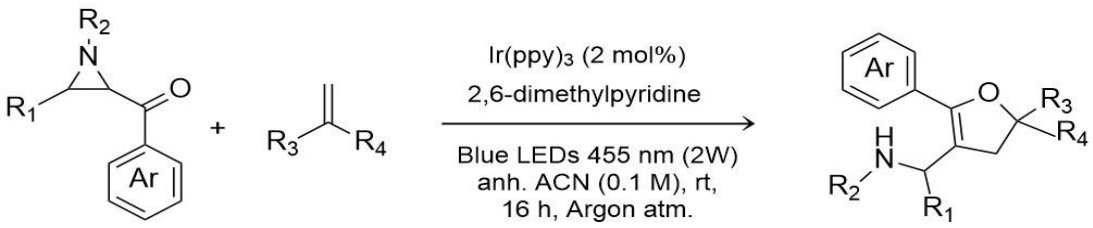
Subject area: Photocatalytic organic transformations

Keywords: photoredox catalysis ● ring expansion ● radical polar crossover ● α-ketoaziridines ● dihydrofurans

Photoredox catalysis driven by visible light has become a powerful and established strategy in organic synthesis to allow the precise formation of radical intermediates under very mild conditions.[1] One of the most noteworthy reaction models enabled by this methodology is the radical-polar crossover (RPC) pathway, in which these radical species undergo single-electron transfer (SET) to yield ionic intermediates, employing the complementary properties of both radical and polar chemistry.[2]

In this context, an interesting class of versatile building blocks for the synthesis of functionalized heterocycles through photocatalysis are the ring-strained α-ketoaziridines. These substrates have been studied for the possibility of photocatalytic ring opening and ketyl radical-anion formation, followed by radical trapping.[3] Along this line, our group has recently reported the first intramolecular photocatalytic ring-expansion of N-arylsulfonyl α-ketoaziridines into d-sultams.[4] I

n this work, we present our latest studies on the preparation of amino-2,3-dihydrofurans by a photoredox-catalyzed radical-polar crossover intermolecular approach, implying a visible light photo-induced ring opening of α-ketoaziridines, followed by radical trapping with alkenes and final polar cyclization.



The generality of the reaction was explored across a broad range of substrates, showing a good functional group tolerance as well as a ten-fold upscaling robustness, opening new possibilities for the construction of functionalized heterocycles by photoredox-mediated RPC ring expansion reactions.

Acknowledgements

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OC3: Redox-potential-controlled Thioxanthylium Organophotoredox Catalysis

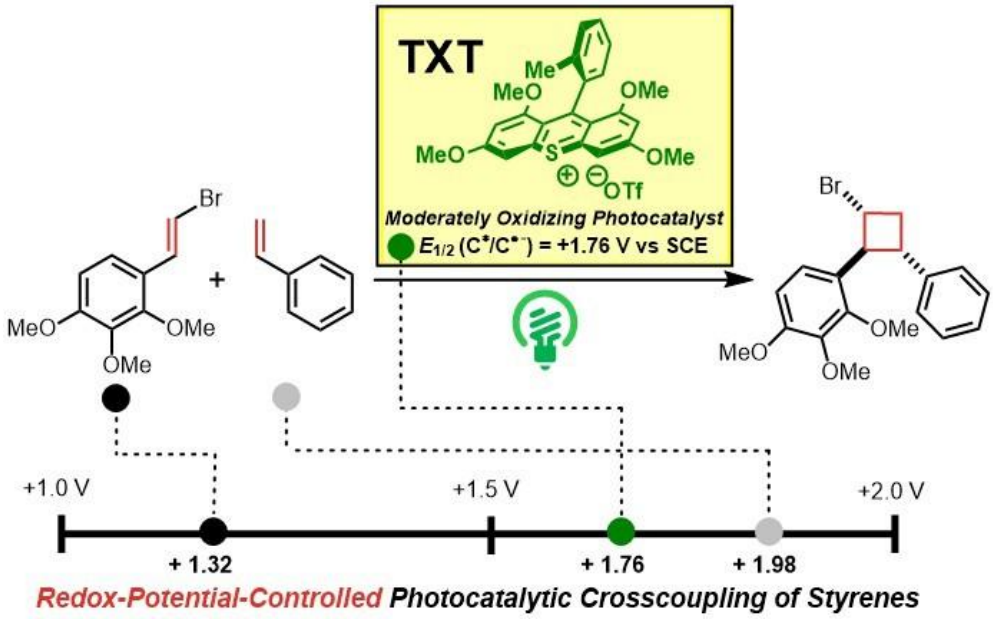
Kenta Tanaka (1)

(1) Okayama University, Japan

Subject area: Photocatalytic organic transformations

Keywords: Organophotoredox Catalysts, Visible light, Redox potential, [2+2] cycloaddition

The redox potential is an important factor for controlling the outcome of photoredox catalysis. Especially the selective oxidation of substrates and establishing control over reaction outcomes are challenging when using photoredox catalysts that have high excited-state reduction potentials. Recently, we have designed and synthesized organophotoredox catalysts and developed visible-light-induced various photochemical transformations. In this study, a redox-potential-controlled intermolecular [2+2] cycloaddition of styrenes using a thioxanthylium organophotoredox (TXT) catalyst has been developed. This TXT catalyst selectively oxidizes ß-halogenostyrenes and smoothly promotes the subsequent intermolecular [2+2] cycloadditions to give multisubstituted halogenocyclobutanes with excellent regio- and diastereoselectivity, which has not been effectively achieved by the hitherto reported representative photoredox catalysts. The reaction system also could be applied to radical cation Diels-Alder reactions. The present reaction contributes to the field of redox-potential-controlled electron-transfer chemistry.



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OC4: Earth-Abundant Metal Photodecarboxylation for Radical Fluoroalkylations

Francisco Juliá-Hernández (1)

(1) University of Murcia, Spain

Subject area: Photocatalytic organic transformations
Keywords: Earth-abundant metal photocatalysis, LMCT, photodecarboxylation, fluoroalkylation

Visible-light photoredox catalysis has significantly advanced the development of more efficient and sustainable synthetic methods, enabling the construction of molecular complexity through single-electron transfer (SET) processes. State-of-the-art photoredox catalysts, typically based on precious metals or organic compounds, facilitate these pivotal SET events via an outer-sphere mechanism.[1] Similar to ground-state redox reactions, this pathway requires precise alignment between the redox potentials of the excited-state photocatalyst and the substrate.[2]

Despite remarkable progress in the field, this redox compatibility constraint has limited the broader application of these transformations. In my talk, I will highlight my group's strategies to overcome these limitations through the design of Earth-abundant metal photocatalysts derived from inexpensive and readily available base metals such as iron and copper. These catalysts operate through a complementary inner-sphere mechanism involving the population of dissociative ligand-to-metal charge-transfer excited states (LMCT), offering enhanced reactivity compared to canonical photoredox catalysts.[3]

Our reactivity platform has enabled the discovery of novel decarboxylation reactions of fluorinated carboxylic acids, thereby repurposing these feedstocks and demonstrating strong potential for synthetic applications, including late-stage diversification.[4] Our synthetic methods exhibit unique reactivity and selectivity patterns that extend beyond the capabilities of canonical redox-based approaches, including traditional photoredox catalysis. Collectively, these advances address long-standing challenges in organic synthesis and contribute significantly to the derivatization of complex molecules, highlighting their potential for impactful applications in small-molecule drug discovery and development.

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OC5: Triazole substitution turns cyanine dyes into viable probes for straightforward three-colour bacterial cell tracking

Valeska Viereckt (1), Olalla Vázquez (1)

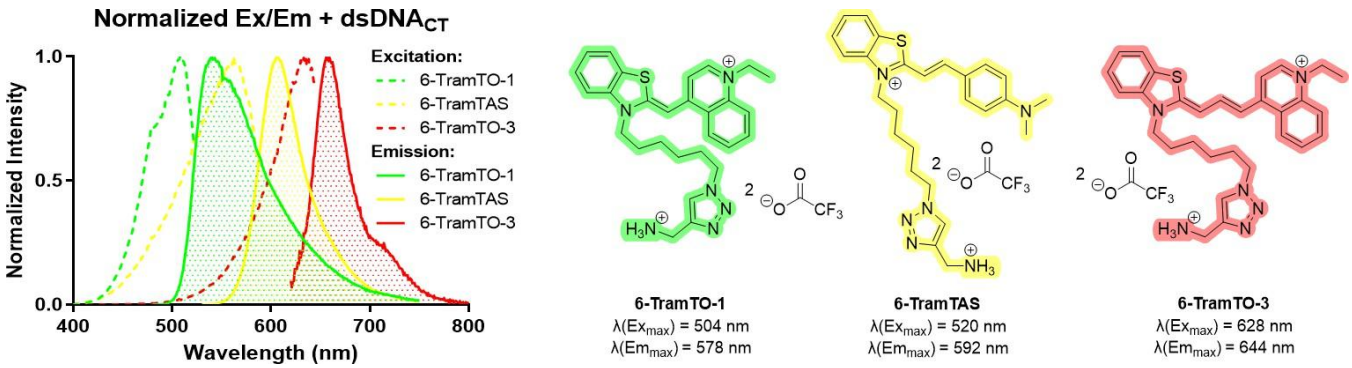
(1) Marburg University, Germany

Subject area: Mechanistic studies in photo- and bio-catalysis

Keywords: Multidrug-resistant bacteria, multicolour labelling, fluorescent DNA binder, viable probes

The rise of multidrug-resistant bacteria is a major global health challenge, highlighting the need for advanced methodologies to study bacterial infection and support antibiotic development.[1]

Here, we present triazole-substituted fluorescent DNA binders for efficient (>99%) multicolour labelling and real-time analysis of live bacteria without genetic manipulation or loss of viability. Trialzole modification of the probes resulted in an up to 400-fold fluorescence enhancement while restoring DNA-binding affinity with no apparent toxicity, which enabled multicolour labelling of live bacteria by flow cytometry and microscopy. As a proof-of-concept, we tracked macrophage uptake of *Escherichia coli* and antibiotic-resistant *Klebsiella pneumoniae*, revealing distinct immune clearance strategies in co-infection settings. These findings demonstrate the potential of triazole-substituted cyanine dyes as versatile chemical probes for chemical biology, microbiological research, diagnostics, and the investigation of antibiotic-resistant pathogens.[2-4]



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OC6: Dual-role Iron Species in Photoelectrocatalytic Radical Trifluoromethylation with Trifluoroacetates

Sara Cuadros (1), Sara Fernández García (2), Irene Bosque (1), Jose C. Gonzalez-Gomez (1), Francisco Juliá-Hernández (2)

(1) University of Alicante, (2) University of Murcia, Spain

Subject area: Photocatalytic organic transformations

Keywords: synthetic methods, photoelectrocatalysis, iron catalysis, radical trifluoromethylation

Trifluoromethylation is a fundamental transformation in pharmaceutical research, contributing to the success of numerous marketed drugs. Recent advances in iron ligand-to-metal charge transfer (LMCT) catalysis have enabled the use of trifluoroacetates as CF_3 radical sources in (hetero)arene trifluoromethylation.[1] However, current approaches often rely on inorganic stoichiometric oxidants to regenerate photoactive iron species, thereby restricting functional group compatibility and broader applicability.

In this work, we report a photoelectrocatalytic strategy that uses in situ-formed multifunctional iron catalysts to achieve C(sp^2)–H trifluoromethylation without external oxidants, producing traceless byproducts.[2] Mechanistic investigations reveal catalytically active iron species that simultaneously drive trifluoroacetate photodecarboxylation and facilitate redox turnover. The method operates under mild, tunable and scalable conditions using visible light and electrical current, and demonstrates broad substrate compatibility, including challenging electron-rich and easily oxidizable substrates. Overall, this strategy offers a practical and sustainable approach for late-stage trifluoromethylation in drug discovery workflows.

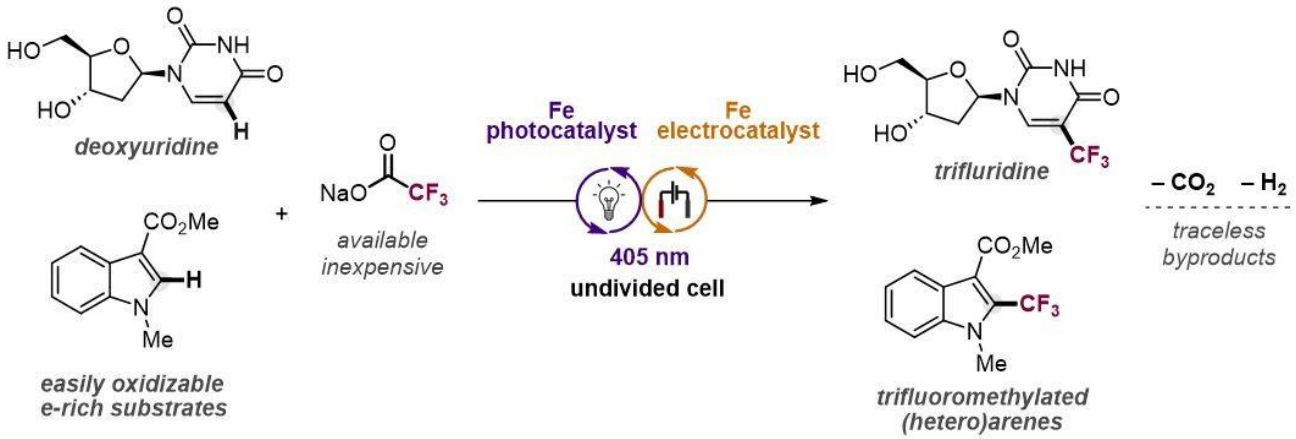

Figure 1. Radical C-H trifluoromethylation of (hetero)arenes with trifluoroacetates by synergistic iron electro- and photocatalysis.

Acknowledgements

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OC7: Learning from and Teaching Nature with Light

Uxía Deus-Lorenzo, Adrián Rivas-Saborido, Alba Casas-Pais, David Montoto, María Tomás-Gamasa, José L. Mascareñas, Mauro Mato (1)

(1) Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CiQUS) and Departamento de Química Orgánica, Universidade de Santiago de Compostela, 15705 Santiago de Compostela, Spain

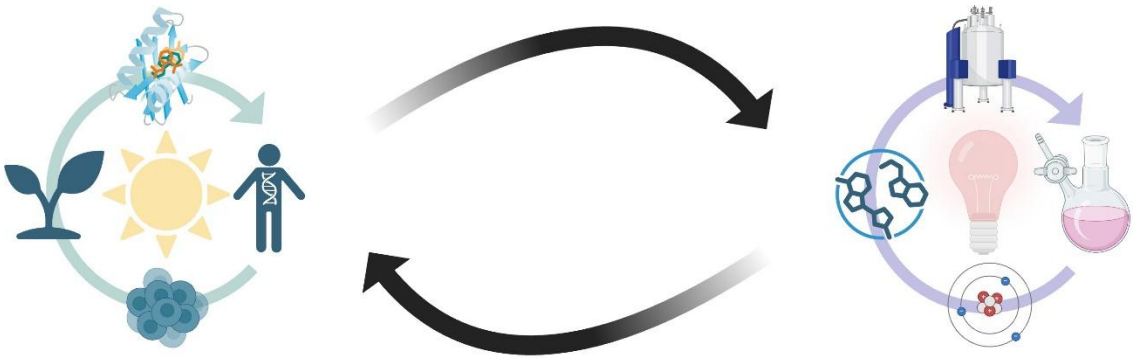
Subject area: Photocatalytic organic transformations

Keywords: photoredox catalysis, bioinspired catalysis, radical chemistry, bioorthogonal chemistry

Since the emergence of modern photocatalysis, nature has inspired chemists to harness light for chemical reactivity. In this regard, we pursue a bidirectional strategy: we use natural redox principles to guide the development of new synthetic radical chemistry, while also attempting to introduce artificial photochemical reactivity into living systems.[1]

For example, we have found that NADH can be repurposed both as a reagent or as a catalytic redox mediator to promote the generation of alkyl radicals from redox-active precursors using biocompatible red light. This approach provides systems with highly reducing activation potentials which are inaccessible under low-energy irradiation alone.[2]

An analogous approach can be used to efficiently activate aryl thianthrenium salts under low-energy-light conditions, leading to aryl radicals. We have exploited this to develop an unprecedented uncaging approach that bypasses the need for heteroatom handles, based on the reversible masking of aromatic C–H bonds with a thianthrenium group. This established the feasibility of performing artificial radical chemistry within living cells, and is leading to proof-of-concept applications of this strategy for the modulation of drug activity.[3]



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OC8: A de novo Approach to 3-Azabicyclo[3.1.1]heptanes via the Synergistic Combination of Odd-Alternant Photocatalysis and Orthogonal Lewis Acid Activation

Nayan Saha (1), Burkhard König (1)

(1) Universität Regensburg, Germany

Subject area: Photocatalytic organic transformations

Keywords: 3-Azabicyclo[3.1.1]heptanes, Azomethine ylide, Phenalenyl Photocatalysis

3-Azabicyclo[3.1.1]heptanes have recently emerged as valuable saturated bioisosteres of pyridines and privileged six-membered N-heterocycles, yet their modular synthesis remains challenging. Herein, we report a synergistic photo/Lewis acid mediated catalytic strategy that enables the direct conversion of free N–H aziridines and monosubstituted bicyclo[1.1.0]butane ketones into densely functionalized 3-azabicyclo[3.1.1]heptanes under redox-neutral conditions.

Central to this approach is a phenalenyl-based odd-alternant hydrocarbon photocatalyst that selectively engages the aziridine substrate while remaining orthogonal to the BCB component. Consecutive single-electron oxidation and reduction of the aziridine rapidly furnishes an azomethine ylide through a redox-neutral photocatalytic manifold. Concurrently, coordination of $Sc(OTf)_3$ to the BCB ketone lowers its LUMO and weakens the central C–C bond, transforming an otherwise poor dipolarophile into a highly reactive cycloaddition partner. The resulting dual activation strategy promotes rapid [3+2] cycloaddition to deliver a broad range of 3-azabicyclo[3.1.1]heptanes in short reaction times. This work establishes free N–H aziridines as azomethine ylide precursors and broadens the synthetic utility of bicyclo[1.1.0]butanes, providing efficient access to medicinally relevant three-dimensional N-heterocycles.

OC9: New photochemical reactions for C(alkenyl)-S bond formation

Manuel Plaza Martinez (1)

(1) Universidad de Oviedo, Spain

Subject area: Photocatalytic organic transformations

Keywords: C-S bond formation, EDA complex, exciplex, alkenyl radical, photochemistry

The discovery of new activation modes for the creation of carbon-centered radicals is a task of great interest in organic chemistry. In this context, the photochemical halogen-bonding (HaB) assisted generation of carbon-centered radicals has risen as a powerful synthetic tool for the creation of radical intermediates under mild reaction conditions.(1) While all of the transformations enabled thanks to this reactivity have been applied to the creation of aryl and alkyl-centered radicals, our research group has pioneered synthetic applications based on the generation of alkenyl radicals. Our approach utilizes alkenyl halides as starting materials,(2) enabling C–S bond forming reactions including thioetherifications,(3a) carbothiophosphorylations,(3b) sulfonylations,(3c) and thiocyanations.(3d) These transformations exhibit exceptional functional group tolerance, simplicity, and scalability. Moreover, recent progress in our group has shown that photoexcited thiophenolate anionic compounds can react with alkenyl bromides through exciplex-type complexation for the preparation of functionalized imidazoles.(4)

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OC10: Aldehydes as CO releasing molecules: in-situ and ex-situ Giese reactions and Palladium catalyzed aminocarbonylations

Elena Cassera (1), Maurizio Fagnoni (1)

(1) PhotoGreen Lab, Department of Chemistry, University of Pavia, Italy

Subject area: Photocatalytic organic transformations

Keywords: Decatungstate anion ● Hydrogen Atom transfer ● Pd catalysis ● Photocatalysis ● Giese reaction

Carbon monoxide (CO) represents a fundamental C1 synthon, widely utilized in valuable carbonylation reactions. Its hazardous nature, however, has made necessary the development of proper strategies for its safe manipulation, e.g. the use of stable CO precursors, known as CORMs (CO-releasing molecules). These surrogates allow for a smooth, controlled release of CO – whether through thermal or photochemical activation – within the reaction mixture. A drawback of this approach, however, is that the remaining part of the CORM (after CO loss) is wasted thus impacting the atom economy of the reaction.[1]

Recently, we successfully tested some aldehydes where the formyl group was dubbed as "HAcTive group" having the role to direct the photocatalyzed hydrogen atom abstraction in the substrate. In such a way, an acyl radical resulted and upon CO loss easily gave access to various substituted carbon-based radicals (e.g. tertbutyl, benzyl, α-oxy etc).[2]

We then envisaged a two-chambers photoreactor (**Figure 1a**), where in Chamber A, the CORM, i.e. a proper aldehyde, was activated, upon light irradiation at 390 nm, by a decatungstate anion (TBADT)-photocatalyzed hydrogen atom transfer, to the corresponding acyl radical, which spontaneously decarbonylated, releasing an alkyl radical. The latter underwent a Giese reaction, via conjugate addition onto a Michael acceptor, while the photogenerated carbon monoxide, once reached Chamber B, was exploited in the Palladium photocatalyzed aminocarbonylation of an aryl iodide triggered by the same wavelength (390 nm).[3]

Both types of reactions showed a remarkable efficiency, allowing to obtain several Giese adducts and benzamides in good yields, and assuring a full incorporation of the CORM structure in the final products.

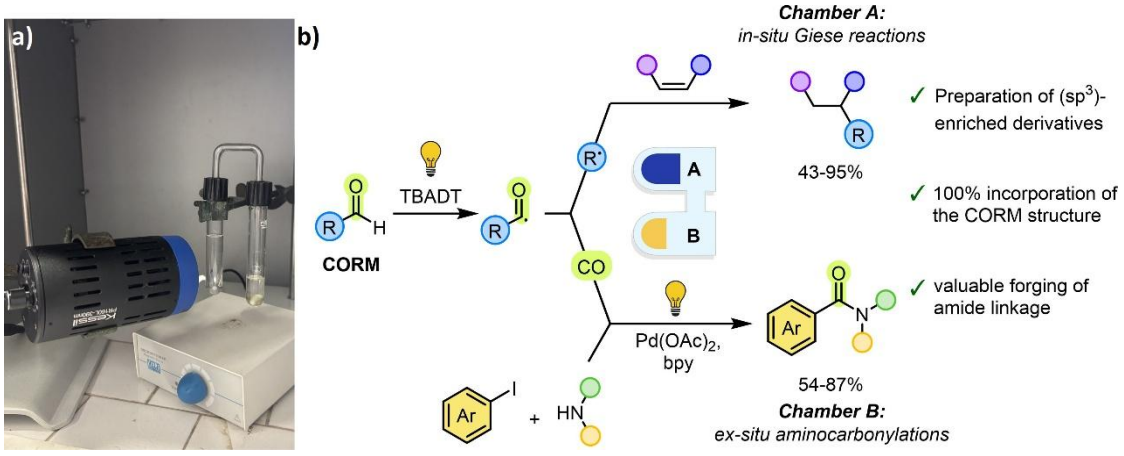

Figure 1: a. Two chambers setup employed for the reaction (Chamber A on the left, Chamber B on the right) **b.** Aldehydes as CORMs

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OC11: Surpassing Photon Limits In Earth-Abundant Photoredox Catalysis

Felicity Draper (1), Cui Wang (1), Time Connell (2)

(1) University of Konstanz, Spain, (2) Deakin University, Australia

Subject area: Mechanistic studies in photo- and bio-catalysis

Keywords: Photoredox catalysis, red-light photocatalysis, earth-abundant photochemistry

Photoredox catalysis harnesses visible light to drive synthetic transformations, but its reach is fundamentally limited by photon energy. By acting as redox mediators, photocatalysts convert light into chemical potential while avoiding direct substrate activation with high-energy UV irradiation. While blue light is typically required, lower-energy red or green light offers advantages in chemoselectivity, penetration, and energy efficiency.[1] However, limited photon energy and inherent losses restrict access to thermodynamically demanding substrate transformations with conventional single-photon photoredox systems.

Here we show an unconventional approach to push the single-photon photoredox chemistry beyond the intrinsic energy limits by decoupling redox reactivity from excitation wavelength and excited state decay.[2-4] Sacrificial redox agents, typically used to close the catalytic cycle, are repurposed as additional energy inputs, generating reactive radical intermediates following photoinduced electron transfer. Earth abundant Fe(III) N-heterocyclic carbene photocatalysts enable photochemical upconversion to drive challenging reductive transformations under green and red light. Oxalate derived $CO_2^{\bullet-}$ generation serves as a proof of concept, enabling reactivity of challenging aryl halides under low-energy irradiation, supported by efficient quenching and cage escape steps. This strategy establishes a general framework for extending photoredox catalysis into low-energy visible light regimes, positioning Fe(III)-based photocatalysts as sustainable platforms for demanding chemical transformations beyond the conventional limits.

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OC12: Ferrioxalate Photocatalysis

Fabio Juliá

(1) University of Murcia, Spain

Subject area: Photocatalytic organic transformations

Keywords: photocatalysis, ferrioxalate, ligand-to-metal charge-transfer (LMCT), organic synthesis, radical chemistry, iron catalysis

The use of transition-metal catalysis has become an indispensable asset for organic synthesis, particularly for the assembly of C-C bonds.[1] Among all possible metals, the use of Earth-abundant iron for this task would represent a promising and sustainable new tool for synthesis.[2] However, the challenging reduction of benchmark iron salts to active species represents an important obstacle that hinders the broad development of reductive iron catalysis.

Inspired by the classic photochemistry of ferrioxalate, which is known for 130 years[3] and is routinely used as standard for quantum yield determination, we have developed the use of oxalate salts as photo-activable, traceless 2-electron reductants for iron catalysis. This new activation mode, unprecedented within the arena of transition-metal catalysis, enable access to versatile reduced Fe species exploiting the innate reactivity of ligand-to-metal charge-transfer (LMCT) excited states of iron complexes. In this communication it is presented the discovery and development of ferrioxalate photocatalysis,[4] a general catalytic platform with multiple synthetic applications featuring mild conditions and broad functional group compatibility.

The multitasking ability of iron complexes to act as photocatalysts, reductants and organometallic intermediates enable transformations hitherto inaccessible to previous strategies based on iron catalysis or LMCT reactivity, representing a privileged new system to discover unprecedented transformations for organic synthesis.

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OC13: Radical Approaches to Saturated Analogues of Aryl C–Glycosides

Giulio Goti (1), Alessia Marrese, Simone Baldon, Chun Qi, Patricia Gómez Roibás, Giorgio Pelosi, Andrea Sartorel, Luca Dell'Amico

(1) Department of Chemical Sciences, University of Padova, Italy

Subject area: Photocatalytic organic transformations

Keywords: radicals; carbohydrates; strain-release; photocatalysis; bioisosteres

Aryl *C*-glycosides—saccharides directly linked to aryl fragments through a C–C bond—constitute an important class of biologically active molecules widely found in nature.[1] These compounds exhibit resistance to enzymatic hydrolysis, a property that has been successfully leveraged in the development of metabolically stable drugs.[2]

Recently, we envisaged the replacement of the planar aromatic ring with a three-dimensional fragment to access saturated analogues of aryl *C*-glycosides, which are expected to show enhanced physicochemical properties.[3] Here, we present our efforts to explore this chemical space. Specifically, we developed two distinct synthetic methods to prepare analogues featuring a bicyclo[1.1.1]pentane (BCP) fragment at the anomeric position.[4] Both protocols share a strain-release strategy in which glycosyl radicals **I** are intercepted by [1.1.1]propellane **2** to afford BCP *C*-glycosides **4**.

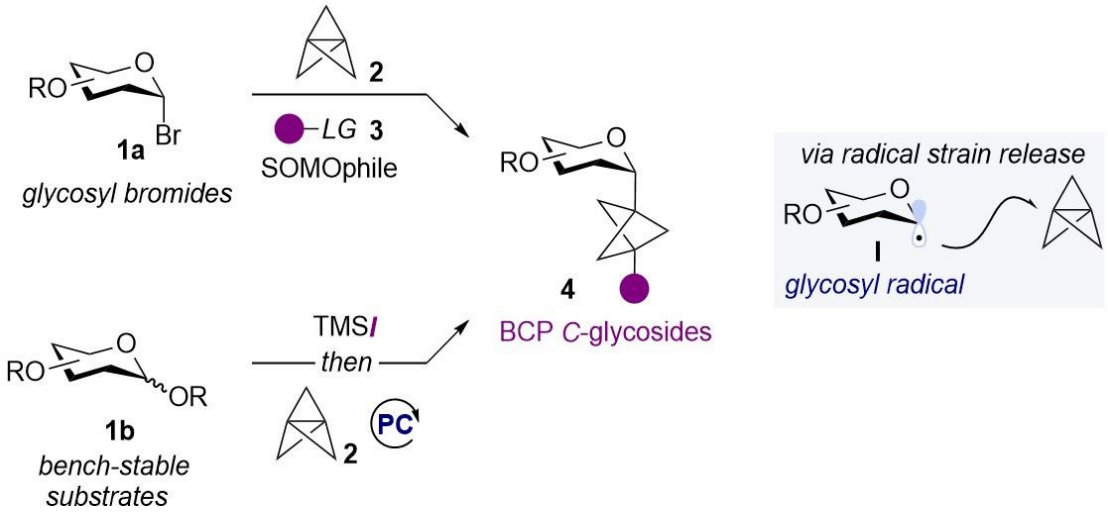

Figure 1. Radical strategies for the synthesis of BCP C–glycosides.

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OC14: Mechanophotochemistry: Lighting up EDA complexes in the Solid-State

Aniket Kumar Srivastawa (1), Eli Zysman-Colman (1)

(1) University of St Andrews, Scotland

Subject area: Sustainable and Green Photochemical Applications

Keywords: Electron donor acceptor complex, photochemistry, mechanochemistry, mechanophotochemistry, solvent-minimized

Photochemistry is an indispensable tool for the synthetic organic chemist. In a typical photochemical reaction, solvent constitutes the dominant waste stream by mass. Mechanophotocatalysis, the synergistic union of mechanochemistry and photocatalysis provides an alternative route to these photochemical reactions, enabling them to be performed in the absence of solvent using a ball mill irradiated by visible light.[1]

Here we report mechanophotochemistry driven by the in situ formation of visible-light absorbing Electron Donor–Acceptor (EDA) complexes. This photocatalyst-free approach is demonstrated across five synthetically valuable transformations: a Giese reaction,[2] a C–S cross-coupling,[3] a phosphorylation,[4] a sulfonylation,[5] and a Povarov reaction[6] — all performed under air.

EDA complex formation in the solid state was confirmed by solid-state UV–Vis absorption spectroscopy, which revealed characteristic charge-transfer bands absent in the individual components. Four of the five reactions proceeded competitively with their solution-state counterparts. The Povarov reaction revealed that transformations requiring O_2 as a terminal oxidant are not feasible in the mechanophotochemical setup, despite the formation of the EDA complex.

This work establishes EDA mechanophotochemistry as a viable, simple, and sustainable alternative to solution-state photochemistry.

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OC15: DIASTEREOSELECTIVE RADICAL HYDROALKYLATION OF CYCLOPROPENES ENABLED BY EDA COMPLEXES

Jorge García-Lacuna (1), Angel Manu Martínez (1), Gema Dominguez (1), Pau Prats-Colàs (1), Inés Alonso (2), Marcus Baumann (3), Javier Pérez-Castells (1)

(1) Universidad San Pablo CEU, Spain (2) Universidad Autónoma de Madrid (UAM), Spain (3) University College Dublin, Ireland

Subject area: Photocatalytic organic transformations

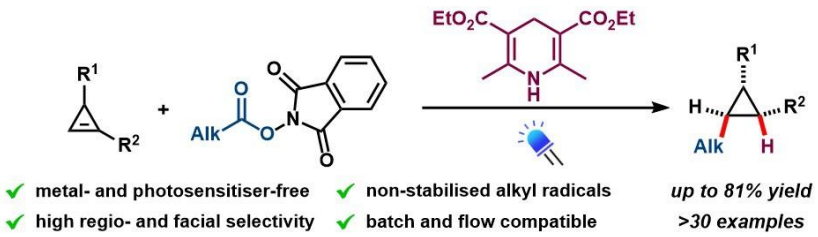
Keywords: cyclopropene, hydrofunctionalisation, radical chemistry, EDA complex, continuous flow

Cyclopropanes are valuable structural motifs widely found in natural products and bioactive molecules, and constitute versatile building blocks in synthetic chemistry due to their inherent ring strain.[1] Among the available strategies, the ring-retentive hydrofunctionalisation of cyclopropenes has emerged as an efficient and atom-economical approach to access highly substituted cyclopropanes.[2]

However, the direct hydroalkylation of cyclopropenes via radical pathways remains underdeveloped,[3] as it requires the controlled generation and selective trapping of highly reactive, non-stabilised alkyl radicals, which are often prone to undesired side reactions.

Contributing to this field, we have developed a metal-free strategy based on electron donor–acceptor (EDA) complexes that enables the visible-light-driven hydroalkylation of cyclopropenes.[4] This approach allows the decarboxylative generation of alkyl radicals from readily available NHPI esters, followed by regio- and facial-selective addition to cyclopropenes and subsequent hydrogen-atom transfer to afford polysubstituted cyclopropanes.

The protocol operates under mild conditions and shows broad substrate scope, delivering the desired products in moderate to good yields with excellent diastereoselectivity (>20:1 dr) and no detectable ring opening. In addition, the methodology can be translated to continuous-flow conditions, highlighting its scalability and operational robustness. Mechanistic investigations, supported by experimental studies and DFT calculations, are consistent with an EDA-initiated radical pathway involving selective radical addition to cyclopropenes followed by hydrogen-atom transfer.



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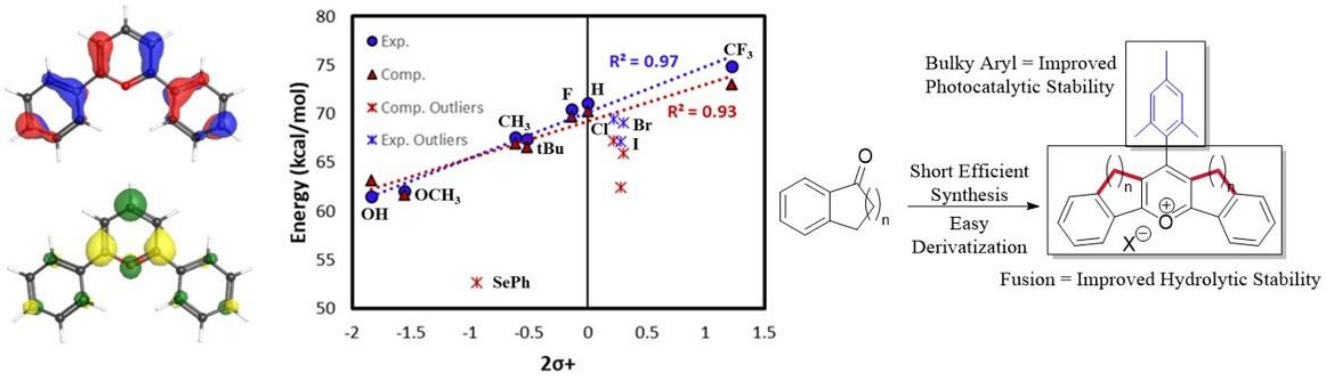
OC16: Predictive Control over Photocatalytic Properties in Improved Pyrylium Photocatalysts

Ian MacKenzie (1)

(1) Muhlenberg College, Pennsylvania, USA

Subject area: Mechanistic studies in photo- and bio-catalysis

The field of synthetic photocatalysis has witnessed a major renaissance in the last 15 years. Much of the focus for photocatalysts has been given to organometallic complexes of ruthenium and iridium, the photophysical and electrochemical properties of which are widely tunable via judicious choice of ligands. However, a single unified-yet-tunable fully organic photocatalyst platform has yet to emerge. Much of this is due to the fact that tuning the photophysical or electrochemical properties of organic photocatalysts is usually nontrivial, sometimes requiring a completely different chemical synthesis in order to produce a relatively minor change in substitution, and in many cases not well studied.
Pyrylium salts represent an easily tunable class of photocatalysts. Previous studies have shown clear relationships between substitution on the external aromatic rings and the resulting photophysical properties. However, there are limited studies on the effects of substituents on the electrochemical properties of pyryliums and no quantitative correlations have been made for substituent effects on the excited state reduction potentials, one of the key properties for oxidizing photocatalysts. As part of our ongoing interest in the development of new pyrylium photocatalysts, we have studied the photophysical and electrochemical properties of a series of substituted 2,6-diarylpyrylium structures. Using Hammett analysis and computational calculations, we provide some quantitative relationships with predictive use for future photocatalyst design. We also briefly detail our work towards a final library of structurally improved pyrylium photocatalysts for broad synthetic utility.



OC17: Enantioselective Hydrogen Atom Relay via Non-covalent Catalyst Assembly

Giuseppe Zuccarello (1)

(1) EPFL, Switzerland

Subject area: Photocatalytic organic transformations
Keywords: asymmetric photocatalysis, deracemization, catalyst design

Hydrogen atom transfer (HAT)[1] is a powerful technology in organic synthesis especially when coupled with photoredox catalysis. However, inducing enantioselectivity in these transformations proceeding through neutral radical intermediates is an outstanding challenge.[2] While traditional approaches to chiral catalyst design rely on constructing a covalent chiral environment around the active site, we have disclosed a distinct approach. We have paired chiral phosphate ions, derived from privileged chiral phosphoric acids with commercial 2-mercaptopyridines.[3] The chiral counterions render the achiral HAT catalysts (2-mercaptopyridines) effectively chiral.[4] The two-component catalyst design is highly tunable and interchangeable, giving potentially access to numerous chiral HAT catalysts while maintaining a low synthesis demand. We have applied our conceptual catalyst design to the photochemical deracemization of 2-aryl pyrrolidines. Mechanistic studies reveal that ion-pairing is the main non-covalent interaction shaping the assembly and that enantioenrichment occurs via enantioselective hydrogen atom relay.

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OC18: Atomic-level engineering of carbon nitride via heteroatom doping for solar-driven hydrogen peroxide production

Hugo Salazar (1)

(1) BCMaterials, Basque Center for Materials, Applications and Nanostructures, Spain

Subject area: Sustainable and Green Photochemical Applications

Keywords: carbon nitride; defect engineering; atomic-level; metal-free doping; hydrogen peroxide; photocatalysis

The photocatalytic production of hydrogen peroxide (H_2O_2) from water is a promising approach for achieving solar-to-chemical energy conversion as a suitable alternative to obtain hydrogen fuel. This work explores metal-free defect engineering by heteroatom doping (B, O, P, and S) into graphitic carbon nitride (C_3N_4) to modulate its structural and electronic properties and enhance its solar-driven H_2O_2 production. Morphological analysis revealed that doping induced morphological and structural modifications, including increased disorder, nanosheet exfoliation, and variations in interlayer spacing, indicating a successful heteroatom incorporation and perturbation of the electronic and optical properties. DFT insights indicate that the impact of doping depends strongly on the heteroatom and its substitution site. Heteroatom doping at C sites induces spatial separation of HOMO and LUMO states across layers, in-plane deformation, and delocalization of both HOMO and LUMO states.

Photocatalytic tests under solar radiation demonstrate the influence of sacrificial agent, pH of the media, and the presence of scavengers[3,4] on the H_2O_2 yield. A significant enhancement in H_2O_2 yield was achieved for all doped-catalysts, with 9.6, 14.8, 11.0, and 16.4-fold enhancement for B-, P-, O-, and S-doped C_3N_4, respectively, compared to the pristine catalyst. S-doped C N catalyst achieved the highest yield of 3022.1 μmol h^{-1} g^{-1} and an apparent quantum yield of 8.1%, due to improved charge separation and optimized 2e^- oxygen reduction selectivity. The stability of the catalysts is also demonstrated, with S-doped C_3N_4 maintaining over 95% efficiency after five cycles. These results demonstrate that tailored defect engineering through heteroatom doping is a robust strategy for developing high-performance solar-to-chemical energy conversion systems.

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10. Poster Presentations

P1: Photochemical valorization of lignin

Leandro Cid Gomes (1), Alexander Riddell (1), Hafsa Mohammad Khalid (1), Diana Bernin (1)

(1) Chalmers University of Technology

Subject area: Sustainable and Green Photochemical Applications
Keywords: lignin, biobased materials

Lignin is a potential sustainable source of carbon-based materials and chemicals, yet, its recalcitrancy and heterogeneity hinder its depolymerization and chemical modification. Light-driven methods often provide milder reaction conditions and higher selectivity than thermochemical routes, which could facilitate tailoring of lignin into applications. Direct irradiation of lignin with UV-light can indeed promote its fragmentation. Our group has previously shown that UV-light can be used to produce small molecules from lignin without the use of photocatalysts,[1] which allows milder and metal-free conditions to be used. However, the direct irradiation of lignin with UV-light often leads to oxidation of the aromatic rings and repolymerization reactions, which motivated us to explore the use of a photosensitizer with Kraft lignin.[2] Lignin can also act as a photocatalyst itself, and some studies have shown its use in aqueous solutions to catalyse the formation of hydrogen peroxide,[3,4] which can be used for further in-situ oxidation reactions. However, aqueous systems limit the use of a wide range of lignin types due to their low solubility.

In this presentation, we will discuss the use of different photocatalysts to achieve more controlled reactions to modify both the functional groups and size of lignin under near UV-light and visible light irradiation. It will also address the use of lignin in the light-driven production of hydrogen peroxide in non-aqueous solvents, which allows a wider range of lignin types to be used due to its higher solubility in organic solvents.

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P2: Scalable Solar Evaporator Based on Bandgap Engineered $CuMnCrO_4$ Spinel Oxide with Salt-Resistant Property for Contaminated Seawater

Rana Muhammad Irfan

Subject area: Sustainable and Green Photochemical Applications
Keywords: Photothermal materials, spinel oxides, solar evaporation

Freshwater scarcity demands innovative solutions that combine efficiency, durability, and scalability. Here, $CuMnCrO_4$ (CMCO), is presented as a ternary spinel oxide photothermal absorber introduced for the first time in solar desalination, synthesized via co-substitution of Mn_3O_4 with Cu and Cr. This multi-cation design narrows the bandgap from 2.3 to 1.49 eV, markedly enhancing solar absorption across the visible and near-infrared spectrum and enabling efficient light-to-heat conversion. Unlike conventional carbon or single-oxide-based systems, CMCO demonstrates record-high evaporation performance of 4.1 kg m−2 h−1 under 1-sun, positioning it among the most efficient oxide-based ISSG materials reported to date. Equally novel is the integration of CMCO with a cotton fabric substrate and hydrophobic polyester strips in an inverted U-shaped configuration, which ensures continuous water wicking, localized salt separation, and mechanical robustness. This architecture delivers stable operation over three weeks without salt accumulation, overcoming a long-standing challenge in ISSG. Furthermore, the system retains high efficiency under strongly acidic/alkaline conditions and in oil- or dye-contaminated water, demonstrating unique resilience rarely reported in solar desalination systems. Finally, the modular design enables straightforward scalability from laboratory-scale strips to large-area panels. Together, these advances establish CMCO-based systems as a new materials platform for practical, durable, and scalable solar desalination, offering a sustainable pathway toward addressing global water scarcity.

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P3: Multimeric Norbornadiene/Quadricyclane Photoswitches as Potential Candidates for Molecular Solar Thermal Application

Christian Traut (1), Andreas Hirsch (1)

(1) Friedrich Alexander Universität Erlangen Nürnberg

Subject area: Sustainable and Green Photochemical Applications

A major challenge associated with the utilization of the sun as a sustainable energy source is the storage of solar energy.[1] A promising approach to tackle this problem is the use of molecular solar thermal (MOST) systems.[2] Upon irradiation with sunlight a stable parent compound A undergoes isomerization towards a meta-stable isomer B. If the system is converted back to compound A, the stored energy can be released in the form of heat.[3] The Norbornadiene (NBD)/Quadricyclane (QC) interconversion couple is a well-researched candidate for MOST applications due to its potential for high energy storage density.[4] By attaching multiple NBD scaffolds to one linker, the gravimetric energy density of the system can be increased and the absorption properties of the NBD photoswitch enhanced.[5] We present a library of multimeric NBD derivatives featuring a central electron withdrawing unit. The photophysical properties of all compounds were investigated employing UV/Vis and NMR spectroscopy as the main characterization methods.

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P4: Harnessing Photocatalytic HAT Chemistry for Lignin Depolymerization and Diversification

Xavier Marset (1), Elio Rico (1), Javier Fernández-Catalá (1), Néstor Guijarro (1)

(1) University of Alicante

Subject area: Sustainable and Green Photochemical Applications
Keywords: Lignin, Photocatalysis, Valorization, HAT

The sustainable valorization of lignin remains a central challenge in the transition toward renewable chemical feedstocks. A photocatalytic strategy for the selective depolymerization and functional upgrading of lignin under mild conditions is presented. This methodology relies on hydrogen atom transfer (HAT) catalysis to promote the selective cleavage of β-O-4 linkages, the most abundant structural motif in lignin, through the generation of reactive radical intermediates.

Under visible-light irradiation, controlled lignin fragmentation is achieved, affording well-defined aromatic monomers without the need for harsh reagents or conditions. Gram-scale reactions using organosolv lignin demonstrate the practical applicability of the system, delivering vanillin in synthetically relevant yields. In parallel, the process produces functional oligomeric fractions that act as effective bioplasticizers, significantly improving the mechanical properties of polylactic acid (PLA).

Beyond depolymerization, interception of the in situ generated radical intermediates enables access to a diverse array of value-added chemicals, including commodity building blocks and pharmaceutically relevant scaffolds. This dual reactivity highlights lignin as a versatile platform not only for aromatic monomer production but also for direct synthetic diversification.

Overall, this work underscores the potential of photocatalytic radical chemistry to transform lignin from a recalcitrant waste polymer into a tunable feedstock for the sustainable synthesis of high-value molecules

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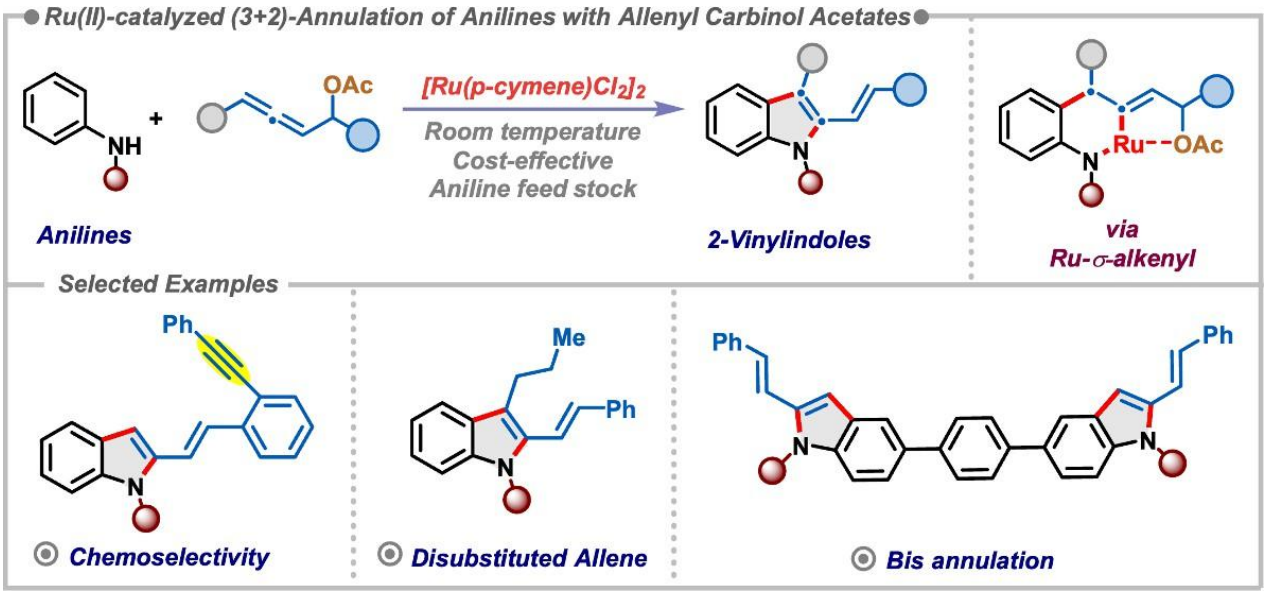
P5: Ru(II)-Catalyzed Regioselective (3+2)-Annulation of Anilines with Allenyl Carbinol Acetates to Access 2-Vinylindoles

Om Prakash Dash (1)

(1) IIT Bombay

Subject area: Sustainable and Green Photochemical Applications
Keywords: Allene, 2-vinylindole, photophysical studies, C-H activation

We report a cost–effective Ru(II)–catalyzed regioselective (3+2) annulation of readily available anilines with allenyl acetates for the efficient synthesis of biologically relevant 2–vinylindole scaffolds under mild conditions at room temperature. The developed protocol proceeds through a key Ru–alkenyl intermediate, an elusive species in C–H activation reactions involving allenyl acetates, providing new mechanistic insight into allene functionalization. The transformation exhibits broad substrate scope and excellent regioselectivity, enabling the rapid construction of a diverse library of 2–vinylindole derivatives from commercially available starting materials in good to moderate yields. The synthetic utility of the methodology was further demonstrated through gram–scale synthesis, late–stage functionalization of complex natural product derivatives, and diverse downstream transformations of the vinylindole products. Furthermore, photophysical investigations of selected products revealed promising optical properties, highlighting the potential of these compounds as functional molecular scaffolds in addition to their synthetic and medicinal relevance.



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P6: Ionic Microenvironment Engineering of Carbon Nitrides Enables Proton-Coupled Oxygen Reduction to Hydrogen Peroxide

Luis Fernando Guimarães Noleto (1), Ivo Freitas Teixeira (2), Christian Mark Pelicano (1)

(1) Max Planck Institute of Colloids and Interfaces, (2) Federal University of São Carlos

Subject area: Sustainable and Green Photochemical Applications
Keywords: Poly(heptazine imide) (PHI); Cation exchange; Ionic microenvironment; Photocatalytic H2O2 production

Photocatalytic hydrogen peroxide (H_2O_2) production via the selective two-electron oxygen reduction reaction ($2e^-$ ORR) offers a sustainable alternative to the energy-intensive anthraquinone process. Crystalline poly(heptazine imides) (PHIs) are promising photocatalysts owing to their ordered ionic framework and exchangeable cations, yet engineering of their ionic microenvironment remains largely unexplored. Herein, we report a post-synthetic cation-exchange strategy to introduce trace amounts of Al^{3+} into crystalline Na-PHI while preserving its structural integrity. Comprehensive structural and spectroscopic characterization confirmed successful Al incorporation without framework reconstruction, while revealing subtle electronic polarization of the PHI network. The optimized catalyst, containing only 0.23 wt% Al, exhibited a six-fold enhancement in H_2O_2 production compared with pristine Na-PHI, reaching 10.98 mmol L^{-1} after 1 h under 427 nm irradiation without cocatalysts and maintaining excellent long-term stability (>70 mmol L^{-1} after 24 h). UV-Vis, photoluminescence, electrochemical impedance, and photocurrent measurements demonstrated enhanced charge separation and interfacial charge transfer, whereas TG-MS revealed stronger water-framework interactions following Al exchange. Electrochemical ORR measurements showed that Al incorporation shifts oxygen reduction toward the selective two-electron pathway for H_2O_2 formation, while radical trapping and EPR spectroscopy confirmed the participation of oxygen-derived intermediates. These findings demonstrate that trace multivalent cation exchange effectively engineers the ionic microenvironment of crystalline PHIs, providing a complementary strategy to conventional electronic structure engineering for the rational design of highly efficient photocatalysts for sustainable H_2O_2 production.

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P7: Supramolecular Light-switchable Triazole Hosts for Photoadaptive Anion Binding

Yannik Steinberg (1), Alisa Kondrateva (1), Monika Schönhoff (1), Olga Garcia Mancheño (2)

(1) University of Muenster, (2) University of Rostock

Subject area: Sustainable and Green Photochemical Applications
Keywords: Photoswitches, Adaptiv Systems, Anion Binding

While responsive materials are well-established[1], the development of truly adaptive materials remains a formidable challenge. Achieving adaptivity is essential for the evolution of intelligent materials capable of information processing[2], offering a potentially greener and more sustainable alternative to existing technological frameworks. Due to its precision and versatility, light is an ideal trigger[3], driving the development of photoswitchable hosts for anionic guests[4].

Hereby, we present our latest results on the development of photoadaptive supramolecular anion binding hosts. We aim to engineer host structures that achieve a high degree of binding contrast between *E* and *Z* isomers, thereby enabling adaptive behavior in anion binding that can be photochemically controlled. Expanding on our previous work in anion binding catalysis with supramolecular tetrakistriazole-based hosts[5], we focus on photoswitchable architectures with a central switching unit which allows for the precise, light-driven regulation of reactivity. Systematic in situ NMR titration studies were employed to evaluate the influence of various structural motifs on host performance, with the most promising results yielded by an arylazopyrazole switch paired with a 1,3-phenyl linker. Furthermore, cyclic azobenzene derivatives will be also presented. They exhibit reversed thermodynamic stability compared to conventional systems, positioning them as compelling candidates for the realization of a genuinely photoadaptive system.

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P8: Merging Deep Eutectic Solvents and $FeCl_3$ LMCT Photochemistry for Sustainable Decarboxylative Giese Type Couplings

Alejandro Cores (1), Diego J. Ramón (1), Xavier Marset (1), Gabriela Guillena (1)

(1) Universidad de Alicante

Subject area: Sustainable and Green Photochemical Applications
Keywords: Deep Eutectic Solvents, Decarboxylation, Photochemistry, Sustainability, LMCT

The development of sustainable synthetic methodologies aligned with the Sustainable Development Goals and Green Chemistry principles has become a priority in organic synthesis, particularly in medicinal chemistry. In this field, the extensive use of volatile organic solvents, precious metal catalysts, and energy-intensive reaction conditions poses significant environmental challenges.[1] Among the emerging sustainable alternatives, photochemical transformations performed in eutectic mixtures have attracted considerable attention due to the tunability, low toxicity, safety, and renewable nature character. In addition, light represent a clean, inexpensive, and efficient energy source for promoting a broad range of chemical transformations.[2,3] In parallel, iron has emerged as an attractive substitute for precious metals owing to its natural abundance, low cost, and reduced environmental impact.[4] Herein, we report a sustainable, base-free decarboxylative Giese-type reaction enabled by $FeCl_3$ ligand-to-metal charge transfer (LMCT) in deep eutectic solvents. The sustainability of the methodology was evaluated using green metrics and benchmarked against conventional protocols. The results revealed substantial improvements in both environmental performance and overall process efficiency.

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P9: Towards photoactive Cu(I) coordination compounds for light-driven applications

Ragavan Rajendran (1)

(1) KTH Royal Institute of Technology

Subject area: Sustainable and Green Photochemical Applications
Keywords: Cu(I) coordination compounds, Redox-active imide ligands, Photocatalysis

Cu(I)–based coordination compounds have attracted growing interest as photoactive materials owing to their tunable electronic structures, excited–state behaviour and potential applications in photochemistry and photocatalysis. Here, we report the investigation and structural characterization of Cu(I) coordination compounds derived from redox–active imide–based chromophores. These ligands exhibit strong visible–light absorption, tunable redox properties and facilitate photoinduced electron transfer.

Imide–based chromophores, including phthalimide, pyromellitic diimide, perylene diimide and related derivatives possess electron–deficient π–systems that stabilize charge–separated states. Their incorporation into Cu(I) coordination compounds combines the light–harvesting properties of the ligands with the coordination versatility of Cu(I) centers.

Seven imide–based ligands have been synthesized and characterized, and their reactions with Cu(I) iodide have yielded new coordination compounds. Varying the CuI to ligand stoichiometry produces distinct crystalline phases, with powder X–ray diffraction confirming the formation of unique coordination architectures.

These results highlight the potential of redox–active imide ligands for constructing structurally diverse Cu(I) photoactive materials. Future work will correlate structure with photophysical properties and evaluate the photocatalytic performance of these compounds in visible–light–driven transformations.

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P10: Photophysics of TADF push-pull naphthalimide derivates for advanced bioimaging and optoelectronics

Virginia Trotti (1), Pietro Mancini (1), Rajneesh Misra (2), Benedetta Carlotti (1)

(1) University of Perugia, (2) Indian Institute of Technology (IIT)

Subject area: Sustainable and Green Photochemical Applications

In response to the growing demand for efficient, heavy-metal-free organic compounds for biological, photocatalytic and optoelectronic applications, novel potential TADF push-pull systems are investigated.

These molecules consist of electron-donating and electron-accepting units connected through a π-bridge in different configurations. This structural motif gives rise to unique optical properties due to their excited-state dynamics, generally involving the formation of ICT states[1], which make these systems particularly attractive for a wide range of applications. Very high fluorescence quantum yields were observed, with some dependence on the medium, reaching values close to 100% in certain cases. However, significant triplet production was also detected even in cases where the fluorescence was very efficient. In fact, the photophysical behavior of TADF dyes is governed by efficient RISC between singlet and triplet excited states enabled by a small singlet tripletenergy gap (ΔEST)[2]. Ns-TA measurements and gated emission measurements at 77 K have verified the population of the triplet excited state and the small ΔEST. Furthermore, through long-scale time-resolved singlet photon counting experiments both the prompt and delayed fluorescence components were detected. Fs-TA spectroscopy provided insight into ISC and ICT processes, while fs TPEF measurements highlighted the nonlinear optical properties relevant for two-photon microscopy.

The obtained results are promising for the applicability of these materials in the optoelectronic and biological field, where the ability to populate triplet states makes them suitable for photodynamic therapy (PDT), while their delayed fluorescence can be exploited for time-resolved luminescence imaging (TRLI). Finally, their long-lived excited states and strong redox potentials will be explored for photocatalytic applications.

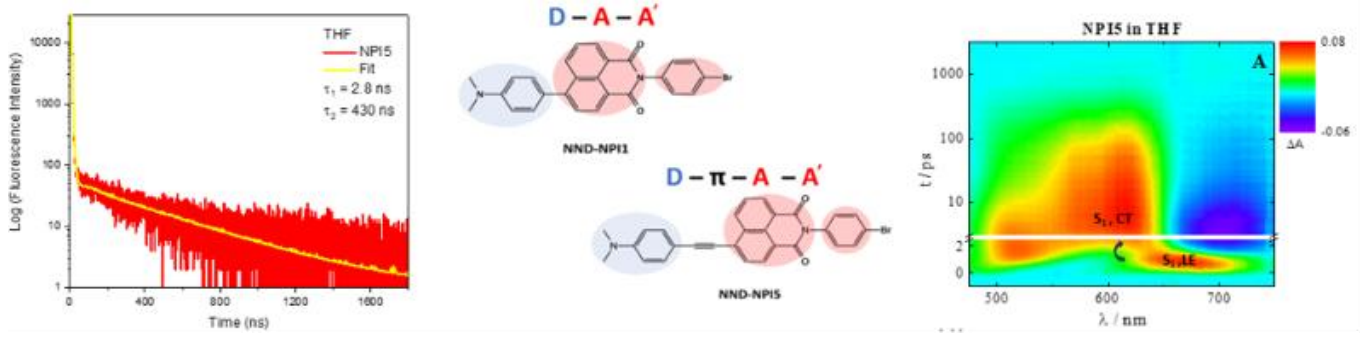

Figure 1. Left: fluorescence decay kinetics recorded by TCSPC for NPI5 in THF. Right: fs-TA for NPI5 in THF.

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P11: Advanced Oxide Ceramic Nanofibers: From Needleless Electrospinning to Photocatalytic Environmental Remediation

Iván Shepa (1), Erika Múdra (1), Kateryna Nemesh (1), Alexandra Kovalčíková (1), Veronika Kuchárová (2), Richard Smolko (2), Maksym Lisnichuk (1), František Kromka (1), Saeed Sajjadi (3), Surjyakanta Rana (3), Michal Žitňan (3), Marzieh Ghadamyari (3), José Velázquez (3), Dušan Galusek (3)

(1) Institute of Materials Research, Slovak Academy of Sciences, Watsonova 47, 040 01 Kosice, Slovak Republic, (2) Institute of Experimental Physics, Slovak Academy of Sciences, Watsonova 47, 040 01 Kosice, Slovak Republic, (3) Centre for Functional and Surface Functionalized Glass, Alexander Dubček University of Trenčín, Študentská 2, 911 50 Trenčín, Slovakia

Subject area: Sustainable and Green Photochemical Applications
Keywords: Needleless electrospinning, Oxide ceramic nanofibers, High-entropy ceramics, Nanofibers, Nanophotocatalysts.

One-dimensional ceramic nanofibers are highly sought after for functional applications due to their exceptional porosity, high surface-area-to-volume ratio, and mechanical strength. This work describes a scalable fabrication route utilizing high-throughput, reactive, needle-less electrospinning from polymer-precursor blends, bypassing conventional sol-gel steps to reduce the preparation times. The precursor blend composition critically governs the fiber morphology; reducing the metal precursor concentration smoothly transitions the structures from round to ribbon-like shapes. Post-spinning processing converts these pre-ceramic precursors into crystalline ceramics. Conventional calcination in air at temperatures up to 600 °C successfully yields pure, carbon-free oxides such as TiO_2, ZnO, and Nb_2O_5.

This versatile approach is extended to complex multi-element transition metal systems (Ti, Zr, Hf, Nb, Ta), producing single-phase or dual-phase high-entropy ceramics ($TiZrHfNbTaO_{11}$). The photocatalytic viability of these systems—either as high-entropy configurations or as TiO_2 nanofibers modified with green-synthesized noble metal (e.g., Ag, Au) nanoparticles—was evaluated through the degradation of model organic pollutants (including dyes and emerging antibiotics) under both UV and visible light irradiation. Mineralization pathways and reaction intermediates were comprehensively identified via UV-Vis spectrophotometry and HPLC. This combination of lattice-distortion effects in high-entropy structures or noble metal modification with high-aspect-ratio architectures demonstrates an exceptionally active platform for advanced environmental remediation.

This work was supported by the Scientific Grant Agency of the Ministry of Education, Science, Research and Sport of the Slovak Republic and the Slovak Academy of Sciences, project No. VEGA 2/0106/26. Funded by the EU Next Generation EU through the Recovery and Resilience Plan for Slovakia under the project No. 09I03-03-V04-00579.

P12: Simplicity by design. Sustainable late-stage functionalization of peptides, amino-acids and alcohols through the Zimmerman-O'Connell-Griffin (ZOG) reaction

Sara Bacaicoa, Yanira Pérez-Almarcha, Mario Martos (1), Wilma Y. Graf, Ganesh H. Shinde, August Runemark, Henrik Sundén

(1) University of Gothenburg

Subject area: Sustainable and Green Photochemical Applications
Keywords: ZOG reaction, late-stage functionalization, visible light, sustainable photochemistry

The development of late-stage functionalization protocols is one of the main fields of research within organic and medicinal chemistry, targeting the modification of bioactive molecules with functional units, linkers or warheads. Given the relative complexity and reactivity of the molecules of interest, his process is rarely straightforward, often requiring protection-deprotection steps and strenuous purification protocols.1 In this work, we present our findings on the late-stage functionalization of nitrogen and oxygen-containing biomolecules through the Zimmerman-O'Connell-Griffin (ZOG) reaction. This transformation involves the visible-light induced rearrangement of dibenzoylethylene derivatives into highly reactive ketene species that can be trapped by nucleophiles.2,3 The whole process takes place in the absence of photocatalysts or additives in environmentally friendly ethyl acetate as a solvent, with few to no byproducts and often not requiring chromatographic purification. We have successfully applied this strategy to unprotected heterocycles, aminoacids and peptides, observing full selectivity towards N-functionalization with excellent sustainability metric scores (E-factor, AE, SF, RME, EcoScale).4 Alcohols are also well tolerated, including aromatic substrates and N-hydroxycarbamates, with a marked preference for primary alcohols. Current work focuses on a dual wavelength strategy to enhance reaction rates and adaptation to flow conditions.

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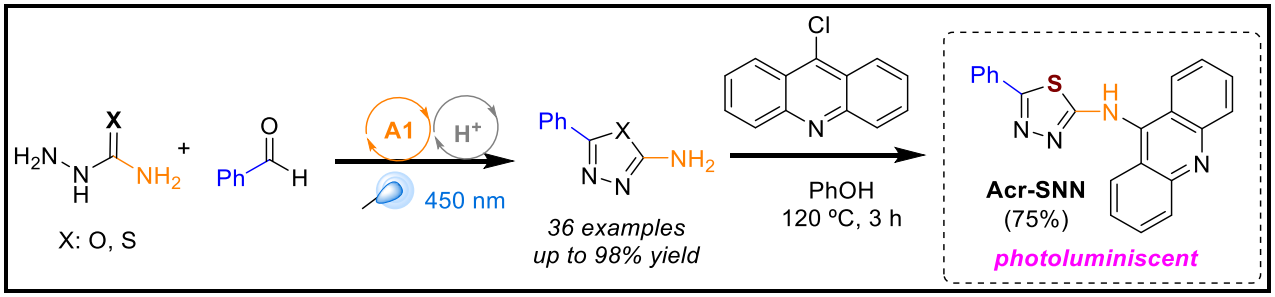
P14: Direct Photocatalytic Synthesis of 1,3,4-Oxa(thia)diazoles from aldehydes and (thio)hydrazides

Nuria Soler-Segura (1), Beatriz Quevedo-Flores(1), Jose C. Gonzalez-Gomez (1), Irene Bosque (1)

(1) Instituto Universitario de Síntesis Orgánica, Universidad de Alicante

Subject area: Photocatalytic organic transformations
Keywords: Photocatalysis, Visible Light, Acridine, 1,3,4-Oxadiazole, 1,3,4-Thiadiazole.

1,3,4-Oxadiazoles and their structural counterparts, 1,3,4-thiadiazoles, are crucial heterocyclic building blocks widely found in nature and in biologically active compounds.[1,2] Herein, we describe a simple, operationally straightforward photocatalytic strategy for the synthesis of 1,3,4-oxadiazoles and thiadiazoles using the acridine derivative 9-(2-chlorophenyl)acridine (**A1**) as a pre-photocatalyst (Scheme 1).[3] Photophysical and electrochemical studies, including Stern-Volmer quenching analysis, quantum-yield measurements, radical-trapping experiments, cyclic voltammetry, and control reactions, validate the proposed mechanism. To demonstrate its synthetic utility, we applied this photocatalytic protocol to the concise synthesis of an acridine-based heterocyclic derivative (Acr-SNN) for materials science.



Scheme 1

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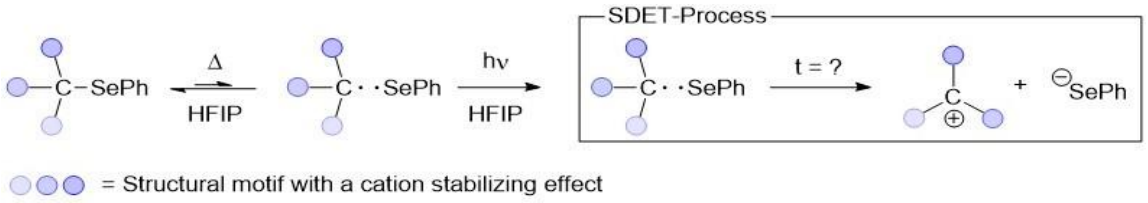
P15: Atypical SN1 Reactions at Carbon Enabled by σ-Bond Quantum Poling

Markus Seidl (1), Alexander Breder (1)

(1) University of Regensburg

Subject area: Mechanistic studies in photo- and bio-catalysis
Keywords: Quantum poling, SDET, Photochemistry, radical clocks



In classical S_N1 reactions, the heterolytic cleavage of polarized σ-bonds – typically between carbon and electronegative groups such as halides or sulfonates – leads to ion pair intermediates.[1] In contrast, homopolar bonds like C–Se (EN = 2.55 for both atoms) lack this intrinsic polarization and preferentially undergo homolysis under thermal or photochemical conditions, yielding radical pairs.[2] Conventional methods to induce heterolysis in such systems rely on stoichiometric activation of selenium, often at the expense of chemoselectivity.[3]

We report a conceptually distinct approach in which C–Se bond cleavage is directed via sequential modulation of the substrate's electronic and vibrational states. Initial thermal homolysis generates a neutral radical pair, followed by selective photoexcitation of the selenium-centered radical. This triggers a stimulated doublet–doublet electron transfer (SDET) from the carbon-centered donor to the selenium acceptor, resulting in net heterolysis and formation of an ion pair from homopolar precursors.[4] The characteristic timescales of the SDET process have previously been determined by transient absorption spectroscopy using photothermally generated radicals. To provide synthetic validation, a series of radical clock substrates was employed. These radical clocks also offer insight into the relevant timescale of the SDET when initiated via thermophotonic activation. The obtained results support the proposed timing of the electron transfer and confirm the occurrence of SDET within distinct, experimentally resolvable temporal regimes. This method enables S_N1-type reactivity in substrates traditionally restricted to homolytic pathways, offering new avenues for selective bond activation via internal excitation control.

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P16: Net heterolysis of homopolar and symmetric σ-bonds via thermophotonically controlled internal poling

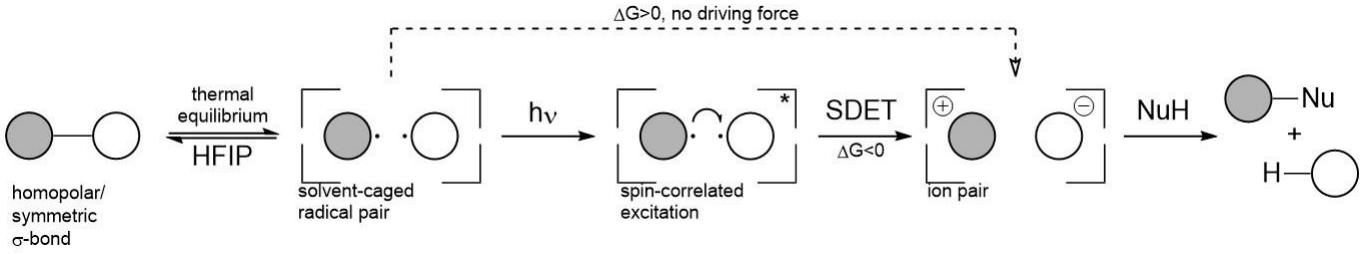
Breder Alexander (1), Tiefel Anna (1), Zunhammer Georg (1)

(1) Universität Regensburg

Subject area: Mechanistic studies in photo- and bio-catalysis
Keywords: SDET Photochemistry Excited States Reaction mechanisms

The differentiation between heterolysis and homolysis of σ–bonds is usually predetermined by their surrounding molecular environment. That is, the symmetry of the molecule across the bond, the electronegativity or polarity of the bond constituents, or external influences. In the absence of catalysts or additives, the course of a bond cleavage is determined by the intrinsic properties of the molecule.

As ion pairs are key reactive intermediates in organic synthesis, their formation is limited to either an inherently polarized bond or to the use of external polarizing activators. As a counter–design, our group developed a method for the net heterolytic fission of homopolar σ–bonds, using two separate but correlated activation steps (Fig. 1).[1]



1)Homolytic cleavage of a homopolar or symmetric σ–bond. 2) Photochemical excitation of the solvent–caged, geminate radical pair to induce an electron transfer in the geminate stage to form an ion pair.

Whereas a single–step heterolysis of homopolar bonds is thermodynamically unfavorable (ΔG>0), the electron transfer within the geminate radical pair becomes exergonic (ΔG<0) after homolysis and photoexcitation.[2] Since the two radical fragments are (for symmetric bonds) electronically equivalent in their ground doublet states, the driving force allowing an otherwise symmetry–forbidden electron transfer is provided by a photon. This by–chance promotion into an excited doublet state gives rise to the term stimulated doublet–doublet electron transfer (SDET). This novel paradigm is illustrated in the net heterolysis of symmetric Se–Se bonds and homopolar, heteronuclear C–Se bonds, enabling broad synthetic applications, such as lactonization of β,γ–unsaturated carboxylic acids, atypical SN1–type reactions, and Friedel–Crafts alkylations.[1] The concept of state–directed charge distribution (i.e. internal poling) may be applicable to any geminate radical pair in which two fragments differ in their excited–state electron affinities.

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P17: Modelling of hemithioindigo-based photoswitches across scales

Elias Harrer (1), Carolin Müller (2), Dirk Zahn (2)

(1) Friedrich-Alexander-Universität Erlangen-Nürnberg, CCC, (2) CCC, Friedrich-Alexander-Universität Erlangen-Nürnberg

Subject area: Mechanistic studies in photo- and bio-catalysis
Keywords: photoswitches, computational chemistry, molecular dynamics

In the realm of nanotechnology and molecular engineering, photoswitches play a key role as structural elements converting light into mechanical work. In particular, switchable chromophores embedded in complex molecular environments – such as molecular machines and self-assembled monolayers on surfaces – offer unique opportunities for the precise control of material properties and molecular motion. [1] A relatively new but emerging class of photoswitches is based on hemithioindigo (HTI) chromophores, which feature high thermal bistability, bright absorption bands in the visible region of the electromagnetic spectrum, and chemical durability. Upon photon absorption, HTIs readily undergo double bond isomerization, resulting in the formation of either Z- or E-isomers. By using HTI photoswitches as core structures, future photoresponsive (nano) devices are accessible via HTI functionalization to tailor the light-induced motion, aggregation, and self-assembly on substrate surfaces. [2]

Excited state dynamics simulations are powerful tools to investigate the photoinduced processes in individual photoswitchable molecules. [3–5] However, in most light-responsive devices, the motion of the photoswitch is strongly coupled to a complex environment – e.g. explicit solvent shells or ensembles of photoswitches – requiring an atomistic treatment of 1000s of molecules paired with ns-scale dynamics. While this presents a significant challenge for fully ab initio treatment, an approximate approach involves multiple molecular mechanics models, each describing a separate electronic state under consideration. [6] Here, we present an adaption of this methodology to the widely employed HTI chromophors. For this, we revisit the static theoretical description of the excited states of HTI model systems [7–8] using high-level calculations. The multi-state molecular mechanics are demonstrated for photoswitches in highly complex environments such as self-assembled monolayers.

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P18: From sequence to mechanism in light-activated proteins through structure-based discovery and photostate-aware classical molecular dynamics

Pedro Ribeiro Faria (1), Douglas Lopes Borges (1), Arthur Wakim Enrici (1), Douglas Weber (1), Eduardo Crespi Souza Rocha (1), Awana da Silva Lima (1), Leticia M. Zanphorlin Murakami (1), Célio Cabral Oliveira (1)

(1) The Brazilian Center for Research in Energy and Materials (CNPEM)

Subject area: Mechanistic studies in photo- and bio-catalysis
Keywords: photobiocatalysis; microbial rhodopsins; fatty acid photodecarboxylase; molecular dynamics; protein discovery; photostability

Light-driven microbial proteins are promising green biocatalysts, from rhodopsin ion pumps driving light-gated ATP synthesis in vivo[1] to algal FAD-binding photoenzymes turning fatty acids into biofuel hydrocarbons[2]. Yet discovering them, purifying transmembrane pumps, and stabilizing soluble photoenzymes under variable light, temperature and pH remain major bottlenecks. Here we combined in silico strategies, from state-aware modeling to photostate-aware molecular dynamics (MD), with bench biophysics to guide and explain wet-lab work on two light-activated proteins. Structure-based mining and deep-learning/metagenomic prediction of absorption and stability clustered to nominate proton-pump candidates. A lead expressed at high yield in E. coli, pumped strongly under green light in vivo as predicted, and, after guided purification, was monodisperse in digitonin micelles, 12 nm by SEC/DLS. Its predicted pentamer was confirmed by electron microscopy; storage stability exceeded the ultrastable Tara76[3], thermostability by circular dichroism matching it above 90 °C. Secondary carotenoid chromophores[3,4] broadened absorption and raised activity under blue, green and white RGB light, MD resolving the drivers. Our group also identified new photostable FAPs from red algae whose photostability, the main bottleneck for FAD-based oxidoreductases, exceeds green-algal reference CvFAP. Evolutionary and structural analysis with condition-matched MD traced this to substrate-tunnel selectivity blocking water and oxygen from the flavin: the green-algal enzyme showed ~2× higher throughput, a wider bottleneck, more frequent, longer-lived pocket water in its main tunnel. A divergent gate on that tunnel drove red-algal selectivity and photostability while keeping broad scope, validated by site-directed mutagenesis. Finally, pairing multifeature discovery and biophysics with in silico tools establishes pipelines to dissect light-driven biocatalysts for sustainable light-powered aviation fuels.

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P19: Stereodynamism in Pentacoordinate Al(Salen) (Photo)Catalysts

Emanuel Studer (1), Walter R. Linke (1), Mia A. Müller (1), Constantin G. Daniliuc (1), Michael Ryan Hansen (1), Johannes Neugebauer (1), Ryan Gilmour (1)

(1) Universität Münster

Subject area: Mechanistic studies in photo- and bio-catalysis
Keywords: Asymmetric Photocatalysis; Al(Salen) Photocatalysis; Stereodynamism; Mechanistic Investigations; Helical Chirality

Owing to their ability to simultaneously regulate reactivity and selectivity over a wide range of transformations, M(Salen) complexes are considered to be "privileged" scaffolds in ground-state asymmetric catalysis,[1] and Al(Salen) complexes have most recently emerged as powerful contenders in asymmetric photocatalysis.[8–13] Their ease of preparation and synthetic modification provide handles for the fine-tuning of photophysical and catalytic properties.[14] In contrast to contemporary designs, transfer of stereochemical information from catalyst to substrate proceeds in the absence of precision-binding motifs. Hence, establishing stereochemical models is essential for guiding future innovations for the application and evolution of these highly dynamic structures. The interdisciplinary analysis of Jacobsen's Al(Salen)Cl by manners of dynamic NMR (^{1}H, ^{13}C, ^{19}F, line-shape analysis), solid-state (^{27}Al MAS NMR) and computational (DFT) investigations reveals unprecedented insight into the dynamic stereochemistry of these chiral operators in-solution: Pentacoordinate metal centers populate the spectrum between square based pyramidal (sbp, $\tau = 0$) and trigonal bipyramidal (tbp, $\tau = 1$) coordination geometries: This was shown to govern the sense of helicity (*P*/*M*) in Al(Salen) complexes, where a critical flip in helicity is predicted at the diagnostic Addison parameter $\tau = 0.15$. Mechanistic investigations further suggest a halide-catalyzed interconversion of stereoisomers proceeding via an associative interchange (I_A) mechanism. Contrary to established models, inversion of helicity proceeds with retention of backbone conformation, which gives rise to pseudo-enantiomeric diastereomers (*R*,*R*-(*M*); *R*,*R*-(*P*)) for the popular 1,2-*trans*-diamino backbone. The presence of helical diastereomers with orthogonal helicity naturally invokes a Curtin-Hammet scenario and converges on a revised stereodynamism model for pentacoordinate Al(Salen) complexes.

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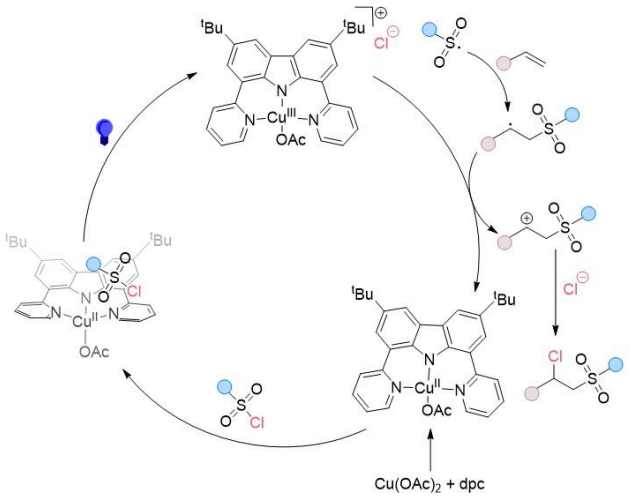
P20: Advanced Spectroscopic Insights into an Unconventional Cu(II)/Cu(III)-Driven ATRA Pathway for Chlorosulfonylation of Alkenes

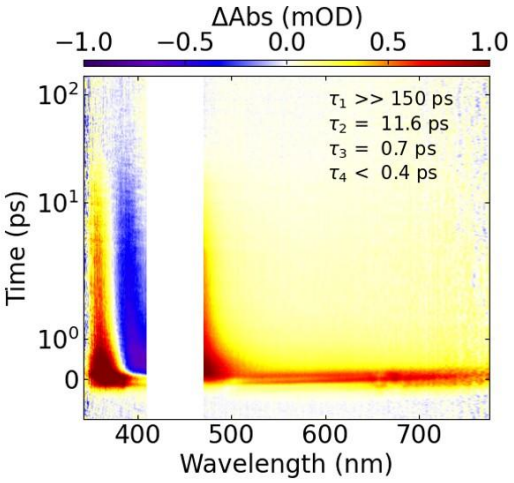
Max Schadenfroh (1), Isabell Reinberger (1), Patrick Nuernberger (1), Oliver Reiser (1)

(1) Universität Regensburg

Subject area: Mechanistic studies in photo- and bio-catalysis

Photocatalytic atom transfer radical addition (ATRA) reactions are conventionally governed by Cu(I)/Cu(II) redox cycles.[1] In the present study, however, we demonstrate that the structurally rigid complex Cu(dpc)OAc (dpc = 3,6-di-tert-butyl-1,8-di(pyridin-2-yl)-9H-carbazol) [2] enables an alternative photocatalytic pathway operating through a Cu(II)/Cu(III) manifold. Central to this reactivity is the enforced planar geometry of the ligand scaffold, which effectively suppresses the flattening distortion typically associated with photoexcited copper complexes.[3] Using alkene chlorosulfonylation as a representative ATRA transformation, we further establish that preorganization of the Cu(II) catalyst with the sulfonyl reagent is essential for both initiation and maintenance of the catalytic cycle. The existence of this preassembled complex is substantiated by complementary transient absorption spectroscopy on fs to ns an ms timescales, fluorescence studies, and quantum-chemical calculations. Upon photoexcitation, the preorganized complex undergoes homolytic activation to generate a highly reactive Cu(III) intermediate alongside a sulfonyl radical. The Cu(III) species was characterized through a combination of spectroelectrochemical measurements, irradiation experiments, and computational analysis. Subsequent addition of the sulfonyl radical to the olefin substrate, followed by single-electron transfer, regenerates the Cu(II) catalyst while simultaneously producing a carbocationic intermediate. Trapping of this intermediate by chloride furnishes the corresponding ATRA product. Collectively, these findings establish a previously underexplored Cu(II)/Cu(III) photocatalytic framework for ATRA-type transformations and provide mechanistic insight into how ligand-imposed geometric constraints can fundamentally alter the photoredox behavior of copper complexes.





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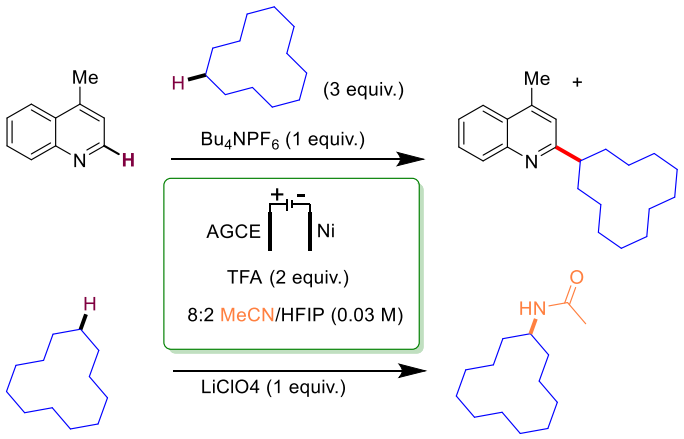
P21: Activated Glassy Carbon Electrodes for Electrochemical Heteroarylation and Amidation of Alkanes without mediators

Loris Laze, Jose C. Gonzalez-Gomez, Irene Bosque

(1) Instituto Universitario de Síntesis Orgánica, Universidad de Alicante

Subject area: Photocatalytic organic transformations

Aliphatic compounds are ubiquitous and essential building blocks across the pharmaceutical and agrochemical industries. [1] Among modern synthetic methodologies, the direct functionalization of unactivated \(\text{C(sp}^{3}\text{)--H}\) bonds offers an exceptionally efficient and selective strategy for structural modification. [2] While electrochemical oxidation has recently emerged as a premier green alternative, traditional methods often rely heavily on chemical redox mediators. To address this limitation, we developed a mediator-free electrocatalytic system for \(\text{C(sp}^{3}\text{)--H}\) functionalization via direct hydrogen atom transfer (HAT) (Scheme 1). [3] This approach utilizes a standard glassy carbon electrode electrochemically pretreated in a phosphate buffer. The resulting surface-bound oxygenated functional groups efficiently abstract hydrogen atoms from inert alkanes, driving subsequent Minisci- and Ritter-type transformations under mild conditions.



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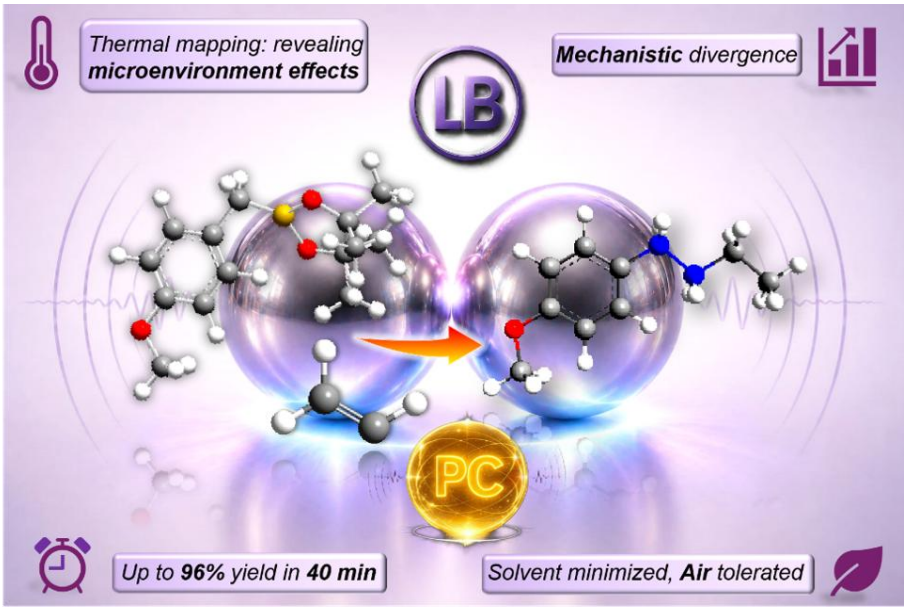
P22: Dual Ir/Lewis base Mechanophotoredox catalysis: Solvent-free Air-tolerant Giese-type Addition of Boronic esters onto Electron-Deficient Olefins

Suraksha Rajan (1), Eli Zysman-Colman (1)

(1) University of St-Andrews

Subject area: Mechanistic studies in photo- and bio-catalysis
Keywords: Mechanophotocatalysis, Mechanochemistry, Ir/LB dual mechanophotocatalysis, thermal-reaction kinetics

In this work, we report the first example of a dual Lewis Base photocatalysis reaction conducted under mechanophotocatalysis conditions, using a custom-built ball-milling photoreactor.[1,2] We investigate how mechanical agitation, temperature, and liquid-assisted grinding (LAG) each influence the reaction kinetics. Using a Giese-type coupling between alkyl boronic esters and electron-deficient olefins as a model system,[3] MeOH-assisted LAG conditions afforded near-quantitative yields of the coupled product within 40 min under aerobic conditions, compared to 24 h for the corresponding solution-state transformation. The reaction without MeOH LAG agent proceeds more sluggishly. Time-resolved infrared thermography revealed a direct correlation between reactor temperature and reaction progression under LAG agent-free mechanophotocatalytic conditions. Comparative fan-cooled and non-cooled experiments revealed a pronounced temperature dependence under LAG-free milling conditions despite the absence of any external heating source. These studies provide the first direct comparison of reaction kinetics as a function of temperature between solution-state photocatalytic and mechanophotocatalytic reactions and demonstrate that efficient dual Lewis base photoredox catalysis can be achieved under solvent-minimized mechanophotochemical conditions.



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P23: Sulfoxonium Ylides as Versatile Platforms for Photocatalytic and Electrochemical C–C Bond Formation.

Juan Salvador Dato Santiago (1), Arsala Kamal (1), Olga García Mancheño (1)

(1) Leibniz Institute for Catalysis

Subject area: Photocatalytic organic transformations
Keywords: Sulfoxonium ylides; photocatalysis; electrocatalysis; cyclopropanation; hydrogen atom transfer

Sulfur ylides (S-ylides) represent a versatile and long-standing class of reagents in organic synthesis. In particular, sulfoxonium ylides have attracted considerable attention owing to their bench stability and straightforward large-scale preparation, providing a practical and safer alternative to diazo compounds.[1] Under traditional thermal conditions, their well-established reactivity enables a wide range of transformations, including cyclizations, ring expansions and carbon-carbon bond-forming reactions, providing access to valuable motifs found in natural products.[2] More recently, sulfoxonium ylides have emerged as attractive substrates in photocatalysis, particularly through ketyl radical generation via reductive proton-coupled electron transfer (PCET).[3] In contrast, their activation through oxidative single-electron transfer (SET) to generate carbon-centered radicals remains far less explored, despite recent examples in photocatalysis and electrochemistry demonstrating valuable transformations.[4]

To address these challenges and further expand the oxidative SET reactivity of sulfoxonium ylides, we propose a photocatalyzed cyclopropanation through a radical-polar crossover (RPC) process between sulfur ylides and electron-rich alkenes under mild, additive-free, and transition-metal-free conditions. Unlike traditional methods such as the Corey-Chaykovsky reaction, which generally require electron-deficient acceptors, this approach provides access to valuable cyclopropanes. In parallel, we propose the use of these ylides as direct HAT electrocatalysts for carbon-carbon bond formation. Compared to photochemical and transition-metal-catalyzed systems, the range of direct HAT mediators available in electrochemistry remains limited and is mainly confined to oxidation reactions.[5] Furthermore, their application in carbon-carbon bond-forming processes is still underexplored, with most reported methods relying on stoichiometric or substoichiometric amounts of mediator.[6]

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P24: Selective Excitation of an Electrochemically Generated Acridine Radical Cation Enables Oxidative C–N Bond Formation

Stefano Visentini (1), Luca Dell'Amico (1), Sara Bonacchi, Elena Bassan (2), Oliver Wenger (2)

(1) University of Padova, (2) University of Basel

Subject area: Mechanistic studies in photo- and bio-catalysis
Keywords: electro-photocatalysis, mechanistic investigation,

Herein, we report the use of an acridine-derived organic catalyst for an electro-photocatalytic C-N coupling reaction between mesitylene and pyrazole. The catalytic cycle relies on the anodic oxidation of the neutral acridine derivative forming the corresponding radical cation, which is subsequently excited under visible-light irradiation [1,2]. The photoexcited radical cation displays sufficient oxidizing power to activate mesitylene (1) through single-electron transfer, enabling its subsequent coupling with pyrazole (2) to afford the desired product (3).

The mechanistic features of the process were investigated through a combination of spectroelectrochemical (SPEC), ultrafast transient absorption spectroscopy (TAS) in the femto-second time scale, and electrochemical studies (Cyclic Voltammetry, CV) in presence of light irradiation, confirming the generation and characterization of the acridine radical cation under electrochemical conditions and the quenching of the radical cation's excited state in the presence of mesitylene, proving the interaction between the excited radical cation and the substrate.

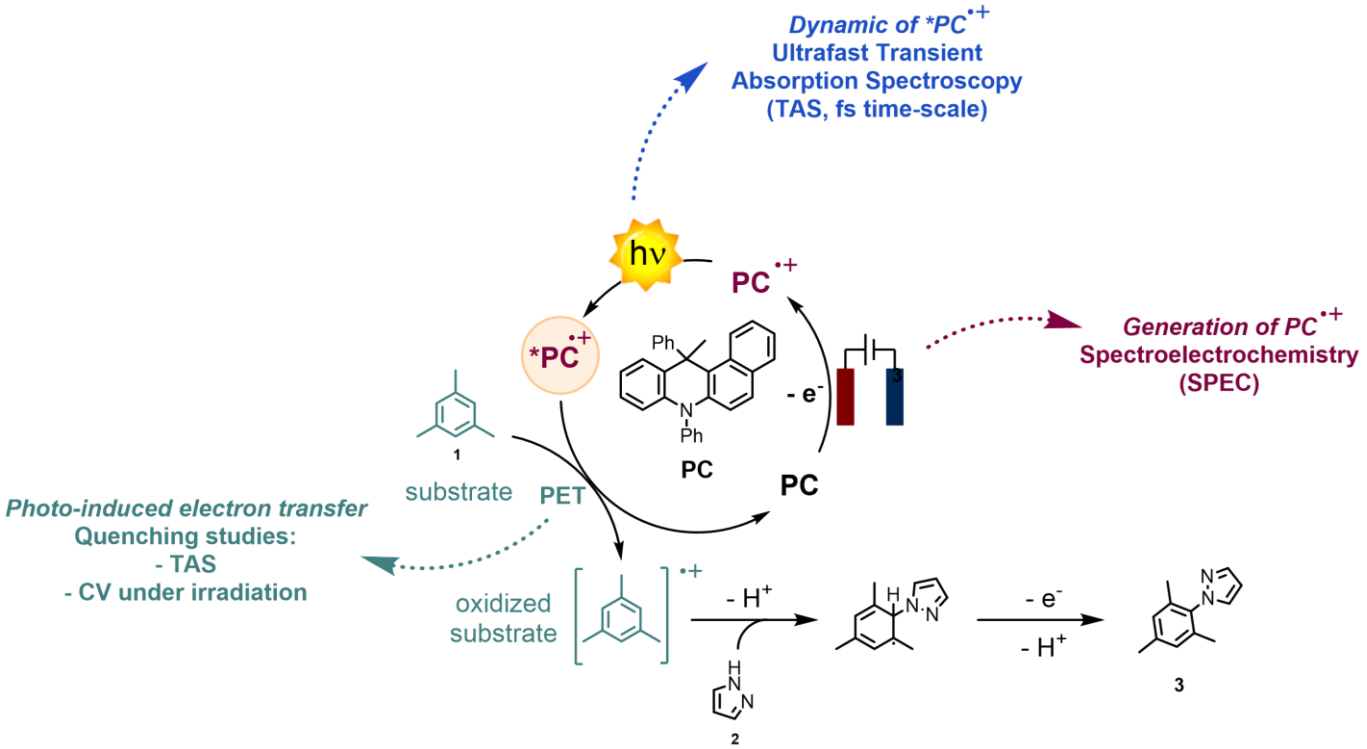

Figure 1. Electro-photocatalytic C-N coupling cycle mediated by an acridine-derived catalyst. Proposed catalytic cycle involving electrochemical generation and photoexcitation of the acridine radical cation, followed by the photo-reactivity with the substrate, and the mechanistic investigation of the critical steps of the electro-photocatalytic cycle.

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P25: Recyclable IPN Photocatalysts Supported by Polymer Matrices: From Soluble Copolymers to Core-Polymer Brush Shell Nanostructures

Elena Avanzini (1), Alessio Lobocchiaro (1), Agata Checcozzo (1), Luis Izquierdo Aranda (1), Eric Ruzicka (1), Jorge Humbrías Martín (1), Gianluca Gazzola (1), Francesca Lorandi (1), Luca Dell´Amico (1), Edmondo Maria Benetti (1)

(1) Dipartimento di Scienze Chimiche, Università degli Studi di Padova

Subject area: Hybrid Catalytic Systems
Keywords: ●IPN photocatalysts ●polymer brushes ●recyclable photocatalysis ●visible-light catalysis ●Aqueous photoredox catalysis

Isophthalonitrile (IPN)–based organic photocatalysts are powerful platforms for visible–light synthesis owing to their tunable redox properties, long–lived excited states, and thermally activated delayed fluorescence (TADF). However, their broader use is limited by difficult recovery, photochemical fragility, and poor compatibility with aqueous media. Here, we report a polymer–supported strategy that addresses these limitations by integrating IPN photocatalysts into either soluble amphiphilic copolymers or silica nanoparticle–supported polymer brushes. A library of carbazole– and diphenylamine–substituted IPN photocatalysts was synthesized, characterized, and screened in a benchmark Povarov–type cycloaddition, identifying the most active and stable candidates. These photocatalysts were converted into methacrylate monomers and copolymerized with oligo(ethylene glycol) methyl ether methacrylate by ARGET ATRP, or grafted from silica nanoparticles by surface–initiated ARGET ATRP. The soluble copolymers retained the photophysical properties and catalytic activity of the parent photocatalysts, giving high yields at low catalyst loadings, although recovery by precipitation was only moderate. In contrast, silica–supported polymer brushes preserved efficient photocatalytic performance while enabling simple centrifugation–based recovery and reuse over several cycles, with catalyst recoveries around or above 90%. The amphiphilic polymer environment further expanded IPN photocatalysis to water without additional surfactants, enabling both photoredox transformations and energy–transfer [2 + 2] cycloadditions. These results show that polymer architecture is decisive for balancing activity, recyclability, and medium compatibility, establishing polymer–supported IPN photocatalysts as practical and sustainable systems for visible–light–driven organic synthesis.

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P26: Engineering floatable Janus CNF–silane aerogels decorated with metal-doped ZnO nanoparticles for solar-driven water treatment

Andreea Laura Scutaru (1), Gabriela Biliuta (1), Raluca Baron (1), Viorica Podasca (1), Violeta Melinte (1), Madalina Elena Bistriceanu (1), Coseri Sergiu (1)

(1) Petru Poni Institute of Macromolecular Chemistry

Subject area: Hybrid Catalytic Systems

The development of sustainable photocatalytic platforms capable of operating at the air–water interface represents a promising strategy for efficient solar-driven water remediation. In this work, we propose the fabrication of floatable Janus nanocellulosic hybrid aerogels consisting of a hydrophobic photocatalytic upper layer and a hydrophilic supporting layer. The floating architecture is designed to maximize light harvesting while ensuring continuous water supply and efficient mass transfer of pollutants.

The photocatalytic layer is based on cellulose nanofibers (CNFs), vinyltrimethoxysilane (VTMS), and metal-doped ZnO nanoparticles (doped with Co, Ag or Eu). VTMS serves both as a network-strengthening agent and as an interface modifier capable of forming Zn-O-Si linkages with ZnO nanoparticles, thereby reducing particle agglomeration and promoting charge separation. The hydrophilic supporting layer is prepared from poly(vinyltrimethoxysilane) (PVTMS)-reinforced CNF aerogels, providing mechanical stability and efficient water transport.

The influence of CNF structure, silane chemistry, and ZnO composition on aerogel morphology, floatability, and photocatalytic performance will be investigated. The resulting floating assemblies will be characterized by FTIR, SEM, TEM, EDX analyses and evaluated for the degradation and mineralization of representative textile dyes under UV and visible light irradiation. The proposed Janus architecture offers a promising route toward efficient, recyclable, and sustainable photocatalytic platforms for water purification applications.

Acknowledgement

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P27: Enantioselective Organocatalytic Synthesis of Cyanocoumarins Derivatives

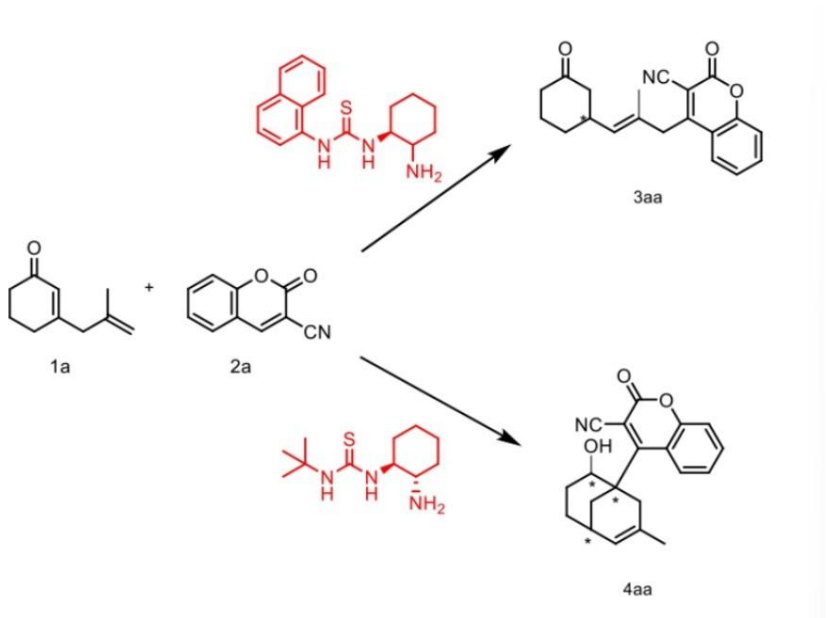
Francisca Medina-Medina (1), José Trujillo-Sierra (1), Raquel Hidalgo-León (1), José Miguel Sansano (1), Ana Sirvent (1), María de Gracia Retamosa (1)

(1) Universidad de Alicante, Carretera de San Vicente del Raspeig, S/N, 03690

Subject area: Hybrid Catalytic Systems
Keywords: coumarins, organocatalysis, bifunctional organocatalyst, enantioselective

Coumarin derivatives are prominent motifs in medicinal chemistry due to their diverse biological profiles and relevance in drug discovery. [1] As a result, the development of efficient approaches to access functionalized coumarins continues to attract considerable interest. In parallel, previous work from our group demonstrated that organocatalyzed reactions of 2,5-dienones provide an effective route to chiral spiro-fused coumarins frameworks. [2]

In the present project, it was observed that the structure of the thiourea catalyst strongly influences the reaction outcome. While the use of a naphthalene-derived thiourea leads selectively to the formation of the linear product, the tert-butyl-substituted thiourea promotes the formation of the bicyclic compound. These results underscores the key role of catalyst design in steering the reaction pathway toward distinct molecular architectures.



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P28: From Hybrid C3N4/WS2 Heterostructures to Reusable PVDF-HFP Composites: Synergistic Sonophotocatalytic Degradation of Trimethoprim

Dominika Czekanowska (1), Hugo Salazar (2), Jorge Saiz (2), Anatolijs Sarakovskis (3), Senentxu Lanceros-Méndez (2), Andrei Kholkin (3), Paweł Głuchowski (1)

(1) Graphene Energy Ltd., (2) BCMaterials - Basque Center for Materials, Applications and Nanostructures, (3) Institute of Solid State Physics, University of Latvia

Subject area: Hybrid Catalytic Systems
Keywords: sonophotocatalysis, C3N4@WS2, water remediation, trimethoprim, polymeric composites

The increasing presence of pharmaceutical contaminants in aquatic environments poses a serious challenge to ecosystem integrity and public health, creating a need for efficient and sustainable water treatment technologies. In recent years, semiconductor-based sonophotocatalysis (**SPC**) has emerged as a promising strategy for water remediation, owing to the synergistic effects arising from the combined use of light and ultrasound [1,2,3].

Herein, a series of 2D/2D **C_3N_4@WS_2** with different mass ratios (85:15, 65:35, 50:50, 35:65, and 15:85) were synthesized and evaluated for the SPC degradation of trimethoprim (**TMP**), a widely detected antibiotic pollutant. Among the investigated compositions, the **65:35** hybrid demonstrated the highest synergy factor (2.71), indicating a pronounced cooperative effect between photo- and sonocatalysis.

The enhanced performance was attributed to efficient charge separation and transfer across the C_3N_4@WS_2 heterointerface, promoting the generation of reactive oxygen species. Radical scavenging experiments identified superoxide radicals ($\cdot O_2^-$) and photogenerated electrons (e^-) as the main active species responsible for TMP degradation. For practical application, the optimal hybrid catalyst was immobilized in reusable PVDF-HFP composite films, maintaining high SPC activity while ensuring mechanical stability, easy recovery, and reusability.

Structural, optical, and electrochemical analyses (XRD, TEM, DRS, FT-IR, XPS, Raman, photocurrent measurements, and EIS) confirmed successful hybrid formation, enhanced visible-light absorption together with improved charge transfer properties.

This work introduces a reusable sonophotocatalytic platform based on C_3N_4@WS_2 heterostructures and PVDF-HFP composites for efficient removal of pharmaceutical contaminants from water. The findings provide valuable insights into the design of advanced hybrid catalysts and highlight the potential of ultrasound-assisted photocatalysis for sustainable water purification.

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P29: Alkyne-Assisted Stereospecific Skeletal Rearrangement via Non-Classical Carbocations

Rajan Kumar Kharwar (1)

(1) Technion Institute of Technology

Subject area: Hybrid Catalytic Systems

We report stereospecific nucleophilic substitutions of homopropargylic alcohols enabled by anchimeric assistance from an alkyne. Upon activation, alkyne participates generates a cyclopropylidene methyl cation, a non-classical carbocation featuring an sp-hybridized center. The rigid, bridged geometry of this intermediate governs both regio- and diastereoselectivity, promoting selective C-C bond cleavage and nucleophilic substitution at quaternary centers with a complete skeletal rearrangement. The transformation provides access to densely substituted tertiary homopropargyl fluorides with broad functional group tolerance and proceeds with efficient transfer of chirality from enantioenriched substrates.

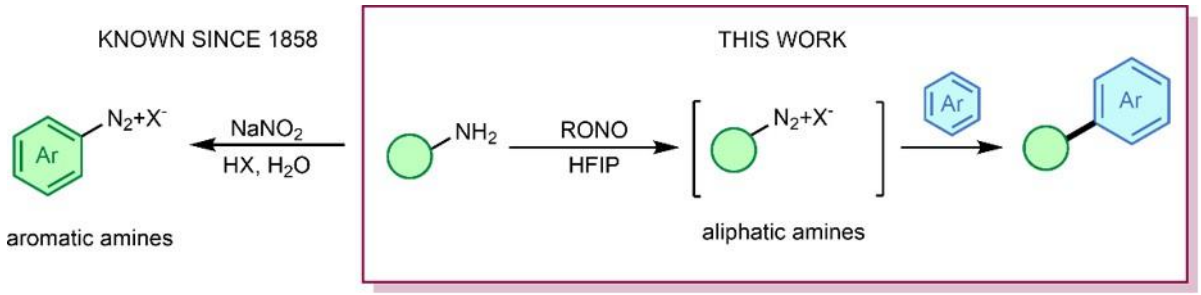
P30: Aliphatic amines unlocked as efficient carbocation precursors

Barbara Fabjanowicz (1), Jakub Durka (1), Dorota Gryko (1)

(1) Institute of Organic Chemistry Polish Academy of Sciences

Subject area: Hybrid Catalytic Systems

While aromatic diazonium salts obtained from aryl amines are important reagents in organic synthesis, 'Diazonium ions generated from ordinary aliphatic primary amines are usually useless for preparative purposes, since they lead to a mixture of products giving not only substitution by any nucleophile present, but also elimination and rearrangements if the substrate permits', as stated in an organic chemistry textbook[1]. Nevertheless, aliphatic amines are highly abundant compounds thus methodologies that would allow for their controlled activation are of high demand. Recently, we have demonstrated that the cited statement is no longer valid and diazotization of aliphatic amines can serve preparative purposes[2][2]. The key to success lies in the use of hexafluoroisopropanol as a reaction medium that enables application of these reagents as precursors of carbocations. Here, these reactive intermediates are trapped by the solvent in a less reactive state thus enabling selective reactions to take place. The diazotization process followed by subsequent acid–catalyzed alkylation of aromatic compounds enables Friedel–Crafts–type reactions in good yields.



In addition to solving a long–standing issue, the two–step sequence procedure brings several additional benefits. Given the vast availability of the amines, from natural or commercial sources, and no need for prefunctionalization, this method provides practical and scalable access to a wide variety of compounds. It allows for the generation of alkylated products involving highly destabilized carbocations, such as ones derived from aminoacids, which are inaccessible from traditionally used alkenes, alcohols or alkyl halides. Furthermore, the developed methodology is not limited to Friedel–Crafts type reactivity, other nucleophiles were successfully employed in this transformation as well. This methodology opens an avenue for reactions involving aliphatic amines via diazotization thus expanding the degree of chemical space

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P31: Expanding Light-Driven Multi-Enzyme Cascades with Novel Fatty Acid Photodecarboxylases

Eduardo Rocha (1), Leticia Zanphorlin (1), Robert Kourist (2)

(1) Brazilian Center for Research in Energy and Materials (CNPEM), (2) Technische Universität Graz (TU Graz)

Subject area: Enzyme-catalyzed organic reactions
Keywords: Photobiocatalysis Photodecarboxylases Renewables

The transition toward a sustainable bio-based economy requires efficient technologies for the production of renewable fuels and value-added chemicals. Photobiocatalysis has emerged as a promising strategy by combining the high selectivity of enzymes with light as a clean and renewable energy source. Among the known photoenzymes, fatty acid photodecarboxylases (FAPs) catalyze the blue-light-driven decarboxylation of fatty acids into hydrocarbons under mild conditions, making them attractive biocatalysts for renewable chemical synthesis. Building on the identification of novel FAPs displaying enhanced photodecarboxylation activity toward fatty acids compared with the benchmark *Chlorella variabilis* FAP (*Cv*FAP), this work investigates their application in a previously reported photobiocatalytic multi-enzyme cascade. The cascade combines an oleate hydratase (Ohy) for the regioselective hydration of renewable unsaturated fatty acids with FAP-catalyzed photodecarboxylation, enabling the synthesis of secondary fatty alcohols. By introducing these newly identified FAPs into the cascade, this study expands the available photobiocatalyst toolbox and explores their potential to improve the efficiency of light-driven multi-enzyme transformations. Preliminary GC-MS analyses confirmed the formation of the target secondary fatty alcohols using the novel FAPs, demonstrating for the first time their applicability in this photobiocatalytic cascade. Ongoing work focuses on the quantitative evaluation of cascade performance, direct comparison with CvFAP under identical reaction conditions, and the development of enzyme immobilization strategies to improve catalyst stability, reusability and operational robustness. By integrating novel photoenzymes, cascade biocatalysis, enzyme immobilization and photobioreactor engineering, this work advances the development of scalable photobiocatalytic platforms for the sustainable production of renewable chemicals.

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P32: Catalytic enantioselective [2 + 2] photocycloadditions for the dearomatization of heterocycles

Vasco Corti, Gianluca Simionato, Lorenzo Rizzo, Stefano A. Serapian, Giorgio Pelosi, Mirco Natali, Luca Dell'Amico

University of Padova, Italy

Subject area: Photocatalytic organic transformations
Keywords: Asymmetric synthesis, Photochemistry, Organocatalysis, Photocycloadditions, Dearomatizations

The direct transformation of readily available aromatic feedstocks into structurally diverse three-dimensional heterocycles makes catalytic asymmetric dearomatization (CADA) reactions[1] of broad interest, providing a sustainable and straightforward synthetic route to medicinally relevant archetypes. However, the inherent difficulty of the disruption of aromaticity demands a large energy input during the dearomatization process, which could be incompatible with the typical conditions required by asymmetric catalysis. One promising approach to overcome this issue is the investigation of the excited-state reactivity of (hetero)arenes that may display different reactivity patterns compared to the original ground-state ones.

In this contribution, the successful combination of asymmetric organocatalysis with the direct activation of visible light[2] to develop an array of interesting organocatalytic asymmetric [2 + 2] dearomative photocycloadditions of the indole core[3] is presented. This methodology[4] relies on the excited state reactivity of transiently generated catalytic intermediates, thus enabling the construction of optically active polycyclic products in high levels of yield and stereoselectivity. The scope of the reaction was explored using a broad range of alkene partners, including strained substrates such as bicyclobutanes (BCBs). In addition, the catalytic system was successfully translated to flow conditions, demonstrating promising improvements in reaction efficiency and scalability.

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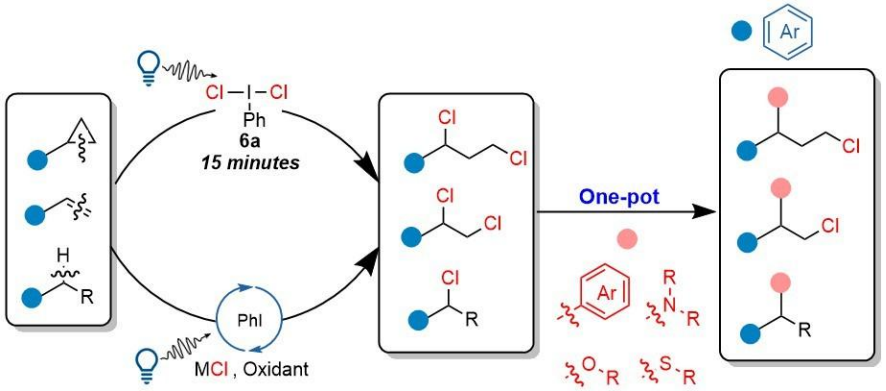
P33: Unified Photochemical Approach to C(sp³) Chlorinated Compounds from Cyclopropanes, Olefins, and C–H Bonds Using Willgerodt-Type Reagents

Tin Vu-Trung Nguyen (1)

(1) University of Medicine and Pharmacy and Ho Chi Minh city

Subject area: Photocatalytic organic transformations

C(sp³)–Cl bonds are essential intermediates in organic synthesis and are widely found in natural products and biologically active molecules.[1] Their role as versatile diversification handles underscores the need for efficient and selective chlorination strategies.[2] Herein, we report a general and practical protocol for the selective formation of C(sp³)–Cl bonds from readily available substrates, including aryl cyclopropanes, olefins, and activated C–H bonds.[3]



This transformation is enabled by the direct photoexcitation of Willgerodt-type reagents, which serve as convenient chlorine radical precursors for the transformation with π- and σ-bonds, as well as functionalizing activated C–H bonds. The reaction proceeds under mild, operationally simple conditions with short reaction times. The method demonstrates broad substrate scope and good functional group tolerance, including compatibility with commercially available drug molecules, highlighting its potential for late-stage functionalization of complex molecules. In addition to the stoichiometric protocol, preliminary studies toward an iodine(I/III)-mediated catalytic system are presented, employing abundant and inexpensive chloride salts as the chlorine source. This approach aims to further improve practicality of radical chlorination processes.

Furthermore, a one-pot telescoped protocol has been developed for the direct functionalization of benzylic chlorides with a variety of nucleophiles, including carbon-, nitrogen-, oxygen-, and sulfur-based species. This streamlined strategy eliminates intermediate purification steps and enhances overall efficiency. Notably, this approach enables rapid access to 1,1-diaryl motifs, which are key structural elements in numerous pharmacologically relevant compounds.

Overall, this work establishes a unified photochemical platform for C(sp³) chlorination and downstream diversification, providing practical tools for applications in synthetic and medicinal chemistry.

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P34: Selective C-H Bond Activation via Acridine Photocatalysis

Jose C. Gonzalez-Gomez(1), Irene Bosque (1), Loris Laze (1), Beatriz Quevedo-Flores (1), Mario Martínez (1)

(1) Instituto Universitario de Síntesis Orgánica, Universidad de Alicante

Subject area: Photocatalytic organic transformations

Extensive studies by the Larionov [1] and Dilman [2] groups have demonstrated that acridine derivatives can promote the radical decarboxylation of carboxylic acids upon irradiation at 400 nm via proton–coupled electron transfer. More recently, we discovered that protonation of the ground state of acridine photocatalysts enables their photoactivation under blue–light irradiation. Building on this finding, we developed a strategy for the selective generation of benzyl radicals through the photooxidation of toluene derivatives (Figure 1a). This activation mode was subsequently applied to a three–component coupling of toluene derivatives, aldehydes, and anilines, providing modular access to bioactive 1,2–diarylethylamines [3].
We have also developed a dual catalytic system in which pyridine N–oxide is combined with an acridine photocatalyst to facilitate hydrogen atom transfer (HAT) from otherwise unactivated C(sp^3–H) bonds (Figure 1b). This catalytic system was successfully applied to a Minisci–type reaction that proceeds without the need for sacrificial oxidants [4].
In this conference, we will present the latest advances from our research group in the development and application of acridine–based photocatalytic methods.

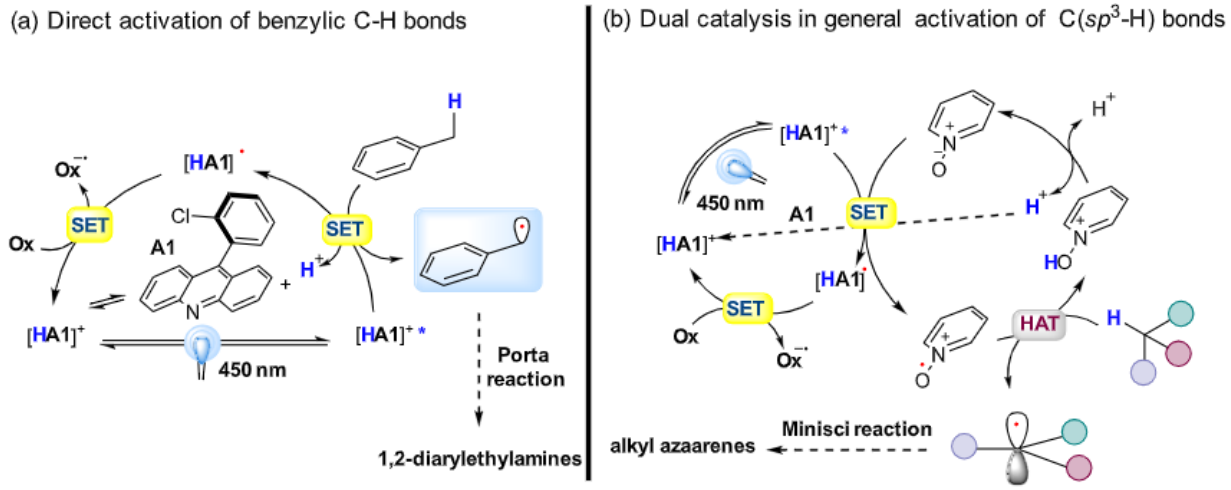

Figure 1

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P35: Exclusively Light-Induced Bidirectional Photoswitching of Norbornadiene using Perylene diimide as Photocatalyst

Simone Pintér (1), Andreas Hirsch (1)

(1) Friedrich-Alexander University Erlangen-Nürnberg

Subject area: Photocatalytic organic transformations

The norbornadiene/quadricyclane (NBD-QC) isomer couple is a well-studied photoswitch for molecular solar thermal energy storage.[1] UV irradiation converts NBD to the energy-storing, metastable QC, while regeneration of NBD with simultaneous energy release can be triggered by various stimuli. Achieving complete, on-demand energy release over many switching cycles remains a key challenge for practical deployment. We present the use of perylene diimide (PDI) as a photoactive redox catalyst to trigger energy release upon blue-light (475 nm) irradiation. As previously shown by our group, this process does not require a covalent connection between the two organic frameworks.[2] This enables an autonomously operating system solely based on organic compounds and eliminates the need for critical-metal catalysts commonly employed for the QC-to-NBD back-conversion. Crucially, on-demand activation by irradiation at longer wavelengths allows the PDI catalyst to coexist with the photoswitch without unintentionally inducing back-isomerization. We exploit this feature by investigating PDI/NBD mixtures in solution as well as in polymer matrices, targeting the optimization of interconversion performance and controllability toward applications such as coatings and domestic heating. In addition to that, we report the first fully conjugated NBD-PDI hybrid systems, in which PDI serves as the electron-accepting unit within a push-pull architecture. This design offers a promising route to strongly red-shift NBD absorption, addressing the second major challenge for NBD applications, namely the poor overlap between NBD absorption and the solar spectrum.

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P36: Photocatalitic radical cyclization of fluorinated sulfoximines for the synthesis of seven-membered heterocycles

Simone Baldon (1), Julien Paut (2), Elsa Anselmi (3), Emmanuel Magnier (4), Luca Dell'Amico (1)

(1) Università degli Studi di Padova, (2) Université Paris-Saclay, (3) Université de Tours, (4) Universit´e Paris-Saclay

Subject area: Photocatalytic organic transformations
Keywords: sulfoximine; fluorine; photoredox; cyclization

Sulfoximines have recently gained increasing popularity in pharmaceutical and agrochemical research as versatile bioisosteric replacement of different functional groups, such as sulfones and ketones.[1] On the other hand, fluorine-containing molecules are of great interest because of their significant pharmacological properties. Despite their value, the synthesis and use of cyclic sulfoximines remains largely unexplored, as well as their fluorinated variants.[2] Building on our previous studies on the photocatalytic difluorosulfoximination of olefins and propellanes,[3] we have now investigated a peculiar radical ring-closing process that grants selective access to complex seven-membered heterocyclic systems.

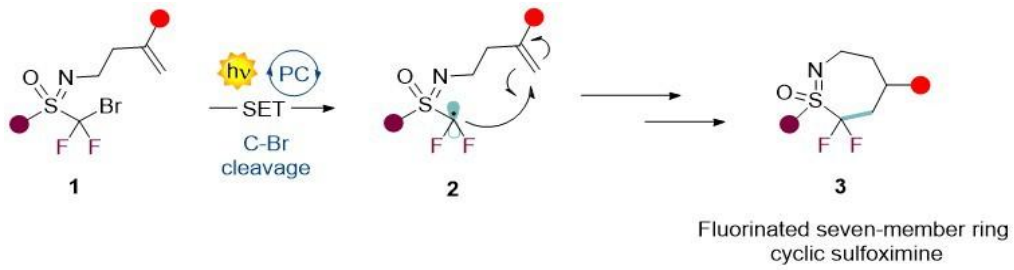

Figure 1. Photoredox synthesis of fluorinated seven-membered cyclic sulfoximines.

Here, a wide variety of seven-member cyclic sulfoximines are obtained under mild organophotoredox conditions. Using this synthetic strategy, we accessed structurally diverse cyclic derivatives **3** (25 examples, up to 88% yield), with high tolerance toward different functionalities, including halogens, amide, alkyne, etc.

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P37: Visible-Light-Initiated, Nickel-Catalyzed Aminocarbonylation of Alkynyl Iodides to 2-Ynamides

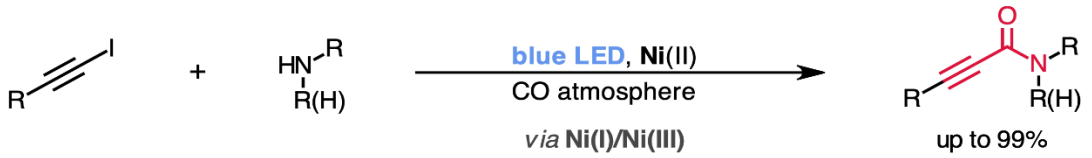
Michael Weiser (1), Alexander Frischauf (1), Berthold Stöger (2), Ertan Turhan (3), Dennis Kurzbach (3), Katharina Bica-Schröder (1)

(1) Institute of Applied Synthetic Chemistry, TU Wien, (2) X-Ray Center, TU Wien, (3) Institute of Biological Chemistry, University of Vienna

Subject area: Photocatalytic organic transformations
Keywords: aminocarbonylation, visible-light, nickel-catalysis, carbon monoxide, 2-ynamide

The development of new, broadly applicable methods for amide bond formation remains a central objective in synthesis, particularly given the prevalence of amides in medicinally relevant compounds. Despite the value of 2-ynamides as versatile structural motifs, existing aminocarbonylative approaches rely exclusively on Pd catalysis and require relatively harsh conditions.[1]

Herein, we disclose a visible-light-initiated, Ni-catalyzed aminocarbonylation of alkynyl iodides that proceeds under low carbon monoxide pressure, providing an earth-abundant catalytic platform for accessing 2-ynamides. Mechanistic investigations support the light-triggered generation of catalytically active Ni(I) species that initiate a thermally sustained carbonylative Ni(I)/Ni(III) manifold. The method features operational simplicity and a broad substrate scope, accommodating a wide range of alkynyl iodides and amines to afford the corresponding 2-ynamides in good to excellent yields.



- Pd-free synthesis of 2-ynamides
- earth-abundant Ni-catalyst
- low CO pressure
- visible-light irradiation
- broad substrate scope

Acknowledgements: This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement no. 864991). Moreover, this research was funded in part by the Austrian Science Fund (FWF) [10.55776/COE5, Cluster of Excellence MECS]. DK acknowledges support by the Austrian FWF (grant agreement I5771-N). The authors acknowledge support by the NMR center of the University of Vienna.

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P38: Functionalization of Methane and Other Gaseous Alkanes under Visible Blue Light

Jose Manuel Malga Diaz (1), Nicolás Martínez Acevedo (1), Martín Fañanás Mastral (1)

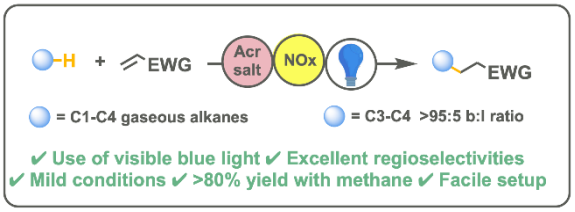
(1) Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CiQUS), Departamento de Química Orgánica, Universidade de Santiago de Compostela, 15782 Santiago de Compostela (Spain)

Subject area: Photocatalytic organic transformations
Keywords: C-H Activation, Methane, Gaseous alkanes, HAT, photocatalysis, blue light

The use of simple and abundant molecules as raw materials in chemical synthesis is one of the fundamental aspects that society must study to move towards a more sustainable future. Methane, the simplest alkane and a potent greenhouse gas, is one of the most abundant carbon feedstocks on the planet[1]. Currently, methane and other gaseous alkanes are primarily used as fuels and in industrial processes such as steam cracking. These applications raise significant environmental concerns, as they are highly energy-intensive and lead to substantial greenhouse gas emissions. As a result, the development of novel protocols that allow the utilization of gaseous alkanes as alkylating agents is crucial.[2]

However, the inertness of C–H bonds (BDE~105 kcal/mol, pKa~50) in methane makes its functionalization highly challenging.[3] Consequently, strategies for efficient methane functionalization remain scarce. One of the current methodologies to functionalize these gaseous alkanes relies in the use of HAT photocatalysis. Some of these methodologies consist in the use of TBADT[4–5] to do direct hydrogen atom transfer (HAT) or the use of metal chlorides to perform ligand to metal charge transfer (LMCT)[6–7]. Nevertheless, these methodologies rely on the use of UV-A light sources to activate the photocatalyst and, when C3–C4 alkanes such as propane or n-butane are used, poor regioselectivity is obtained. Given the advantages of blue light over higher-energy UV-A irradiation, the development of methodologies for the functionalization of gaseous alkanes under such conditions is highly desirable.

Inspired by the work of Nicewicz[8] and Deng[9] with liquid alkanes, we hereby report a metal-free indirect HAT strategy to activate gaseous alkanes under blue light by using an acridinium salt as photocatalyst and pyridine oxides as HAT agents. This methodology provides high yields when methane is used and excellent branched regioselectivities when C3-C4 gaseous alkanes are employed.



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P39: Photocatalysis with Modified Quinones Aided by Machine Learning

Juho Savola (1)

(1) University of Helsinki

Subject area: Photocatalytic organic transformations
Keywords: Photocatalysis, Machine Learning, structure optimization, catalyst synthesis

There are countless transformations and equally as many catalysts in photocatalysis. Many great discoveries have been made in terms of multi use catalysts that work for a variety of reactions. However, these rarely are the best ones for the case at hand and many metal-based catalysts are expensive. How great would it be to be able to tailor a photocatalyst for your specific reaction, metal free?

Here I present a machine learning-guided workflow for the systematic optimization of quinone-based photocatalysts through the integration of virtual library generation, statistical selection methods, synthesis, and experimental evaluation. Rather than relying on traditional trial-and-error catalyst development, the work introduces a data-driven strategy in which catalyst structures are selected to maximize structural diversity and information content prior to synthesis. The approach enables efficient exploration of catalyst chemical space while minimizing experimental workload.

A large virtual catalyst library consisting of millions of potential quinone derivatives was generated from cheap starting materials. Following structural and synthetic feasibility filtering, molecular and atomic descriptors were calculated for the remaining candidates using AQME. Clustering was employed to identify a representative set of 30 catalysts spanning the accessible structural space. This strategy was designed to maximize the usefulness of the resulting experimental dataset for machine learning applications. Several machine learning models were then evaluated with ROBERT, and the best performing one was selected for structure optimization. The suggested structures could then be screened and the results fed back into the ML model. This loop can be iterated until desired results are achieved.

The study demonstrates how statistically informed dataset construction combined with iterative machine learning can accelerate photocatalyst discovery while reducing the need for exhaustive synthesis.

P40: B/O Doped MR-TADF Photocatalysts for Photoinduced Electron and Energy Transfer Reactions

Valerio Cerrato (1), Lea Hämmerling (2), Marco Villa (1), Paola Ceroni (3), Eli Zysman-Colman (2)

(1) Department of Chemistry "G. Ciamician", Alma Mater Studiorum - University of Bologna, (2) Organic Semiconductor Centre, EaStCHEM School of Chemistry, University of St Andrews, (3) Department of Chemistry "G. Ciamician", Alma Mater Studiorum - University of Bologna

Subject area: Photocatalytic organic transformations
Keywords: MR-TADF; Photocatalysis; Electron Transfer; Energy Transfer; Stern-Volmer quenching; Photophysics.

Multi–resonant thermally activated delayed fluorescence (MR–TADF) materials are widely used as emitters in high–performance organic light–emitting diodes (OLEDs)[1] and have recently emerged as promising photocatalysts for photoinduced electron transfer (PET) and photoinduced energy transfer (PEnT) reactions.[2,3] MR–TADF compounds exhibit small singlet–triplet energy gaps that enable efficient reverse intersystem crossing, leading to long–lived excited states with strong redox capabilities.[2,3]

In this presentation, three B/O–doped MR–TADF photocatalysts with high photoreducing power and elevated triplet energies are introduced, and their performance is demonstrated through selected examples of PET and PEnT reactions, designed to probe the redox and energy–transfer capabilities of these materials. Mechanistic insights are supported by Stern–Volmer quenching experiments and photophysical investigations on representative systems.

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P41: Sustainable Triple-Network Eutectogels for Photocatalytic Soft Materials

Sergiu Coseri (1), Catalin Chersan (1), Raluca Baron (1), Gabriela Biliuta (1)

(1) "Petru Poni" Institute of Macromolecular Chemistry Iasi

Subject area: Photocatalytic organic transformations
Keywords: photochemistry, deep eutectic solvents, photocatalysis, eutectogel, green solvents, soft robotics

Deep Eutectic Solvents (DES) are an emerging class of green solvents formed by combining hydrogen–bond donors (HBDs) and hydrogen–bond acceptors (HBAs) in specific molar ratios, resulting in extensive hydrogen–bonding interactions and significant melting–point depression [1]. Cellulose, a renewable and biocompatible polysaccharide with a highly organized hydrogen–bonding network, represents an attractive platform for the development of advanced hydrogel and eutectogel materials due to its excellent mechanical properties and chemical versatility [2]. In this work, a triple–network eutectogel was developed using a novel DES. The DES was successfully prepared by lyophilization of precursor solutions containing choline chloride in water and 4–carboxyphenylboronic acid in DMF at an optimized 1:1 molar ratio. Structural and physicochemical characterization by FTIR, NMR, thermal analysis, and microscopy confirmed the formation of a stable supramolecular network. The obtained eutectogel is expected to exhibit enhanced mechanical robustness, autonomous self–healing capability, and ionic conductivity owing to the synergistic combination of hydrogen bonding, Schiff–base interactions, and dynamic boronic linkages within the triple–network structure. Moreover, the boronic functionalities and conductive eutectic environment offer promising opportunities for the incorporation and stabilization of photocatalytically active species. These features make the developed material a potential candidate for photocatalysis, environmental remediation, light–responsive sensing, healthcare technologies, and soft robotic applications. The study highlights the potential of cellulose–based eutectogels as sustainable multifunctional materials integrating green chemistry and photocatalytic functionality.

Acknowledgment: This work was supported by a grant from the Ministry of Education and Research, CNCS – UEFISCDI, project number PN–IV–P1–PCE–2023–0558, within PNCDI IV.

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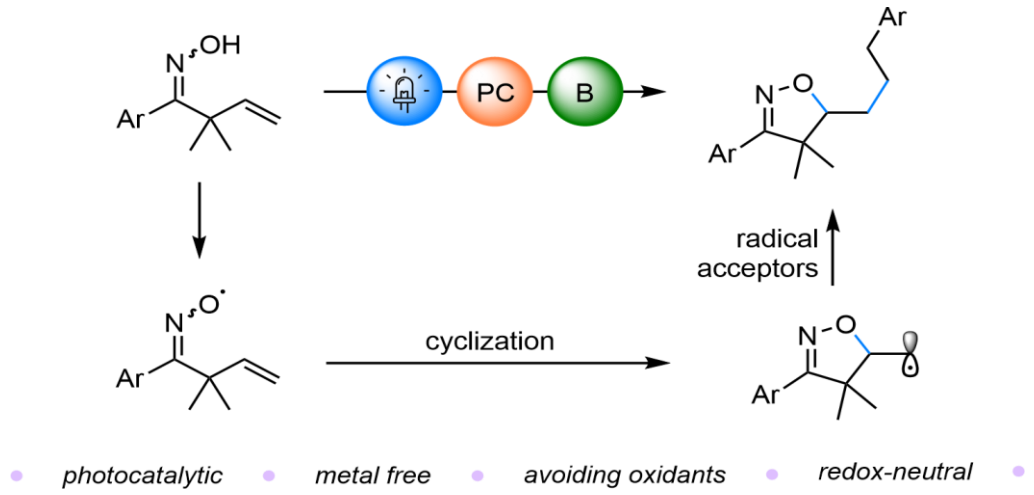
P42: Photocatalytic Iminoxyl Radical Generation from β,γ-Unsaturated Oximes for Isoxazoline Formation and Styrene Functionalization

Stefan Kellnberger (1)

(1) University of Regensburg

Subject area: Photocatalytic organic transformations
Keywords: Iminoxyl radicals, Photocatalysis, β,γ-unsaturated oximes, Radical cascade, Isoxazolines

Iminoxyl radicals represent versatile intermediates for the synthesis of nitrogen-containing molecules, yet their photocatalytic generation remains comparatively underexplored[1]. In addition, many established approaches rely on stoichiometric oxidants and, in several cases, iridium-based photocatalysts[2,3,4]. Herein, we report a light-driven, oxidant and metal free method for the generation of iminoxyl radicals from β,γ-unsaturated oximes, providing a mild, redox-neutral, and atom-economical alternative. The generated iminoxyl radicals undergo a 5-exo-trig cyclization onto the pendant alkene of the β,γ-unsaturated oxime to form a cyclic radical intermediate, which is subsequently trapped by styrenes, delivering functionalized isoxazoline products in a single cascade process. This study highlights the untapped potential of photocatalytic iminoxyl radical chemistry and establishes β,γ-unsaturated oximes as efficient precursors for cascade radical transformations toward functionalized heterocycles.



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P43: Trifluoromethylative bifunctionnalisation of alkenes via Copper LMCT

Quentin ORDAN (1), Francisco Julia-Hernandez (1)

(1) Universidad de Murcia

Subject area: Photocatalytic organic transformations
Keywords: trifluoromethylation ● visible light ● decarboxylation ● radical-polar crossover

The trifluoromethyl groups (CF_3) are key components in pharmaceuticals and agrochemicals.[1]

Many strategies and reagents design have been developed to introduce these fluoroalkyl groups into organic molecules. Yet, most of them rely on reagents with poor atom economy and limited scalability.[1] In another hand, trifluoroacetates are the most abundant and accessible sources of CF3 groups through decarboxylation, which makes them very attractive candidates as trifluoromethylating reagents. However, their very high oxidation potential constitutes a major obstacle.

In the recent years, alongside other groups with various metals [2][3], we developed a methodology to enable the direct decarboxylation of trifluoroacetates with iron photocatalysts for the trifluoromethylation of (hetero)arenes.[4] Under visible light irradiation, the decarboxylation is triggered through an inner-sphere electron transfer (LMCT), which operates independently of redox potentials.

In this communication, we show the decarboxylation step thanks to copper salts to broaden the scope of this reactivity to the versatile difunctionalisation of alkenes, introducing both a CF_3 group and a range of nucleophiles across the double bond. The reaction conditions are very simple and practical, requiring only a readily available copper salt [5] that serves a dual role: triggering photoinduced decarboxylation and acting as an oxidant to facilitate the radical–polar crossover (RPC). Taken together, our protocol enables rapid access to a diverse array of densely functionalized products bearing industrially relevant fluoroalkyl groups, starting from available and inexpensive chemical feedstocks.

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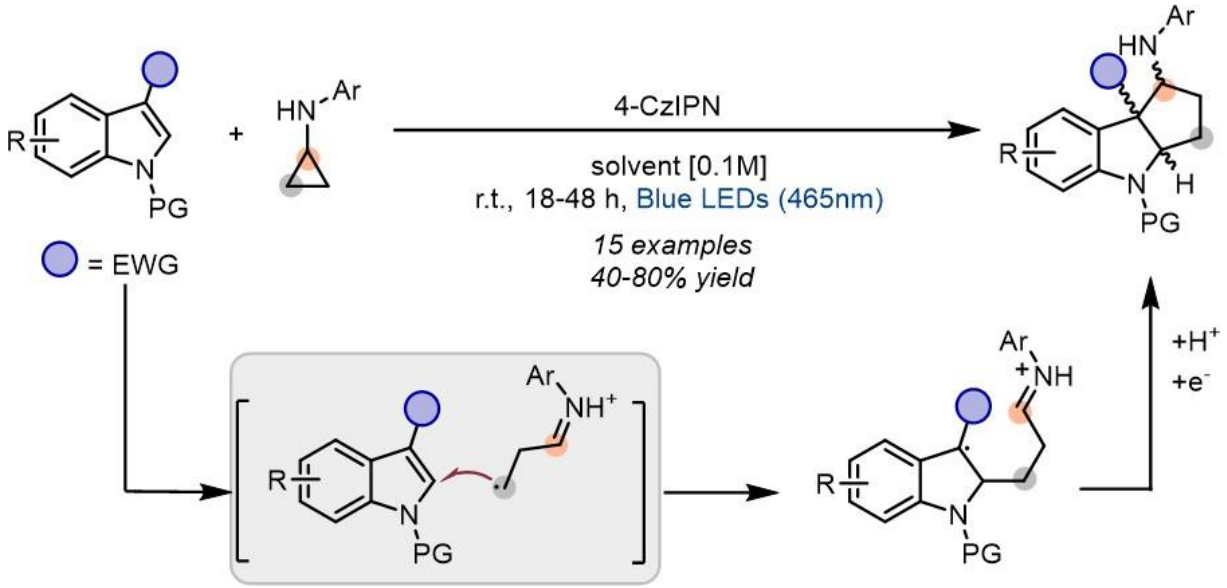
P44: Photoredox Dearomative [3+2] Cyclisation of Electron-Deficient Indoles with N-Cyclopropylarylamines

Anastasia Katsatou(1), Volker Derdau(2), José Alemán,(1,3) Jose A. Fernández-Salas(1,3)
(1) Organic Chemistry Department, Science Faculty, Universidad Autónoma de Madrid, 28049 Madrid, Spain
(2) Integrated Drug Discovery, Isotope Chemistry Sanofi-Avertis Deutschland, 65926, Höchst, Germany.
(3) Institute for Advanced Research in Chemical Sciences (IAdChem), Universidad Autónoma de Madrid, Madrid, Spain.

Subject area: Photocatalytic organic transformations

Visible-light photoredox catalysis has emerged as a powerful platform for the generation of reactive radical intermediates under mild conditions. Visible-light oxidation of N-cyclopropylarylamines generates nitrogen radical cations that undergo rapid ring opening to distonic radical cation intermediates[1-3]. Albeit this ambiphilic character has supported annulations with olefins and alkynes, heterocycles have not yet been reported as model substrates[4-5]. Herein, a visible-light-mediated dearomative formal [3+2] cyclisation of electron deficient indoles with N-aryl cyclopropyl amines for the formation of fused indoline frameworks is reported. This strategy enables the formation of complex polycyclic structures from simple starting materials under notably mild conditions both in batch and continuous-flow.



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P45: From aldehydes to pyridazines in flow: a modular photocatalytic approach to privileged heterocycles

Amy Nicole Corridori (1), Filippo Sacchelli, Luca Capaldo

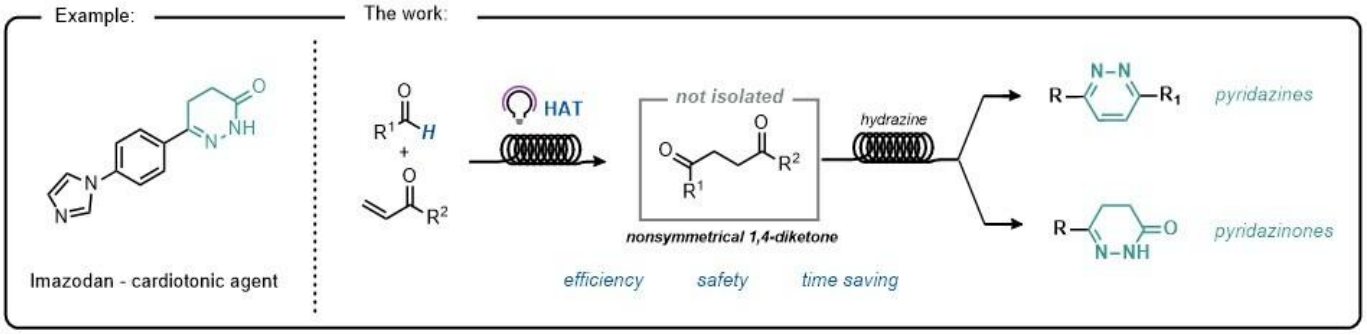
(1) University of Parma

Subject area: Sustainable and Green Photochemical Applications
Keywords: Flow chemistry, Photocatalysis, Heterocycles synthesis

Six-membered heterocycles such as pyridazine and pyridazinone derivatives are recognized as privileged scaffolds in medicinal chemistry. These motifs have been extensively explored in the pharmaceutical field against a wide range of biological targets and for diverse therapeutic applications. However, compared to other diazine isomers, particularly pyrimidines, pyridazines remain relatively underexplored, mainly because they do not occur naturally and are not readily accessible through biochemical nitrogen transformations.

Herein, we report a practical and sustainable flow protocol for the telescoped synthesis of pyridazine and pyridazinone derivatives. Since access to these heterocycles is often limited by the scarce availability of unsymmetrical 1,4-diketones, our approach starts with a decatungstate-photocatalyzed hydrogen atom transfer (HAT) from aldehydes to generate acyl radicals, which undergo regioselective addition to functionalized enones. The resulting diketones are then directly transferred, without purification, into a second reactor, where they undergo a stepwise condensation-cyclization sequence with aqueous hydrazine.

This modular strategy provides rapid access to densely substituted and biologically relevant heterocycles bearing unconventional substitution patterns.



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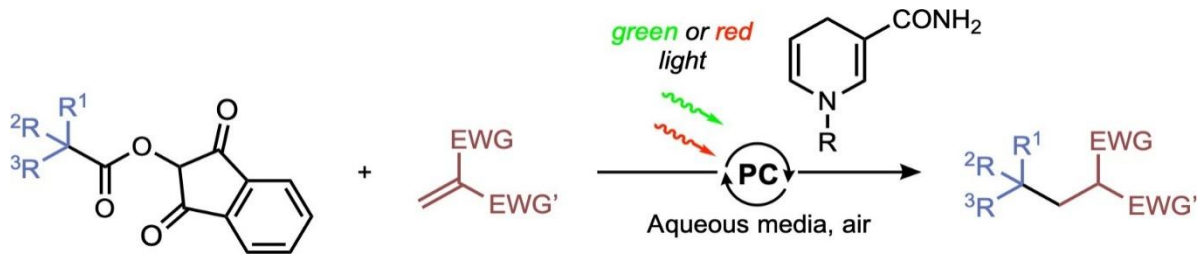
P46: Red-shifted photoredox carbon–carbon bond-forming reactions in biorelevant media

David Montoto (1), Uxía Deus-Lorenzo (1), María Tomás-Gamasa (1), José Luis Mascareñas (1), Mauro Mato (1)

(1) Center for Research in Biological Chemistry and Molecular Materials (CiQUS), and Department of Organic Chemistry, University of Santiago de Compostela

Subject area: Photocatalytic organic transformations
Keywords: Photoredox catalysis, bioorthogonal chemistry, Giese reaction

Photocatalysis has emerged as a promising strategy for the development of bioorthogonal chemical reactions—reactions that can be performed in live settings without interfering with native biochemical processes—thanks to its mild conditions and exceptional spatiotemporal control. However, most synthetic photochemical transformations have been studied in the context of synthetic chemistry, requiring organic solvents and high-energy light sources that are incompatible with biological systems.[1] Here, we present new photoredox systems that harness green- or red-light irradiation to generate alkyl radicals for subsequent Giese-type trapping. These reactions display compatibility with air, aqueous solvents, and biologically relevant media, including cell lysates, enabling photocatalyzed carbon-carbon bond-forming reactions in biological settings. This paves the way for the further development of bioorthogonal radical photocatalytic synthetic chemistry.[2]



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P47: Post-Synthetic Modification of Cu-, Ca-, and Zr-Based MOFs for Enhanced Photocatalytic Activity

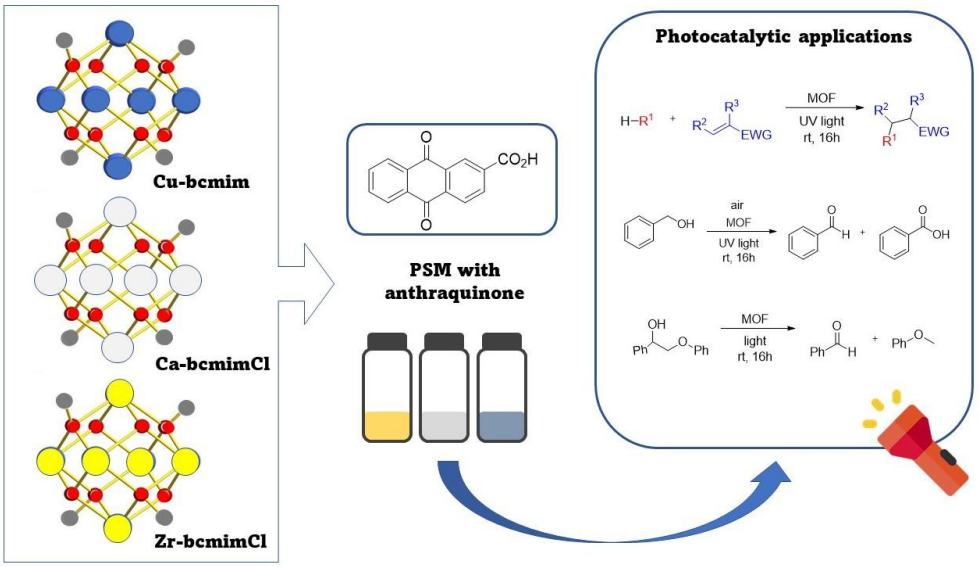
Yanira Pérez Almarcha (1), Alberto Mijangos Ochoa (2), Anna Nacher Luis (2), Xavier Marset (3), Irene Bosque (1), Isidro M. Pastor (1)

(1) Instituto de Síntesis Orgánica (Universidad de Alicante), (2) Universidad de Alicante, (3) Instituto de Electroquímica (Universidad de Alicante)

Subject area: Photocatalytic organic transformations
Keywords: Metal Organic Frameworks (MOFs), Photocatalysis, Post-synthetic Modifications (PSM), Anthraquinone

Metal–organic frameworks (MOFs) have emerged as highly versatile platforms for photocatalysis due to their tunable porosity, structural diversity, and capacity for post–synthetic modification. In this work, we report the synthesis and functionalization of copper–,[1] calcium–, and zirconium–based MOFs and explore their potential as photocatalysts for organic transformations. Previous studies have demonstrated that post–modification strategies—such as halogenation of copper and calcium MOFs,[2] or the transformation of zirconium MOFs into xerogel–like structures [3]—significantly enhance catalytic activity by improving light absorption and charge–transfer processes. Building on these findings, the present project focuses on the incorporation of an anthraquinone derivative into the parent MOF structures as a photoactive modifier.

The introduction of anthraquinone units is expected to extend the light–harvesting capability of the materials and promote efficient photoinduced charge separation, thereby amplifying photocatalytic performance.[4] The resulting modified MOFs are systematically characterized and evaluated in representative photocatalytic reactions, including the oxidation of benzylic alcohols and selected carbon–carbon bond–forming reactions. Comparative studies with the corresponding unmodified MOFs are carried out to elucidate structure–activity relationships and the role of the organic modifier. Overall, this work aims to provide insights into rational post–synthetic modification strategies for MOF–based photocatalysts and to expand their applicability in sustainable organic synthesis.



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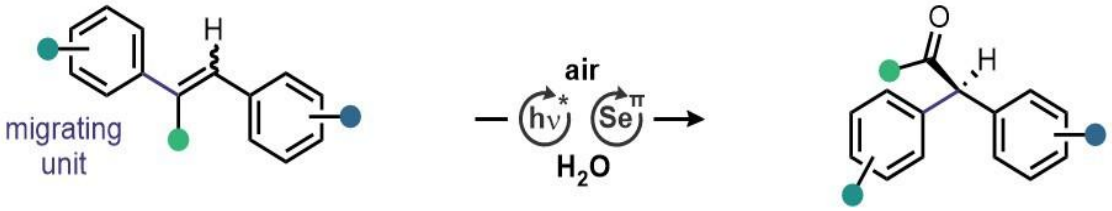
P48: Chiral diarylmethanes via an asymmetric Tsuji–Wacker oxidation

Eduard Frank, Sooyoung Park, Elias Harrer, Jana-Larissa Flügel, Marcel Fischer, Julia Stoiber (1), Partick Nuernberger (1), Julia Rehbein (1), Alexander Breder (1)

(1) University of Regensburg

Subject area: Photocatalytic organic transformations
Keywords: Photocatalysis, diarylmethanes, enantioselectivity

As enantiomerically enriched diarylmethanes are key structural motifs in pharmaceuticals[1] and agrochemicals,[2] their enantioselective synthesis has become an important area of research in recent years. Established strategies typically rely on enantioselective desymmetrization of the central sp^3–hybridized carbon atom,[3] stereocontrolled substitution,[4] and asymmetric 1,2–additions or insertion reactions involving 1,1–diarylated alkenes.[5] However, certain arene residues, such as para–substituted benzenes or unsubstituted heteroarenes, are challenging to install, as chiral catalysts are often unable to distinguish between these isosteric residues.[5] Consequently, for the stereoselective incorporation of isosteric (hetero)arenes into chiral diarylmethane scaffolds stoichiometrically differentiated building blocks are required, which are generally obtained through prior redox–modifications, such as metalation or halogenation, leading to a poor step– and redox–economy.[3–5] As an alternative approach, we report the first example for the synthesis of chiral diarylmethanes via an asymmetric selenium–π–acid catalyzed migratory Tsuji–Wacker oxidation using simple, unactivated 1,2–diarylated alkenes as starting materials.[6] The α–alkyl substituent allows the selenium catalyst to differentiate between the two π–faces of the substrate, enabling the use of isosteric arene residues without prior activation and thus overcoming previous limitations. Overall, this multicatalytic platform exhibits broad functional group tolerance, provides access to diarylmethanes with high levels of enantioselectivity (up to 97% ee), and has been successfully applied in the synthesis of antihistaminic agents (e.g. (R)– and (S)–neobenodine).



Scheme 1. Enantioselective synthesis of diarylmethanes via an asymmetric migratory Tsuji–Wacker oxidation.

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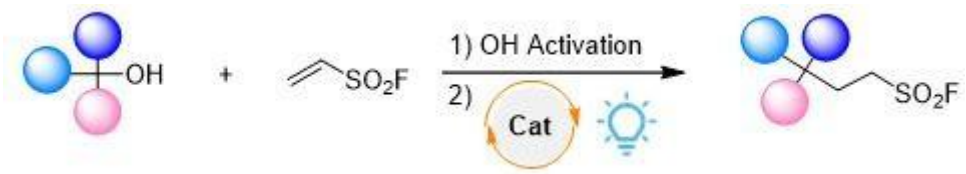
P49: Radical Deoxygenative Synthesis of Sulfonyl Fluorides via Photoredox Catalysis

Iñaki Fernández Yagüe (1), Álvaro Castilla Mocholí, Marc Montesinos Magraner, Carlos Vila, Gonzalo Blay Llinares

(1) Universitat de València

Subject area: Photocatalytic organic transformations

Sulfonyl fluorides have emerged as versatile functional groups due to their interesting applications in SuFEx chemistry in fields such as medicinal chemistry and chemical biology.[1] As a result, the synthesis of SO_2F-containing compounds has attracted the attention of organic chemists over the last decade. Among the possible disconnection, the radical addition of carbon-centred radicals to ethenesulfonyl fluoride is one of the most interesting possibilities.[2] Moreover, alcohols represent an attractive source of alkyl radicals owing to their abundance and widespread availability.[3] In this work, we explore a radical deoxygenative strategy for the synthesis of sulfonyl fluorides through visible-light-mediated photoredox catalysis. The transformation relies on the generation of carbon-centered radicals from activated alcohols under mild conditions, and their subsequent addition to ethenesulfonyl fluoride, Preliminary studies demonstrate the feasibility of the methodology and highlight the potential of radical deoxygenation as an approach for the preparation of structurally diverse sulfonyl fluorides.



Acknowledgments

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P50: Selenium photo-π-acid catalysis enables regio- and redox-orthogonal semipinacol rearrangements

Daniela Fritsch (1), Carina Allacher (1), Christian Walbrunn (1), Kilian Müller (1), Daniel Grenda (1), Tao Lei (2), Patrick Nuernberger (1), Julia Rehbein (1), Alexander Breder (1)

(1) University of Regensburg, (2) Hainan University

Subject area: Photocatalytic organic transformations
Keywords: Photoacids - Selenium Lewis acids - Semipinacol rearrangement

Photoacids are versatile, emerging tools in the field of catalysis. They offer modes of reactivity that remained elusive to their thermal counter parts.[1] The key feature of their reactivity is the control of their catalytic performance, which can be easily regulated by light.[2,3] Yet, many photoacids exhibit short excited-state lifetimes on the order of pico- to early nanoseconds, which is often inadequate for synthetic applications.[3,4,5] However, we found diaryldiselanes promising Lewis photoacids, as they still show absorption in the visible and near UV region under experimental conditions. The distinctive feature of selenium Lewis acids lies in their carbophilicity. This circumstance can be used for the activation of C−C double bonds. We were able to perform catalytic semipinacol rearrangements of 1-vinylcyclobutan-1-ols into 2-methylenecylopentan-1-ones.
The developed conditions are less sensitive to diffusion-limited side reactivity compared to traditional photoredox catalysts, and allow the use of atmospheric oxygen as a green oxidant. After reaction optimization, we applied the title protocol to a broad array of 1-vinylcyclobutan-1-ols. Many common functional groups such as halogens, carboxylic esters or sulfones are well tolerated. With yields of up to 91%, the title method complements cognate transition metal-catalyzed methods that are associated with orthogonal regioselectivities. Further mechanistic studies, including computations, ultrafast spectroscopy and mechanistic investigations gave comprehensive insight into the catalytic cycle.[6]

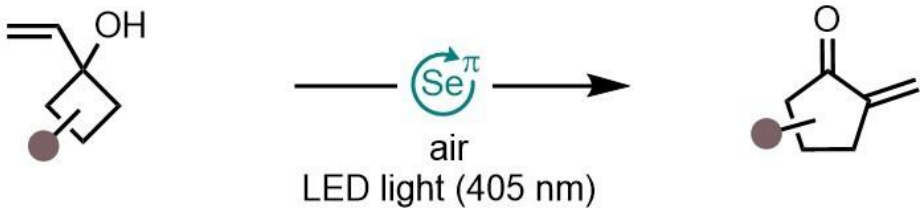

Figure 1: Synthesis of 2-methylenecylopentan-1-ones by photo-π-acid catalysis conditions.

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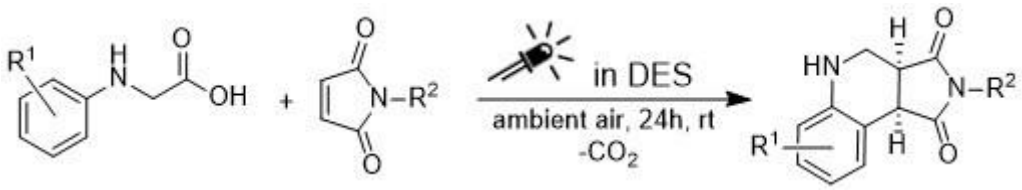
P51: Visible Light-Induced Catalyst-Free Decarboxylative Povarov-Type Reaction of N-Aryl Glycines with Maleimides in Deep Eutectic Solvents

José Antonio Ñiguez Elena (1), Francisco José Sierra Molero (1), Luis Paredes Soler (2), Diego Antonio Alonso Velasco (1), Rafael José Chinchilla Cruz (1)

(1) Instituto de Síntesis Orgánica, (2) Instituto de Síntesis Orgáica

Subject area: Photocatalytic organic transformations
Keywords: Green Chemistry, Deep Eutectic Solvents, Povarov, Decarboxylation.



Scheme 1

Photoredox reactions, particularly those induced by visible light, have considerably expanded the utility and scope of radical chemistry in organic synthesis in recent years.[1] However, these reactions are usually conducted using Volatile Organic Compounds (VOCs) as reaction media, which pose inherent environmental risks. To avoid these drawbacks, different alternative solvents have emerged as a convenient alternative to VOCs in organic transformations, specially Deep Eutectic Solvents (DES), owing to their low volatility, ease of preparation, and biodegradability.[2]

Despite these advantages, reported examples of visible-light-promoted synthetic transformations in DES remain scarce.[3] In this communication, we present the synthesis of polycyclic tetrahydroquinoline derivatives in DES via a visible-light (blue LED)-induced, catalyst-free Povarov-type cyclization in ambient air, based on the decarboxylation of N-aryl glycines and subsequent cyclization of the formed α-aminoalkyl radical with maleimides (Scheme 1).

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P52: Chalcogen Bonding enabled, Visible Light Driven radical Diels-Alder cyclization

Robin Groeters, Augustinus Künzel, Jens Peternathe (1), Olga García Mancheño

(1) Leibnitz Institut für Katalyse e.V.

Subject area: Photocatalytic organic transformations
Keywords: Photocatalyis Sigma-hole catalysis Chalcogenbonding

Over the last years, the interest in visible light, metal–free photocatalysis has increased and many different catalytic systems in this field have been developed. Alternatively, sigma–hole catalysis has recently emerged as a powerful tool for the activation of substrates, leading to the development of new methodologies in organocatalysis, as well as photochemical transformations. However, no photocatalytic system based on sigma–hole interactions have been described to date.

In this work, an unexpected novel photocatalyst based on a chalcogen–bond donor and its application in visible–light mediated Diels–Alder reactions is presented. Telluronium salts are mostly known for their application in chalcogen bonding catalysis due to their enlarged sigma–hole. During our research in the field of s–hole organocatalysis, we found that some of these salts can also be used to initiate chemical reactions by irradiation with blue light, making them interesting for photocatalysis. In particular, the Diels–Alder of anethol with various dienes as model test reaction has been investigated, allowing for a mild and effective transformation in the presence of diaryl methyl tellurium salts. Interestingly, the used telluronium salts do not absorb light in the visible spectra, suggesting the formation of a complex with the electron rich conjugated substrate, similar to electron donor–acceptor (EDA) or charge transfer (CT) complexes. Experimental and computational studies supporting this key complexation through sigma–hole interactions will be presented, as well as the scope of the method and extension to other light driven cycloaddition reactions.

P53: Streamlining Large Helicene Synthesis Through Modular Design: Theory Driven Mapping of Photochemical Pathways

Pawel Jaroslaw Bronk (1), Bianca Catalina Baciu (1), Albert Guijarro (1)

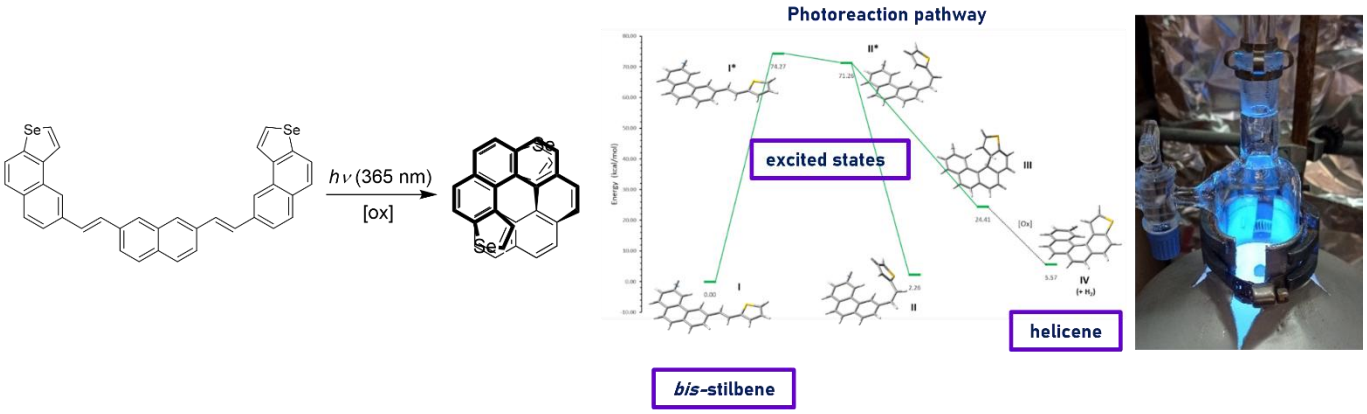
(1) Instituto de Síntesis Orgánica, Universidad de Alicante

Subject area: Mechanistic studies in photo- and bio-catalysis
Keywords: helicenes, oxidative photocyclization, LED, modular synthesis, DFT

Helicenes are a family of non-planar polycyclic aromatic hydrocarbons with helical shape. Their inherent chirality and unique helical architecture endow them with remarkable properties that can be exploited in a wide range of applications. Over time, a range of synthetic methodologies has been developed for the preparation of helicenes, with oxidative photocyclization standing out as the most widely adopted strategy in the literature. In this work, the technique has been advanced by implementing selective irradiation using LED technology, replacing conventional broadband sources to enhance reaction control and efficiency.[1],[2]

The implementation of a 365 nm LED irradiation system has enabled the efficient synthesis of a broad range of helicenes, providing cleaner crude reaction mixtures and improved overall reaction efficiency. Selective irradiation at this wavelength specifically targets the stilbene-type precursors, obtained through an efficient modular synthesis, thereby suppressing competing photochemical processes and minimizing the formation of undesired by-products.

The feasibility of this synthetic strategy was evaluated by comparing the experimental outcomes with DFT calculations, providing theoretical support for the efficiency of the process.[3]



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P54: Porphyrin SURMOF (Surface Coordinated Metal Organic Framework) for carbon dioxide photoreduction

Marta Grota (1)

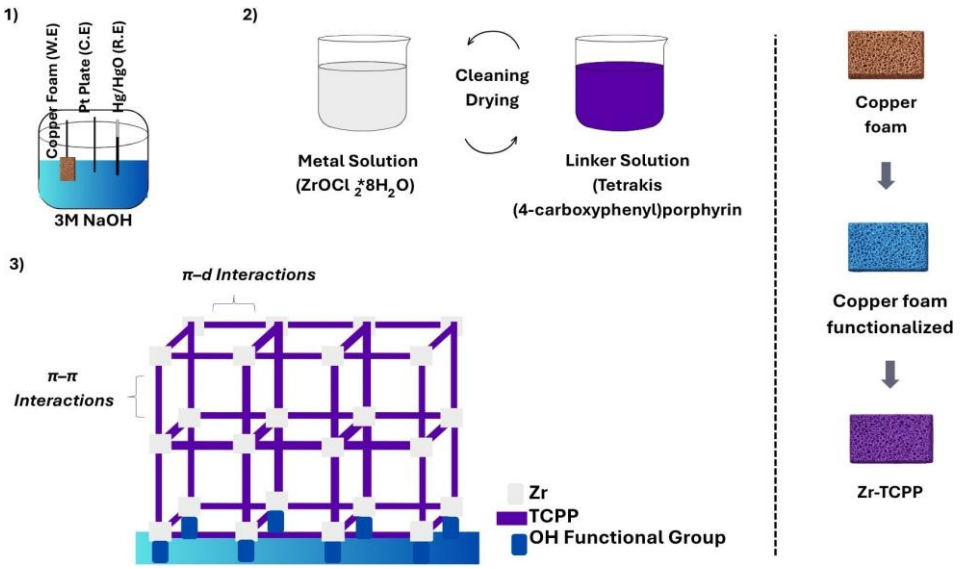
(1) Gdansk University of Technology

Subject area: Photocatalytic organic transformations
Keywords: Photocatalysis, SURMOF, CO_2 photoreduction

According to the latest data, global GHG emissions in 2024 reached 53.2 Gt CO_2eq. This marks an increase of 1.3%, or 665 Mt CO_2eq, compared to 2023.1 The overproduction of carbon dioxide necessitates the development of technologies capable of reducing this amount. Heterogeneous photocatalysis with the use of semiconductors appears to be a promising solution.

One of the promising semiconductor materials is MOF (Metal Organic Framework). A MOF is a hybrid material consisting of organic linkers and inorganic metal centers. Compared to powder MOFs, SURMOFs offer several advantages. The main advantages include easier processability, greater control over the MOF structure, and higher photocatalytic activity. To obtain a SURMOF, a substrate must be functionalized with appropriate functional groups to ensure the formation of a uniform and stable film. Before the deposition process, the substrate was functionalized via electrochemical way.2 The functionalized substrate was first immersed in a metal precursor solution ($ZrOCl_2 \cdot H_2O$) for 30 min, then rinsed with water and ethanol for 5 min. Next, the substrate was immersed in the linker solution (Tetrakis (4-carboxyphenyl)porphyrin) for another 30 min. Finally, the sample was dried at 60°C overnight. As a result of the deposition, the substrate color changed from blue to purple.3

To evaluate the activity of the SURMOF, a series of photocatalytic experiments was performed. The results showed the presence of formic acid and an increase in its concentration over time.



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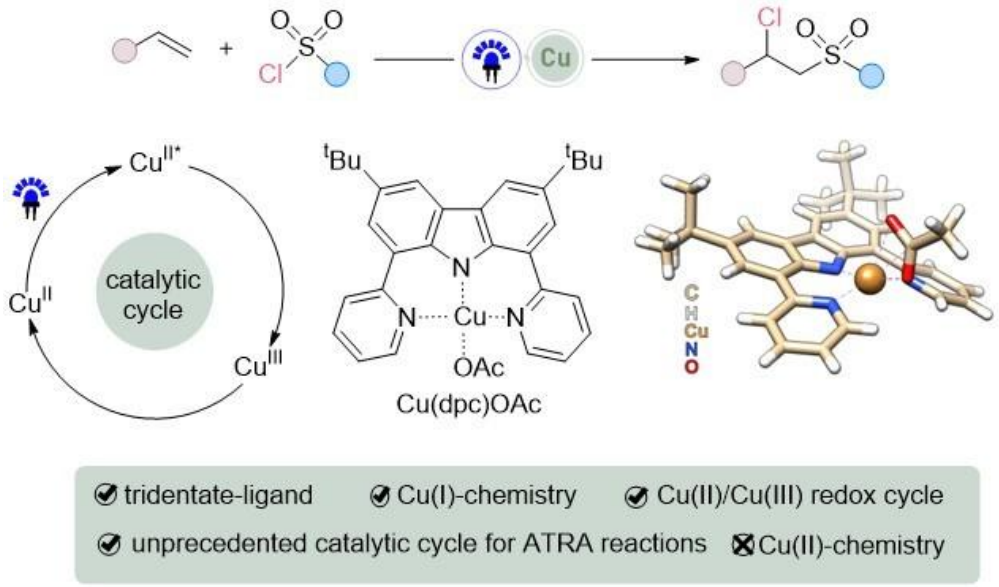
P55: Rewriting Copper Catalysis for Photocatalyzed ATRA reactions: Chlorosulfonylation of Alkenes through a Cu(II)/Cu(III) Pathway

Isabell Reinberger (1), Max Schadenfroh (2), Patrick Nürnberger (1), Oliver Reiser (1)

(1) Universität Regensburg, (2) Universiät Regensburg

Subject area: Photocatalytic organic transformations

Inspired by recent advances in Cr(III) photophysics reported by Oliver Wenger, tridentate chelating frameworks such as the dpc ligand (3,6-di-tert-butyl-1,8-di(pyridin-2-yl)-9H-carbazole) have emerged as promising alternatives to classical polypyridine ligands.[1] In this work, we extend this ligand design strategy to copper complexes to investigate whether analogous improvements in photophysical and catalytic properties can be achieved. The copper (II) complex Cu(dpc)OAc was synthesized and evaluated as a photocatalyst. Its catalytic activity was assessed using Chlorosulfonylation as a benchmark reaction for copper-mediated photocatalysis.[2] In addition, electrochemical measurements and time-resolved spectroscopic studies were conducted to elucidate the mechanistic pathway. While photocatalytic atom transfer radical addition (ATRA) reactions are typically associated with a Cu(I)/Cu(II) redox cycle[3], in contrast, Cu(dpc)OAc operates through an alternative Cu(II)/Cu(III) cycle. This work highlights the potential of rigid tridentate ligand frameworks to modulate copper redox chemistry and enable non-classical photocatalytic pathways.



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P56: Unique Reactivity of Copper Complexes in Photoredox-Catalyzed SO_2 fixation

Nejc Petek (1), Till Opatz

(1) University of Ljubljana, Faculty of Chemistry and Chemical Technology

Subject area: Photocatalytic organic transformations
Keywords: Photoredox catalysis, copper complexes, sulfur dioxide, sulfones

While photoredox catalysis has long contributed towards the synthesis of sulfonyl-containing compounds, copper complexes have only recently emerged as an important class of photoredox catalysts. They have not only proven as a more sustainable alternative to costly iridium- and ruthenium-based catalysts for promoting atom transfer radical addition reactions to alkenes or alkynes, but have also enabled transformations not accessible with other catalysts.[1]

In addition to the existing repertoire of copper-catalyzed photoredox reactions, we have recently demonstrated their use in the fixation of SO_2 to α-bromoamides and styrenes, resulting in α-(styrylsulfonyl)amides.[2] Such compounds usually require multiple steps to synthesize, while the newly developed method affords them in a single step. Moreover, copper complexes were the only ones among the tested catalysts to enable this transformation, indicating that copper complexes may play a dual role as photoredox catalysts and in promoting C-S bond formation.

The developed method was used to synthesize 21 α-(styrylsulfonyl)amides, as well as 5 esters and a ketone analogue.[2]

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P57: Photocatalyzed Polarity-Reversed Corey–Chaykovsky Cyclopropanation via Radical-polar Crossover

Arsala Kamal (1), Juan S. Dato-Santiago (2), Vittoria Martini (3), Olga García Mancheño (2)

(1) Leibniz Institute for Catalysis e.V. LIKAT, (2) Leibniz Institute for Catalysis e.V. LIKAT Rostock, (3) University of Muenster

Subject area: Photocatalytic organic transformations
Keywords: Photoredox catalysis; sulfoxonium ylides; Corey-Chaykovsky reaction; radical umpolung; radical-polar crossover; cyclopropanation

Cyclopropanes are valuable structural motifs in pharmaceuticals, natural products, and functional materials.[1,2] However, classical Corey–Chaykovsky cyclopropanation relies on the nucleophilic reactivity of sulfur ylides and is largely restricted to electron–deficient alkenes, limiting its broader synthetic applicability.[3] In this work, we report a photochemical cyclopropanation enabled by the radical umpolung reactivity of sulfoxonium ylides under visible–light irradiation at room temperature. In contrast to the conventional two–electron pathway, photoredox single–electron transfer (SET) activation of sulfoxonium ylides generates electrophilic radical cation intermediate. This reactivity inversion enables efficient engagement of electron–rich olefins that are typically inaccessible in traditional sulfur ylide cyclopropanation chemistry. Following radical addition, a radical–polar crossover[4,5] process induces a second polarity inversion, furnishing carbanionic intermediates that undergo intramolecular ring closure to deliver cyclopropane products. The transformation proceeds under mild conditions, requires no external additives or transition metals, and employs bench–stable sulfoxonium ylides as practical and versatile reagents.

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P58: Ketone-alkene radical cross coupling through ferrioxalate photocatalysis

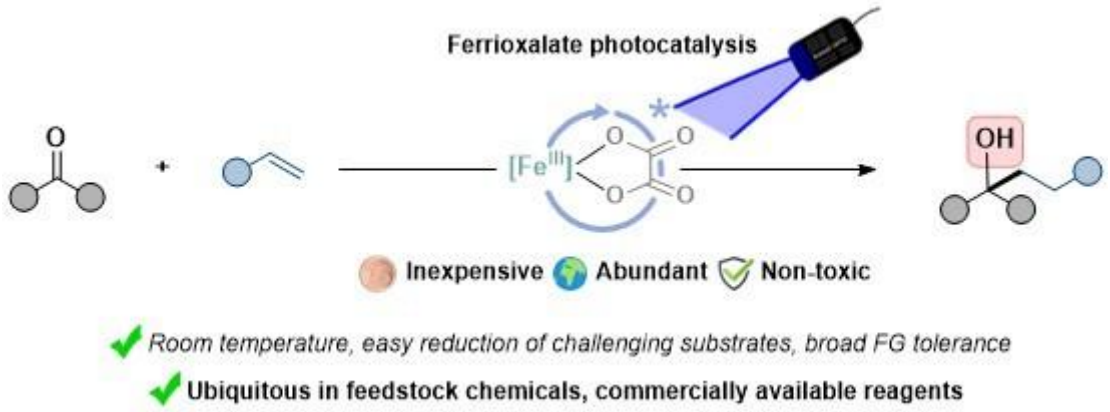
Dalila Arnaldi (1), Niccolò Intini, Fabio Juliá Hernandez, Partha Pratim Sen, Sergio Adalid, Kristýna Kellovská

(1) Universidad de Murcia

Subject area: Photocatalytic organic transformations
Keywords: ketone-olefin cross coupling ● iron photocatalysis ● radical chemistry

Ketones and alkenes are ubiquitous in feedstock chemicals or bioactive compounds. These two functional groups are archetypal textbook examples of reactivity handles for organic synthesis,[1] however, the direct coupling between them to obtain tertiary alcohols remains limited. Some of the most successful strategies rely on radical chemistry to assembly new C–C bonds, are mediated by SmI2, metal hydrides or photoredox catalysis.[2] Nevertheless, reported strategies are mainly focused on intramolecular couplings or require the use of activated substrates. In this context, the intermolecular coupling between unactivated alkenes and ketones with broad scope remains a longstanding ambition.[3]

Recently, our group introduced the use of ferrioxalate photocatalysis in diverse reductive transformations based on the effective generation of catalytic species with unexplored synthetic potential.[4] In this work we present how ferrioxalate catalysis can enable ketone–olefin coupling reactions. Photoactivation of iron catalysts allows to perform this challenging transformation under exceptionally mild reaction conditions (visible light, room temperature), without the use of strong bases or stoichiometric metal reductants, and present a broad scope in both coupling partners. The implementation of this blueprint has unlocked the use of ketones and alkenes as building blocks for intermolecular C–C bond formation in presence of multiple functionalities, opening new opportunities for fragment coupling strategies.



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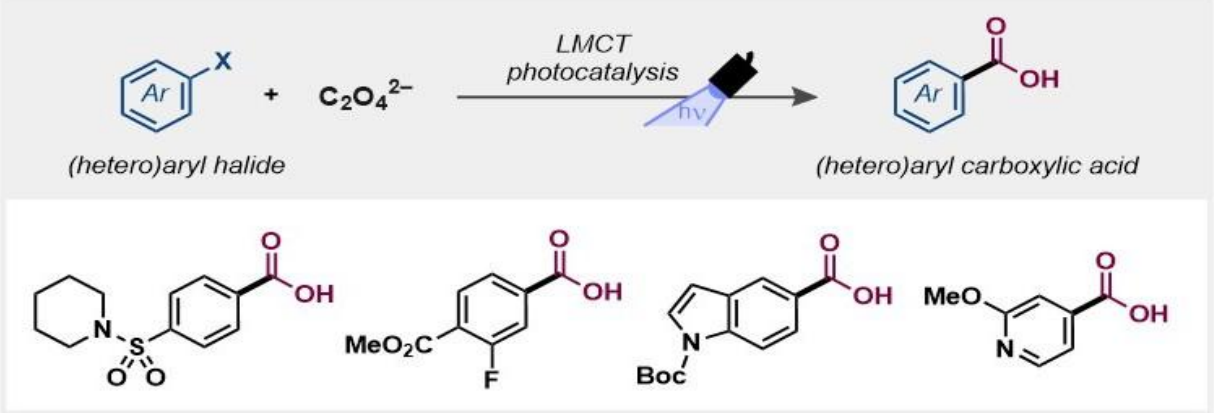
P59: Photoinduced Carboxylation of (Hetero)aryl Halides

Kristýna Kellovská (1), Fabio Juliá (1)

(1) Universidad de Murcia

Subject area: Photocatalytic organic transformations
Keywords: photocatalysis, carboxylation, aryl halides

Carboxylic acids and their derivatives are one of the most employed functional groups in organic chemistry with great importance in the fields of organic synthesis, medicinal chemistry and drug discovery.[1] Traditionally, carboxylic acids are synthetized by reacting organometallic reagents, such as Grignards or organolithiums, with CO gas.[2] However, high nucleophilicity and hydrolytic lability of these organometallics together with relatively harsh reaction conditions often limits functional group compatibility and hampers broader applicability of these methods. More recently, transition-metal catalyzed carboxylation of organic (pseudo)halides with CO_2 gas has emerged as an attractive alternative to the traditional approaches.[3] While these methods offer improved chemoselectivity, better atom-economy and proceed under milder conditions, one of the main drawbacks is the need for stoichiometric metal-based reductants, such as Mn and Zn powder or pyrophoric Et_2Zn and $AlMe_3$. In this work, we present a complementary approach for carboxylation of (hetero)aryl halides which does not require the use of gaseous CO_2 and strong metal-based reductants. Instead, our method utilizes an inexpensive and easy-to-handle oxalic acid salt as a solid CO_2 surrogate and proceeds under mild conditions of visible light irradiation in the presence of a metal salt. The reaction showed excellent functional group compatibility and enabled preparation of a wide scope of (hetero)aromatic carboxylic acids in good yields.



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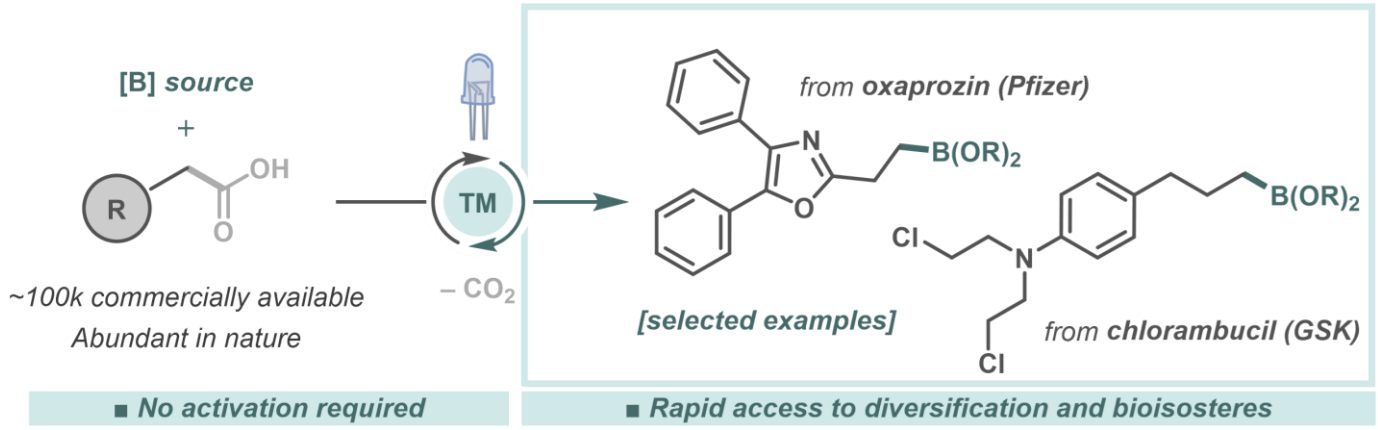
P60: Direct Photodecarboxylative Borylation

Paula Visiedo Jiménez (1), Sarah Jayne Burlingham (1), Quentin Émile Léon Ordan (1), Francisco Juliá Hernández (1)

(1) Facultad de Química, Centro Multidisciplinar Pleiades-Vitalys, Universidad de Murcia, Campus de Espinardo, 30100 Murcia (Spain)

Subject area: Photocatalytic organic transformations
Keywords: iron, photocatalysis, borylation, decarboxylation, radical chemistry

Carboxylic acids are widely found in nature and are key structural motifs in industrially important compounds,[1] which makes them a highly appealing feedstock for the development of new synthetic routes. Specially, their conversion into boronic esters is particularly attractive because organoboron compounds are versatile intermediates for the construction of C–C and C–heteroatom bonds,[2] with significant relevance in drug discovery. However, direct access to alkyl boronic esters from aliphatic carboxylic acids remains underdeveloped. Current decarboxylative borylation strategies generally rely on prior activation of the acids through redox-active derivatives,[3,4] often compromising step economy and efficiency. Herein, we describe a direct decarboxylative borylation of carboxylic acids mediated by photocatalysis using Earth-abundant metals. The method displays broad substrate scope and great functional group compatibility, including applicability to structurally complex molecules. Altogether, this approach offers a straightforward, efficient, and practical route to valuable boron-containing building blocks from readily accessible carboxylic acids, while also enabling late-stage functionalization.



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P61: Suzuki-type reaction via Ferrioxalate Photocatalysis

Niccolò Intini (1), Carlos Bernabeu (1), Fabio Juliá (1)

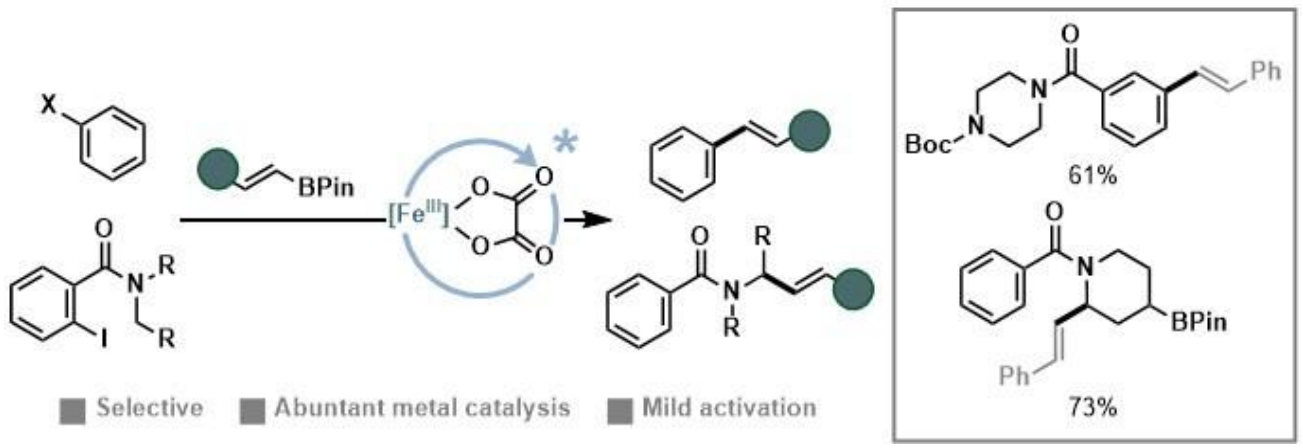
(1) Edificio Pleiades-Vitalis, Campus de Espinardo, 30100 Murcia (Spain)

Subject area: Photocatalytic organic transformations
Keywords: Iron catalysis, LMCT, Cross-Coupling

The use of palladium in cross-coupling reactions is particularly common to synthetize pharmaceuticals, agrochemicals and materials. In particular, the coupling between an organoboron and aryl halides, better known as Suzuki-type reaction, plays a leading role in the coupling between two C(sp^2) fragments[1]. While highly versatile, Palladium suffers from critical geopolitical supply and high cost. This led the community to investigate the replacement of palladium and ithers abundant metals with alternatives based on abundant and sustainable ones[2].

Among the various alternatives, iron has emerged to be one of the most attractive and promising due to its high abundance and low toxicity[3]. Unfortunately, the Suzuki-types reactions catalyzed by iron relieve the use of strong bases, such as LDA, Grignard, or organolithium or the presence of directing groups. These drawbacks dramatically limit the applicability of iron catalysis in Suzuki-type transformations[4].

In this work, we present the use of a radical approach based on ferrioxalate catalysis[5] to overcome this limitation. Thanks to this approach, we can achieve highly reducing iron species able to activate aryl halides to aryl radicals. These can engage an orthogonal approach to standard Suzuki reaction based on transmetallation. We developed also a regioselective 1,5-HAT on amides thanks to the installation of a directing group to obtain a C(sp^3)-C(sp^2) bond formation. Thus, this new method constitutes a sustainable and fast method in the absence of strong bases, with reaction conditions that show exceptional tolerance to functional groups and a wide structural diversity in the coupling between aryl halides and alkenyl organoboron compounds inaccessible under iron-catalysed methodologies.



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P62: Bicyclic Pyrazoles as Versatile Platforms for Photocatalyst-Free Light-Driven Skeletal Diversification

Ines Babnik (1), Nejc Petek, Jurij Svete, Uroš Grošelj, Bogdan Štefane

(1) Faculty of chemistry and chemical technology, University of Ljubljana

Subject area: Photocatalytic organic transformations
Keywords: pyrazoles, photocatalyst-free, skeletal editing, diazepines, 3D-rich compounds

Pyrazole-containing compounds are relevant nitrogen heterocycles in medicinal chemistry, exhibiting a wide range of biological activities and being frequently encountered in approved pharmaceuticals.1 In recent years, photochemical methodologies have been developed for the synthesis and selective functionalization of monocyclic pyrazoles, providing efficient access to structurally diverse derivatives under mild reaction conditions.2 In contrast, despite the growing pharmaceutical relevance of pyrazole-fused bicyclic systems,3 their photochemical reactivity remains largely unexplored.

Herein, we demonstrate that pyrazolo[1,2-a]pyrazolones and pyrazolo[1,2-a]pyridazinones constitute versatile platforms for photocatalyst-free photochemical transformations. These heterobicycles are readily accessible through a one-pot synthetic protocol and absorb visible light, enabling direct photoactivation without the need for external catalysts. By tuning the irradiation wavelength and substrate structure, the bicyclic pyrazoles can be selectively converted into a variety of valuable heterocyclic scaffolds, including pyrazole-fused 1,2-diazepines, aldehydes, and stereochemically defined tricyclic products. Combined experimental and DFT studies enabled the elucidation of the underlying photochemical mechanism, including the participation of triplet-state intermediates, and rationalized the torquoselectivity responsible for the high stereoselectivity of the transformations. Furthermore, the methodology was successfully translated to continuous-flow conditions, allowing straightforward scale-up of the photochemical processes.

These results establish bicyclic pyrazoles as a previously underexplored class of photochemical building blocks and provide new opportunities for the synthesis of structurally complex and biologically relevant heterocyclic architectures using only substrate, solvent, and light.

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P63: Visible-Light-Driven Benzylation of In Situ-Formed Imines Using Toluenes and Acridine Photocatalysis

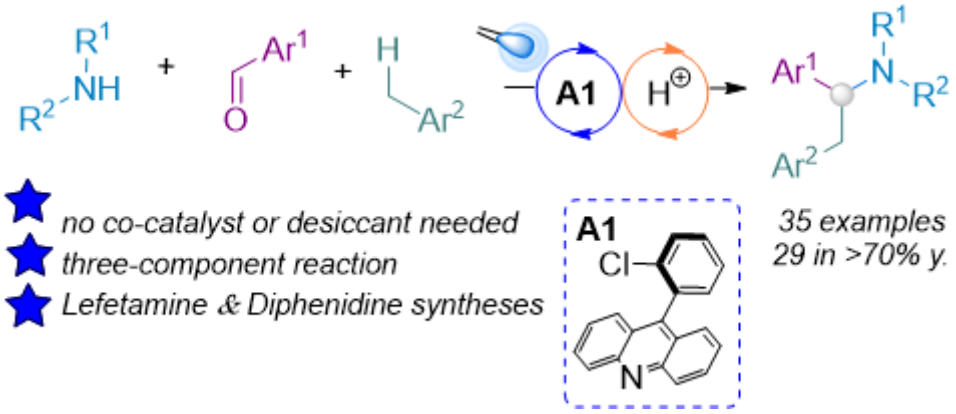
Mario Martinez-Lopez (1), Beatriz Quevedo-Flores (1), Loris Laze (1), Manuel A Ortuño (1), Irene Bosque (1), Jose C. Gonzalez-Gomez (1)

(1) Universidad de Alicante

Subject area: Photocatalytic organic transformations
Keywords: acridine photocatalysis, visible light, benzyl radicals, three-component reaction, metal-free

The 1,2-diarylethylamine framework is an important pharmacophore found in numerous biologically active compounds, including agents with anticonvulsant, analgesic, and neuroprotective activities, as well as NMDA receptor antagonists.[1] Nevertheless, efficient, modular synthesis of these structures from readily available starting materials remains a significant challenge, particularly via radical benzylation strategies. In this context, the homogeneous photooxidation of toluene derivatives to generate benzyl radicals is often problematic, especially for substrates with relatively high oxidation potentials, which restricts the scope of conventional methodologies.

In this work, we describe a visible-light-mediated three-component coupling that enables the synthesis of 1,2-diarylethylamines from simple toluene derivatives, aldehydes, and anilines using acridine as an organic photocatalyst (Scheme 1).[2] The process involves the *in situ* generation of an iminium ion, which subsequently undergoes radical benzylation promoted by the photoexcited acridine catalyst. The presence of trifluoroacetic acid (TFA) or *p*-toluenesulfonic acid (*p*-TsOH) is crucial, as these additives fulfill three complementary functions: activation of the photocatalyst, facilitation of iminium ion formation, and suppression of undesired product oxidation. Notably, unlike previously reported acridine-mediated photochemical transformations,[3,4] the present protocol does not require an additional cocatalyst for catalyst turnover, thereby simplifying the overall reaction system. The practical value of the methodology was further demonstrated through the synthesis of several bioactive targets, underscoring its potential utility in medicinal chemistry and drug discovery.



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P64: Acridinium Amidates as Versatile N-centered Direct Hydrogen Atom Transfer Catalysts

Neele Gause (1), Lukas-Maximilian Entgelmeier (2), Soichiro Mori (3), Olga García Mancheño (1), Kohsuke Ohmatsu, Takashi Ooi (4)

(1) Leibniz-Institut für Katalyse, (2) Organic Chemistry Institute, University Münster, (3) Scripps Research, (4) Department of Molecular and Macromolecular Chemistry, Graduate School of Engineering, Nagoya University

Subject area: Photocatalytic organic transformations

The utilization of photocatalysis for the functionalization of non-activated C(sp^3)–H bonds is a research area of high interest.[1] Among different strategies, the activation of aliphatic hydrocarbons though direct photoinduced hydrogen atom transfer (d-HAT) has attracted wide attention. However, the so far used catalytic systems primarily rely on oxo-groups, e.g. aromatic ketones and inorganic polyoxometalates,[2] while nitrogen-based d-HAT catalyst are still elusive.

Herein, we present zwitterionic acridinium amidates as a new class of N-based d-HAT catalysts able to form the corresponding amidyl radical as an excited-state triplet diradical under visible light irradiation.3 The generated radical can undergo HAT processes and enables C(sp3)–C(sp3) bond formations through Giese type addition reactions. The mechanistic investigations suggest a necessary stabilizing non-covalent interaction of the amidate nitrogen and a hydrogen-bond donor, such as hexafluoroisopropanol (HFIP). This study represents a new concept in d-HAT catalysis and opens new venues for C–H functionalization reactions through N-centered d-HAT.[3]

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P65: Photoredox Catalytic Synthesis of Quinolines and Indoles with Phenanthrenequinone Derivatives

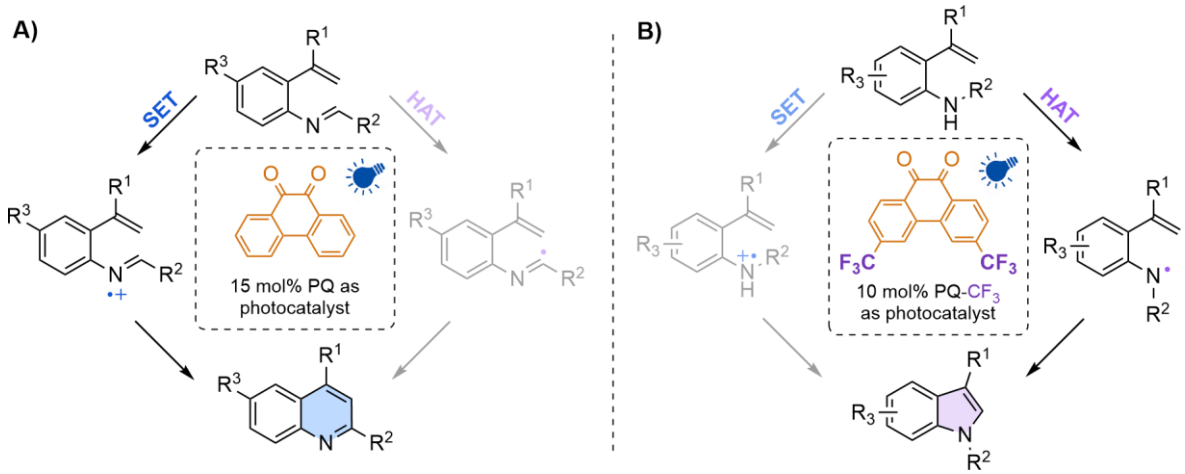
Juulia Talvitie (1), Juho Helaja (1)

(1) University of Helsinki

Subject area: Photocatalytic organic transformations
Keywords: organophotocatalysis, hydrogen atom transfer, single-electron transfer, quinones, electrocyclization

9,10-Phenanthrenequinone (PQ) can act as a photoactivated oxidant, and its use as a photocatalyst has increased rapidly during 2020s. In our developed method, blue-light-excited PQ catalyzes the electrocyclization of 2-vinylarylimines to polysubstituted quinolines.[1] Experimental and computational DFT studies indicated that excited-state PQ induces a single-electron oxidation of the imine which subsequently triggers the electrocyclization. (Scheme 1A).

To alter the redox properties of PQ, we modified its structure by designing a synthesis route for a novel electron-deficient 3,6-bis(trifluoromethyl)-substituted PQ-derivative (PQ-CF_3).[2] Its catalytic efficacy was shown to be superior to PQ in the oxidation of secondary alcohols, and further studies revealed that the mechanism of the oxidation depends both on the starting material and the catalyst. As the key mechanistic finding, we showed that PQ-CF_3 acts as a highly effective hydrogen atom transfer (HAT) catalyst instead of inducing single-electron transfer (SET). To investigate if this property could be utilized in direct N-H activation, we developed a method for the synthesis of polysubstituted indoles via electrocyclization of 2-vinylarylamines. The computational and experimental data was strongly opposing the SET pathway, suggesting that the cyclization progresses via a neutral nitrogen radical (Scheme 1B).[3]



Scheme 1. Proposed mechanistic pathways. A) The PQ-catalyzed synthesis of quinolines via SET. B) The PQ-CF_3-catalyzed synthesis of indoles via HAT.

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P66: Visible-Light-Driven Oxidative Coupling of Benzylamine Under O_2 and CO_2 Atmosphere Using a Single Ru–BODIPY Conjugated Dyad

Supriya Das (1), Chhanda Mondal (1), Sanjib K. Patra (1)

(1) Indian Institute of Technology Kharagpur, Kharagpur

Subject area: Photocatalytic organic transformations
Keywords: Ru(II)-BODIPY dyad, Oxidative coupling, Visible light, O_2/CO_2-mediated transformations

The oxidative transformation of amines to imines is an important reaction, as imines are versatile intermediates in pharmaceuticals, ligands, and functional materials, and serve as precursors to diverse architectures while enabling a key C–C bond–forming reactions.1,2 However, conventional methods often require harsh conditions and are not sustainable. In this context, visible–light–driven oxidative coupling provides a green, mild, and selective approach. Molecular oxygen is widely used oxidant, typically operating via reactive oxygen species such as singlet oxygen or superoxide radicals.3 In contrast, carbon dioxide, an abundant and sustainable C_1 feedstock, remains largely underexplored as an alternative electron acceptor in such oxidative transformations.

We have developed Ru(II)–BODIPY conjugated dyad as a visible–light–active photocatalyst (PC) for the oxidative coupling of benzylamines under both O_2 and CO_2 atmospheres, affording the corresponding N–benzylidenebenzylamines in high yields (95%) with a broad substrate scope. A series of control experiments, quenching studies, and spectroscopic studies were performed to elucidate the reaction mechanism, confirming the involvement of reactive oxygen species (under O_2) and radical intermediates (under CO_2). Our attempt to develop a non–heme organometallic photocatalyst enabling dual oxidative pathways as sustainable and versatile platform for imine synthesis will be presented.

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P67: Flow Chemistry Approach to Pyrazole Synthesis via 1,3-Dipolar Cycloaddition

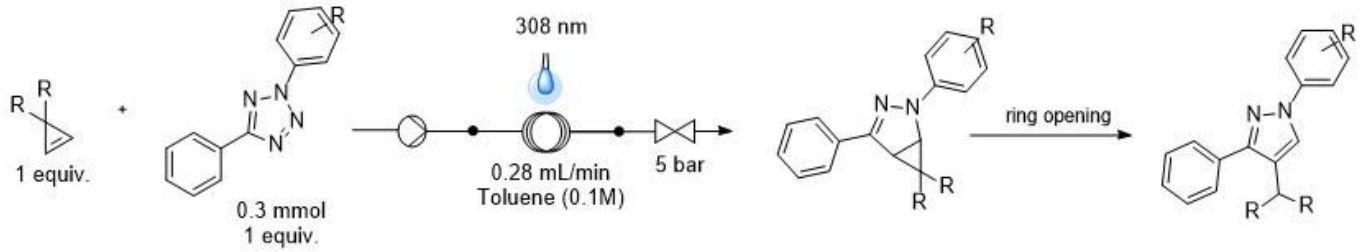
Beatriz Quevedo Flores (1,4), Jorge García Lacuna (2), Angel Martínez Garzón (3), Marcus Baumann (1)

(1) University College Dublin, School of Chemistry, Science Centre South, Belfield, Dublin 4, Ireland., (2) Universidad San Pablo CEU, School of Pharmacy, 28668, Madrid., (3) Universidad San Pablo CEU, School of Pharmacy, 28668, Madrid.(4) (1) Instituto de Síntesis Orgánica, Universidad de Alicante

Subject area: Photocatalytic organic transformations

Pyrazoles are a class of pharmaceutically relevant five-membered heterocycles that can be accessed through a variety of synthetic approaches, including condensation reactions, the Pechmann synthesis, and 1,3-dipolar cycloadditions.[1] Herein, we present a novel photochemical 1,3-dipolar cycloaddition between tetrazoles and cyclopropenes to afford pyrazoles. Tetrazoles are attractive precursors, whose major drawback is the release of nitrogen gas, which increase safety concerns and complicates scale-up in industrial venues. On the other hand, cyclopropenes are valuable structural motifs with high strain energy and subsequent instability.[2]

To address these challenges, flow chemistry is a powerful and innovative technology that enables safer handling of hazardous reactions through enhanced control of temperature and pressure, as well as uniform photochemical irradiation.[3,4] The reaction was performed using a flow reactor equipped with a 308 nm UV lamp and a back-pressure regulator to safely manage N_2 evolution. Under optimized conditions, a wide range of pyrazoles were synthesized in moderate to excellent yields in only 10–20 minutes. Interestingly, resulting pyrazoles suffer a ring opening in most of the cases. Furthermore, a continuous long-run experiment demonstrated the scalability of the process, delivering 1.5 g of product within 3 hours. These results highlight the method as a safe, reliable, and industrially relevant approach for pyrazole synthesis.



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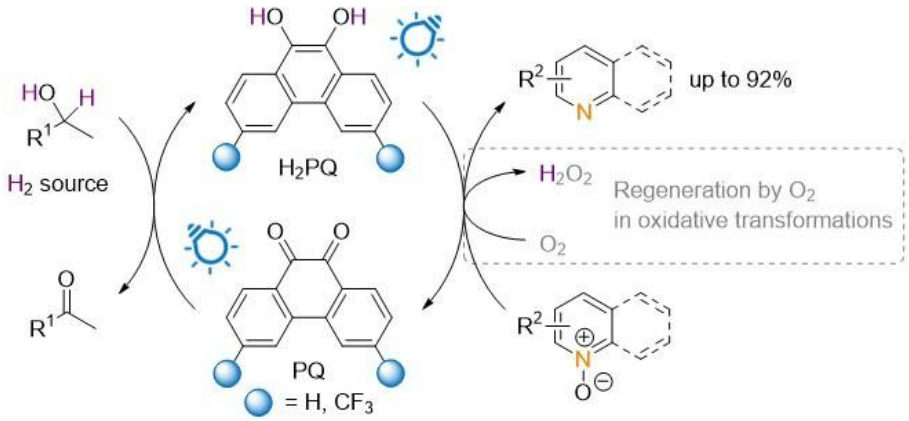
P68: Hydroquinone/Quinone Cycle for Reductive Photocatalytic Transformations

Iida Alanko (1), Juho Helaja (1)

(1) Department of Chemistry, University of Helsinki

Subject area: Photocatalytic organic transformations
Keywords: 9,10-phenanthrenequinone, photoredox catalysis



Over the past few decades, the shift from metal-based to organic photocatalysts has motivated the exploration of quinones as photoredox catalysts. Seminal work by Fukuzumi and co-workers showed that phenanthrenequinone (PQ) can act as a photoactivated oxidant in alcohol oxidations.[1] Building on this concept, we have enhanced the redox properties of PQ by tailoring it with CF_3 substituents.[2]

In PQ catalyzed oxidative protocols, terminal oxidants, such as oxygen or metal salts, are needed to regenerate PQ for the next oxidative cycle. Instead of regenerating PQ, we envisioned utilizing the regenerative cycle for photoactivated reductive transformations. To test this concept, we investigated photoactivated deoxygenation of N-heterocyclic *N*-oxides.[3] The developed method utilizes simple molecules, such as alcohols, as hydrogen sources to generate *in situ* phenanthrenehydroquinones (H_2PQs) which act as photoactivated reductants enabling deoxygenation of pyridine and quinoline *N*-oxides. Combined experimental and computational mechanistic studies revealed H_2PQs to act as potent photoacids and electron donors in their excited singlet state. To the best of our knowledge, this is the first organic transformation mediated by photoactivated H_2PQs.

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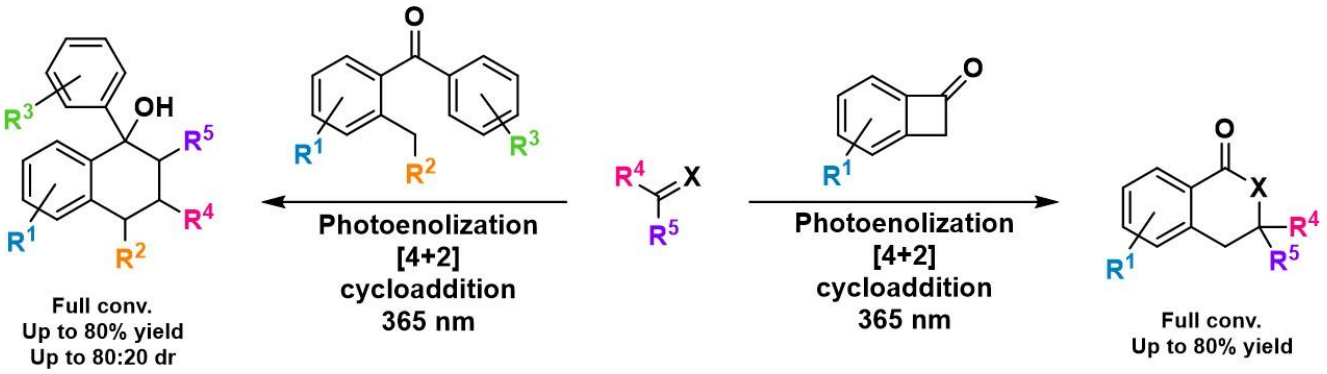
P69: Diastereoselective synthesis of Photochemically Generated Hydroxy-o-Quinodimethanes via [4+2] cycloaddition

María González Marcos, José Trujillo-Sierra, Maria de Gracia Retamosa-Hernández, Nerea Sanchez-Montesinos, Francisco Foubelo, José Miguel Sansano Gil, Ana Sirvent Verdú

University of Alicante

Subject area: Photocatalytic organic transformations
Keywords: Photochemistry, photoenolization, diastereoselective, [4+2] cycloaddition, Diels-Alder Reaction



In recent decades, synthetic photochemistry has evolved into a highly sophisticated field.[1] A wide variety of light-mediated transformations have been employed for the construction of structurally complex organic molecules,[2] considerably expanding the toolbox available to synthetic chemists. Among these transformations, the photoenolization of ortho-alkyl aromatic ketones and aldehydes represents a classic photochemical process, first reported in 1961, that generates the corresponding hydroxy-o-quinodimethanes.[3] These electron-rich intermediates possess sufficient lifetimes to participate efficiently in subsequent reactions, most notably as dienes in [4+2] cycloadditions with electron-deficient alkenes. The resulting benzannulated carbocyclic scaffolds constitute valuable chiral frameworks commonly encountered in both approved pharmaceuticals[4] and naturally occurring bioactive compounds.[5]

Due to the versatility and the synthetic potential of the photoenolization/Diels-Alder (PEDA) reaction, in this work, we successfully developed a [4+2] cycloaddition between hydroxy-o-quinodinomethanes and different alkenes and ketones under very mild conditions. The study explored the impact of different substituents on both, affording the corresponding cycloadducts in excellent diastereomeric ratios and yields.

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P70: Visible-Light-Driven Perylenemonoimide Mediated Photooxidation of Alcohols toward Synthesis of Bis(indolyl)methanes

Premnath Das (1), Moromi Nath (1), Priyanath Das (1), Sabyashachi Mishra (1), Sanjib K. Patra (1)

(1) Indian Institute of Technology Kharagpur

Subject area: Photocatalytic organic transformations
Keywords: interrupted borrowing hydrogen, visible light, metal-free, perylenemonoimide

Interrupted borrowing hydrogen (IBH) strategies, though less explored than conventional borrowing hy0drogen approaches, hold significant promise for advancing sustainable catalysis. However, the development of efficient metal–free catalytic systems for IBH remains limited.[1] In this context, perylenemonoimide (PMI), owing to its structural tunability and exceptional photophysical properties, emerges as a promising yet underutilized organic photocatalyst. In this work, we exploit the photo-dehydrogenating capability of PMI to develop a metal–free approach for the synthesis of bis(indolyl)methanes (BIMs) via an IBH pathway. The reaction employs alcohols and indoles under visible–light irradiation and open–air conditions, affording moderate to good yields. Mechanistically, the transformation proceeds through a synergistic interplay of single electron transfer (SET) and hydrogen atom transfer (HAT). Upon photoexcitation, PMI undergoes SET with KOtBu to generate a reduced species capable of abstracting hydrogen atoms from alcohol substrates, forming a dearomatized PMI intermediate that drives the catalytic cycle under aerobic conditions.[2] Notably, this strategy mimics traditional transition–metal–mediated IBH processes, which typically require harsh conditions and inert atmospheres, while operating under mild, sustainable, and metal-free conditions without significant side–product formation.[3,4] Mechanistic insights were obtained through control experiments, intermediate characterization, EPR spectroscopy, and DFT studies. Our attempt to develop sustainable, metal–free photocatalytic strategy for BIMs synthesis under open–air conditions will be presented.

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P71: A heterogeneous photocatalytic strategy for the aerobic conjugate addition of pyrrolidines to electron-deficient olefins

Paula Romero-Navarro (1), Francisco Alonso (1)

(1) Instituto de Síntesis Orgánica, Universidad de Alicante

Subject area: Photocatalytic organic transformations
Keywords: Conjugate addition, heterogeneous photocatalysis, pyrrolidines, nitrogen heterocycles, titania.

Pyrrolidines are structural units of great importance in asymmetric organic synthesis[1] and privileged motifs in bioactive compounds and drugs of interest (Scheme 1).[2] However, catalytic methods that enable direct C–C bond formation at the α–position of saturated amines under operationally simple and sustainable conditions remain limited.[3][4]. This work describes a heterogeneous photocatalytic methodology that enables the efficient and regioselective conjugate α–C–H addition of N–protected pyrrolidines and related saturated N–heterocycles to electron–deficient olefins.[5] The process employs commercial titanium dioxide –an economical, stable and environmentally friendly material– as a photocatalyst under UVA irradiation in air. The method is compatible with a broad range of substrates, provides the corresponding adducts in modest–to–good isolated yields, and allows straightforward recovery and reuse of the photocatalyst. Mechanistic experiments support the involvement of α–amino radical intermediates and a photoinitiated chain component in which the solvent likely serves as the principal H–atom donor. Overall, these findings establish an "aerobic titania photocatalysis" platform for synthetically useful α–C–H bond constructions adjacent to nitrogen and provide a basis for extending heterogeneous photocatalysis to related bond–forming transformations.

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P72: Diastereoselective [4 + 2] Cycloadditions of Photogenerated o-Quinodimethanes with Olefinic Oxindoles

José Trujillo Sierra (1), María González-Marcos, Enara Esteban-Hidalgo, Ana Sirvent, María de Gracia Retamosa

(1) Universidad de Alicante

Subject area: Photocatalytic organic transformations
Keywords: Photochemistry, photoenolization, diastereoselective, [4+2] cycloaddition, Diels-Alder Reaction

In the last decades, synthetic photochemistry has grown increasingly sophisticated.[1] Numerous light–induced reactions have been developed for the preparation of structurally complex organic compounds,[2] greatly broadening the range of tools available to modern chemists. One representative example is the photoenolization of ortho–alkyl aromatic ketones and aldehydes, which generates hydroxy–o–quinodinomethanes through a well–established photochemical process first reported in 1961.[3] These highly reactive, electron–rich intermediates possess sufficient stability to participate effectively in further transformations, most notably as dienes in [4+2] cycloaddition reactions with electron–deficient alkenes. Such processes provide access to chiral benzannulated carbocyclic frameworks, structural motifs commonly present in pharmaceutical agents[4] and natural products.[5]

Given the versatility and significant synthetic utility of the photoenolization/Diels–Alder (PEDA) reaction, this work describes the successful development of a [4+2] cycloaddition between hydroxy–o–quinodinomethanes and olefinic oxindoles under mild reaction conditions. The influence of various substituents on both the ketone and olefin components was systematically investigated, leading to the formation of the corresponding cycloadducts with good yields and excellent diastereoselectivities.

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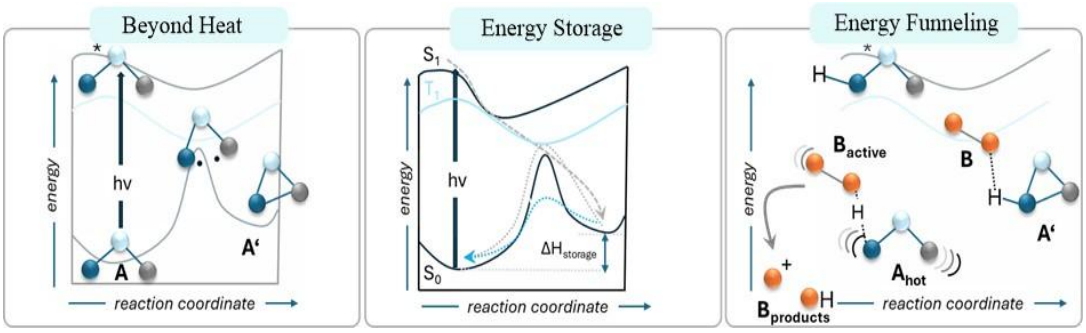
P73: Harnessing Stored Molecular Energy for Intermolecular Activation

Vanshika Raheja (1), Aryaman Pattanaik (1), Mary Gaber (1), Julia Rehbein (1)

(1) Universität Regensburg

Subject area: Photocatalytic organic transformations
Keywords: solar energy storage, norbornadiene-quadricyclane, strain-release, H-bond-assisted vibrational energy transfer

NBD/QC photoisomers are promising candidates for solar energy storage owing to high-energy double cyclopropane ring structure. In such systems, irradiation generates metastable isomer from which stored energy can be released on demand via thermal, photochemical, or electrochemical activation.[1] Herein, we focus on fundamental question whether **strain-release energy** associated with QC-to-NBD back-conversion can be **directly harnessed to promote chemical transformations** rather than being dissipated thermally.



To address this challenge, we investigate strain-release energy from QC to NBD **(A´→A)** that can be channelled through hydrogen-bond-mediated vibrational mode coupling into bound reactants **(B),** thereby enabling strain-driven chemical activation. We designed substituted NBD/QC systems bearing push-pull substituents (-COOH, -CN, -Ph, -Np) to tune visible light absorption and introduce directional hydrogen-bonding sites. DFT calculations reveal that increasing push-pull character at 2,3-positions enhances strain-release energy, while phenyl substitution with EWGs attenuates it. We monitored photochemical NBD-to-QC interconversion and catalytic QC back-conversion by UV/Vis under thermal and photocatalytic conditions, using Rh- and Ir-photocatalysts as well as PDI sensitizers[2]. Various catalyst materials were examined to investigate catalytic reaction governing back conversion via a singlet-triplet mechanism.[3] Ground-state Born-Oppenheimer molecular dynamics simulations indicate that QC ring-opening produces vibrationally hot NBDs. Excess vibrational energy localizes along breaking C-C bonds in these NBDs, enhancing acidity at carboxylic acid sites and facilitating proton shuttling and stronger hydrogen bonding. Together, these results establish direct link between molecular strain release, vibrational energy redistribution[4], and acidic protonation, demonstrating that stored energy can be converted into chemically productive activation rather than being dissipated as heat.

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P74: Visible-light cobalt(II)-catalysed synthesis of aroyl amides from arylazo sulfones

Komal Jaiswal (1)

(1) Universität Regensburg

Subject area: Photocatalytic organic transformations
Keywords: Dyed Auxiliary, Arylazo Sulfones, Carbonylation

A strategy combining the unique properties of arylazo sulfones as dyed auxiliary group–bearing substrates for arylation reactions and $Co_2(CO)_8$ as a catalyst in carbonylation processes was used to prepare aromatic amides. This versatile method was utilized to create a library of aroyl amides with good to excellent yields.

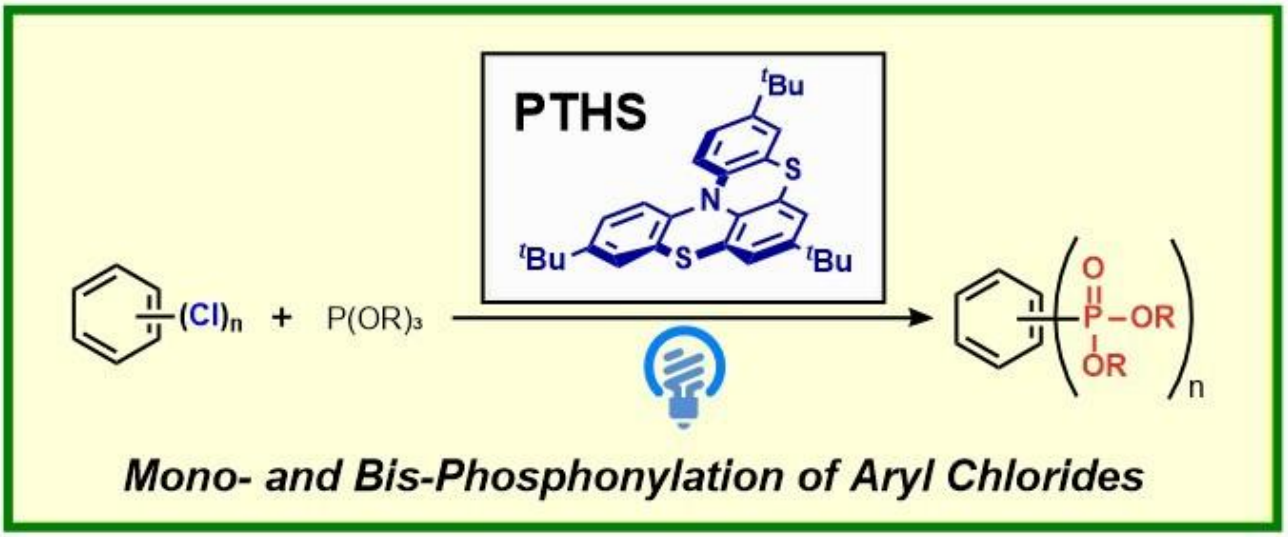
P75: Mono- and Bis-Phosphonylation of Aryl Chlorides via Helical Phenothiazine Organophotoredox Catalysis

Kenta Tanaka (1)

(1) Okayama University

Subject area: Photocatalytic organic transformations
Keywords: Organophotoredox Catalysts, Visible light, Phenothiazine, phosphonylation

Aryl phosphonates are important structural motifs in a variety of fields, including pharmaceuticals and functional materials. While methods for the phosphonylation of aryl iodides and bromides have been widely developed, the corresponding transformation of aryl chlorides remains relatively unexplored due to the high energy barrier associated with the activation of C(sp2)−Cl bonds. In particular, bis-phosphonylation of aryl chlorides remains largely unexplored.1 Recently, we have designed and synthesized organophotoredox catalysts and developed visible-light-induced various photochemical transformations.2 Here, we report the mono- and bis-phosphonylation of aryl chlorides using a strongly reducing helical phenothiazine organophotoredox catalyst (PTHS).3 The reaction is applicable to various mono- and bis-chlorinated benzenes to obtain the corresponding aryl phosphonates. This method offers versatile access to functionalized aryl phosphonates, thus rendering it a promising tool for the synthesis of pharmaceuticals and functional materials.



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P76: "On-water" Photosensitization Enables Redox-Neutral Acylation and Alkylation of Quinones

Rohan Sharma (1), Burkhard König

(1) University of Regensburg

Subject area: Photocatalytic organic transformations

Water–oil interfaces have a high cohesive energy density and form a supramolecular hydrogen-bonding network that supports organic reactions in multiple ways. Here, we introduce a redox-neutral photo-Friedel-Crafts acylation and alkylation of quinones at the aqueous–organic interface. Spectroscopic and computational studies reveal extensive hydrogen bonding at the water surface, stabilizing the quinone's photo-excited state and lowering its energy, while also increasing the excited state energy of the photosensitizer Eosin Y. This combined behavior allows photosensitization of quinone under visible light at the oil–water interface, promoting the desired transformation. Mechanistic studies show that C–C bond formation occurs via hydrogen atom transfer (HAT) from the aldehyde or alkyl reactant to the quinone, following a redox-neutral pathway, with radical recombination producing 2-functionalized quinols. The method demonstrates broad applicability with aromatic and aliphatic aldehydes, including natural and synthetic drug molecules, as well as ethers, thioethers, alkanes, silanes, and amines, which act as acylating or alkylating agents. The reactions have been successfully scaled up, and the resulting acylated quinol products have undergone further functionalization to showcase their synthetic utility.

P77: Photocatalytic Oxide Ceramic Nanofibers Synthesized from Recycled Industrial Waste for Degradation of Organic Pollutants

Kateryna Nemesh (1), Erika Mudra, Ivan Shepa, Jana Piroskova, Alexandra Kovalčíková, Dávid Jáger, Maksym Lisnichuk, František Kromka, Saeed Sajjadi, Surjyakanta Rana, Michal Žitňan, Marzieh Ghadamyari, José Joaquín Velázquez García, Dušan Galusek

(1) Institute of Materials Research of SAS Slovak Academy of Sciences

Subject area: Photocatalytic organic transformations
Keywords: Electrospinning, hydrometallurgical treatment, waste recycling, nano/microfibers, ceramics, photocatalysis

Significant quantities of zinc are contained within secondary resources generated during both primary and secondary production stages, such as slag, fly ash, dross, and foam. Due to their heterogeneous nature, these by-products are frequently classified as hazardous waste. Hydrometallurgical processing utilizing either acidic or alkaline aqueous media presents an efficient pathway for leaching target metals into solution.

ZnO-based ceramic nanofibers were made from sal ammonia skimming waste from a wet-piece hot-dip galvanizing process. The raw material was studied using phase analysis and atomic absorption spectroscopy. Zinc was extracted using three different solutions (HCl, $(NH_4)_2CO_3$, and H_2SO_4). After that, spinning solutions were prepared using poly(vinylpyrrolidone). Nanofibers were fabricated via needleless electrospinning and subsequently calcined in air at 600 °C to obtain crystalline ceramic structures.

The resulting fibers were characterized by SEM, EDX, XRD, and BET analysis. The results show that the type of leaching solution affects fiber shape, crystal structure, and surface area. These differences also change the photocatalytic activity. The materials were tested for the degradation of organic pollutants, including dyes (Methylene Blue and Reactive Black 5) and an antibiotic (tetracycline). After the tests, HPLC was used to check the remaining solution and identify possible reaction products. The results show that waste zinc materials can be successfully turned into useful photocatalytic nanofibers for cleaning polluted water.

This work was supported by the Scientific Grant Agency of the Ministry of Education, Science, Research and Sport of the Slovak Republic and the Slovak Academy of Sciences, project No. VEGA 2/0106/26. Funded by the EU Next Generation EU through the Recovery and Resilience Plan for Slovakia under the project No. 09I03-03-V02-00013.

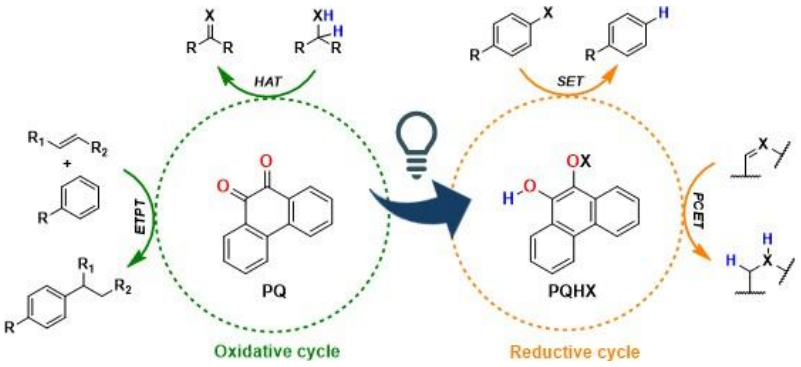
P78: Hydroquinone Anion (HPQ^-): The Key Active Species for Efficient Hydrodehalogenation of Aryl Halides

Andrés Mollar Cuni (1), Juho Helaja (1)

(1) University of Helsinki

Subject area: Photocatalytic organic transformations
Keywords: Photoredox catalysis, Hydroquinone anion, Photoreduction, Hydrodehalogenation

During the last decades, the development of photoredox catalysis has revolutionized the means of performing organic transformations. The use of organic dyes as photocatalyst, instead of classical metal-based photosensitizers, has increased interest in this methodology due to its availability and lower cost.[1] However, one well known weakness of the method is the requirement for (over)stoichiometric amounts of sacrificial oxidants/reductants, co-catalysts or additives, such as HAT agents, which produce both economic burden and chemical waste. In recent years, phenanthrenequinones (PQs) have emerged as promising catalysts due to its versatility, as it can act as direct HAT photocatalyst, as well as reacts through SET or ETPT mechanisms.[2,3] Additionally, phenanthrenehydroquinones derivatives (PQHX), reduced forms of PQs which can be obtained in situ using different types of reductants, are good reductant photocatalysts proceeding via SET or PCET mechanism.[4] In view of this versatility, PQs could be considered as Swiss army knife in photocatalysis.



A clear example of this versatility is the combination of PQ photocatalysts with formate salts, which act as green reductants. Upon blue-light irradiation, the PQ catalyst activates and oxidizes the formate, generating a previously unreported intermediate under catalytic conditions, namely the hydroquinone anion (HPQ^-). This newly identified species is capable of efficiently promoting the dehalogenation of aryl halides with catalyst loadings in the ppm range, thereby establishing a benchmark for this type of transformation.

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P79: Visible Light-Mediated Synthesis of Perfluoroalkylated Heteroarenes

Yassine Benhamidat (1), Gianluca Montella (2), Rosaria Schettini (2), Ibrahim Khettar (2), Giorgio Della Sala (2), Leyre Marzo (3), Jose Lara Alemàn (3)

(1) Università Degli Studi di Salerno, (2) University of Salerno, (3) Universidad Autónoma de Madrid

Subject area: Photocatalytic organic transformations
Keywords: perfluoroalkylation ● visible light ● amino acids ● photoredox catalysis ● heteroarenes

Five membered heteroarene compounds, such as azoles and their derivatives, are known for their biological and chemical properties.[1] As a result they present a high potential application in agricultural supramolecular and especially medicinal chemistry.[2] For this, increasing their lipophilicity and enhancing their metabolic stability can be achieved by the insertion of fluorine atoms improving their physicochemical and pharmacokinetic properties.[3] Consequently, developing a novel synthetic approach for their functionalization is highly important and challenging. Photocatalysis has recently emerged as an unavoidable methodology for fluoroalkylation reactions avoiding the conventional harsh conditions for such reactions.[4] Although visible-light-promoted fluoroalkylation has developed rapidly in recent years, the fluoroalkylation of such azole analogues remains poorly explored. The few reported examples are limited to the installation of trifluoromethyl or sulfonyldifluoromethyl groups on substrates lacking aromatic substituents, avoiding regioselectivity issues, and rely on synthetically demanding fluoroalkyl radical precursors.[5]

Herein, we report the first photoredox-catalyzed perfluoroalkylation of oxazoles and thiazoles using commercially available perfluoroalkyl iodides in the presence of a silver salt additive. The developed visible-light-driven protocol exhibits broad substrate and perfluoroalkyl group compatibility, including substrates bearing aromatic substituents at the C-2 position. In addition, mechanistic investigations provide insight into the reaction pathway.

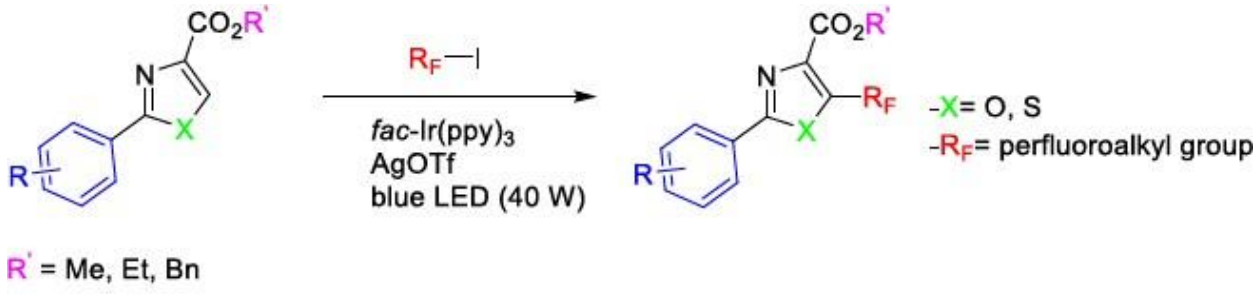

Figure 1: Current approach for photoredox-catalyzed perfluoroalkylation reaction.

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P80: Regioselective Functionalization of Propane and *n*-Butane through Nickel-mediated Radical Locking

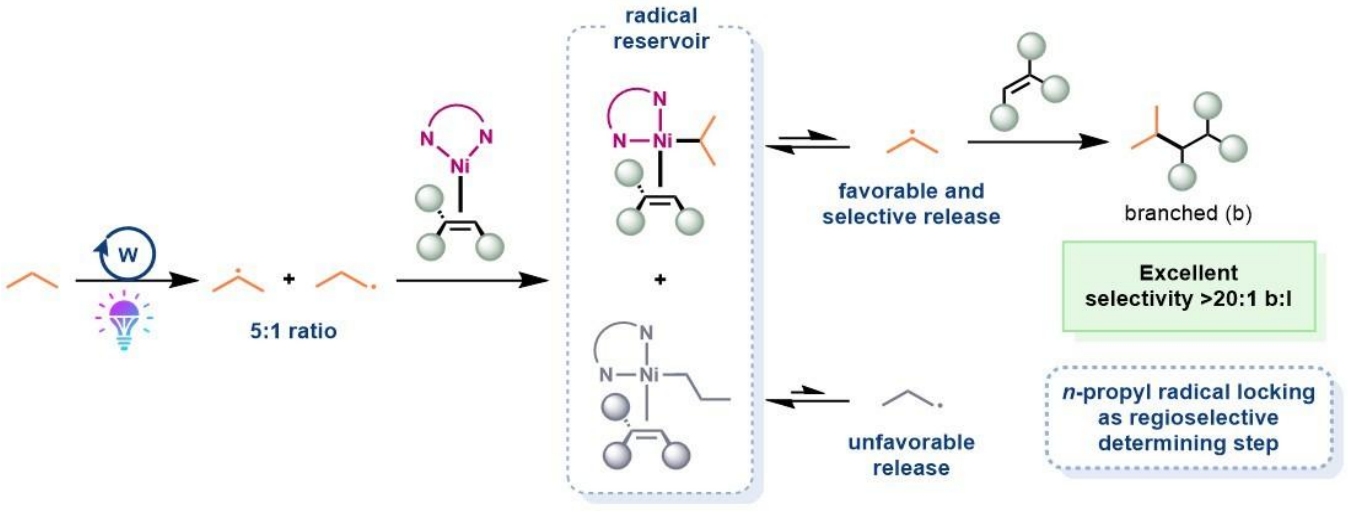
Hugo Jiménez-Cristóbal (1), Akshay M. Nair (2), Poulami Mukherjee (3), Adhya Suresh (3), Hanshika Arya (3), Ángel Rentería-Gómez (3), Osvaldo Gutierrez (3), Martín Fañanás-Mastral (1)

(1) CiQUS Universidade de Santiago de Compostela. Spain, (2) CiQUS Universidade de Santiago de Compostela. India, (3) University of California Los Angeles. USA.

Subject area: Photocatalytic organic transformations
Keywords: Gaseous alkanes, Hydrogen Atom Transfer (HAT), Regioselectivity

Gaseous alkanes are the most abundant carbon feedstock, yet their direct functionalization remains challenging due to their gaseous nature and the inertness of their C(sp^3)–H bonds. Photocatalytic hydrogen atom transfer (HAT) has emerged as a powerful strategy for activating these unreactive molecules by generating alkyl radicals.[1] However, control over the regioselectivity in the functionalization of C_3 and C_4 alkanes, such as propane and n-butane, still remains as an unresolved challenge. In reported strategies, site-selectivity is dictated by the nature of the HAT agent. Existing methodologies based on ligand-to-metal charge transfer (LMCT) involving chlorine or oxygen radicals or tetrabutylammonium decatungstate (TBADT) photocatalysis typically yield mixtures of branched and linear (b:l) products, with regioisomeric ratios ranging from 1:1 to 5:1 (b:l).[2]

Herein, we report a dual TBADT/nickel catalytic platform for gaseous alkanes functionalization, in which site-selectivity is not dictated at the HAT step. As demonstrated by DFT studies, the nickel co-catalyst serves as an alkyl radical reservoir, selectively releasing the secondary alkyl radical in a controlled manner, while locking the linear primary one (Scheme 1). This off-cycle mechanism provides excellent regioselectivity (>20:1 b:l) and broad applicability across Giese-type additions, alkene dicarbofunctionalizations, and defluorinative alkylations.



Scheme 1. Ni-mediated radical locking for the regioselective functionalization of propane.

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P81: *N*-doped carbon quantum dots as sustainable photocatalysts for the degradation of organic dyes in aqueous media

Cristina Mellinas (1), María de la O Martínez (1), Alfonso Jiménez (1), María del Carmen Garrigós (1)

(1) University of Alicante

Subject area: Sustainable and Green Photochemical Applications

The development of sustainable photocatalysts from agro-industrial residues offers a promising approach for combining environmental remediation with biomass valorisation. In this work, nitrogen-doped carbon quantum dots (N-CQDs) were synthesised from grape pomace extract through a rapid microwave-assisted process and evaluated as photocatalysts for the degradation of methylene blue in aqueous media.

The synthesis was optimised using a Box-Behnken experimental design considering reaction time, microwave power and the urea-to-extract ratio as key variables, while methylene blue degradation was used as the response. Optimal conditions were identified at 10 min, 900 W and a urea-to-extract ratio of 4.87 g/g. Under these conditions, elemental analysis revealed a 38.7% increase in nitrogen content compared with the precursor grape pomace extract, while X-ray photoelectron spectroscopy confirmed the incorporation of nitrogen-containing surface functionalities, including C-N and N-H groups. UV-Vis spectroscopy, FTIR and electron microscopy further confirmed the formation and optical characteristics of the N-CQDs.

The resulting nanomaterial exhibited pronounced photocatalytic activity towards methylene blue degradation under both UV and simulated solar irradiation. The rapid degradation kinetics observed under irradiation highlight the strong photoactivity of the N-CQDs and suggest the involvement of reactive oxygen species in the degradation process. In particular, the performance under solar irradiation demonstrates the potential of these biomass-derived quantum dots as sustainable light-responsive materials for aqueous-phase photocatalytic applications.

Overall, this work demonstrates a fast and resource-efficient route to produce nitrogen-doped carbon quantum dots from grape pomace, integrating agro-industrial by-product valorisation with photocatalytic water treatment. The results contribute to the development of sustainable carbon-based photocatalysts for advanced environmental remediation.

P82: In Situ Single-Particle Studies of Distance-Dependent Energy Transfer and Singlet Oxygen Generation

Oleg Semenov (1)

(1) AMOLF, The Netherlands

Subject area: Sustainable and Green Photochemical Applications

The performance of surface-supported photochemical systems is often governed by nanoscale interfacial effects that remain obscured in ensemble measurements. Distance-dependent interactions at photoactive interfaces can strongly influence excited-state dynamics and chemical transformation, yet these effects are often difficult to isolate in bulk measurements.

This work examines singlet oxygen generation at the single-particle level using surface-bound particles immobilized on glass substrates with controlled spacer layers. The influence of spacer thickness affects on optical coupling, nanosurface energy transfer, and the resulting photoactivity of individual particles under irradiation. The experimental platform enables in situ observation of individual particles during optical excitation and chemical exposure, allowing changes in fluorescence response and reactivity to be monitored in real time, primarily by total internal reflection fluorescence (TIRF) microscopy. In this system, silicon phthalocyanine dihydroxide ($SiPc(OH)_2$) acts as the photocatalyst, and its fluorescence signal response varies with alumina spacer thickness, indicating that the separation between interacting components influences its excited-state behavior. To probe the photochemical consequences of these changes, 1,3-diphenylisobenzofuran (DPBF) is used as a singlet-oxygen-sensitive probe. These studies help establish structure-function relationships between spacer distance, $SiPc(OH)_2$ emission, and local photoactivity, providing insight into the design of surface-supported photochemical systems for reactive oxygen generation, sensing, and offering guiding principles for the future development of fiber-based photoreactors.

P83: Hybrid catalytic conversion of functionalized alkane building blocks into chiral amines

Sara Arteche Echeverría (1), Sébastien Roy (1), Vitaly Ordomsky (2), Egon Heuson (2)

(1) Sanofi, (2) Unité de Catalyse et Chimie du Solide

Subject area: Hybrid Catalytic Systems and Enzyme-catalyzed organic reactions
Keywords: Hybrid catalysis, photocatalysis, biocatalysis, amines, alkanes.

The pharmaceutical industry is demanding sustainable amine synthesis methods. Transaminases, catalyzing the transfer of an amino group from an aminated donor substrate to an acceptor keto one, stand as suitable catalysts. However, since keto-substrates may not be directly available in nature, enzyme-compatible approaches for keto-product synthesis are needed. A strategy is the biocatalytic oxidation of sp3 C-H bonds. Despite coupling enzymes enhances one-pot synthesis by reducing intermediate purification steps, the resulting enzymatic cascades often inquire the stabilization of coexisting substrates and availability of expensive cofactors. Plus, for higher reaction control, pure enzymes may be used, the preparation of which iscostly and time-consuming.[1] Hybrid catalysis couples chemical catalysts with enzymes and can provide a solution to such systems. Among the reported chemical catalysts for alkane oxidation, photocatalysts use light as energy source under mild conditions, increasing their potential enzyme-compatibility. Recent works mainly couple homogeneous photocatalysts withdifferent families of enzymes.[2] From an industrial perspective, however, switching to heterogenous catalysts is more attractive as it can facilitate catalyst recycling and process scale-up.

This work aims to design a hybrid system coupling a heterogeneous photocatalyst with a transaminase in one-pot. Alkanes are first photocatalytically oxidized to ketones, followed by their transamination to chiral amines. 7 reported heterogeneous photocatalysts working under mild conditions were screened towards methylcyclohexane, and 9 *(S)*-transaminases were produced and characterized. At this stage, a one-pot/two-step reaction was achieved in a biphasic system. To the photo-oxidized organic mixture, the aqueous phase with all components for the transamination was added, where keto-products were converted to their corresponding amines.

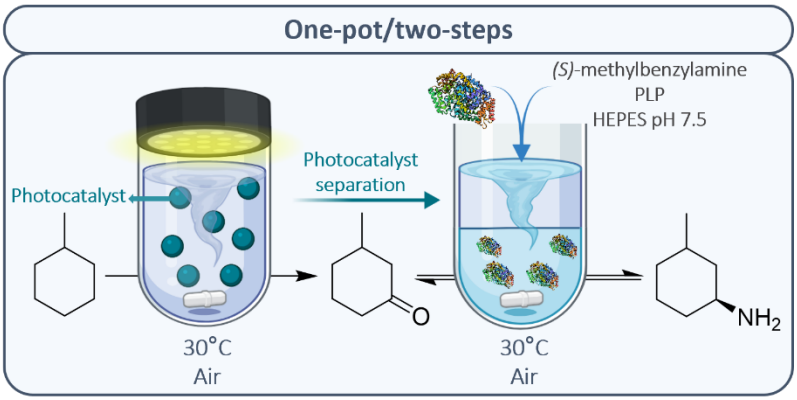

Figure 1. One-pot/two-step photobio-amination of methylcyclohexane.

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11.SOCIAL PROGRAM

Participants and accompanying persons of PHOTOCAT26 are invited to all the activities detailed in this social program.

Monday, 21st September 2026
Welcome reception at the Museum of the University of Alicante (MUA). It will take place from 18:30 to 20:00 h.

Tuesday, 22nd September 2026
Beach Volley tournament, at Playa de San Juan

- From San Vicente del Raspeig to Tournament place/beach:

MEETING POINT18:00 · Bus stop opposite Lecture Hall II (Aulario II)

- From Tournament place/beach to San Vicente del Raspeig:

Bus will leave from Tournament place/beach around 20:30 h or when the tournament finishes.

Wednesday, 23rd September 2026
Visit to Alicante city.

- From San Vicente del Raspeig to Alicante city:

MEETING POINT18:00 · Bus stop opposite Lecture Hall II (Aulario II)

Thursday, 24th September 2026
Conference Banquet at Meliá Hotel (Address: Plaza del Puerto 3, Alicante)
Participants who booked accommodation through the Photocat26 webpage:

- From San Vicente del Raspeig to Meliá Hotel:

MEETING POINT 20:00 · Hotel Universa (Avda. Vicente Savall Pascual, 33, San Vicente del Raspeig) & the roundabout near Micampus residence, in front of the main entrance of the university.

- From Meliá Hotel to San Vicente del Raspeig:

Bus will leave from Meliá Hotel at 00:30.
Participants who arranged their accommodation independently:

- Bus 24 (From Stop at C/Alicante 135, to Stop at Mercado) or Tram L2 (From Stop Universidad to Stop at Mercado) then, 10 min walk.

Friday, 25th September 2026
Suggested visit to the 'European Research Night 2026' situated at the University of Alicante, all around campus.

12. Sponsors

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