

CataLysis



CataLysis Networking Conference 2026

20.05.2026 - 22.05.2026

Leonardo Hotel Weimar, Weimar,
Germany

Organizing CRCs and TRRs

CRC 1333 | Stuttgart www.crc1333.de

CRC/TRR 247 | Duisburg, Essen and Bochum www.trr247.de

CRC/TRR 234 | Ulm and Jena www.catalight.eu

CRC 1441 | Karlsruhe www.trackact.kit.edu

CRC 325 | Regensburg, München, Leipzig, Saarbrücken, Mainz
www.crc325.de

CRC 1633 | Göttingen <https://www.uni-goettingen.de/de/683468.html>

Administration & Organization

Dr. Elisabeth Rütthlein (CRC 1333)

Dr. Carina Marek (CRC/TRR 247)

Dr. Philipp Traber (CRC/TRR 234)

Dr. Florian Maurer (CRC 1441)

Dr. Alena Hölzl-Hobmeier (CRC/TRR 325)

Dr. Janina Dürr (CRC 1633)

Acknowledgements

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20.05.2026	Goethe-Saal 1+2 (Plenum)	Goethe-Saal 3+4
11:00 – 12:00	Reception & pre-meetings	
11:00 – 13:30	Lunch Snack	
13:30 – 14:00	Welcome Felix Schacher (TRR 234)	
14:00 – 14:30	Introduction CRC 1615 Raimund Horn (CRC 1615) - Bringing Operando Spectroscopy to the Reactor	
14:30 – 14:40	Change of rooms	
14:40 – 15:05	Stéphane Kenmoe (TRR 247) - Ethylene glycol partial oxidation on Co3O4 surfaces: interplay between endogenous and exogenous factors	René Peters (CRC 1333) - Mesoporous Confinement Enables Enzyme-Like Rate Acceleration in Cooperative Asymmetric Catalysis
15:05 – 15:30	Catalina Leiva-Leroy (TRR 247) - Bridging Heterogeneous Liquid-Phase Thermal and Electrocatalytic Oxidation of Ethylene Glycol over Co3O4 Nanoparticles	Deven Estes (CRC 1333) - The Effects of Selective Substrate Adsorption on Catalytic Reactions in Confinement
15:30 – 16:00	Break & Snack	
16:00 – 16:40	Keynote CRC 1333 Mircea Dincă - MOF-Enabled Catalysis for Commodity Chemicals	
16:40 – 16:50	Change of rooms	
16:50 – 17:15	Sofia Kolin (CRC 1333) - Who sets the pace? How functionalization and defects control diffusion in UiO-67 frameworks	Alexander Breder (CRC 325) - Translocal Control in Symmetric σ -Bond Net Heterolysis
17:15 – 17:40	Felix Fischer (CRC 1333) - Hard X-ray Spectroscopy of Molecular Heterogeneous Catalysts in Confined Geometries	Oliver Reiser (CRC 325) - When the same is not the same: Divergent reactivity of radicals generated from different metal complexes or organic dyes through photoredox catalysis.
17:40 – 18:55	Poster Session 1 CRC1333, CRC1441, TRR325	
18:55 – 19:00	Break	
19:00	Dinner	
20:30	Get together and Networking	

21.05.2026	Goethe-Saal 1+2 (Plenum)	Goethe-Saal 3+4
08:50 – 09:00	Intro (Coordination Team)	
09:00 – 09:40	Keynote CRC 1633 Vincent Artero - From Proton Relays to Microenvironments: Harnessing PCET processes in molecular catalysis for H ₂ and CO ₂ Conversion	
09:40 – 09:50	Change of rooms	
09:50 – 10:15	Lingli Ni (TRR 234) - Porous Carbon Nitride: Nanostructure-Controlled Bandgap and Photocatalytic H ₂ O ₂ Generation	Felix Studt (CRC 1441) - Simulating the effect of Pt particle sizes for ammonia oxidation
10:15 – 10:40	Stephan Kupfer (TRR 234) - Photo-induced Electron Transfer within the Marcus Picture and Beyond	Di Wang (CRC 1441) - Operando (S)TEM insights on mass selected Pt ₂₀₀ /CeO ₂ as model catalyst for CO oxidation
10:40 – 11:10	Break & Snack	
11:10 – 11:50	Keynote TRR 325 Ming-Yu Ngai - Excited-State Catalysis in Organic Synthesis	
11:50 – 13:30	Group Picture, then Lunch	
13:30 – 14:10	Keynote CRC 1441 Valerie Briois - Hyperspectral Full Field Quick EXAFS Imaging for Looking at the Dynamic of Spatial Heterogeneities along a Catalyst Bed	
14:10 – 14:20	Change of rooms	
14:20 – 14:45	Patrick Lott (CRC 1441) - Dynamic Catalyst Operation: A Pathway to Enhanced Modern Emission Control	Benjamin Dietzek-Ivanšić (TRR 234)
14:45 – 15:10	Shweta Sharma (CRC 1441) - Multiscale X-ray Imaging of Washcoated Monolith Catalysts: From Structural Heterogeneity to Operando Chemical Transformation	Radim Beránek (TRR 234) - Ionic Carbon Nitrides in Photo(electro)catalysis: Achievements and Challenges
15:10 – 15:40	Pause & Snack 30 min	
15:40 – 16:05	Julia Westermayr (TRR 325) - Machine Learning for Excited States and Catalysis: From Transferable Models to Experiment	Franz Meyer (CRC 1633) - Mechanism-Based Mono- and Bimetallic Approaches for Catalytic Ammonia Oxidation at Low Overpotentials
16:05 – 16:30	Simone Stegbauer (TRR 325) - Chromophore Activation by Lewis Acid Coordination – NovelPhotoreaction of Carbonyl Compounds	Vera Krewald (CRC 1633) - Ab initio quantification of the nuclear dimensions for electron transfer and proton-coupled electron transfer
16:30 – 16:40	Change of rooms	
16:40 – 17:10	Scientific Publishing - Q&A for Early-Career Researchers - Dr. Sandra González Gallardo (Editor in Chief - ChemCatChem - Advanced Synthesis & Catalysis, Wiley-VCH GmbH)	Walk & Meet/ Networking (Park at the Ilm - UNESCO World Cultural Heritage)
17:10 – 17:40	Impulse Talks - Research Data Science	
17:40 – 18:55	Poster Session 2 CRC1633, TRR234, TRR247	
18:55 – 19:00	Break	
19:00	Get together and Networking	

22.05.2026	Goethe-Saal 1+2 (Plenum)	Goethe-Saal 3+4
08:50 – 09:00	Intro (Coordination Team)	
09:00 – 09:40	Keynote CRC 1633 Ive Hermans - TS-1: The Gift that Keeps on Giving	
09:40 – 10:10	Break and Snack	
10:10 – 10:40	Introduction CRC 1487 Ulrike Kramm - Iron-up!	
10:40 – 10:50	Change of rooms	
10:50 – 11:15	Inke Siewert (CRC 1633) - Base-Metal and Metal-Free Hydride Donor Reagents – From Fundamentals to Applications in Electrocatalysis	Mahnaz Azimzadeh Sani (TRR 247) - Probing Intrinsic Oxygen Evolution Kinetics at Single Nanocatalysts
11:15 – 11:40	Christian Jooß (CRC 1633) - Atomic scale ordering of liquid water at a dynamic Pt(111) interface under electrochemical conditions imaged by electron holography	Swetlana Schauer mann (TRR 247) - Molecular systems for reversible hydrogen storage: atomistic-level insights
11:40 – 13:10	Lunch	
13:10 – 13:50	Keynote TRR 234 Ken Sakai - Molecular Catalysis of Water Splitting and CO ₂ Reduction	
13:50 – 14:30	Poster Awards and Short Poster Presentations, Final Remarks and Goodbye Sven Schneider (CRC1633)	

Plenary and Keynote Talks

Bringing Operando Spectroscopy to the Reactor

Raimund Horn^{1,2}

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The Hamburg-based Collaborative Research Center 1615 develops “SMART Reactors” which are Sustainable, Multipurpose, Autonomous, Resilient and Transferable (SMART). Of particular importance for these developments is the ability to monitor the structure and performance of catalysts inside these reactors. Solid catalysts are highly dynamic systems which change their geometric and electronic structure, adsorbates, active sites and reactivity in response to the local chemical environment. The Institute of Chemical Reaction Engineering (ICRT) at TUHH and Reacnostics GmbH, a spin-off from ICRT, jointly develop technologies to perform operando measurements inside of reactors and single pellets. This talk will give an overview of some of these developments including spatial profile reactors for kinetic measurements, Raman spectroscopy, XAS, XRD, XRD-CT, Neutron scattering and single-pellet measurements. The concept of Iso-Potential Operando Spectroscopy (IPOS) will be introduced allowing to couple catalytic reactors of arbitrary size and shape with any spectroscopic method applicable to the temperature, pressure and chemical conditions inside the reactor. First steps to run such measurements in a Self-Driving Lab and to analyze the data by AI-methods will be presented.

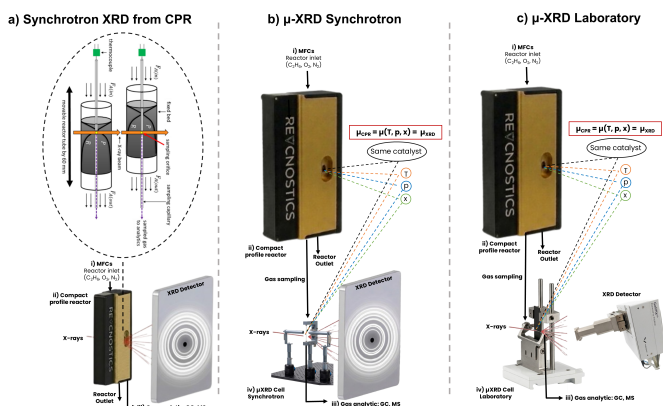


Figure 1: Spatially Resolved Operando X-Ray Diffraction in a Catalytic Fixed Bed Reactor: a) Measured directly through the reactor at a synchrotron, b) measured in Iso-Potential Coupling at a synchrotron and c) measured in Iso-Potential Coupling on a laboratory diffractometer.

MOF-Enabled Catalysis for Commodity Chemicals

Mircea Dincă¹

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Abstract text:

The metal nodes, or secondary building units (SBUs) of MOFs are molecular species that often do not have equivalents in homogeneous chemistry. As such, they allow fine structural and electronic tuning, and exhibit reactivity that is similar to that of homogeneous catalysts. Yet, they are site-isolated and fixed within solid matrices, in that sense acting as heterogeneous catalysts. With these two virtues, MOF catalysts can address challenges in industrially-relevant catalytic transformations that thus far have been the exclusive purview of homogeneous catalysts. This presentation will focus on various aspects of MOF-driven catalysis, especially as applied to commodity chemical transformations.

From Proton Relays to Microenvironments: Harnessing PCET processes in molecular catalysis for H₂ and CO₂ Conversion

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Catalysis in hydrogenases and other metalloenzymes involved in CO₂ transformation only requires Earth-abundant metal centers, the reactivity of which is enhanced thanks to the presence of basic sites acting as proton relays [1] at their vicinity. Such active sites have been used as an inspiration to design new synthetic catalysts harnessing PCET processes to enhance catalytic performance for H₂ and CO₂ conversion. We will show how detailed molecular electrochemistry studies can help understanding and quantifying the role of the proton relays related to these remarkable behaviors [2]. We will then show how the immobilization of such catalytic platforms onto surfaces allows the preparation of electrode materials operating with the same principles [3-4]. Then we will focus on the assessment of the intrinsic activity of the metal centres and exemplify how multiple populations of catalysts can be identified, with variable contributions to the electrocatalytic process depending on their micro-environment. Finally, we will report on post-operando characterisation and investigate how the same micro-environment impact deactivation pathways of such surface-confined molecular catalysts [5].

[1] Haake, M.; Reuillard, B.; Chavarot-Kerlidou, M.; Costentin, C.; Artero, V., *Angew. Chem. Int. Ed.* 2024, 63, e202413910.

[2] Reuillard, B.; Costentin, C.; Artero, V. *Angew. Chem. Int. Ed.* 2023, 62, e202302779.

[3] Katipamula, S.; Wagner, H.; Kuin, S.; Reuillard, B.; Costentin, C.; Artero, V.; <https://doi.org/10.26434/chemrxiv.10002033/v1>

[4] Haake, M.; Aldakov, D.; Pérard, J.; Veronesi, G.; Aguilar Tapia, A.; Reuillard, B.; Artero, V.; *J. Am. Chem. Soc.* 2024, 146, 15345-15355.

[5] Haake, M.; Caumes, C.; Saint-Pierre, C.; Gasparutto, D.; Veronesi, G.; Aguilar Tapia, A.; Artero, V.; Reuillard, B.; *J. Am. Chem. Soc.* 2026, accepted; <https://chemrxiv.org/doi/full/10.26434/chemrxiv-2025-0w2l9>.

Excited-State Catalysis in Organic Synthesis

Ming-Yu Ngai

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Abstract text: The development of efficient strategies for the synthesis and diversification of complex molecules remains a central challenge in organic chemistry. The Ngai laboratory seeks to address this challenge by developing new approaches to build and modify molecules, with the long-term vision of *turning light into medicine*. Our research focuses on the use of visible-light-driven excited-state catalysis to transiently reprogram molecular reactivity and enable transformations that are difficult to achieve under conventional ground-state conditions. By combining photochemistry, radical reactivity, and transition-metal catalysis, we aim to establish general platforms for selective bond construction and late-stage functionalization of structurally complex molecules. These efforts include the development of new catalytic strategies for site-selective modification, carbon–heteroatom bond formation, and the introduction of functional groups relevant to medicinal, agrochemical, and materials chemistry. This seminar will highlight recent advances from our laboratory illustrating how excited-state catalysis can enable new strategies for molecular functionalization and provide streamlined access to bioactive molecular architectures.

[1] Khosravi, A.; Zhang, Y.; Zhao, G.; Radefeld, K. J.; Sharma, S.; Pannilawithana, N. A.; Zhang, Y.; Liu, P.*; Ngai, M.-Y.*, *J. Am. Chem. Soc.* **2025**, *147*, 27197, DOI: 10.1021/jacs.5c08537.

[2] Zhao, G.; Mukherjee, U.; Yao, W.; Ngai, M.-Y.*, *Acc. Chem. Res.* **2025**, *58*, 1815, DOI: 10.1021/acs.accounts.5c00205.

[3] Zhao, G.; Lim S.; Musaev, D. G.; Ngai, M.-Y.*, *J. Am. Chem. Soc.* **2023**, *145*, 8275, DOI: 10.1021/jacs.2c11867.

[4] Zhao, G.#; Yao, W.#; Mauro, J. N.; Ngai, M.-Y.* *J. Am. Chem. Soc.* **2021**, *143*, 1728, DOI: 10.1021/jacs.0c11209.

hyperspectral full field Quick exafs imaging for looking at the dynamic of spatial heterogeneities along a catalyst bed

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The second time-resolution provided by Quick-EXAFS beamlines on 3rd generation synchrotron radiation facilities makes the technique powerful for unraveling reaction pathways of catalysts in working conditions. Recently, the Full Field (FF) hyperspectral Quick-XAS imaging, offering micrometer-scale spatial resolution in addition to the time resolution together with the element-specific information provided by X-ray Absorption Spectroscopy (XAS), has been implemented at the ROCK-SOLEIL beamline [1]. FF XAS imaging is based on the recording of the visible light emitted by a scintillator imaging the sample absorption by a pixelated CMOS camera (ORCA Flash 4.0 V3, Hamamatsu) equipped with a X4 magnification objective (pixel size and Field of View (FoV) 1.625 μm and 3.3 mm, respectively). Images at different energies of the XAS spectrum are collected during the monochromator energy scan yielding to one complete hyperspectral cube every 2 to 11 s depending on the oscillation frequency. Spectra normalization, energy alignment, spatial pixel binning or cube binning are based on home-made Jupyter notebooks. Speciation in the cube is obtained by Multivariate Curve Resolution with Alternating Least Square (MCR-ALS) analysis.

In this lecture, we will illustrate the capability of the full-field hyperspectral spatio-temporal technique implemented at ROCK for monitoring the thermal activation of catalysts [1] and their regeneration after use [2].

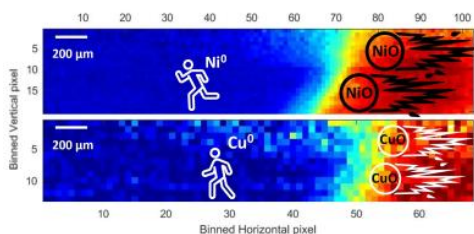


Figure 1: FF Quick-EXAFS hyperspectral imaging of the monitoring of the oxidative regeneration of a NiCu-based spent catalyst used for Ethanol Steam Reforming [2]

[1] V. Briois *et al.*, J. Synch. Rad., **2024**, 31, 1084, 10.1107/S1600577524006581

[2] V. Briois *et al.*, ChemCatChem, **2024**, 16, e202400352, 10.1002/cctc.202400352

TS-1: The Gift that Keeps on Giving

Ive Hermans¹

¹Johns Hopkins University, Department of Chemical and Biomolecular Engineering,
Department of Chemistry, Ralph O'Connor Sustainable Energy Institute, Baltimore, USA

E-Mail presenting author: hermans@jhu.edu

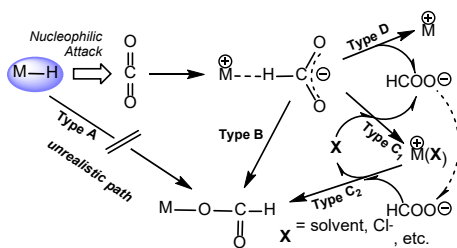
Titanium silicalite-1 has long been known as an excellent catalyst for the epoxidation of propylene with hydrogen peroxide. Although this technology has been commercialized in many plants across the globe, many peculiar aspects remain enigmatic such as the precise role of the solvent and promoters/feed modifiers. In this presentation I will demonstrate the power of combining traditional chemical engineering experiments (such as break through curves) with state-of-the-art in situ spectroscopic studies to begin elucidating effects that so far remained largely empirical. One powerful tool that I will highlight is Modulation Excitation Spectroscopy, a dynamic technique where the concentration of one of the reagents is periodically altered. By studying the response of the system to this perturbation we can filter out noise and signals stemming from spectator species and obtain kinetic insights in the activation and transformation of reagents over participating sites at the fluid-solid interface.

Molecular Catalysis of Water Splitting and CO₂ Reduction

Ken Sakai

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One of our works in the last decade has focused on the development of photocatalytic and electrocatalytic CO₂ reduction to fuels under fully aqueous conditions where proton reduction to H₂ may cause inhibiting factors in promoting the catalysis. With appropriate choices of conditions, we were able to demonstrate highly efficient and selective CO₂ reduction to CO under pH 7 conditions.¹⁻⁴ Thereafter, we shifted our interest to the selective formate formation due to its potential application in reversible hydrogen storage technology. To have a higher selectivity for formate over CO, the key is to stabilize a hydride intermediate responsible for the formate formation rather than to accelerate the CO₂ binding to give a CO₂²⁻-coordinated intermediates.^{5,6} Among various hypothetical paths A-D (see figure), our studies evidenced that the nucleophilic attack of a metal-hydride (M-H) at the carbon center of CO₂ (Types B-D), ruling out the classical definition called “CO₂ insertion”. Remarkably, [Rh^{III}Cp*(dihydroxy-bpy)Cl]⁺ catalysts were demonstrated to show water-induced switching in formate selectivity to boost CO₂-to-HCOOH.⁶ In addition to the above catalytic CO₂ reduction topics, we were also able to advance our on-going studies on (i) water oxidation catalysis,⁷ (ii) highly active cobalt NHC catalysts for H₂ evolution,^{8,9} and the H₂ evolution reactions catalyzed as well as photosensitized by platinum(II) photocatalysts.^{10,11}



- [1] A. Call, M. Cibian, K. Yamamoto, T. Nakazono, Yamauchi, K. Sakai, *ACS Catal.* **2019**, 9, 4867-4874. [2] X. Zhang, M. Cibian, A. Call, K. Yamauchi, K. Sakai, *ACS Catal.* **2019**, 9, 11263-11273. [3] X. Zhang, K. Yamauchi, K. Sakai, *ACS Catal.* **2021**, 11, 10436-10449. [4] F. Sueyoshi, X. Zhang, K. Yamauchi, K. Sakai, *Angew. Chem. Int. Ed.* **2023**, 62, e202217807. [5] C. Liao, K. Yamauchi, K. Sakai, *ACS Catal.* **2024**, 14, 11131-11137. [6] D. Lee, K. Yamauchi, K. Sakai, *J. Am. Chem. Soc.* **2024**, 146, 31597-31611. [7] Y. Aimoto, A. Parent, K. Yamauchi, K. Sakai, *J. Am. Chem. Soc.* **2024**, 146, 16866-16877. [8] K. Yamauchi, K. Sakai et al. *J. Am. Chem. Soc.* **2025**, 147, 5602-5614. [9] M. Kan, K. Yamauchi, K. Sakai, *ChemRxiv* **2025** (under revision). [10] K. Sakai, M. Murugesu, J. Brusso, H. Ozawa et al. *Angew. Chem. Int. Ed.*, **2025**, 64, e202418884. [11] K. Sakai, M. Murugesu, J. Brusso, H. Ozawa et al. *Chem. Sci.* **2025**, 16, 22580-22587.

Regular Talks

The Effects of Selective Substrate Adsorption on Catalytic Reactions in Confinement

Erik J. Wimmer,¹ Zeki Beydeda,¹ Hoang-Huy Nguyen,¹ Marc Högl,² Nadine Schnabel,¹ Thomas Sottmann,¹ Nikolaj Wendland,¹ Niels Hansen,² Deven P. Estes¹

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²Faculty of Energy-, Process-, and Bioengineering, University of Stuttgart, Stuttgart, Germany

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Abstract text:

Catalytic reactions of using molecular catalysts confined in mesoporous materials, such as are investigated in the CRC 1333, often differ from analogous homogeneously catalyzed processes in ways that are difficult to understand and quantify. One critical difference is that the chemical environment inside the materials often differs very strongly from bulk solutions. In particular, substrates, intermediates, and products can often selectively adsorb inside the materials such that the local concentrations of the reactants inside the pores differ greatly from those in bulk solutions. By understanding how substrates adsorb inside of the materials, we understand the physicochemical origins of such confinement effects. We have shown via neutron scattering and MD simulations that formic acid selectively adsorbs inside of mesopores to form a shell of formic acid along the pore wall. This results in ca. 20x slower formic acid dehydrogenation at intermediate concentrations (1.2 M) but 2x faster catalysis at high formic acid concentrations (80 wt%), due to variations in the local concentration of formic acid inside the pores versus bulk solution. Similarly, we saw that some organic enyne cycloisomerization reactions give higher conversions and yields when carried out in confinement versus in solution, due to selective adsorption of the substrate giving high local concentrations in the pores.

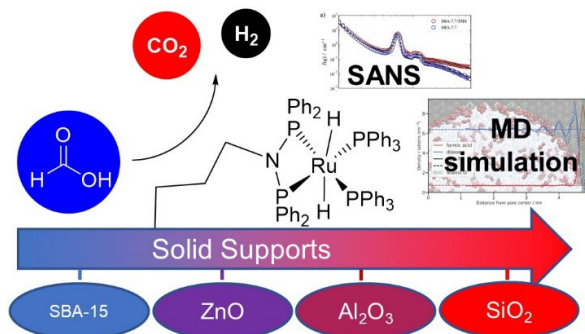


Figure 1: Effect of substrate adsorption on the rate of formic acid dehydrogenation.

Hard X-ray Spectroscopy of Molecular Heterogeneous Catalysts in Confined Geometries

Jun.-Prof. Felix R. Fischer¹, Prof. Dr. M. Bauer¹

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The overarching objective of CRC 1333 is to realize molecular heterogeneous catalysis in confined geometries by immobilizing molecular catalysts within mesoporous materials and exploiting confinement effects as a key determinant of catalytic selectivity. Confinement parameters, such as pore size and pore geometry, are expected to exert a pronounced influence not only on catalytic reactivity but also on the coordination chemistry of the immobilized species. In this context, hard X-ray spectroscopy is employed to probe these effects via the excitation of core-level electrons, predominantly 1s electrons. Owing to their high penetration depth, hard X-rays enable the investigation of the molecular structure of catalytic complexes independently of their state of aggregation. The methodological portfolio comprises X-ray absorption spectroscopy (XAS) and X-ray emission spectroscopy (XES). Belonging to XAS, XANES (X-ray absorption near-edge structure) provides insight into the oxidation state and local structure around the metal center, while EXAFS (extended X-ray absorption fine structure) yields information on distances, identities and numbers of coordinating donor atoms. Complementarily, advanced X-ray emission techniques such as HERFD-XANES (high-energy-resolution fluorescence-detected XANES) and valence-to-core XES (VtC-XES) offer enhanced sensitivity to frontier orbital characteristics, whereas core-to-core XES (CtC-XES) enables the determination of spin states (Figure 1). The combined spectroscopic data allow for a direct comparison of the electronic and structural parameters of molecular (pre)catalysts and their immobilized counterparts, thereby providing detailed insight into the origin of confinement effects on the modified catalytic activity and selectivity of immobilized complexes.[1-4]

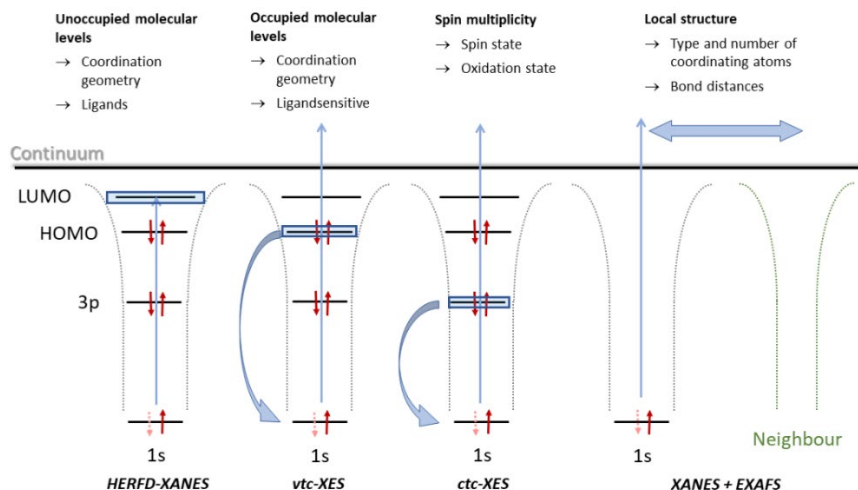


Figure 1: Hard X-ray methods and provided information for the example of K-edge spectroscopy.

- [1] S. Bhattacharya, M. Höglér, J. R. Bruckner, B. Atwi, M. Bauer, N. Hansen, F. R. Fischer, M. R. Buchmeiser, *Catal. Sci. Technol.* **2026**, *16*, 2170, DOI: 10.1039/D5CY01483B.
- [2] A. Allgaier, F. R. Fischer, S. Bhattacharya, K. Balliet, M. R. Buchmeiser, M. Bauer, J. van Slageren, *Inorg. Chem.* **2026**, XXX, XXX-XXX, doi.org/10.1021/acs.inorgchem.6c00208.
- [3] P. Probst, M. Lindemann, J. R. Bruckner, B. Atwi, D. Wang, F. R. Fischer, M. Höglér, M. Bauer, N. Hansen, M. Dyballa, M. R. Buchmeiser, *J. Am. Chem. Soc.* **2025**, *147*, 8741, doi.org/10.1021/jacs.4c18171.
- [4] A. Rodríguez-Camargo, E. Yildiz, D. Juela, F. R. Fischer, D. Graf, B. B. Rath, C. Ochsenfeld, M. Bauer, M. Sitti, L. Yao, B. V. Lotsch, *J. Am. Chem. Soc.* **2025**, *147*, 33472, doi.org/10.1021/jacs.5c07787.

Who sets the pace? How functionalization and defects control diffusion in UiO-67 frameworks

Sofia Kolin¹, Hassan Shatla^{2,3}, Ardeshtir D. Yeganeh^{2,3}, Sadia Noor⁴, Sabine Laschat⁴, Simon Krause^{2,3}, Kristyna Pluhackova¹

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³Nanochemistry Department, Max Planck Institute for Solid State Research, 70569 Stuttgart, Germany

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Molecular diffusion within metal-organic frameworks (MOFs) critically governs their performance in catalytic processes, yet remains challenging to rationalize due to the complex interplay of pore geometry, linker functionalization, framework defects and guest loading. Here, we use all-atom molecular dynamics (MD) simulations to investigate how linker functionalization and position and framework defects influence the diffusion of nitrobenzene in UiO-67-based MOFs. We systematically vary the loading and attachment position of proline-functionalized biphenyl linkers, introduce missing linker or missing cluster defects and probe a wide range of different guest loadings to determine their role in nitrobenzene diffusion. This computational approach allows us to disentangle the individual and combined contributions of steric effects, pore accessibility, and guest-framework interactions to molecular mobility, which are difficult to resolve experimentally. Our findings establish a molecular-level understanding of diffusion in functionalized MOFs and set solid ground for design of catalytically active materials.

[1] S. Kolin, H. Shatla, A. D. Yeganeh, S. Noor, S. Laschat, S. Krause, K. Pluhackova. Preprint available at ChemRxiv, **2026**, 10.26434/chemrxiv.15000388/v1

[2] Z. Dilruba, A. D. Yeganeh, S. Kolin, S. Noor, H. Shatla, C. Wieland, B.-H. Yu, K. Gugeler, A. Zens, J. Kästner, D. P. Estes, K. Pluhackova, S. Krause, S. Laschat. *Inorg. Chem. Front.* **2025**, 10.1039/d4qi02724h

Mesoporous Confinement Enables Enzyme-Like Rate Acceleration in Cooperative Asymmetric Catalysis

L. Rautenbach¹, M. Nandeshwar¹, E. Goldstein¹, M. Högler², M. Häußler¹, A. Allgaier¹, A. Bauer¹, D. Hornung¹, A. Beck¹, C. Franke¹, J. Osterbrink¹, J. R. Bruckner¹, J. Kästner¹, F. R. Fischer³, M. Bauer³, J. van Slageren¹, J. Pleiss¹, N. Hansen², M. R. Buchmeiser¹, R. Peters¹

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Enzymes achieve outstanding rate accelerations by combining cooperative functional group activation with confinement inside precisely organized active sites, reducing entropic costs and enforcing productive orientations of the substrates. These principles are shown to be transferable to artificial cooperative asymmetric catalysts by mesoporous confinement. Embedding a chiral bifunctional catalyst into ordered mesoporous silica creates a synthetic analogue of enzymatic pockets, in which cooperative activation and nanoscale confinement act synergistically. By such confinement, reaction half-lives could be reduced by up to 97% in asymmetric 1,4-additions. Kinetic analyses attribute this enhancement to entropic advantages of confinement, while molecular dynamics simulations reveal narrowing of the catalyst's conformational space closely paralleling precise enzymatic preorganization as molecular origin. Unlike enzymes, however, the mesoporous framework remains

tunable, allowing linker length and pore size to systematically adjust reactivity. This work establishes confinement engineering as a versatile strategy to design “unnatural active sites” that merge enzymatic efficiency with synthetic catalyst flexibility.

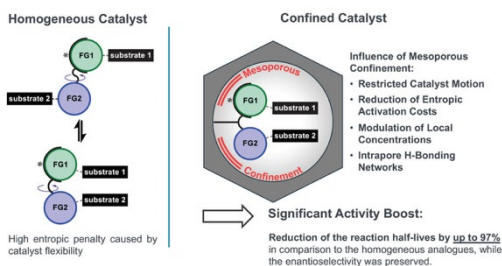


Figure 1: Comparison of homogeneous cooperative catalysis and under confinement.

[1] L. Rautenbach, M. Nandeshwar, E. Goldstein, M. Högler, M. Häußler, A. Allgaier, A. Bauer, D. Hornung, A. Beck, C. Franke, J. Osterbrink, J. R. Bruckner, J. Kästner, F. R. Fischer, M. Bauer, J. van Slageren, J. Pleiss, N. Hansen, M. R. Buchmeiser, R. Peters, *ChemRxiv* (preprint), 2025, [10.26434/chemrxiv-2025-b8gqs](https://doi.org/10.26434/chemrxiv-2025-b8gqs).

Dynamic Catalyst Operation: A Pathway to Enhanced Modern Emission Control

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Meeting increasingly stringent emission standards requires strategies that maximize catalyst efficiency. Against this background, forced dynamic operation (FDO) offers a means to overcome kinetic and thermodynamic limitations in emission control. This work investigates FDO in three applications: three-way catalysis, methane oxidation, and selective ammonia oxidation. For this, Pd-based catalysts were synthesized and evaluated through kinetic studies and *ex situ/in situ* characterization as powders and washcoated substrates. In three-way catalysis, high-frequency lean–rich cycling mitigates CO and O₂ poisoning, enabling frequency-dependent optimization of activity and selectivity. For methane oxidation, short rich pulses during lean operation improve light-off performance and long-term stability, with spatiotemporal studies identifying palladium redox gradients and hydroxyl removal as key to sustained CH₄ activation. In NH₃ oxidation, FDO promotes coexistence of metallic Pd and PdO, enhancing activity and selectivity beyond state-of-the-art catalysts. These results demonstrate that rational dynamic operation enables low-temperature abatement while reducing catalyst volume, cost, and reliance on scarce materials.

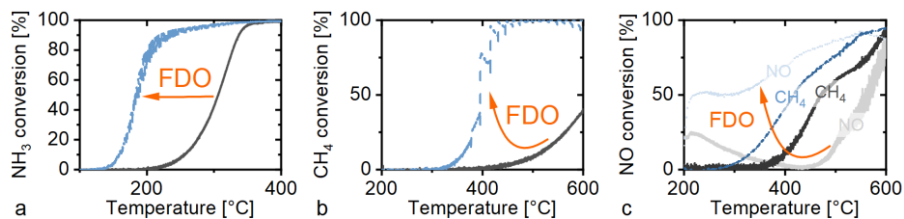


Figure 1: Performance improvement driven by FDO (dashed lines) compared to time-invariant constant gas streams (solid lines) for a) selective ammonia oxidation in excess oxygen, b) lean methane oxidation, and c) three-way catalysis. Data from [1-3].

[1] D. Hodonj, B. Thiele, O. Deutschmann, P. Lott, Chem. Eng. J., **2024**, 499, 155852, DOI: 10.1016/j.cej.2024.155852.

[2] K. Keller, D. Hodonj, L. Zeh, L. Caulfield, E. Sauter, C. Wöll, O. Deutschmann, P. Lott, Catal. Sci. Technol., **2024**, 14, 4142-4153, DOI: 10.1039/D4CY00625A.

[3] T. Häber, C. Cárdenas, O. Deutschmann, P. Lott, **2026**, submitted.

Multiscale X-ray Imaging of Washcoated Monolith Catalysts: From Structural Heterogeneity to *Operando* Chemical Transformations

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Structured emission control catalysts are typically implemented as washcoated monolithic honeycombs, where catalytic performance is governed not only by intrinsic reaction kinetics but also by catalyst architecture and spatially heterogeneous aging phenomena[1]. In this work, complementary hard X-ray imaging techniques were applied to investigate structured catalysts across multiple length scales. Multiscale X-ray tomography was used to characterize the architecture of washcoated Pd/Al₂O₃ monolith catalysts, enabling quantitative three-dimensional analysis of washcoat morphology, channel accessibility, and structural changes during catalyst aging. Complementary X-ray absorption spectroscopy was employed to investigate chemical transformations in washcoated Cu-SSZ-13 monolith catalysts under reaction conditions[2]. This enabled spatially resolved mapping of Cu speciation within the washcoat, providing insight into catalyst deactivation processes and the spatial distribution of active species during operation. Together, these studies demonstrate how multimodal and multiscale X-ray imaging provides a powerful framework for linking catalyst structure, chemical state, and performance in technically relevant emission control catalysts.

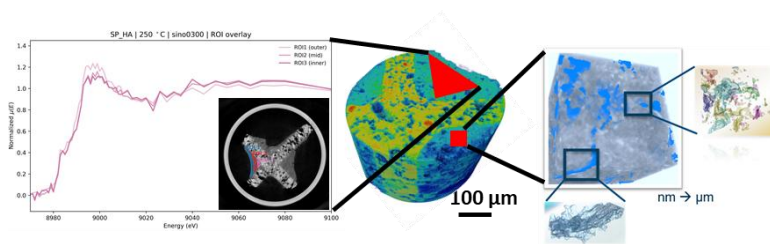


Figure 1: Structural and chemical investigation of washcoated monolith.

[1] J. Becher *et al.*, JPCC, **2019**, 123, 41, 10.1021/acs.jpcc.9b06541.

[2] J. Becher *et al.*, Nat. Catal., **2021**, 4, 46-53, 10.1038/s41929-020-00552-3.

Simulating the effect of Pt particle sizes for ammonia oxidation

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Density functional theory (DFT) calculations are now routinely used to understand the functioning of heterogeneous catalysts. However, there is still the formidable challenge to identify and construct valid active site motifs of working catalysts at the atomic scale, while also keeping the methodology computationally feasible. Herein, we report a DFT-based Monte Carlo method that can simulate the atomic-scale structure of oxide supported metal particles of sizes up to 10 nm (see Figure 1) Sk.[1] This method revealed new sites for CO splitting on supported Co particles,[2] and we will show here how Pt particles change their surface structure with particle size and what that means for the key selectivity determining steps of ammonia oxidation, namely N-N recombination as well reaction steps towards NO, N₂O and NO₂ formation. Further, we will also shed light on Pt single atoms supported on the CeO₂(111) facet that show an unexpected stability within subsurface interstitial sites as evidenced by IR spectroscopy and DFT calculations.[3]

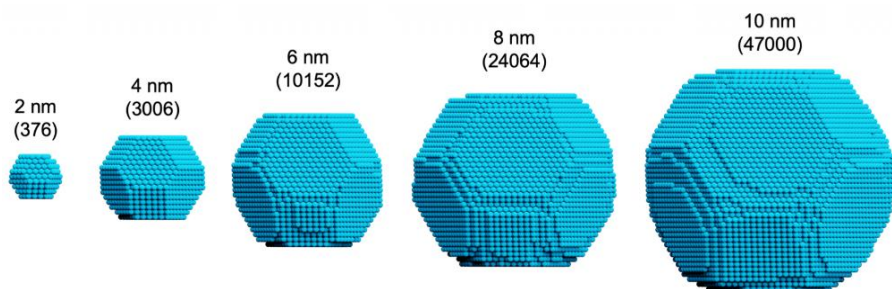


Figure 1: Performance Structural models of Co nanoparticles obtained with a DFT-based Monte Carlo algorithm. The number of Co atoms composing the NPs are given in parentheses. Data from [1].

[1] E. Sireci, T. D. Grüger, P. N. Plessow, D. I. Sharapa, F. Studt, J. Phys. Chem. C, **2025**, 129, 13232, DOI: 10.1021/acs.jpcc.5c02777

[2] E. Sireci, D. I. Sharapa, F. Studt, J. Phys. Chem. C, **2025**, 129, 21634, DOI: 10.1021/acs.jpcc.5c07278.

[3] S. Chen, Z. Yu, J. Wang, J. Jelic, W. Li, F. Studt, Y. Wang, C. Wöll, Angew. Chem. Int. Ed. **2026**, e22372.

Operando (S)TEM insights on mass selected Pt₂₀₀/CeO₂ as model catalyst for CO oxidation

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Mass-selected metal clusters supported on oxide surfaces serve as powerful model catalysts for probing fundamental aspects of heterogeneous catalysis. In our work, we investigate Pt₂₀₀ clusters supported on pulsed laser-deposited CeO₂, prepared via Cluster Ion Beam Deposition (CIBD)¹ directly onto a MEMS reactor device. This setup facilitates operando Scanning Transmission Electron Microscopy (STEM), allowing real-time imaging under controlled heating and gas flow. During CO oxidation, the CO₂ generation and the level of conversion at different temperatures have been monitored using a high sensitivity residual gas analyzer (RGA). In addition, identical location STEM experiments are also conducted to understand the effect of e⁻ beam on the cluster dynamics and to assess its effect on the catalytic process. Beyond operando catalytic conditions, the catalyst is examined in oxidative and reductive environments to visualize Pt-CeO₂ interactions in fresh, spent and rejuvenated states. Under oxidative treatment (≥ 600 °C), Pt₂₀₀ clusters disperse into single atomic sites, forming PtO_x and Ptn⁺-O-Ce species². Upon reduction with H₂ at 800 °C, cluster reformation is observed, revealing reversible structural dynamics and Strong Metal-Support Interactions (SMSI). The Ce oxidation states at both oxidized and reduced states have been analyzed using electron energy loss spectroscopy (EELS). The observations are compared to an analogous model catalyst tested independently in a flow reactor to validate the operando STEM findings. This integrated approach bridges atomic-scale imaging with catalytic performance, offering comprehensive insights into structure-activity relationships in cluster-based model catalysts.

[1] A. Fischer *et al.*, Rev Sci Instrum. **2015**, 86, 023304, DOI: 10.1063/1.4908166.

[2] F. Maurer *et al.*, Nat. Catal. **2020**, 3, 824–833, DOI: 10.1038/s41929-020-00508-7.

Ab initio quantification of the nuclear dimensions for electron transfer and proton-coupled electron transfer

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Electron transfer and proton-coupled electron transfer are ubiquitous in chemistry, for instance in catalysis, along enzymatic charge transport chains, or as intramolecular events in some mixed-valent compounds. In the Marcus–Hush model, electron transfer (ET) results in a change in diabatic potential energy surfaces, separated along an ET nuclear coordinate. This coordinate accounts for all nuclear motions that promote electron transfer. It is usually assumed to be dominated by a collective asymmetric vibrational motion of the redox sites involved in the ET, but it is rarely quantitatively specified.

We have recently proposed an *ab initio* approach for quantifying the ET coordinate in mixed-valence compounds.^[1] Using sampling methods at finite temperature combined with density functional theory calculations, we find that the electron transfer can be followed using the energy separation between potential energy surfaces and the extent of electron localization. The precise nuclear motion that leads to electron transfer is then obtained as a linear combination of normal modes. We demonstrate this approach for a series of dinitroradical anions^[1] and the famous Creutz–Taube ion.^[2, 3]

We will then discuss how our approach for quantifying ET coordinates can be translated to proton-coupled electron transfer reactivity.^[4] Using examples that are representative of concerted proton-electron transfer and hydrogen atom transfer –two distinct regimes within proton-coupled electron transfer– we discuss how the nature of the process is reflected in the *ab initio* calculations.

[1] A. Šrut, B. J. Lear, V. Krewald, *Chem. Sci.* **2023**, *14*, 9213-9225.

[2] C. Creutz, H. Taube, *J. Am. Chem. Soc.* **1969**, *91*, 3988.

[3] A. Šrut, B. J. Lear, V. Krewald, *Angew. Chem.* **2024**, *63*, e202404727.

[4] A. Šrut, M. Diefenbach, M. L. Kronenberger, B. J. Lear, V. Krewald, preprint available on *ChemRxiv*. **2025**, DOI: 10.26434/chemrxiv-2025-36d35.

Base-Metal and Metal-Free Hydride Donor Reagents – From Fundamentals to Applications in Electrocatalysis

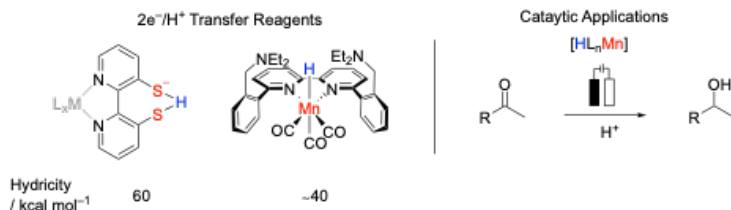
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Hydride transfer reactions are fundamental functional group transformations in chemical synthesis, especially for the reduction of polar double bonds. Hydride donors proceed a two-electron, proton-coupled reduction in a concerted fashion thereby circumventing the formation of high energy intermediates. Noble metalhydrides, particularly Rh, Pd and Pt, are generally excellent hydride donors and can often be used in catalytic amounts in thermal hydrogenation reaction protocols. However, due to the low abundance of noble metal-based hydrides, recent scientific efforts have investigated base-metal and metal-free hydride donor and their utilization in (electro)catalytic reduction processes.

In an electrocatalytic application, the conjugated reagent must be regenerated by consecutive single electron transfer steps and protonation, which is usually challenging. I will present the electrochemical formation of a base-metal and metal-free hydride donor reagents for storing multiple electrons and protons focusing of the distinct differences and similarities in their formation and reactivity.^[1,2] Furthermore, I will show the application of such hydride transfer reagents in the electrochemical hydrogenation of C=O bonds in ketones, aldehydes using electrons and protons.^[2]



[1] M. Cattaneo, C. E. Schiewer, A. Schober, S. Dechert, I. Siewert, F. Meyer, *Chem Eur J* **2018**, 24, 4864-4870; S. A. Hua, L. A. Paul, M. Oelschlegel, S. Dechert, F. Meyer, I. Siewert, *J. Am. Chem. Soc.* **2021**, 143, 6238-6247.

[2] I. Fokin, I. Siewert, *Chem. Eur. J.* **2020**, 26, 14137-14143; M. H. Rønne, D. Cho, M. R. Madsen, J. B. Jakobsen, S. Eom, É. Escoudé, H. C. D. Hammershøj, D. U. Nielsen, S. U. Pedersen, M.-H. Baik, T. Skrydstrup, K. Daasbjerg, *J. Am. Chem. Soc.* **2020**, 142, 4265-4275; I. Fokin, K.-T. Kuessner, I. Siewert, *ACS Catal.* **2022**, 12, 8632–8640.

Atomic scale ordering of liquid water at a dynamic Pt(111) interface under electrochemical conditions imaged by electron holography

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Imaging atomic structure and electric fields of the electric double layer at electrode-water interfaces is essential for understanding electrochemical reactions. The wave properties of electrons in an environmental transmission electron microscope were used to reconstruct the atomic scale electric potentials of a platinum (111) interface in water by phase shifting electron holography [1]. This progress allowed the observation of ordered water layers at the dynamic state of the platinum (111) surface and the water reorganization under applied electric potentials. The obtained projected electric potential of the Pt-water interface is quantitatively compared to ab-initio molecular dynamics (AIMD) simulations, revealing an extended ordered water region. Such ordered water layers form despite the presence of a dynamic adatom layer, also being observed at other oxide water interfaces [2,3]. We conclude, that the potential drop at the solid-H₂O interface is mainly carried by the polarization field of the ordered water structure.

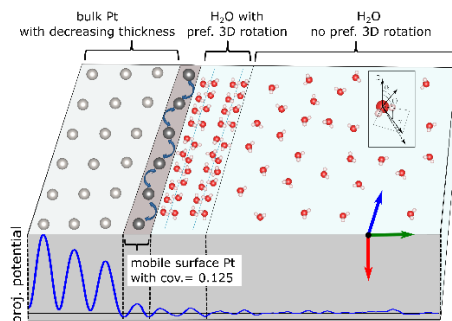


Figure 1: Atomic scale model of the platinum-water interface derived by combined in-situ environmental electron holography and AIMD simulations at zero voltage conditions.

[1] J. Lindner et al, *Advanced Energy Materials*, 2026: e05756.

[2] G. Lole *et al.*, *Comm Mat*, 2020, **1**, 68, doi.org/10.1038/s43246-020-00070-6

[3] E. Ronge *et al.*, *J Phys Chem C*, 2021, **125**, 5037-5047

Mechanism-Based Mono- and Bimetallic Approaches for Catalytic Ammonia Oxidation at Low Overpotentials

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In the context of sustainable energy scenarios and the quest for carbon-free energy vectors, NH₃ is considered an attractive fuel since it is produced globally on a huge scale from N₂, has a high energy density and is readily transported. NH₃ stores energy in its N–H bonds, but the ammonia oxidation reaction (AOR; NH₃ to N₂) is challenging as it requires orchestration of multiple H⁺ and e[−] transfers as well as the N–N coupling, which can occur from several types of M–NH_x intermediates and may follow different mechanisms (Figure 1). Homogenous AOR catalysts have evolved in recent years and provide mechanistic insight, enabling targeted ligand design for improving catalytic performance and elucidating decomposition pathways.^{1,2} Here we present detailed studies on mono- and dinuclear Ru-based AOR electrocatalysts (**1**, **2**) that mediate N–N bond formation at an early amido stage of the PCET map to avoid higher metal oxidation states and to operate at rather low overpotentials.^{3,4}

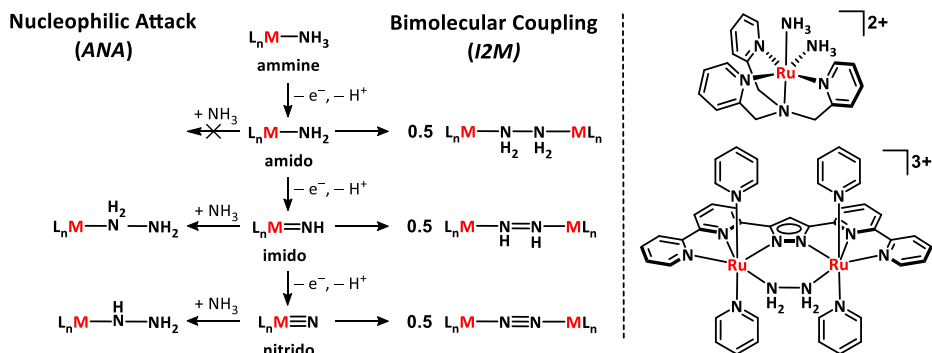


Figure 1: Mechanistic pathways for the metal-mediated ammonia oxidation reaction (AOR)

[1] P.L. Dunn *et al.*, J. Am. Chem. Soc., **2020**, *142*, 17845, DOI: 10.1021/jacs.0c08269.

[2] J. Li *et al.*, Sci. China Chem., **2024**, *67*, 3976, DOI: 10.1007/s11426-024-2137-5

[3] M. Seiß *et al.*, ACS Catal., **2025**, *15*, 20531, DOI: 10.1021/acscatal.5c05769

[4] M. Seiß *et al.*, submitted for publication.

Porous Carbon Nitride: Nanostructure-Controlled Bandgap and Photocatalytic H₂O₂ Generation

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The influence of porosity on the nanostructure and physicochemical properties of graphitic carbon nitride (g-C₃N₄) remains insufficiently understood from both experimental and theoretical perspectives. In this work, three g-C₃N₄ materials with distinct morphologies, layered, rod-like, and curved spherical structures, were systematically studied.^[1] These materials exhibit pronounced differences in porosity, surface hydrophilicity, optical bandgap, charge transport behavior, and photocatalytic performance for oxygen reduction to hydrogen peroxide (H₂O₂). Under 410 nm irradiation, the most porous spherical sample achieves an H₂O₂ production rate of 2.7 mmol·g⁻¹·L⁻¹, which is approximately an order of magnitude higher than that of bulk g-C₃N₄. To interpret these observations, three theoretical models were employed to decouple the roles of curvature effects, quantum confinement, and their combined influence. The results indicate that curvature induces a bandgap widening in g-C₃N₄, however, the formation of intrinsic micro- and mesoporosity associated with curved or distorted surfaces is unlikely due to strong interlayer stacking. Instead, the observed mesoporosity is mainly attributed to the assembly of nanoscale crystallites. Transient absorption spectroscopy further reveals that morphology-induced porosity and increased surface area stabilize long-lived electron populations and promote charge separation, thereby enhancing photocatalytic H₂O₂ production. Overall, this study provides new insights into the relationship between porosity, nanostructure, and photocatalytic function in g-C₃N₄, highlighting the importance of nanostructure engineering for optimizing performance.

[1] L. Ni *et al.*, ChemRxiv, **2025**, DOI: 10.26434/chemrxiv-2025-8x7sd.

Photo-induced Electron Transfer within the Marcus Picture and Beyond

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Photo-induced electron transfer (PET) processes are the cornerstone of natural photosynthetic processes. In this contribution, we present our hierarchical quantum chemical approach to unravel the thermodynamics and kinetics of competitive PET processes associated with catalytic turn-over, charge-recombination and degradation in transition metal-based supramolecular photocatalysts. Within the Marcus picture – a two-state model – both intramolecular and intermolecular PET^[1,2] processes are investigated along efficient internal reaction coordinates and *ab initio* molecular dynamics, respectively. However, such two-state models are insufficient to account for the plethora of electronic excited states involved in photoactive dyad and triad architectures. Therefore, a concept beyond Marcus theory is utilized to cover incomplete population transfer and super-exchange phenomena between an arbitrary number of (excited) states via dissipative quantum dynamics.^[3] Implementation of diabaticization schemes (e.g. Edmiston-Ruedenberg) allowed us to extend our molecular perspective to electrode materials, i.e. to model electron transfer processes of molecular entities embedded in redox-active polymers.^[4]

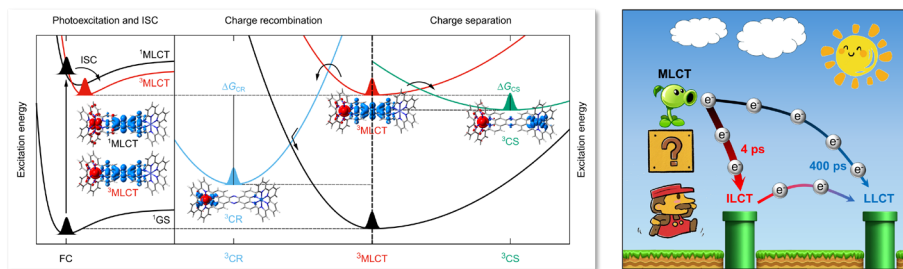


Figure 1: Competitive PET channels in transition metal-based photocatalysts and theoretical extension to model these in a *n*-state model beyond Marcus theory by means of dissipative quantum dynamics.^[3]

[1] G. E. Shillito *et al.*, ChemCatChem, **2023**, 15, e202201489, .

[2] G. Yang *et al.*, Chem. Sci., **2025**, 16, 18113.

[3] G. Yang *et al.*, Chem. – Eur. J., **2025**, 31, e202404671.

[4] C. Zens *et al.*, ChemSusChem, **2026**, 19, e202502645.

Ionic Carbon Nitrides in Photo(electro)catalysis: Achievements and Challenges

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Ionic carbon nitrides based on poly(heptazine imides) (PHI) are a widely studied class of polymeric materials with applications in photo(electro)catalysis and energy storage. This contribution will highlight our recent achievements in developing PHI-based photocatalyst for light-driven H₂O₂ production and PHI-based photoanodes exhibiting interesting properties, including photodoping and very negative photocurrent onset potentials [1–4]. The intriguing properties of PHIs, with particular emphasis on our recent photoelectrochemical, spectroscopic, and theoretical insights into their peculiar photophysics and photo(electro)catalysis, will be discussed [5–8].

- [1] I. Krivtsov, D. Mitoraj, C. Adler, M. Ilkaeva, M. Sardo, L. Mafra, C. Neumann, A. Turchanin, C. Li, B. Dietzek, R. Leiter, J. Biskupek, U. Kaiser, C. Im, B. Kirchhoff, T. Jacob, R. Beranek, *Angew. Chem. Int. Ed.* **2020**, *59*, 487.
- [2] I. Krivtsov, A. Vazirani, D. Mitoraj, M. M. Elnagar, C. Neumann, A. Turchanin, Y. Patiño, S. Ordóñez, R. Leiter, M. Lindén, U. Kaiser, R. Beranek *J. Mater. Chem. A* **2023**, *11*, 2314.
- [3] C. Adler, I. Krivtsov, D. Mitoraj, L. dos Santos-Gómez, S. García-Granda, C. Neumann, J. Kund, C. Kranz, B. Mizaikoff, A. Turchanin, R. Beranek, *ChemSusChem* **2021**, *14*, 2170.
- [4] C. Adler, S. Selim, I. Krivtsov, C. Li, D. Mitoraj, B. Dietzek, J. R. Durrant, R. Beranek, *Adv. Funct. Mater.* **2021**, *31*, 2105369.
- [5] C. Im, B. Kirchhoff, I. Krivtsov, D. Mitoraj, R. Beranek, T. Jacob, *Chem. Mater.* **2023**, *35*, 1547.
- [6] C. Im, B. Kirchhoff, D. Mitoraj, I. Krivtsov, A. Farkas, R. Beranek, T. Jacob, *J. Mater. Chem. C* **2025**, *13*, 8682.
- [7] C. Im, R. Beranek, T. Jacob, *Adv. Energy Mater.* **2025**, *15*, 2405549.
- [8] A. Konar, J. Liessem, Ch. Im, M. M. Elnagar, D. Mitoraj, P. Saini, I. Krivtsov, S. J. Finkelmeyer, J. Griebel, M. Presselt, T. Jacob, R. Beranek, B. Dietzek-Ivanšić, *Adv. Sci.* **2025**, *12*, e09312.

Ethylene glycol partial oxidation on Co_3O_4 surfaces: interplay between endogenous and exogenous factors

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Abstract text: Using ab initio molecular dynamics simulations, we investigate the facet dependent selective oxidation of ethylene glycol (EG) on Co_3O_4 , under thermal and electrocatalytic conditions. We shed light on the complex interplay between key factors governing EG oxidation: solvation, the relevant solute's concentration range, the size of the active surface regions as well as the chemical state of interfacial water and its competition with EG. We further compute and analyze the impact of temperature, pH and applied O_2 concentration on the product selectivity. Our in-depth analyses demonstrate the mechanistic convergence between both catalytic routes, with analogous surface intermediates and pathways, resulting in the same product distribution: glycolate, formate, and oxalate. Co^{3+} centers and OH^- species facilitate oxidation via proton-coupled electron transfer. Molecular oxygen or the applied anodic potential regenerate the active sites. At last, we identify and compare distinctive features between EG's oxidation mechanisms and catalytic trends on Co_3O_4 surfaces to those observed on Au surfaces.

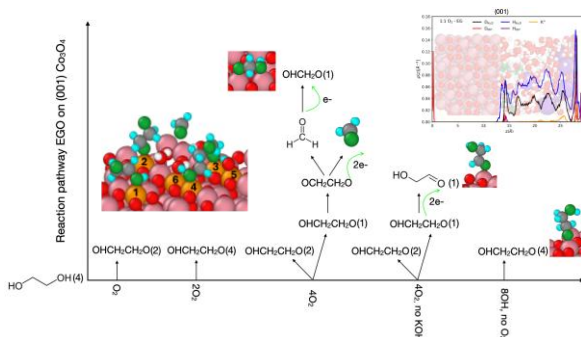


Figure 1: Active centers and Reaction pathway to EG's oxidation intermediates, and products on Co_3O_4 (001) vs. O_2 concentration

[1] C. Leiva-Leroy *et al.*, Angew. Chem. Int. Ed. **2026**, 65, e19188, DOI:

<https://doi.org/10.1002/anie.202519188>

Bridging Heterogeneous Liquid-Phase Thermal and Electrocatalytic Oxidation of Ethylene Glycol over Co_3O_4 Nanoparticles

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Reducing carbon emission requires more efficient selective oxidation reactions for relevant industrial feedstocks using non-precious metals.^[1-3] Recent studies show that thermal redox reactions can be expressed as two half-reactions, suggesting a direct link between thermal and electrochemical reactions.^[1] Here, ethylene glycol (EG) was used as a probe molecule, which can be oxidized to glycolic acid (GA), a key component in adhesives and packing materials.^[1-3] Additionally, cobalt spinel oxides have shown promising results in thermal and electrocatalytic oxidation reactions, along with the known resistance to poisoning and the high thermal stability.^[1-3] Co_3O_4 nanoparticles were synthesized by spray flame synthesis (SF), co-precipitation, and SBA-15 hard templating (HT).^[2]

The SF catalyst achieved the highest yield to GA with low formation of oxalic acid in aqueous thermal oxidation under alkaline conditions.^[2] However, the HT catalyst showed the best stability, which is why it was chosen for EGOR and the combined electrothermal oxidation. Comparable selectivity patterns were observed for thermal oxidation and EGOR under a variety of applied temperatures, pressures, and potentials.^[1] In both reaction systems, Co^{3+} centers and OH^- species facilitate selective oxidation via proton-coupled electron transfer, with molecular oxygen or the applied anodic potential reoxidizing the reduced active sites.^[1] The integration of both oxidation reactions was possible using a unique pressurized electrothermal reactor.^[3] Virtual Faradaic efficiencies over 100% denote the synergistic effects of applying temperature and pressure to EGOR.^[3] Temperature mainly increased the selectivity to GA in short-term experiments, while a remarkable increase in the GA yield was obtained in long-term reactions compared with only anodic EG oxidation.^[3]

[1] C. Leiva-Leroy *et al.*, Angew. Chem. Int. Ed., **2025**, e19188, 10.1002/anie.202519188.

[2] C. Leiva-Leroy *et al.*, ChemRxiv, **2026**, 10.26434/chemrxiv-2025-bdf6c-v2.

[3] A. Koul, C. Leiva-Leroy, M.L. Krebs *et al.*, **2026**, Angew. Chem. Int. Ed., under revision

Probing Intrinsic Oxygen Evolution Kinetics at Single Nanocatalysts

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Ensemble electrochemical measurements of nanocatalysts can obscure intrinsic nanoparticle kinetics because of binders, conductive additives, and interparticle effects.^[1] We probe the intrinsic oxygen evolution reaction activity of individual nanoparticles, including CoFe₂O₄ spinel and IrO_x, using catalytic nano-impact electrochemistry. Single-entity collisions generate discrete catalytic current transients whose amplitudes display a sigmoidal dependence on applied potential, enabling extraction of steady-state single-particle currents and kinetic parameters.^[2] The resulting single-particle Tafel slopes are directly compared with ensemble values to assess whether both configurations reflect the same rate-determining step.^[3] Overall, this binder-free single-entity framework provides a quantitative route to decouple intrinsic catalytic behavior from ensemble artifacts and to establish nanoscale structure–activity relationships for OER catalysts.

[1] N. Blanc *et al.*, J. Electroanal. Chem. **2020**, 872, 114345, <https://doi.org/10.1016/j.jelechem.2020.114345>.

[2] M. Azimzadeh Sani, K. Tschulik, in *Frontiers of Nanoscience Nanoscale Electrochemistry*, (Eds.: A. J. Wain, Ed., E. J. Dickinson), Elsevier, Amsterdam 2021, Vol. 18, p. 203, <https://doi.org/10.1016/B978-0-12-820055-1.00007-1>.

[3] H.M.A. Amin *et al.*, ChemCatChem **17** (22), e70455, <https://doi.org/10.1002/cctc.70455>.

Molecular systems for reversible hydrogen storage: atomistic-level insights

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Hydrogenation of carbonyl compounds to alcohols and selective dehydrogenation of alcohols to their corresponding ketone or aldehyde counterparts are important steps in many technological applications, including the emerging molecular systems for reversible hydrogen storage. In this talk, I will discuss different catalytic systems related to both types of processes and the associated structure-reactivity relationships.

First, the heterogeneous catalysts based on bimetallic single atom alloys (SAA) and their application to selective dehydrogenation of alcohols to ketones will be discussed.¹ Fundamental working principles of these systems remain poorly understood, especially the aspects related to the nanoscopic nature of bimetallic particles. Recently, we developed well-defined SAA catalysts consisting of Pd atomically dispersed in Cu nanoparticles prepared under ultra-high vacuum (UHV) conditions on model $\text{Al}_2\text{O}_3/\text{NiAl}(110)$ support. Employing a unique combination of surface sensitive techniques – scanning tunneling microscopy (STM), infrared reflection absorption spectroscopy (IRAS), molecular beams – and density functional theory (DFT) calculations, we performed detailed structural characterization of these systems at the microscopic level. We demonstrate that Pd disperses atomically in Cu nanoparticles and becomes partly negatively charged. Importantly, these Pd/Cu nanostructured systems show an outstanding catalytic performance in selective dehydrogenation of butanol and exhibit 100 % selectivity toward butanal over a broad range of Pd loadings – the property that cannot be reproduced employing simplified single crystalline Pd/Cu(111) counterparts. The developed approach for preparation and characterization of these nanostructured SAA-catalysts lays a foundation for further fundamental-level catalytic studies on this important class of materials and their rational design for practical applications.

In the second part, the catalytic decomposition of 2-propanol to acetone over Co_3O_4 catalysts will be addressed with the specific focus on the role of water and its derivatives in the reaction mechanism and the overall catalytic activity.² Two types of catalysts were investigated in this study: the powdered materials and their model $\text{Co}_3\text{O}_4(111)$ counterparts. Pre-treatment of both types of catalysts with water at elevated temperatures was shown to result in a substantial increase in the acetone formation rate. Results obtained by a combination of STM and IRAS revealed that pre-

treatment of $\text{Co}_3\text{O}_4(111)$ model surface with water at elevated temperatures leads to the formation of isolated hydroxyls ($\text{O}_\text{s}\text{H}$) involving a lattice oxygen atom (O_s). In contrast, water deposition at lower temperatures leads to the formation of an extended partly dissociated $\text{OH}/\text{H}_2\text{O}$ network layer exhibiting short-range order. The isolated $\text{O}_\text{s}\text{H}$ groups obtained after high temperature pre-treatment with water were observed to play a key role in H abstraction, both from molecular 2-propanol and from the propoxy reaction intermediate, leading to efficient formation of the target product acetone. The promoting role of isolated hydroxyls can be attributed to their function as hydrogen acceptors for H atoms leaving from either 2-propanol or the propoxy intermediate. Our results also suggest that the isolated $\text{O}_\text{s}\text{H}$ group appears to be a substantially more efficient hydrogen acceptor than the adsorbate-free lattice oxygen O_s .

1. *"Pd/Cu single atom alloys for selective alcohol dehydrogenation: from single crystalline to nanostructured model catalysts"*, P. A. Fredersdorff (Haugg), J. Smyczek, C. Schröder, P. Fröhlich, P. Kohlmorgen, S. Appelfeller, K. Neyman*, S. Schauermaun* *Angew. Chem. Int. Edit.* **(2026)** DOI: 10.1002/anie.202521885
2. *"Promoting role of isolated surface hydroxyls on selective dehydrogenation of 2-propanol to acetone over Co_3O_4 catalyst: a mechanistic study."* J. Smyczek, P. Hubert, H. Scheele, C. Schröder, S. Najafishirtari, P. Kohlmorgen, M. Behrens*, S. Schauermaun* *ACS Catalysis* **(2025)** DOI: 10.1021/acscatal.5c05269

Translocal Control in Symmetric σ -Bond Net Heterolysis

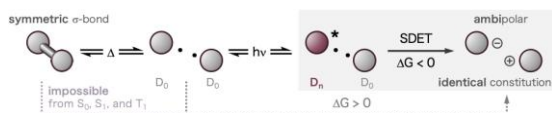
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The unimolecular fission of covalent σ -bonds constitutes an integral elementary step in numerous chemical transformations, such as S_N1 , E1, and intramolecular rearrangement reactions. The decisive factors governing the equal or unequal relocation of electrons during bond cleavage (i.e., homolytic vs. heterolytic) are the electronic state from which a given substrate is about to fragment and the medium in which the bond fission is taking place.[1,2] Regarding unimolecular heterolysis, this circumstance has profound implications on whether a given bond constitution is even amenable to ionic fission. More specifically, if a σ -bond consists of two identical constituents (i.e., a symmetric σ -bond) its unimolecular fission from the ground or chemically most relevant excited states (i.e., S_1 and T_1 according to Kasha's rule) proceeds only homolytically, irrespective of whether the bond activation occurred thermally or photonically.[3]

This fundamental constraint has blended symmetric σ -bonds categorically out of the focus of method-oriented investigations centering on unimolecular heterolyses. However, this state of affairs offers an invaluable opportunity for the development of bond activation principles that are totally outside the realm of conventional protocols. One such auspicious example is the net heterolysis of symmetric and homopolar σ -bonds.[4] This activation principle includes the initial thermal homolysis of a given bond, furnishing a spin-entangled radical pair – a singlet pair consisting of two local doublets. Photoexcitation of one pair member results in a stimulated doublet-doublet electron transfer (SDET), giving access even to constitutionally identical ion pairs.[4] The SDET manifold has profound implications for chemical synthesis and catalysis, as it enables the generation of reactive intermediates previously either inaccessible from apolar precursors or that demanded conditions that are, in part, incompatible with sensitive functionalities.



[1] H.J. Kim *et al.*, J. Am. Chem. Soc. **1992**, 114, 10508, 10.1021/ja00052a055. [2] P.B. Armentrout *et al.*, J. Am. Chem. Soc. **1992**, 114, 8627, 10.1021/ja00048a042. [3] J. Michl, Acc. Chem. Res. **1990**, 23, 127, 10.1021/ar00173a001. [4] A.F. Tiefel *et al.*, Nature **2024**, 632, 550, 10.1038/s41586-024-07622-7.

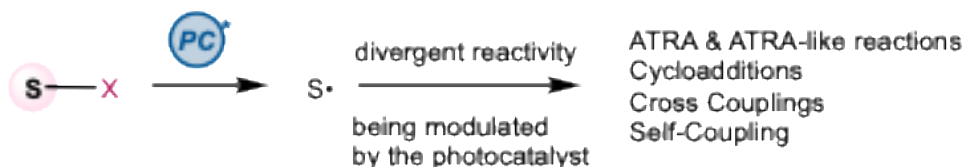
When the same is not the same: Divergent reactivity of radicals generated from different metal complexes or organic dyes through photoredox catalysis.

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The generation of radicals through photoredox catalysis has achieved great success in initiating organic reactions. Typically, a substrate can be reduced or oxidized by a single-electron transfer event from a light-activatable metal complex or organic dye with a suitable reduction or oxidation potential. The resulting radicals can engage in organic transformations. We will show examples of seemingly identical radicals that exhibit divergent reactivity, which is modulated by interactions with the metal- or organophotocatalyst used for their generation.



Leading references:

S. Sardana, A. Pattanaik, J. Rehbein, O. Reiser, *Angew. Chem. Int. Ed.* **2025**, *64*, e202509658, [10.1002/anie.202509658](https://doi.org/10.1002/anie.202509658); A. Reichle, M. Koch, H. Sterzel, L.-J. Großkopf, J. Floss, J. Rehbein, O. Reiser, *Angew. Chem. Int. Ed.* **2023**, *62*, e202219086, [10.1002/anie.202219086](https://doi.org/10.1002/anie.202219086); T. Mandal, M. Ghosh, H. Paps, T. Mandal, O. Reiser, *Nat. Catal.* **2025**, *8*, 605, [10.1038/s41929-025-01357-y](https://doi.org/10.1038/s41929-025-01357-y); V. Klöpfer, A. Chinhole, O. Reiser, *Tetrahedron Chem* **2024**, *10*, 100073, [10.1016/j.tchem.2024.100073](https://doi.org/10.1016/j.tchem.2024.100073); A. Chinhole, M. A. Henriquez, D. Cortes-Arriagada, A. R. Cabrera, O. Reiser, *ACS Catal.* **2022**, *12*, 13549, [10.1021/acscatal.2c03315](https://doi.org/10.1021/acscatal.2c03315).

Machine Learning for Excited States and Catalysis: From Transferable Models to Experiment

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Machine learning (ML) has transformed ground-state molecular predictions using large-scale foundational models such as variants of the message-passing atomic cluster expansion (MACE) model, but excited states and catalysis demand innovative solutions to data scarcity. For theoretical photochemistry, we demonstrate how our excited-state extension, X-MACE [1,2], achieves chemical transferability across electronic states with little additional excited-state data, enabling accurate photochemical property predictions for molecules and extended systems. This method will be showcased on green fluorescent protein chromophores to screen dynamics and revealing rational design principles.

For experimental approaches, we present two algorithms: (1) active curation balancing experiment count, model accuracy, and iterative labeling; (2) subset selection from existing datasets. Both enable robust ML models from sparse data that can be used, for instance, to predict yields or optimize reaction conditions.

[1] Rhyan Barrett, Sophia Wesely, and Julia Westermayr. "Transferable excited-state dynamics enable screening of fluorescent protein chromophores" arXiv preprint **2026** arXiv:2604.12699.

[2] Rhyan Barrett, Johannes CB Dietschreit, and Julia Westermayr. "Incorporating long-range interactions via the multipole expansion into ground and excited-state molecular simulations" npj Computational Materials **2026** 12(135), DOI: 10.1038/s41524-026-02048-3

Chromophore Activation by Lewis Acid Coordination – Novel Photoreaction of Carbonyl Compounds

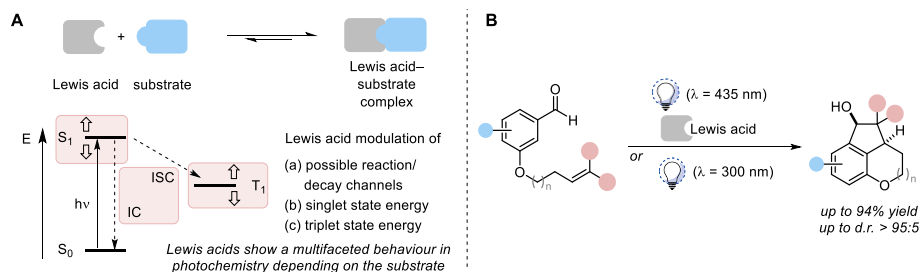
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Lewis acids have been evolved as catalysts, which can change the course of organic reactions dramatically. The application of Lewis acids in light-driven reactions of carbonyl compounds is a powerful instrument to influence the outcome of a photoreaction. Employing Lewis acids, we were able to control the enantioselectivities of an *ortho* photocycloaddition reaction as well as a visible light-triggered cycloaddition / rearrangement cascade of aromatic aldehydes. Furthermore, a fundamental change of the photochemical reactivity pattern of naphthaldehydes with olefins was examined in presence of achiral Lewis acids. Chiral Lewis acids were also successfully applied in an intramolecular *ortho* photocycloaddition reaction of 2-acetonaphthones.



Scheme 1: A: Modulation of Lewis acid–substrate complex. B: Formal [3+2] photocycloaddition.

In a novel formal [3+2] photocycloaddition reaction of benzaldehyde derivatives, Lewis acids are successfully added to increase the yield by using only catalytic amounts (10 mol%). The robustness of this method was proven by the application of the optimized reaction condition to up to 30 different substrates, possessing electron-donating as well as electron-deficient substituents. Mechanistic studies and successful follow-up transformation of the tricyclic aromatic photoproducts in an arene hydrogenation broadens the horizon of the project.

Posters

CO₂ Hydrogenation to Methanol Catalyzed by Phosphine Complexes Immobilized on Lewis Acidic Supports

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Copper hydrides serve as pivotal intermediates in numerous catalytic transformations, including in the hydrogenation of carbon dioxide. Isolating mononuclear copper hydrides remains difficult because they readily aggregate into less active multinuclear clusters such as Stryker's reagent.¹ While bulky ligands or encapsulating agents can provide some stabilization, these approaches often restrict access to the active site. In this study, we introduce a surface-immobilization strategy² that achieves site isolation of reactive Cu–H species. A monomeric Cu(I) complex, ICu(dtbpOH), bearing an alcohol group was investigated and anchored onto aluminum-modified metal–organic frameworks (MOFs)³ through Al–O bonds. Subsequent reaction with hydride sources like HBPi⁴ generated surface-bound copper hydrides. Structural analysis shows that immobilization significantly enhances the stability of the Cu–H centers, which we have characterized by both MAS NMR and by X-ray absorption and emission spectroscopies. These complexes are active catalysts for CO₂ hydrogenation to methanol at low temperature (as low as 110 °C). The identity of the support has a large effect on their activity, with immobilization in the Zr MOF NU-1000 giving ca. 25 times higher activities than non-Lewis acidic supports. These findings demonstrate how confinement within a tailored support can stabilize otherwise transient copper hydrides and provide a versatile platform for developing efficient catalysts for CO₂ reduction and related hydride-mediated reactions.

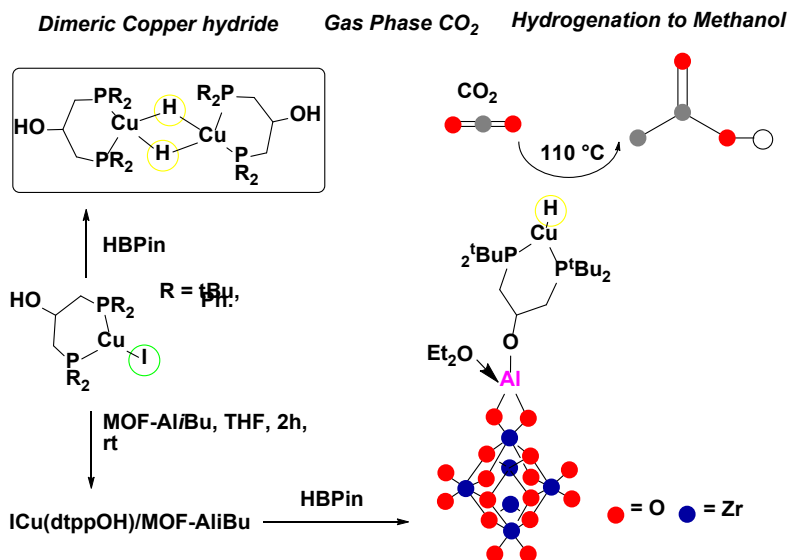


Figure 1. Monomeric Cu catalysts immobilized on NU-1000 as CO₂ hydrogenation catalysts.

[1] S. A. Bezman et al., *J. Am. Chem. Soc.* **1971**, 93, 2063.

[2] L. Castelbou et al., *Chem. Commun.*, **2017**, 53, 3261-3264.

[3] T. C. Wang et al., Scalable synthesis and post-modification of a mesoporous metal-organic framework called NU-1000. *Nat. Protoc.* **2016**, 11, 149-162.

[4] A. W. Beamer, et al., *J. Am. Chem. Soc.* **2023**, 145, 12911-12919.

Ethylene Oligomerization Under Confinement Using Supported Cr(II) and Cr(III) Catalysts

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Supported Cr(II) and Cr(III) catalysts have emerged as versatile systems for the selective ethylene oligomerization, offering easy separation, recyclability, and reduced polymer formation. However, pore confinement, site accessibility, and metal–support interactions can significantly affect performance, altering selectivity compared to homogeneous systems. In this work, we investigated how support morphology and confinement influence the behavior of immobilized Cr catalysts during ethylene oligomerization. Supported catalysts were prepared by selective immobilization of the Cr(II) and Cr(III) complexes, which are all non-selective for ethylene oligomerization in solution, inside the mesopores of ordered mesoporous silica materials with varying pore sizes (**OMS_{66A}**, **OMS_{57A}**, **OMS_{28A}**), as well as amorphous silica (Si60). In comparison to the homogeneous catalysts, upon activation with methylalumoxane (MAO) as cocatalyst, the supported chromium complexes experienced a clear confinement effect. Catalysts **Cr1@OMS_{28A}/MAO** and **Cr2@OMS_{28A}/MAO** immobilized inside well-defined small mesopores demonstrated the ability to generate lower linear α -olefins up to C₁₂ with high selectivity while suppressing PE formation at the same time (Figure 1).

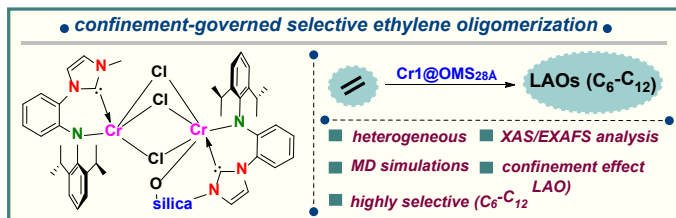


Figure 1. Focus of this work.

[1] S. Bhattacharya *et al.*, *Organometallics*, **2025**, *44*, 315-324, 10.1021/acs.organomet.4c00458.

[2] S. Bhattacharya *et al.*, *Catal. Sci. Technol.*, **2026**, *16*, 2170-2184, 10.1039/D5CY01483B.

Crystalline-Amorphous Reversible Transitions in UiO-67-Proline Functionalized MOFs and Implications in Organocatalysis

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Various pathways of structural transition have been explored within flexible MOFs, commonly referred to as Soft Porous Crystals (SPCs).[1] Nevertheless, the extent of such structural flexibilities in Zr-based UiO MOFs remains unknown. Pallach *et al.* recently reported a new range of alkoxy-functionalized MOF-5 materials that exhibited an innovative type of structural flexibility that responds to both guests and temperature.[2] This flexibility is characterized by the reversible loss and recovery of crystalline order while retaining the framework connectivity and topology. Here, we are aiming to elucidate the underlying mechanisms that govern the flexibility observed in our MOF systems. This entails a thorough investigation into the influence of synthetic parameters, and we have characterized the structural features of the amorphous state through pair distribution function (PDF) analysis, which will be complemented by simulations to develop a structural model. Finally, we will use the flexible frameworks in organocatalytic model reactions to investigate the structural changes influence on the catalytic performance.

[1] S. Krause, N. Hosono, S. Kitagawa. *Angew. Chem.*, **2020**, 36, 15325-15341, doi.org/10.1002/anie.202004535.

[2] R. Pallach, *et al.* *Nat. comm.*, **2021**, 12.1, 4097, doi.org/10.1038/s41467-021-24188-4.

Selective aerobic oxidation of organic molecules by coupled redox catalysis in MOF–COF hybrid frameworks

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Abstract text: Selective oxidation is a core process in organic synthesis. Aerobic O₂ is an ideal green oxidant, but it often leads to low selectivity via peroxide intermediates. Enzymes such as laccase can efficiently catalyze selective aerobic oxidation owing to their spatially separated but electronically coupled dual-site architecture, which couples four-electron reduction of O₂ with one-electron oxidation of substrates. However, such coupled redox catalysis is rarely achieved in artificial materials because of its structural complexity. Recently, we developed MOCOFs (Metal–Organic–Covalent–Organic Frameworks), hybrid frameworks constructed through a combination of MOF-type coordination and COF-type imine linkages.^[1] MOCOFs provide complex structures in MOF-like high crystallinity and COF-like chemical stability, suitable for catalyst confinement. Based on this platform, we aim to achieve coupled redox catalysis by confining O₂ reduction catalysts and single-electron oxidation catalysts with a covalent bridge for electron transfer. So far, we synthesized Co-MOCOF-1-(OH)₂ via Co–amine coordination and imine condensation, and now we are testing the incorporation of secondary metal ions.

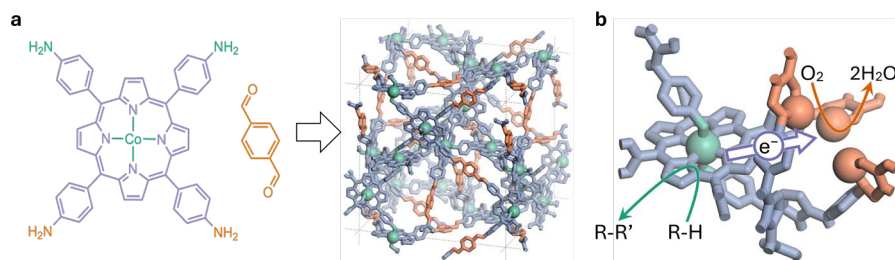


Figure 1: (a) Building blocks and SCXRD structure of Co-MOCOF-1. (b) Planned scheme of coupled redox catalysis.

[1] K. Endo et al., *Nat. Synth.*, **2025**, 4, 603, <https://doi.org/10.1038/s44160-024-00719-x>

Advancing Atom Probe Tomography for Complex Materials: From Organic Liquids to Porous Silica and Polymer Thin Films

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Atom probe tomography (APT) enables nanoscale chemical characterization but faces challenges for soft, liquid, and porous materials. This work presents advances in APT preparation and applications across organic liquids, mesoporous silica, and polymer thin films.

A Micro Cup strategy confines organic liquids within a focused ion beam (FIB)-fabricated cavity, improving reproducibility and reducing beam exposure. Using liquid crystals 8CB and 8OCB, stable field evaporation conditions yield over 70% intact molecular ion detection. Oxygen in 8OCB promotes preferential bond cleavage, while spatial variations reveal differences between smectic-like and crystalline regions.

Al-doped mesoporous silica is analyzed to study dopant distribution. High-quality specimens are prepared via FIB, and APT results agree with ICP-OES measurements, confirming compositional accuracy. Reconstruction and statistical analysis provide insight into aluminum distribution within the silica matrix.

Spin-coated polyvinylpyrrolidone (PVP) thin films are also investigated, with mass spectra identifying key fragments and reconstructions revealing nanoscale organization.

Mechanistic Insights into Enantioselective Alcohol Formation by Cooperative Ni–Al Aldehyde Methylation

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Chiral secondary alcohols are valuable building blocks in fine-chemical synthesis.^[1] To access such motifs, cooperative catalysis offers a powerful strategy by combining complementary activation modes for substrate activation and bond formation.^[2] Here, we present a computational mechanistic study of cooperative Ni–Al aldehyde methylation leading to the selective formation of the *S*-product (Figure 1). Density functional theory calculations were used to characterize the relevant intermediates and transition states, solvent (THF) effects were modeled with implicit solvation and using 0 to 2 explicit THF molecules. Our results show that enantioselective C–C bond formation does not arise from direct methyl transfer from Al to the aldehyde. Instead, the reaction proceeds through an initial methyl transfer from AlMe₃ to the Ni center, forming a Ni–Me intermediate. Subsequent aldehyde coordination to the Al center bound to the binaphthyl-containing catalyst creates a highly organized chiral environment for stereoselective C–C bond formation. Two plausible catalytic cycles were identified, revealing how the second AlMe₃ molecule can play distinct roles in Ni–Me formation, product release, and regeneration of the active Ni–Al species.

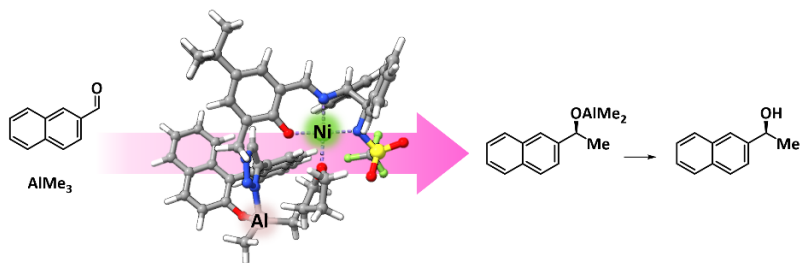


Figure 1: Reaction catalyzed by the Ni–Al complex bearing an axially chiral binaphthyl.

[1] E. S. Isbrandt *et al.*, J. Am. Chem. Soc., **2021**, 143, 14646–14656, DOI:[10.1021/jacs.1c05661](https://doi.org/10.1021/jacs.1c05661).

[2] D. M. Wanner *et al.*, Angew. Chem. Int. Ed., **2023**, 62, e202307317, DOI:[10.1002/anie.202307317](https://doi.org/10.1002/anie.202307317).

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Data science enables computational investigation of mechanisms without relying on time-intensive searches for transition states. In experimental settings, multiple catalysts are often screened, and they can be quantitatively compared using steric or electronic parameters. Carefully combining these descriptors into a model can reveal the underlying factors governing selectivity, with a limited set of data points.

In this work, we applied such an approach to model the selectivity of a metathesis cyclopolymerization catalyzed by molybdenum imido alkylidene complexes with the aim of finding an interpretable polynomial fit function with a limited number of parameters. We found (with an R^2 of 0.854):¹

$$\alpha\text{-selectivity} \sim 47.2 \cdot \% \text{bur}_{\text{NHC},4r-2\alpha} - 82.1 \cdot (\% \text{bur}_{\text{NHC},4r-2\alpha})^2 + 73.9 \cdot Q_{\text{Ocoord},4r-1\alpha} - 105.5 \cdot (Q_{\text{Ocoord},4r-1\alpha})^2$$

Both descriptors, $\%V_{\text{bur},\text{NHC},4r-2\alpha}$ and $Q_{\text{Ocoord},4r-1\alpha}$ indicate a significant role of additional coordination of the monomer to the molybdenum center. The strength of these interactions is mostly determined by the steric hindrance introduced by the NHC-ligand. For medium-sized NHCs, coordination preferentially stabilizes the pathway leading to the major (α) product. In contrast, for smaller NHCs, both paths are stabilized in this way, and for very large NHCs, neither. In both cases, the selectivity is reduced significantly.¹

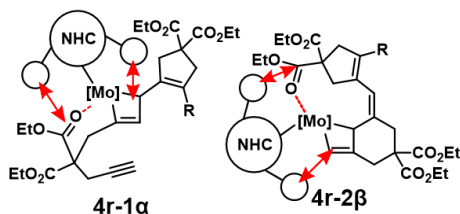


Figure 1: Schematic representation of the stabilizing interactions and the NHC ligands' influence on them for two minimum states in the metathesis formation.

FAIR data management in molecular heterogeneous catalysis and beyond

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The Collaborative Research Center 1333 “Molecular Heterogeneous Catalysis in Confined Geometries” targets the rational development of heterogenized molecular catalyst systems, which are conceptually derived from enzymatic biocatalysts. It integrates several disciplines from experimental and theoretical chemistry. To make the diverse research data generated within this framework findable, accessible, interoperable, and reusable (FAIR), its information infrastructure project (INF) develops a sustainable research data management (RDM) infrastructure grounded in open software and community standards. Its central component, the md-models library, offers a flexible foundation for defining and maintaining machine-actionable data models that are readily integrated into scientific workflows.

Unlike format- or application-specific approaches, the INF project follows a model-centric design philosophy. Data models are expressed as generic, modular object structures that automatically generate Python APIs, which enable developers to implement domain-specific processing, analysis, and visualization tools with minimal overhead. This approach decouples scientific software development from rigid file formats and platform dependencies, thus promoting reuse and interoperability across research domains. The inherent modularity of these data models supports incremental development and community contributions, allowing researchers to evolve and extend data models collaboratively.

Using the same infrastructure, the RDM projects cover various experimental techniques and research questions ranging from analytical techniques over catalysis towards the description of materials synthesis.

By means of md-models the INF project delivers adaptable, model-driven building blocks that empower researchers in CRC 1333 and beyond to establish sustainable RDM practices that scale with evolving methods and standards. The project illustrates how research software engineering principles can transform data management from a secondary concern into a reproducible and collaborative scientific process.

Exploration of Covalent Organic Frameworks on Gas Diffusion Electrodes for Electrochemical CO₂ Reduction

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Covalent organic frameworks (COFs), crystalline porous materials extended through covalently-bonded organic building units, have emerged in the last decade as a promising platform for electrocatalysis due to their precise structural arrangement and tunable chemical and pore environment. COFs have proven to be suitable candidates to study the electrochemical carbon dioxide reduction reaction (eCO₂RR), addressing the climate crisis by mitigating CO₂ levels and, ideally, transforming it into chemical energy value-added chemicals.^[1, 2] On a large scale, eCO₂RR could assist with storing the excess of electricity through energy conversion. To achieve industrial implementation of eCO₂RR with COFs, it is essential to explore the transition from laboratory-scale H-cell setups in their current state to larger-scale electrochemical setups, such as flow cell systems. Hence, we investigate the preparation of gas diffusion electrodes with COF-366-Co in a zero-gap electrolyzer setup coupled with *operando* gas chromatography. This scalable approach, which utilizes humidified CO₂ as a feeding stock, overcomes CO₂ solubility limitations and alleviates mass transport for eCO₂RR, enabling higher current densities than H-cells.^[3] Besides these advantages, the resulting harsher conditions led to a present lack of reports for COFs. Therefore, advancing the exploration of COFs in a novel catalytic environment is bringing them closer to their practical use in terms of industrially relevant conditions.

[1] Z. Chen, N. Li, Q. Zhang, *Small Struct.* **2024**, 5. DOI: 10.1002/sstr.202300495.

[2] S. Lin, C. S. Diercks, Y.-B. Zhang, N. Kornienko, E. M. Nichols, Y. Zhao, A. R. Paris, D. Kim, P. Yang, O. M. Yaghi, C. J. Chang, *Science* **2015**, 349, 1208-1213. DOI: 10.1126/science.aac8343.

[3] D. M. Weekes, D. A. Salvatore, A. Reyes, A. Huang, C. P. Berlinguette, *Acc. Chem. Res.* **2018**, 51, 910-918. DOI: 10.1021/acs.accounts.8b00010.

Leveraging molecular simulations to corroborate confinement effects observed in mesoporous materials

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Understanding the distribution and mobility of molecules under confinement is a prerequisite to utilize confinement effects in the realm of molecular heterogeneous catalysis, liquid chromatography or gas adsorption. Molecular simulation studies offer spatiotemporal resolution for confined systems that is often not accessible experimentally but require structural models that replicate the geometry, dimensions, and chemical structure of a surface-functionalised porous material. We present a software tool that facilitates rapid model building of functionalised silica pores for systematic studies of confinement effects in various applications of relevant materials [1]. The tool allows to choose the chemical structure and density of the ligands and to control the residual hydroxylation of the silica surface. Individual ligands can be placed at a user-defined position on the surface. Moreover, the tool supports an independent functionalisation of the interior and exterior pore surface. We illustrate how the tool can be used to study a diverse set of research questions arising in experimental studies of molecular heterogeneous catalysis in confined geometries [2]. These examples encompass the phase behavior of solvent mixtures under confinement, the distribution of reactants and products in mesoporous silica, and the benefit of confinement to focus the conformational space accessible to a catalytic complex. Moreover, adsorption and diffusion in other mesoporous materials such as metal organic frameworks (MOFs) or covalent organic frameworks (COFs) [3] is discussed with regard to obstacles that often hamper a comparison between simulation and experiment.

Literature:

[1] H. Kraus, J. Rybka, A. Hölzel, N. Trebel, U. Tallarek, N. Hansen, *Mol. Simul.* 2021, 47, 306.

[2] H. Kraus, M. Högler, N. Hansen, *J. Phys. Chem. C* 2023, 127, 14374.

[3] L. Grunenberg, C. Keßler, T. W. Teh, R. Schuldt, F. Heck, J. Kästner, J. Groß, N. Hansen, B. V. Lotsch, *ACS Nano* 2024, 18, 16091.

Role of Spacer Length of Tethered Cationic Molybdenum Complexes in Macrocyclization Efficiency Under Confinement

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Abstract:

Macrocyclic compounds play a vital role in pharmaceutical and industrial chemistry. For entropic reasons, oligomerization dominates over macrocyclization. Many strategies have been developed and used for macrocyclization in recent years. Our group has developed a biomimetic strategy for mono (macro) cyclization (MMC) for the synthesis of macrocyclic products that suppresses oligomerization.¹ Particularly the pore-selective immobilization of highly active cationic olefin metathesis catalysts inside the mesopores of SBA-15 materials allows for up to 98% macrocyclization efficiency using surface organometallic chemistry.² We studied the influence of the spacer length of tethered cationic molybdenum complexes immobilized inside the mesopores of modified SBA-15 materials on both macrocyclization efficiency and Z-selectivity.³ Results are supported by theoretical calculations and will be outlined in detail.

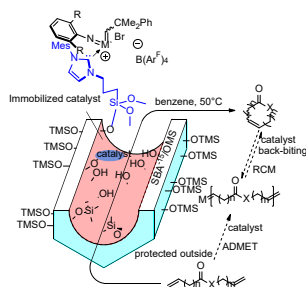


Figure 1: Tethered long-chain cationic molybdenum complexes used for macrocyclization reactions.

References:

- [1] F. Ziegler et al., *J. Am. Chem. Soc.*, **2019**, 141, 19014-19022, 10.1021/jacs.9b08776.
- [2] F. Ziegler et al., *ACS Catal.*, **2021**, 11, 11570, 10.1021/acscatal.1c03057.
- [3] M. Nandeshwar et al., *ChemCatChem*, **2025**, 17, e202401561. 10.1002/cctc.202401561

A Predictive Betaine Organocatalyst Platform for Asymmetric [3+2]-Cycloadditions via Catalyst-Substrate Matching

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Organocatalysts are powerful tools for the efficient and sustainable synthesis of chiral molecules.^[1] The asymmetric [3+2]-cycloaddition of azomethine ylides to dipolarophiles is a well-established strategy for accessing chiral pyrrolidines, key motifs in many bioactive molecules.^[2] Here, we present a new type of metal-free betaine catalyst that competes with the most efficient reported metal catalysts for the reaction of C-H acidic imines with N-methylmaleimide.^[3] DFT analysis reveals a complex, multistep reaction mechanism relying on weak, non-covalent interactions. High conformational flexibility, multiple binding modes and various reaction pathways impeded fast and accurate ab-initio selectivity prediction. Instead, we choose a data-driven strategy based on combinatorial screening of catalyst–substrate screening to identify key interactions. Linear regression models reveal important catalyst–substrate matching effects and accurately predict reaction outcome for new, out-of-sample catalysts and substrates. Our predictive platform enables the selection of the optimal catalyst for a given substrate and provides a foundation for further substrate-space exploration and immobilization of the catalyst into confined pores. This will be used as a strategy to access the space of challenging dipoles and dipolarophiles.

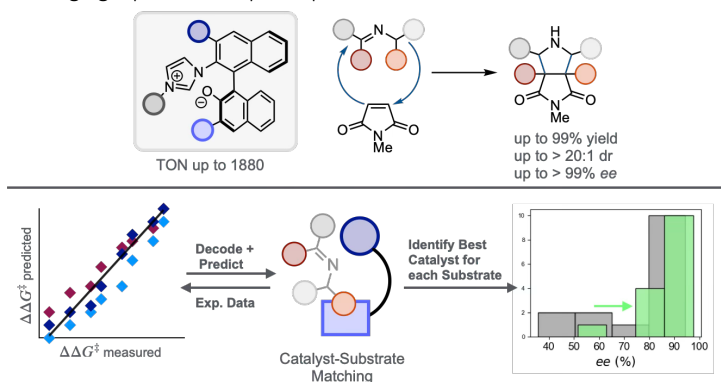


Figure 1: Top: General Structure of the chiral imidazolium-naphthoxide-catalyst and its use in the [3+2]-cycloaddition of imines to N-methylmaleimide. Bottom: Data-driven approach to decode catalyst-substrate interactions and build a predictive platform to find the best catalyst per substrate.

[1] MacMillan, D. W. C. *Nature* **2008**, 455 (7211), 304–308.

[2] Adrio, J.; C. Carretero, J. *Chem. Commun.* **2014**, 50 (83), 12434–12446.

[3] Bürstner, A.; et al. *Angew. Chem. Int. Ed.* **2025**, 64 (34), e202508024.

Ring-Expansion Metathesis Polymerization Under Confinement

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The recently reported ring-expansion metathesis polymerization (REMP) with cationic molybdenum alkylidyne *N*-heterocyclic carbene (NHC) complexes [1] has now been extended to heterogeneous (supported) systems. Complex **1** (Figure 1) was selectively immobilized inside the pores of ordered mesoporous silica with pore diameters of 66 Å, 56 Å, and 28 Å, respectively. REMP of *cis*-cyclooctene (cCOE), 1,5-cyclooctadiene, 2-methyl-2-phenylcycloprop-1-ene and *endo,exo*-2,3-dicarbomethoxynorborn-5-ene with both the homogeneous and the supported catalyst was performed. High molecular weight cyclic polymers were predominantly formed in homogeneous solution with **1** while its immobilization inside small (28 Å) pores of mesoporous silica allowed for suppressing the formation of high molecular weight polymers, thereby offering selective access to low molecular weight oligomers. The oligomers were subjected to MALDI-TOF, confirming the exclusive formation of cyclic polymers. Molecular dynamic simulations and analytical aspects of the heterogeneous system will be outlined.[2]

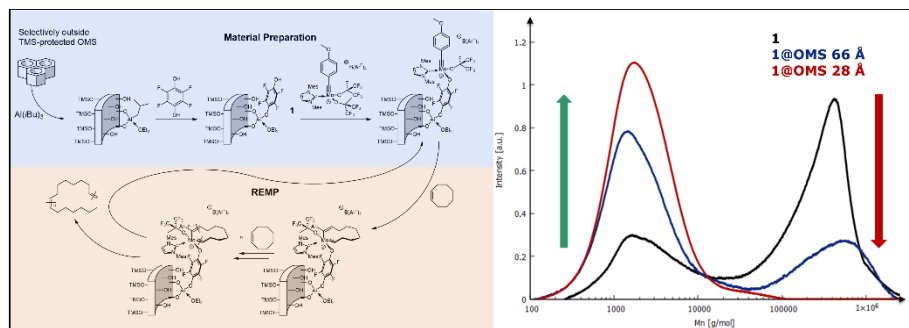


Figure 1. Left: Catalyst immobilization on ordered mesoporous silica, protected with TMS outside, followed by REMP of cCOE. Right: SEC of poly(cCOE) prepared by **1** and on different silica materials.

[1] P. Probst *et al.*, *J. Am. Chem. Soc.*, **2024**, 146, 8435-8446.

[2] P. Probst *et al.*, *J. Am. Chem. Soc.*, **2025**, 147, 8741-8750.

N-Boc-Protected Proline Organic Linkers for Rigid Zr-Metal Organic Frameworks (MOFs) and their Catalytic Potential

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This work focuses on multicomponent metal-organic frameworks (MOFs) as a powerful class of heterogeneous catalysts in which functional groups can be positioned within the pores to influence catalytic transformations. In this project, rigid zirconium-based UiO-67 frameworks containing *ortho*- (red) and *meta*-proline (blue) amide linkers were investigated for their catalytic potential in asymmetric aldol reactions as a benchmark reaction (Figure 1).

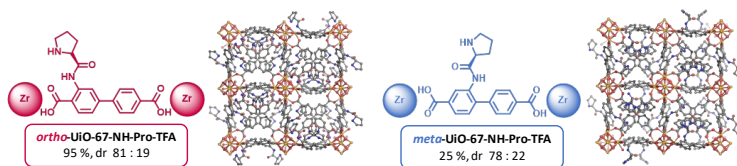


Figure 1: Linkers and their MOFs investigated in this study.

In addition, homogeneous catalysis with the corresponding linker analogues was carried out to analyze the influence of the MOF environment on diastereo- and enantioselectivity. During this work, TFA and other carboxylic acids were introduced as acid modulators in the MOF synthesis. These modulators influenced framework formation, Boc deprotection and the formation of acetals as competing side products. Heterogeneous catalysis showed that the position of the proline unit influenced the catalytic performance, with the *ortho*-functionalized MOF exhibiting higher catalytic activity than the corresponding *meta*-functionalized analogue.

Z. Dilruba *et al.*, Inorg. Chem. Front., **2025**, 12, 5792-5802, Doi:10.1039/D4QI02724H.

Experimentally validated modeling of ordered mesoporous aluminosilicates using *ab initio*-based machine learning interatomic potentials

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Ordered mesoporous silica materials are commonly used as catalyst supports. Introducing small amounts of aluminum into the amorphous silica matrix further enhances their catalytic properties. However, obtaining an atomistic understanding of these ordered mesoporous aluminosilicates (OM2S) experimentally is difficult due to their structural complexity. To address this challenge, we developed an *in silico* synthesis route to generate OM2S models using machine learning interatomic potentials (MLIPs).^[1] This approach enabled us to simulate OM2S with density functional theory (DFT) accuracy at experimentally relevant length scales (see Figure 1). We validated our models by comparing the pair-distribution function, Al-dependent mass density, infrared spectra, and pore surface acid site densities with experimental results.^[2] Furthermore, this model provides a detailed atomistic picture of the acidity and vibrational signatures of functional groups located on the OM2S pore surface.

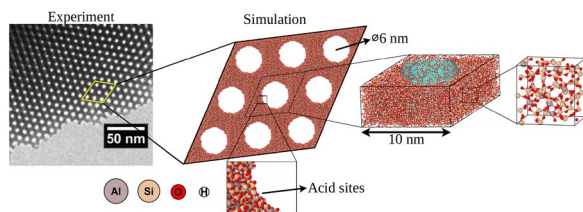


Figure 1: Multi-scale view of simulated OM2S compared to experiment.

[1] J. H. Jung, *et al.*, arXiv, **2025**, 2512.02309.

[2] S. Itzigebl *et al.*, Microporous Mesoporous Mater., **2026**, 402, 113991, <https://doi.org/10.1016/j.micromeso.2025.113991>.

Revealing confinement effects on immobilized group 6 catalysts with hard X-ray spectroscopy

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The overarching objective of CRC 1333 is to realize molecular heterogeneous catalysis in confined geometries by immobilizing molecular catalysts within mesoporous materials and exploiting confinement effects as a key determinant of catalytic selectivity. Elucidating the electronic and structural parameters of molecular (pre)catalysts and their immobilized counterparts provides detailed insight into the origin of confinement effects on modified catalytic activities and selectivities. Owing to their high penetration depth and element specificity, hard X-rays enable the investigation of the molecular structure of catalytically active complexes almost independently of their state of aggregation and the experimental conditions applied.

Via the excitation of 1s electrons, confinement effects on structure and reactivity of immobilized Cr- and Mo-catalysts for ethylene oligomerization and ring-expansion metathesis polymerization (REMP) were elucidated.^[1-3] XANES (X-ray absorption near-edge structure) disclosed significant changes in electron density located at the metal centers, which could be precisely connected to explicit ligand substitution reactions initiated by the immobilization protocol by EXAFS (extended X-ray absorption fine structure). Complementarily, time-dependent DFT (TDDFT) calculations were applied to model the pre-edge fine structures of the investigated complexes and confirm their XAS-derived molecular structures.

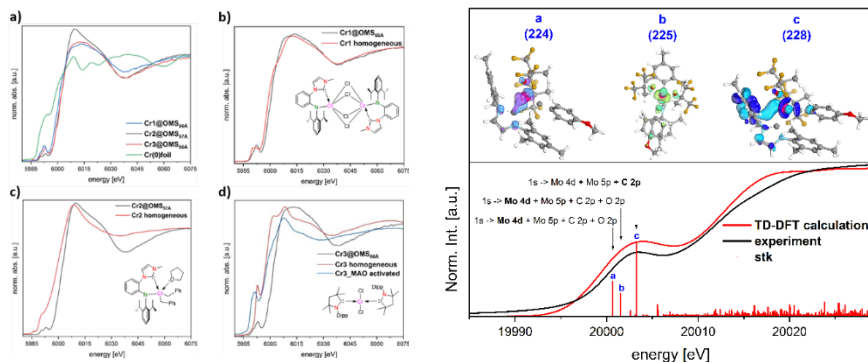


Figure 1: a) – d): XANES spectra of three homogeneous Cr-catalysts for ethylene oligomerization and their immobilized analogues. For Cr3, also the spectrum of the catalytically active species is shown. e): Experimental and TDDFT-calculated XANES spectra of a Mo-alkylidene complex used for ring-expansion metathesis polymerization (REMP).

- [1] S. Bhattacharya, M. Höglér, J. R. Bruckner, B. Atwi, M. Bauer, N. Hansen, F. R. Fischer, M. R. Buchmeiser, *Catal. Sci. Technol.* **2026**, *16*, 2170, DOI: 10.1039/D5CY01483B.
- [2] A. Allgaier, F. R. Fischer, S. Bhattacharya, K. Balliet, M. R. Buchmeiser, M. Bauer, J. van Slageren, *Inorg. Chem.* **2026**, *65*, 13, 7309–7321, doi.org/10.1021/acs.inorgchem.6c00208.
- [3] P. Probst, M. Lindemann, J. R. Bruckner, B. Atwi, D. Wang, F. R. Fischer, M. Höglér, M. Bauer, N. Hansen, M. Dyballa, M. R. Buchmeiser, *J. Am. Chem. Soc.* **2025**, *147*, 8741, doi.org/10.1021/jacs.4c18171.

Defect-Engineered Perovskites: Atomic Scale Nature of A-Site

Vacancy-Stabilized Catalytically Active Phase

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Defect engineering in perovskites offers a sustainable pathway to replace scarce noble metals in heterogeneous catalysis, yet the atomic-scale nature of A-site deficiencies and their role in stabilizing active phases remain poorly understood. Here, we elucidate the structure property relationships in the A-site-deficient perovskite $\text{La}_{0.7}\text{Fe}_{0.7}\text{Mn}_{0.3}\text{O}_3$ ($\text{L}_{0.7}\text{FM}$) during NO reduction by CO using a multimodal approach combining aberration-corrected scanning transmission electron microscopy (STEM), quantitative energy-dispersive X-ray spectroscopy (EDXS), electron energy-loss near-edge structure (ELNES) analysis, in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and in situ X-ray photoelectron spectroscopy (XPS). We reveal a heterogeneous defect landscape: highly A-site-deficient $\text{La}_{0.7-x}\text{Fe}_{0.7}\text{Mn}_{0.3}\text{O}_3$ layers, only 2–3 unit cells thick, are confined to the surfaces and grain boundaries of the perovskite nanoparticles and transition abruptly into stoichiometric bulk $\text{LaFe}_{0.7}\text{Mn}_{0.3}\text{O}_3$. These localized defect regions stabilize the formation of catalytically active FeO_x nanoparticles (≈ 1 –several nm) that are absent in the stoichiometric counterpart. Geometric phase analysis (GPA) confirms that the A-site-deficient matrix remains strain-free, allowing relaxation via FeO_x exsolution rather than lattice distortion. In situ surface characterization and catalytic testing demonstrate that these interfacial FeO_x nanoparticles operate via a Mars–van Krevelen mechanism, markedly lowering the NO reduction onset temperature (≈ 120 °C vs. 180 °C for stoichiometric $\text{LaFe}_{0.7}\text{Mn}_{0.3}\text{O}_3$) while maintaining high N_2 selectivity. Fe^{2+} sites serve as the redox-active centers, with enhanced oxygen vacancy formation and mobility enabled by the confined A-site vacancies. Our results establish a direct atomic-scale link between nanoscale A-site non-stoichiometry and redox-driven catalytic activity, providing a rational design strategy for next-generation defect-engineered perovskite catalysts in exhaust-gas purification and beyond.

[1] Roham Talei, Asghar Mohammadi, Thomas F. Winterstein, Christoph Malleier, Guido Schmitz, Simon Penner, and Nicolas Bonmassar

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DOI: 10.1021/jacs.5c22657

Mesoporous silica materials synthesized via different liquid crystal templating routes: a detailed SAXS study

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The hierarchical structure of ordered mesoporous silica materials (OMS) gives rise to small-angle scattering (SAS) over a wide range of scattering vectors. Based on comprehensive scattering models, small-angle X-ray scattering (SAXS) analysis provides valuable information about the size and arrangement of mesopores, microporous structures, and macropores. These models are usually designed for specific OMS families, such as MCM-41 or SBA-15, which are synthesized via a particular templating route[1]. Here, we present a generalized scattering model that allows for greater variability in the mesopore form factor. Thus, it can be applied to a wide range of OMS materials, even those synthesized via different templating routes, namely conventional liquid crystal templating (LCT) and true liquid crystal templating (TLCT). The results show, among other things, that TLCT leads to a more homogeneous and dense silica matrix between the mesopores.

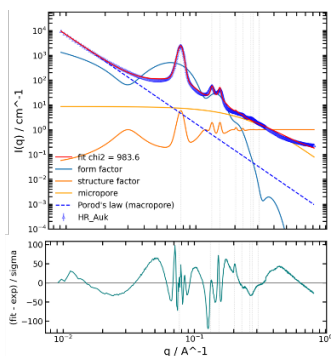


Figure 1: The generalized model fit with TLCT SBA-15 SAXS curve.

[1] J. Gommers et al., J. Phys. Chem. C, **2016**, 120, 1488–1506, DOI: 10.1021/acs.jpcc.5b11070

Spectroelectrochemical Evidence on COF induced Confinement of Water

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The study of nanoscale confinement and its effect on electrochemistry is a rapidly growing field, which however is non-trivial simply due to the inherent complexity of such systems. In this work, we want to present our work on utilizing electrochemical surface enhanced infrared absorption spectroscopy (EC-SEIRAS) to probe such environments and their effect on the potential-dependent behavior of water on Au and covalent organic framework (COF)-modified Au electrodes. Supported by molecular dynamics and solvation shell spectroscopy, we found that in an isorecticular series, the pore size increases the sensitivity of hydrogen-bonded water ($\text{H}_2\text{O}_{\text{HB}}$) to the applied potential.^[1] We also revealed chemical coordinative effects in such systems, which lead to decreased sensitivity. Such insights will allow more facile design of COF systems to induce sought-after (electrocatalytic) behaviour.

[1] Y. Weidemann *et al*, *ChemRxiv* **2026**, <https://doi.org/10.26434/chemrxiv.15000669/v1>

Structure and Chemical Reactivity of size-selected Clusters in Gas Phase

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We study charged cluster ions in the gas phase as a model system for catalysis. Focusing on platinum, ruthenium and palladium clusters, we investigate the relationship between cluster size, structure and catalytic activity. We determine the structural properties of metal clusters and their adsorbates using trapped ion electron diffraction, and measure reactivity in an ion trap under isothermal conditions. Using hydrides as model systems, we observe significant changes in structure and electronic properties induced by hydrogen adsorption.

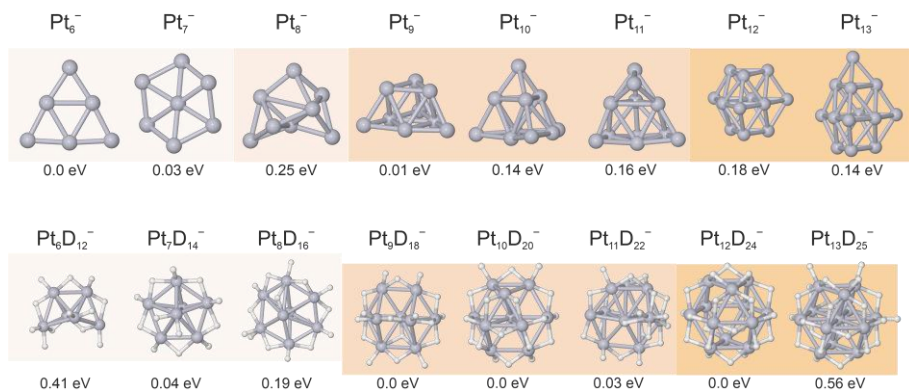


Figure 1: Structure change of small platinum cluster induced by hydrogen adsorption.

[1] D. Bumüller et al., *J. Chem. Phys. A* **2022**, 126, 3502.

[2] S. Gojare et al., *ChemPhysChem* **2024**, 25, e202400649.

Infrared spectroscopy and quantum chemical calculations on oxides and oxide-supported noble metals

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A thorough understanding of structure–activity relationships in metal oxides, as well as the effects of noble metal deposition, remains one of the most important and challenging topics in heterogeneous catalysis. In this work, we investigate the interaction of small molecules (CO, D₂O, HCOOH, NH₃) with metal oxides (CeO₂, Al₂O₃, MgO) and oxide-supported noble metals (Pt, Pd) by combining quantum-chemical embedded cluster calculations with polarization-resolved IRRAS on well-defined single-crystal surfaces. The IR characterization is complemented by XPS and NEXAFS measurements. Building on these comprehensive and reliable reference data, we are able to gain deeper insight into the complex surface chemistry of both pristine and metal–deposited oxide nanoparticles using in-situ IR transmission (UHV-FTIRS). The calculations allow the comparison of spectroscopic data at different adsorption sites and enable assignment and characterization of the active sites. Furthermore, we explore the role of various defects, such as oxygen vacancies and dopants, in governing the reactivity of metal/oxide interfaces. This integrated approach provides a detailed understanding of structural, electronic and reactive properties across model and realistic catalytic systems. [1-5]

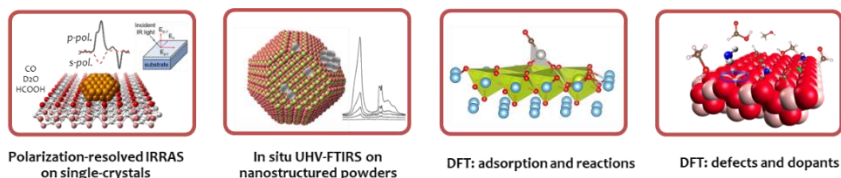


Figure 1: Schematic overview of the research focus

[1] B. Wang, Z. Yu, *et al.*, *Angew. Chem. Int. Ed.*, 2025, 64, e202423273. DOI: 10.1002/anie.202423273

[2] S. Gojare, *et al.*, *ChemPhysChem*, 2025, 26, e202401134. DOI: 10.1002/cphc.202401134

[3] J. Vázquez Quesada, *et al.*, *J. Chem. Phys.*, 2024, 161, 224707. DOI: 10.1063/5.0231189

[4] C. Yang, *et al.*, *Acc. Chem. Res.*, 2024, 57, 3316-23326. DOI: 10.1021/acs.accounts.4c00529

[5] S. Chen, *et al.*, *Angew. Chem. Int. Ed.*, 2024, 63, e202404775. DOI: 10.1002/anie.202404775

Pd nanoparticles supported by CeO₂ nano-islands on α -Al₂O₃ as model catalyst for methane oxidation

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Ceria (CeO₂) is characterized by strong metal-support interactions, high oxygen storage capacity, and unique redox properties based on the facile and reversible change in oxidation state between Ce⁴⁺ and Ce³⁺. Therefore, it is applied in heterogeneous catalysis either as catalytic material or as active support material for noble metals acting as oxygen buffer during oxidation processes [1-3]. However, a detailed description of the oxygen transport between ceria and noble metals remains largely unexplored [3]. This motivates the study of well-defined model systems by surface sensitive X-ray diffraction, combined with atomic force microscopy (AFM), which enables us to uncover atomic scale details of their structure. Here we present the results of the growth and characterization of non-inert CeO₂ nano-islands on inert α -Al₂O₃ substrates, as well as Pd nanoparticles (NPs) on top of this heterogeneous support. These will act as idealized model systems with potentially increased sinter resistance of Pd NPs due to confined Pd movement on the CeO₂ nano-islands [4], and will be investigated further by operando studies under different oxidation reactions, such as methane oxidation, to correlate structural changes with the catalytic activity.

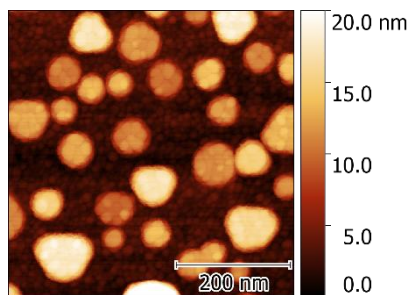


Figure 1: AFM image of Pd NPs (small dots) on triangular/hexagonal CeO₂ islands supported by α -Al₂O₃ (11-20).

[1] A. Trovarelli, Catal. Rev.-Sci. Eng., **1996**, 38, 439-520, DOI:10.1080/01614949608006464.

[2] T. Montini *et al.*, Chem. Rev., **2016**, 116, 5987-6041, DOI:10.1021/acs.chemrev.5b00603.

[3] D. Ciuparu, L. Pfefferle, Catalysis Today, **2002**, 77, 167-179. DOI:10.1016/S0920-5861(02)00243-2.

[4] D. Gashnikova *et al.*, Angew. Chem. Int. Ed., **2024**, 63, e202408511. DOI:10.1002/anie.202408511

Structural and Compositional Evolution of Ru-Bi Catalysts during NH₃ Oxidation Studied by Advanced Electron Microscope

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Ammonia oxidation is a key reaction in emission control, where catalyst stability under oxidizing conditions is essential. Ruthenium-based catalysts [1] show high activity, but multicomponent systems often undergo complex structural evolution.

Additionally, using conventional methods, larger Ru-particles, of the already scarce and expensive element, are forming. Predefined single-site Ru atoms found in the Zintl-cluster $[\{\text{CpRu}\}_3\text{Bi}_6]^-$ were deposited on Al₂O₃ and CeO₂ via incipient wetness impregnation [2]. These Ru-Bi cluster-derived catalysts on oxide supports were studied under different pretreatment conditions and compared before and after NH₃ oxidation.

Rod-like structures with Ru-Bi-O composition form already during preparation and support. On CeO₂, elongated structures are preserved, whereas on Al₂O₃ compact aggregates are observed. After NH₃ oxidation, some structures remain while others show significant changes. These differences correlated with catalytic behavior, showing support-dependent selectivity in NH₃ oxidation.

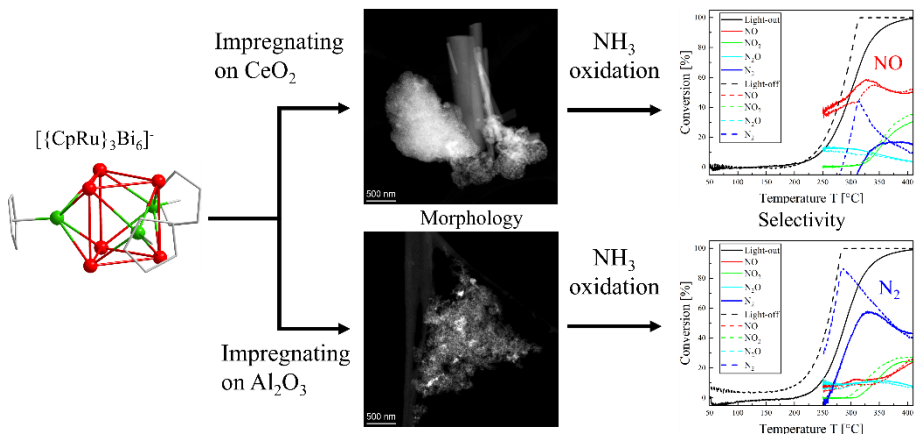


Figure 1: Support-dependent morphology and NH₃ oxidation selectivity of Ru-Bi cluster-derived catalysts. CeO₂ shows rod-like structures, whereas Al₂O₃ forms compact aggregates, with corresponding differences in selectivity.

[1] M. A. Aslam et al., *ACS Catal.*, 15, 18631–18662 (2025).

[2] B. Peerless et al., *Nat. Chem.*, 15, 347–356 (2023).

Nanoscale Pt-CeO₂ Islands on Al₂O₃ Nanosponges as highly active Oxidation Catalysts

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By increasing the surface noble metal concentration (SNMC) of Pt on CeO₂, activity in CO oxidation can be shifted to lower temperatures.^[1] To achieve this without using more noble metal or low surface area CeO₂, Pt can be confined on nanoscale CeO₂ islands supported on porous Al₂O₃.^[2] In our group, we have established liquid phase synthesis of Ce⁰ nanoparticles 2.5±0.4 nm in diameter, which can be oxidized to similarly sized CeO₂ islands on Al₂O₃.^[3] To selectively deposit Pt only on those CeO₂ islands, Ce⁰Pt⁰ nanoparticles are prepared in liquid phase, deposited on highly porous Al₂O₃ nanosponges and oxidized to Pt-CeO₂ islands. Catalytic activity in NH₃ oxidation shows increased activity compared to similarly prepared Pt-Al₂O₃ and Pt-CeO₂ nanosponges.^[4]

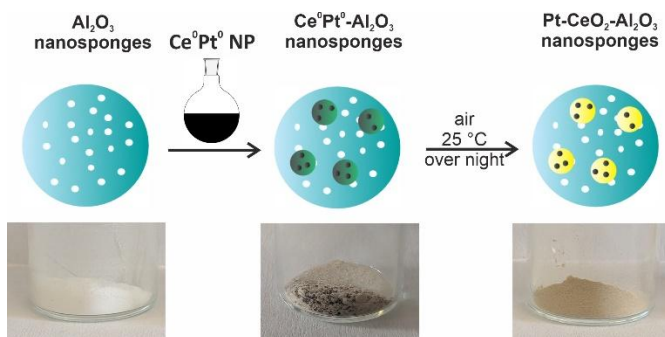


Figure 1: Scheme illustrating the impregnation of Al₂O₃ nanosponges with Pt-CeO₂ islands with corresponding photos of dried powders

[1] F. Maurer *et al.*, *ACS Catal.* **2022**, 12, 2473–2486.

[2] D. Gashnikova *et al.*, *Angew. Chem. Int. Ed.* **2024**, 63, e202408511.

[3] D. Bartenbach *et al.*, *Angew. Chem. Int. Ed.* **2021**, 60, 17373–17377.

[4] S. Falkner *et al.*, **2026**, *in preparation*.

Monodisperse Shape-Controlled PdPtRh Nanoparticles as Model Catalysts for Methane Oxidation

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To understand the effects of surface facets, elemental distribution and size in catalytic reactions, nanoparticles (NPs) with well-defined geometries and sizes can be used as building units for the synthesis of model catalysts.¹ Although monometallic NPs have been the focus of numerous studies,² shape-controlled syntheses of multimetallic NPs remain scarce and poorly understood. They are of particular interest for catalyst design because the combination of two or more noble metals can increase thermal stability during hydrothermal aging, enhance the resistance towards catalyst poisons and create new local electronic sites. Herein, we address the shape- and size-selective synthesis of multimetallic NPs with different constituting elements (i.e. Rh, Pd, Pt). To prepare model catalysts, the NPs were supported on CeO₂ and calcined at 500 °C for 90 seconds. TEM with energy dispersive X-ray (EDS) analysis, PXRD, UV-vis spectroscopy and mass spectrometry were used to study the mechanisms of shape- and size-control synthesis and to derive knowledge-based design principles for shape-controlled, multimetallic NPs. Our recent findings indicate that the shape of such NPs remains unaffected by calcination, suggesting high thermal stability. The catalysts were tested for CH₄ oxidation to assess their stability under catalytic conditions and establish structure-activity relationships.

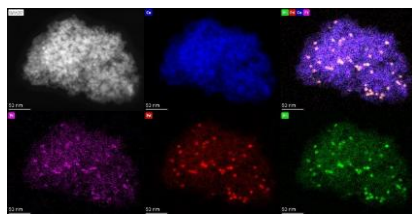


Fig. 1 HAADF-STEM image and EDX maps of RhPdPt NPs on CeO₂. (blue- Ce, pink- Pt, red- Pd, green- Rh)

1. D. I.Sharapa, D. E. Doronkin, F. Studt, J.-D. Grunwaldt, S.Behrens, Adv. Mater **2019**, 31, 1807381.

2. B. Wang, Z.Yu, S.Chen, N.Da Roit, D.Schild, M.Zimmermann, Y.Wang, S.Behrens, Angew. Chem. Int. Ed **2025**, 64, e202423273.

In situ/operando Characterisation of Noble Metal Clusters and Particles on Metal Oxides at Work

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Efficient use of scarce resources such as noble metals (NM) requires new concepts and a thorough understanding of structure–activity relationships. This task is particularly challenging as the structure of the NM clusters/particles and the support material are sensitive to the operating conditions. Therefore, we apply a combination of complementary *in situ/operando* characterisation methods including 1) X-ray absorption spectroscopy to monitor the oxidation state and structure of NMs^[1–3] and 2) surface ligand infrared spectroscopy to track the fate of surface adsorbates and their coordination sites.^[4,5] Based on these two complementary approaches, we identified the crucial role of the NM-support interaction as a function of the exposed CeO₂ surface. In addition, the cluster size formed under reaction conditions plays a significant role. We therefore developed a concept to tune these effects by manipulating the amount of highly interacting support surface that is exposed. By extending our holistic spectroscopic approach towards relevant oxidation reactions, the aim is predicting and controlling the catalytically active sites within their lifecycle during emission control applications and using NMs in a knowledge-based catalyst design as efficiently as possible.

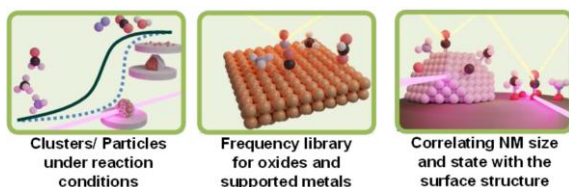


Figure 1: Central focus points of our work

[1] D. Gashnikova, *et al.*, *Angew. Chem.Int. Ed.* **2024**, 63, e202408511. DOI: 10.1002/anie.202408511

[2] D. Gashnikova, *et al.*, *ACS Catalysis* **2024**, 14 (19), 14871. DOI: 10.1021/acscatal.4c02077

[3] D. Gashnikova, S. Struzek, *et al.*, *J. Phys. Chem. C* **2025**, 129 (31), 13923. DOI: 10.1021/acs.jpcc.5c01963

[4] L. Caulfield, *et al.*, *J. Phys. Chem. C* **2025** 129, 39, 17643. DOI: 10.1021/acs.jpcc.5c04507

[5] L. Caulfield, *et al.*, *J. Phys. Chem. C* **2023** 127 (29), 14023. DOI: 10.1021/acs.jpcc.3c03567

A DFT based study on the Oxidative removal of pollutants

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Air pollution [1] and greenhouse gas emissions [2] remain among the most pressing environmental challenges. The catalytic Oxidation of harmful pollutants such as methane and ammonia into less hazardous compounds is a central goal of heterogeneous catalysis research. [3] Supported noble metal catalysts, including Pt, Pd and Rh, are widely employed in automotive and industrial applications for hydrocarbon and nitrogen oxide abatement. However, despite their technological importance, the atomistic mechanisms governing pollutant activation and oxidation over these catalysts are still not fully understood.

This work focuses on the first-principles modelling of methane and ammonia oxidation over Pt-, Pd- and Rh-based model catalysts. Using Density Functional Theory (DFT) calculations, we investigate the key elementary reaction steps underlying C-H and N-H bond activation, their dependence on surface structure and oxygen coverage and product formation. Reaction pathways are systematically analyzed to identify intermediates, transition states, and activation barriers for both direct and oxygen-assisted mechanisms.

The kinetic parameters and mechanistic insights obtained from these DFT studies will serve as critical input for microkinetic modelling and reactor-scale simulations performed within the broader CRC 1441 project. Together, these multiscale modelling efforts aim to identify the key structural and electronic descriptors governing catalytic activity and selectivity for pollutant oxidation.

[1] Afifa; Arshad, et al., Sci. Total Environ. 2024, 928, 172370.
<https://doi.org/10.1016/j.scitotenv.2024.172370>.

[2] Shah, I. H et al., J. Environ. Manage. 2024, 351, 119978.
<https://doi.org/10.1016/j.jenvman.2023.119978>.

[3] He, C. et al., Chem. Rev. 2019, 119 (7), 4471–4568.
<https://doi.org/10.1021/acs.chemrev.8b00408>.

Catalytic Monoliths with Narrow Particle Size Distribution in Washcoats with Well-Defined Gradients

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Noble metal-based catalysts are commonly applied in emission control catalysis, showing high activity. At the subnanometer scale, cluster compounds with precise number of atoms have immense potential, because their catalytic performance not only depends only on size, but also on their specific geometric and electronic structure. Bridging the gap to real world application, these highly active clusters and nanoparticles (NPs) are typically supported on metal oxides and wash-coated on ceramic monolithic honeycombs, yielding hierarchical catalysts.^[1]

However, cluster compounds and nanoparticles are usually synthesized through batch processes that often have a low yield. The continuous flow (CF) synthesis is highly favored for producing of cluster and NPs, as it enhances product yield and reproducibility. Plug flow and microfluidic reactors are commonly used for CF NP synthesis, but they are typically limited to reactions with rapid reaction kinetics. We have developed a CF synthesis platform for reactions with slow kinetics, integrating multiple continuous stirred tank reactors (CSTR) into a cascade.^[2] This multistage platform provides a simple and scalable pathway with flexible but precisely controlled reaction conditions (**Figure 1 left**).

Here, we show the scalable, CF synthesis of $[\text{Pt}_{17}(\text{CO})_{12}(\text{PR}_3)_8]^{n+}$ ($n = 1, 2$) clusters with atomic-level precision in amounts relevant to practical application.^[3] In addition, we demonstrate the CF synthesis of various mono- and multimetallic NPs (based on Pd, Pt, Rh, or Fe_3O_4). Investigating improved washcoat configurations, two-layer structured catalysts, comprising mono and bimetallic Pt and Pd on CeO_2 and Al_2O_3 were prepared by dip-coating. Exemplarily, these catalysts were tested in wet methane oxidation (250 °C -550 °C, 3200 ppm CH_4 , 12% H_2O , 10% O_2 , **Figure 1 right**). A comparison of pristine and hydrothermally aged samples (16 h, 600 °C or 800 °C, 12% H_2O , 10% O_2) revealed that configurations with Pt and Pd in the same layers exhibited the highest activity. Moreover, analysis of different washcoat samples before and after catalytic tests *via* SEM-EDX, XANES and DRIFTS indicated a Pt migration phenomenon from Al_2O_3 to CeO_2 layers. With these insights, future

concepts to avoid loss of catalytic material, as well as designing a stable and long-living catalyst can be developed.

To further improve knowledge-driven catalyst preparation, we aim in monitoring the synthesis of NPs as well as the different coating techniques *in-situ* by different spectroscopy methods (e.g., UV-Vis, DLS, XAS, tomography).

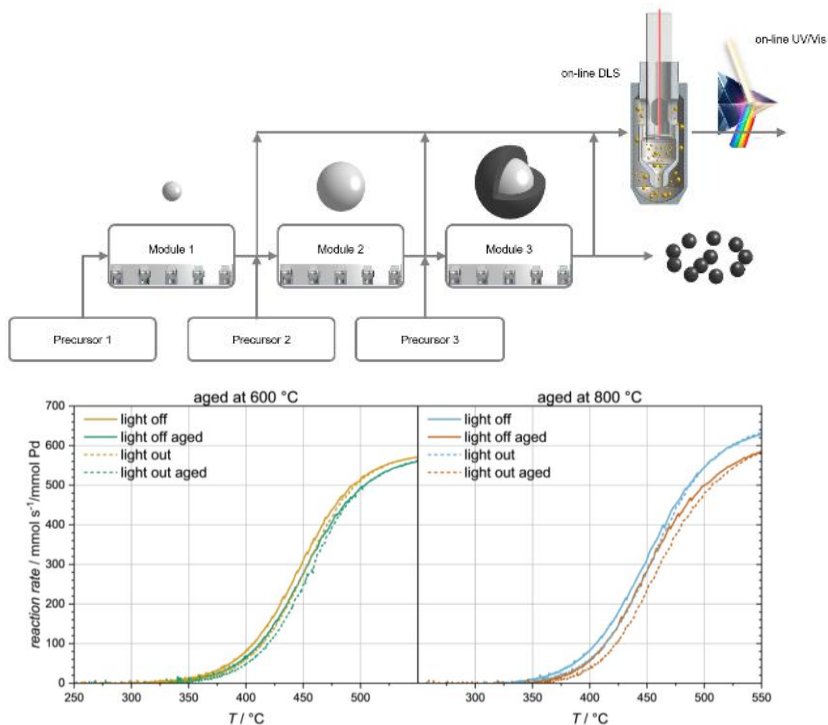


Figure 1 Top: Flow diagram of the continuous flow synthesis of NPs in a CSTR cascade using on-line monitoring by UV-vis spectroscopy and dynamic light scattering. Bottom: Light off and light out curves of monolithic Al₂O₃ // 2 wt% Pd - 1 wt% Pt/CeO₂ catalysts (3200 ppm CH₄, 10 % O₂, 11 % H₂O, N₂, 40,000 h⁻¹). Aging was performed at 600 °C or 800 °C for 16 h (10 % O₂, 11 % H₂O, N₂, 40,000 h⁻¹).

- [1] T. Delrieux *et al.*, React. Chem. Eng., **2024**, 9, 2868–2881, 10.1039/d4re00168k.
- [2] C. Schmitt *et al.*, Nanoscale Adv., **2024**, 6, 2459, 10.1039/D4NA00074A.
- [3] P. Chakraborty *et al.*, ACS Nano **2025**, 19, 3624, 10.1021/acsnano.4c13954.

Multiscale X-ray Imaging of Washcoated Monolith Catalysts: From Structural Heterogeneity to *Operando* Chemical Transformations

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Structured emission control catalysts are typically implemented as washcoated monolithic honeycombs, where catalytic performance is governed not only by intrinsic reaction kinetics but also by catalyst architecture and spatially heterogeneous aging phenomena[1]. In this work, complementary hard X-ray imaging techniques were applied to investigate structured catalysts across multiple length scales. Multiscale X-ray tomography was used to characterize the architecture of washcoated Pd/Al₂O₃ monolith catalysts, enabling quantitative three-dimensional analysis of washcoat morphology, channel accessibility, and structural changes during catalyst aging. Complementary X-ray absorption spectroscopy was employed to investigate chemical transformations in washcoated Cu-SSZ-13 monolith catalysts under reaction conditions[2]. This enabled spatially resolved mapping of Cu speciation within the washcoat, providing insight into catalyst deactivation processes and the spatial distribution of active species during operation. Together, these studies demonstrate how multimodal and multiscale X-ray imaging provides a powerful framework for linking catalyst structure, chemical state, and performance in technically relevant emission control catalysts.

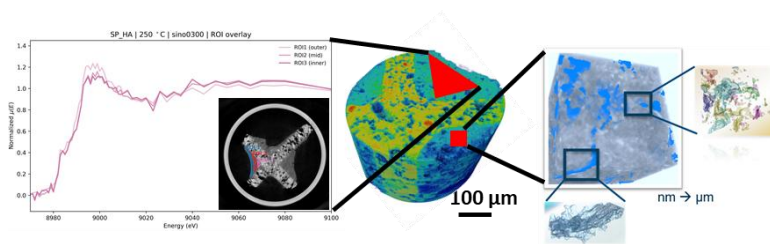


Figure 1: Structural and chemical investigation of washcoated monolith.

[1] J. Becher *et al.*, JPCC, **2019**, 123, 41, 10.1021/acs.jpcc.9b06541.

[2] J. Becher *et al.*, Nat. Catal., **2021**, 4, 46-53, 10.1038/s41929-020-00552-3.

Space and time resolved investigation of the enhanced NH₃ oxidation performance of Pd-based catalysts under dynamic operation

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Establishing structure-activity correlations in heterogeneous catalysts remains challenging as macro- and microkinetic processes on multiple length and time scales have to be considered. Therefore, spatio-temporal resolved studies are key to investigate solid-gas interactions, which is particularly important for highly exothermic and potentially unselective reactions such as the catalytic oxidation of ammonia (NH₃) slip. While Pt-based catalysts enable high NH₃ conversion at low temperatures in the selective catalytic oxidation of ammonia to N₂ and H₂O, they also tend to promote undesired N₂O formation.¹

In the present study, we investigate Pd based catalysts, which are generally less active under static operation, yet more selective toward N₂. Introducing short reductive treatment during lean operation notably improves NH₃ conversion and *operando* spatially resolved X-ray Absorption Spectroscopy (XAS) reveals pronounced structural changes along the bed. In a next step, we will non-invasively follow the selectivity and activity as a function of the local oxidation state by combining Planar Laser-Induced Fluorescence (PLIF) and XAS measurements under realistic conditions.²

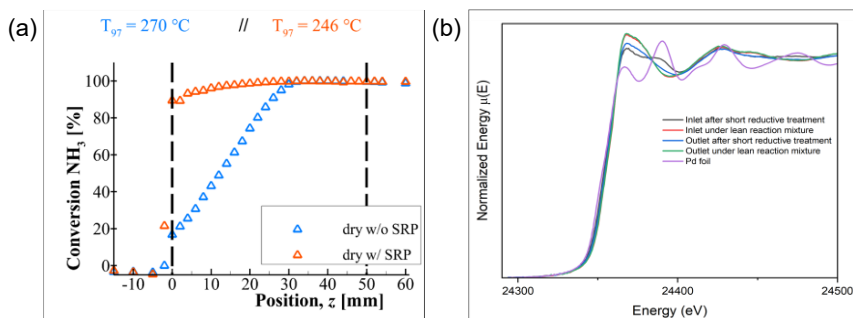


Figure 1: a) Spatial resolved NH₃ conversion and b) Spatially resolved XAS spectra over Pd/Al₂O₃ in static lean mode and in dynamic operation

(1) Shrestha *et al.*, *Catalysis Today* **267** (2016) 130.

(2) Häber *et al.*, *Appl. Catal. A* **712** (2026) 120748.

Induction heating of nickel ferrites and precious metal-based catalysts for CO oxidation

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²Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology, Karlsruhe, Germany

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Electromagnetic induction heating offers strong potential for emission control by enabling dynamic, localized, and rapid heat generation by the use of magnetically susceptible materials under an alternating magnetic field [1]. In this study, precious metal and ferrite catalysts for CO and CH₄ oxidation were evaluated under induction and conventional heating. Ferrites acting as a catalyst and a susceptor were synthesized via hydrothermal synthesis [2] and solvent-deficient precipitation [3]. Colloidal Pt nanoparticles were prepared in a continuous microfluidic setup [4] and deposited on oxide supports to obtain various active phase-support-susceptor combinations. If needed, the catalyst was mixed with carbon steel beads (SB) as bulk susceptor for induction heating. In general, induction heating enabled lower light-off temperatures (T_{50} , T_{90}) when compared to conventional heating (Figure 1).

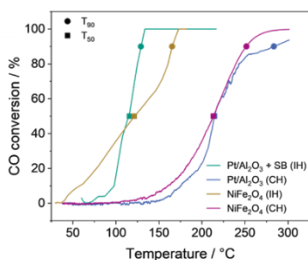


Figure 1: Comparison of light-off-light-out cycles during CO oxidation using NiFe₂O₄ or Pt/Al₂O₃ under induction heating (IH) and conventional heating (CH).

[1] W. Wang *et al.*, ACS Catal, **2019**, 9, 10.1021/acscatal.9b02471.

[2] P. Dolcet *et al.*, Green. Chem., **2018**, 20, 2257, 10.1039/C8GC00086G.

[3] S. J. Smith *et al.*, Nanoscale, **2015**, 7, 144, 10.1039/C4NR04964K.

[4] Y. Mahayni, *et al.*, ChemCatChem, **2025**, 17, e202401762, 10.1012/cctc.202401762.

First steps towards modeling transport inside mesopores of catalytic washcoats for emission control

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The industrial reduction of pollutants and greenhouse gases is mainly carried out in catalytic washcoated monolith reactors. Transport limitations inside the mesoporous catalyst strongly influence the reaction at the catalytic active sites. Spatially resolved modeling of the pore system can significantly contribute to a better understanding of the interplay between surface reaction and transport within catalysts and is a necessary step towards computer-aided catalyst design. However, biggest challenge in modeling transport inside mesopores is that the small pore diameters result in Knudsen numbers greater than 0.01. This causes the continuum assumption to break down, rendering the commonly used Navier-Stokes-Fourier equations invalid. Since molecular dynamic simulations are too computationally expensive for such large and complex geometries, a coarse-grained molecular dynamic method is essential to model the transport coupled with the catalytic reaction within the mesoporous catalyst. In this contribution a novel and general approach to model energy and multicomponent species transport for arbitrary Knudsen numbers is presented. The Boltzmann equation is solved for each component of the mixture using the

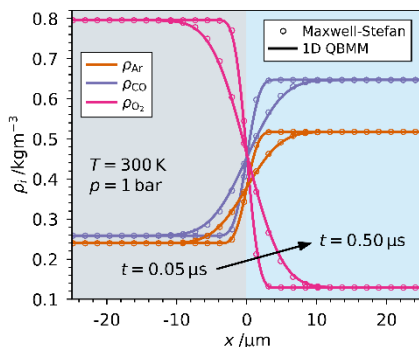


Figure 1: Mixture composition calculated with the Maxwell-Stefan diffusion model and 1D QBMM.

quadrature-based moment method (QBMM) [1]. First, the new approach is tested in 1D within the continuum limit. As illustrated in Figure 1, the developed model aligns well with the Maxwell-Stefan model. This proves the applicability of solving the Boltzmann equation with QBMM for describing multicomponent diffusion for the first time. Future work will extend this concept to 2D and 3D domains and introduce reflecting boundary conditions at the pore walls to model molecule-wall collisions.

Emission Reduction Potential of Three-Way Catalysts in a 100% Ammonia-Fueled Single-Cylinder Engine

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Ammonia is a promising carbon-free fuel for future combustion engines, but its application is associated with elevated emissions of unburned ammonia (NH_3), nitrogen oxides (NO_x) and nitrous oxides (N_2O). In this study, the performance of three-way catalysts (TWC) was investigated on a single-cylinder research engine operated under 100% ammonia combustion. A dedicated exhaust gas sampling system was implemented to extract a defined partial exhaust mass flow and route it through a catalyst test section, enabling controlled and reproducible catalyst evaluation. The experiments were conducted at a fixed operating point of 1500 rpm and 11 bar IMEP. The exhaust gas temperature upstream of the catalyst was approximately 270 °C, with a mass flow rate of 3.4 kg/h. Emissions were measured in ppm upstream and downstream of the catalyst using a FTIR, an AVL AMA and a MS4 hydrogen measurement system. Three ceramic monolith catalysts with identical total loading (100 g cat/l, corresponding to approximately 57 g/ft³ noble metal) were investigated, featuring different coating formulations: 2% Pd/ Al_2O_3 , 2% Pd/CeZr, and 2% Pt/ Al_2O_3 .

The results show that significant reductions in both NH_3 and NO_x emissions can be achieved under slightly rich operating conditions ($\lambda \approx 0.98$) for all investigated catalysts. This indicates that three-way catalysts are generally suitable for ammonia exhaust gas aftertreatment, even at comparatively low exhaust temperatures. At the same time, a strong increase in N_2O emissions was observed under richer conditions.

Overall, the emission behavior exhibits a high sensitivity to the air–fuel equivalence ratio, while differences between catalyst formulations indicate varying activity and selectivity. These findings highlight the importance of precise lambda control and tailored catalyst design for minimizing emissions in ammonia-fueled engine applications.

A surface-preserving sample preparation strategy for high-resolution environmental transmission electron microscopy of oxide catalysts

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A fundamental step in the development of new solid-state catalyst is to understand the underlying surface dynamics of the catalyst at the atomic level. One possible method for achieving this are in-situ ETEM (Environmental Transmission Electron Microscopy) experiments. However, typical TEM sample preparation (using a focused ion beam (FIB)) damages the sample surface or covers it with a non-removable protective layer.

In this study, an unaltered sample surface on a TEM sample was achieved by using a removable, salt-based protective layer during the preparation process. As an example, this process was then used to investigate the surface dynamics of commercially available single-crystal zinc oxide (ZnO) as a model system for photo-electrochemistry. After the single-crystal was covered with the protective layer, TEM samples were prepared using a gallium-ion-based FIB and thinned to a thickness of less than 20 nm. After thinning, the protective layer was removed from the TEM sample surface residue-free by immersion in a solvent and plasma-cleaning. EDX (energy dispersive X-ray spectroscopy) experiments were performed to verify the removal of the protective layer and the absence of implanted gallium in the surface areas.

High-resolution TEM imaging in vacuum showed segments of an ordered ZnO (0001) surface with a high surface mobility under electron beam illumination. We observe reordering of the sample surface, which resulted in a visible growth along the [0001] direction. Additionally, a change in behavior of the sample surface was investigated in-situ for a water atmosphere at high-resolution using the ETEM. Comparative studies on the surface dynamics of differently oriented zinc oxide single crystals as well as differently doped zinc oxide thin-films are first steps into a systematic study of zinc oxide in reactive environments and the suitability of zinc oxide as a catalyst for water splitting.

“POMbranes” – Incorporation of Catalytically Active Polyoxometalates into Integral Asymmetric Block Copolymer Membranes

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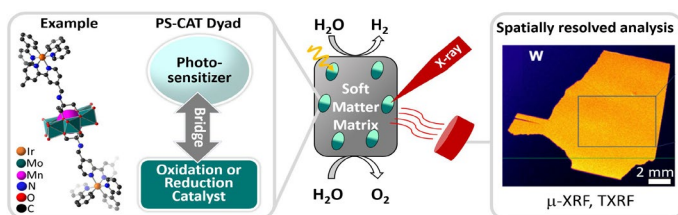
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This project focuses and studies the immobilization of catalytically active building blocks within nanostructured block copolymer membranes, enabling the development of photo-flow reactors for sunlight-driven water oxidation (WOC) and hydrogen evolution (HER). To overcome the challenges inherent in hybrid catalytic systems, catalysts (CAT) and photosensitizers (PS) are integrated into the membrane via electrostatic anchoring, covalent bonding, or a combination of both strategies.



Initial experiments employing electrostatic immobilization revealed promising catalytic activity, with POMbranes facilitating HER under continuous flow conditions [1]. Moreover, heterogeneous WOC was demonstrated using a CoW POM catalyst in combination with $[\text{Ru}(\text{bpy})_3]^{2+}$ [2]. Nonetheless, time-resolved X-ray spectroscopy has revealed partial leakage or degradation of the CAT/PS components in several cases. To address these limitations, we are developing reversible immobilization strategies for suitable CAT building blocks, alongside covalent attachment of organic sensitizers and dyes.

In pursuit of noble-metal-free systems, organic dyes have been investigated as photosensitizers for electrostatic immobilization to support HER. Beyond BODIPY, Ketocoumarines have emerged as promising candidates for the next generation of noble-metal-free sensitizers. We explore 3D printed substrates as alternatives matrices with similar concepts

[1] I. Romanenko et al., J. Mater. Chem. A, **2020**, 8, 6238–6244

[2] J. Kund et al., Angew Chem., **2023**, 62, e2022171

Phenothiazine redox mediators boost photocatalytic hydrogen evolution^[1]

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The photocatalytic production of green hydrogen constitutes an important step towards sustainable energy storage. Herein, we explore a pathway towards such coupled processes by using phenothiazines (PTs) as redox mediators (RMs) in HER. Stern-Volmer experiments show that PTH and derivatives effectively quench the excited state of $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ – independent of pH – enabling the pH to be lowered in the photocatalytic HER from 4^[2] to 2.55, where the catalyst is more active due to a higher availability of protons.^[3–4] A near-linear correlation between the Stern-Volmer-quenching ability of the PT derivatives and the photocatalytic performance suggests the initial reductive quenching step to be an important kinetic factor in the catalytic cycle. These results propose RMs as a strategy to boost the performance of photocatalytic HER systems by mediating efficient electron transfers even at low pH values and paves the way towards coupled reductive and oxidative photocatalysis.

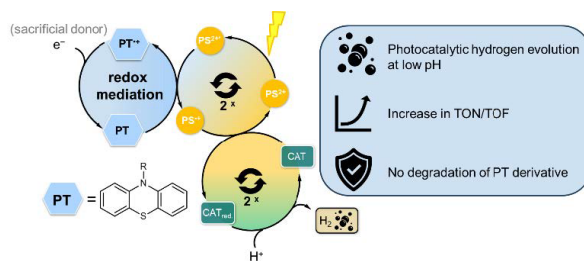


Figure 1: Schematic representation of the reductive photocatalytic cycle utilizing PTH as RM.

References

- [1] D. Baumgarten, M. Gollasch, Y. Gupta, M. Jahn, A. K. Mengele, S. Rau, C. Streb, B. Esser, *EES Catal.*, **2026**, DOI: 10.1039/D6EY00029K
- [2] M. Heiland, R. De, S. Rau, B. Dietzek-Ivansic and C. Streb, *Chem. Commun.*, **2022**, 58, 4603–4606.
- [3] A. Reynal, E. Pastor, M. A. Gross, S. Selim, E. Reisner and J. R. Durrant, *Chem. Sci.*, **2015**, 6, 4855–4859.
- [4] P. D. Tran, T. V. Tran, M. Orio, S. Torelli, Q. D. Truong, K. Nayuki, Y. Sasaki, S. Y. Chiam, R. Yi, I. Honma, J. Barber and V. Artero, *Nature Mater.*, **2016**, 15, 640–646.

Mechanistic Insights into Photocatalytic Hydrogen Evolution with Molecular Thiomolybdates

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Molecular thiomolybdates are well known for their hydrogen evolution reactivity in aqueous photocatalytic systems.^[1] Due to their comparatively simple, modifiable, and observable molecular structure, they serve as excellent homogeneous model complexes for heterogeneous systems. Members of the Transregional Collaborative Research Center TRR234 – CataliGht, with the main contributors from the Streb Group in Mainz, contributed significant efforts to understanding various factors influencing the performance of these catalysts. Both the $[\text{Mo}_2\text{O}_2\text{S}_6]^{2-}$ and $[\text{Mo}_3\text{S}_{13}]^{2-}$ variants were used in multiple studies to determine e.g. the impact of dynamic irradiation on overall performance and solvent composition on terminal ligand exchange. Using a design of experiments approach, spectroscopic studies and DFT calculations, significant mechanistic insights into species formed in situ were gained.

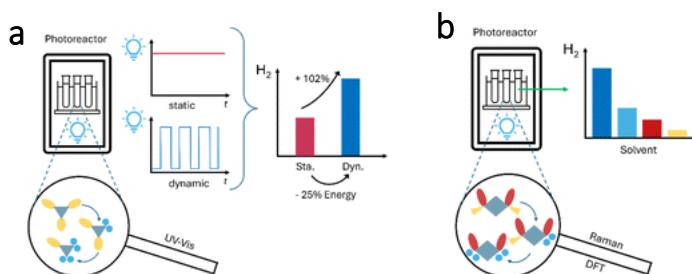


Figure 1: Left: Effects of dynamic irradiation; right: other factors. Both: terminal ligand exchange monitoring

From Oxygen to Hydrogen: Operando insights into water oxidation catalysis and nanoscale structure–function mapping of hydrogen evolution reaction-active PAN fibers

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Renewable energy continues to be a futuristic and sustainable option amidst the high demand for energy resources. In this study we are investigating in operando photocatalytic activity for homo- and heterogeneous systems via Raman spectroscopy. The first system in our investigation builds upon prior research on dynamic irradiation's impact on water oxidation catalysis, aiming to uncover barriers in artificial photosynthesis and mitigate deactivation pathways [1]. Presently, we delve deeper into the influences of dynamic irradiation and its effects on photosensitizer degradation, environmental influences, system stability, and optimization. In our second system we are probing into the matrix of electro-spun fibers that can be used for HER (Hydrogen evolution reaction). In this study we used Optical Photothermal Infrared (OPTIR) to understand the distribution of the active components to better aid in the refinement and optimization of the sample preparation[2]. Since the techniques were non-invasive and requires little to no sample preparation, we were able to study catalytic systems and soft matter matrices in their original state. Together these findings are presented, and the capability of both systems as photocatalytic systems discussed.

References

- [1] Sender, M., et al., Boosting Efficiency in Light-Driven Water Splitting by Dynamic Irradiation through Synchronizing Reaction and Transport Processes. *ChemSusChem*, 2022. 15(12): p. e202200708.
- [2] Tran, J.H., et al., Soft-Matter Confinement Modulates Excited-State Dynamics of Ru Photocatalysts for Hydrogen Evolution in Aqueous Media. *ACS Materials Au*, 2026.

Acknowledgement

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Functionalized liposomes for light-driven H₂ evolution and NADH regeneration

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The growing demand for sustainable energy storage has increased interest in systems that convert solar energy into chemical fuels.^[1] Photocatalytic water splitting is a promising approach because it enables light-driven proton reduction and water oxidation.^[2,3] In natural photosynthesis, these half-reactions are spatially separated by the thylakoid membrane, which limits charge recombination and side reactions.^[4] Inspired by this concept, we developed a liposomal lipid bilayer system for reductive photocatalysis, targeting H₂ evolution and NADH regeneration. The system consists of a rhodium-based catalyst (RhC9), a ruthenium-based photosensitizer (RuC9), different lipids for liposome formation, and either sodium ascorbate or triethanolamine as electron donors. Under blue-light irradiation (453 nm, 8 h), the system reached a turnover number (TON) of approximately 3450 for H₂ production, corresponding to a fivefold improvement over the highest reported related system.^[2] In addition, NAD⁺ was reduced to NADH under 455 nm irradiation with 87% conversion after 50 min. Given the central role of NADH in cellular energy transfer and redox regulation, this platform provides a biomimetic strategy for light-driven fuel formation and cofactor regeneration.^[5]

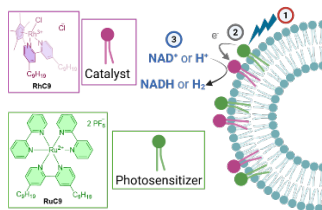


Figure 1: Schematic graph summarizing the H₂ evolution and NADH regeneration from the liposomal system together with the chemical structures of both catalyst and photosensitizer.

[1] [Global Energy Crisis – Topics - IEA](#) [2] A. Abbas *et al.*, Chem. Eur. J., **2023**, 29, e202302284, <https://doi.org/10.1002/chem.202302284>. [3] S. Troppmann *et al.*, ChemistrySelect, **2016**, 1, 1405–1409, <https://doi.org/10.1002/slct.201600032>. [4] D. M. Klein *et al.*, ChemCatChem, **2022**, 14, e202200484, <https://doi.org/10.1002/cctc.202200484>. [5] M. A. Walker *et al.*, Curr. Opin. Physiol, **2018**, 3, 101–109, <https://doi.org/10.1016/j.cophys.2018.03.011>.

Langmuir monolayer matrix impact on photocatalyst activity

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We propose the use of two-dimensional Langmuir monolayers (LM) as photocatalytic membranes that are composed of uniformly aligned^[1] charge-transfer units and matrix amphiphiles, which can be plasticized when the matrix is rigid to achieve a homogeneous LM.^[2] This architecture enables coupling of oxidation and reduction on opposite sides of the molecular membrane, dramatically shortening charge-carrier transport pathways compared to traditional photocatalytic (PC) and photoelectrochemical (PEC) water-splitting approaches, thereby reducing recombination losses. We focus on the photocatalytic hydrogen evolution reaction within the LM.^[3] To increase catalyst loading per volume, we employ a spiral-wound configuration (Fig. 1(b)) that accommodates large membrane areas within a single GC vial (Fig. 1(c)). Embedding the catalyst in the LM membrane yields turnover numbers exceeding those achieved under homogeneous conditions, Fig. 1(d), highlighting a promising route for continuous fabrication of catalytically active two-dimensional membranes.

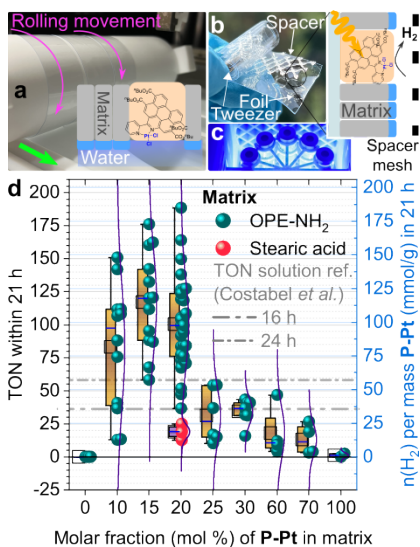


Fig. 1: Light-driven H₂ evolution from dyad-containing mixed Langmuir monolayers: (a) rolling transfer from the air/water interface onto plastic foil, (b) coiling of foil, (c) illuminated samples, (d) TON and P-Pt mass specific H₂ evolution vs. P-Pt dyad molar fraction in the OPE-NH₂ matrix.^[3]

[1] M. L. Hupfer et al., *Adv. Mater. Interfaces*, **2025**, 12, e00550, DOI: 10.1002/admi.202500550.

[2] S. J. Finkelmeyer et al., *J. Colloid Interface Sci.*, **2024**, 680, 1090-1100, DOI: 10.1016/j.jcis.2024.11.020.

[3] S. J. Finkelmeyer et al. *ChemRxiv*, **2025**, DOI: 10.26434/chemrxiv-2025-f4n2t.

Substitution-Dependent Dual Emission and Energy Transfer

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The controlled coupling of organic chromophores to metal-based photosensitizers (PS) is a powerful strategy to tune excited-state properties such as lifetime and energy transfer pathways. In this work, ruthenium-pyrene dyads were synthesized in which the organic dye pyrene is connected to a Ru(II)-polypyridyl PS via an alkynyl linker. This enables electronic delocalization and thus potential electronic communication between both units.^[1]

Pyrene was selected due to its low-lying triplet state, which is energetically comparable to the Ru-centered ³MLCT state.^[2] The pyrene unit was attached at the 5-position of a 1,10-phenanthroline ligand, and the effect of 1- versus 2-substitution at the pyrene moiety was systematically investigated using UV/vis absorption and emission spectroscopy.^[3]

Photophysical studies reveal that 1-substituted dyads exhibit largely independent behavior of the Ru and pyrene moiety, indicating negligible electronic coupling. In contrast, 2-substituted dyads show pronounced electronic communication, resulting in energy transfer between pyrene and the ruthenium center. Notably, dual emission from both the Ru-based ³MLCT state and the pyrene triplet state is observed, a feature, rarely reported in literature. These findings provide valuable insight into structure-property relationships in dyadic systems.^[3]

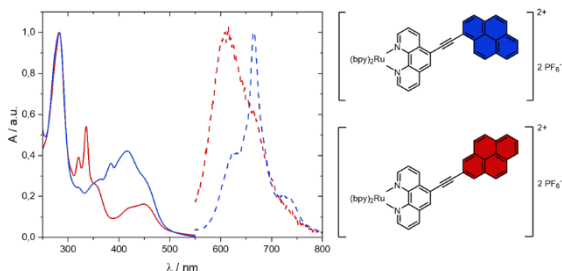


Figure 1: Normalized UV/Vis absorption (solid) and emission (dashed) spectra (left) of the investigated Ru-pyrene dyads with pyrene substituted in its 1-position (red) or its 2-position (blue) and depiction of the respective structures (right). The spectra were measured in 5 μ M acetonitrile solutions under inert conditions and the emission spectra were obtained by excitation of the ¹MLCT bands.

[1] L. Zedler *et al.*, Nat Commun, **2022**, 13, 2538, DOI: 10.1038/s41467-022-30147-4

[2] A. C. Sell *et al.*, **2022**, Dalton Trans. 51, 10799-10808, DOI: 10.1039/D2DT01157C

[3] L. D. Kapp, Master's Thesis "Investigation of Substitution Effects in Ruthenium-Pyrene-Dyads", Ulm University.

Reactor and Cell Design for Integration of Spatially and Temporally Resolved Multi-Spectroscopic Analysis

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Light-driven catalytic systems are known to suffer from degradation due to irradiation or harsh reaction conditions, but the underlying mechanisms are not yet well understood. Analysis often relies on invasive, destructive, ex situ techniques.

As part of the Catalight CRC/TRR 234 project CO₂, this work aims to combine reaction engineering and spectroscopic insights to generate reproducible high-quality data, enhancing understanding and ensuring comparability of light-driven systems. For this purpose, different measurement cells have been developed for flexible integration into analytical and reaction setups.

As one such example, Figure 1 shows a flow-compatible cell for complementary Raman and ATR-IR measurements. It has been successfully integrated into conventional capillary setups, *e.g.*, for the analysis of a Ru-based light-driven water splitting system^[1], allowing high-resolution tracking of reaction components. Extended by continuous optical oxygen sensing and UV-Vis measurements, a full multi-spectroscopic data set was generated to compare static and dynamic radiation conditions. Results indicate that the previously assumed reaction mechanism is incomplete, and that the analysis of dark periods plays a significant role in getting the full picture of complex photochemical processes.

Further cells have been developed, such as for in-situ elemental mapping of wet native soft matter materials using μ XRF spectrometry. These enable representative qualitative and quantitative comparison of photocatalytically functionalized matrixes, and was demonstrated by the analysis of active component distribution homogeneity before and after loading and leaching procedures in polyoxometalate cluster functionalized nanoporous block copolymer membranes, *i.e.*, POMbranes^[2].

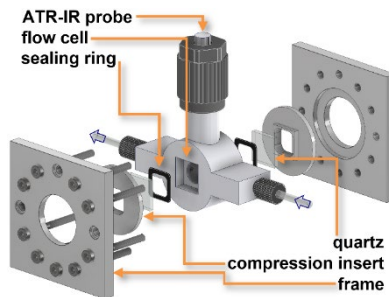


Figure 1: Multi-spectroscopy flow cell for in-situ Raman and ATR-IR analysis.^[1]

[1] A. Koba *et al.*, Zenodo, 2025, 10.5281/zenodo.17867914

[2] A. Koba *et al.*, Zenodo, 2025, 10.5281/zenodo.17867940

Demonstrating solar hydrogen evolution using thiomolybdate-modified carbon nitrides in a mass transport intensified 3 L loop photoreactor – A feasibility study

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In this contribution a feasibility study on hydrogen production was conducted in a scaled 3 L stirred loop photoreactor (SLPR) using natural sunlight. Mo₃S₁₃-loaded carbon nitride particles were used as a heterogeneous model system for the feasibility studies^[1]. The SLPR concept has been validated on a 0.5 L scale in a previous studies using Pt-loaded carbon nitride particles for hydrogen production^[2]. To ensure sufficient irradiance incident to the slurry-type SLPR, a combined specular/diffuse solar collector was designed and evaluated using ray tracing simulations, resulting in an increase of the irradiance incident to the SLPR by a factor of 2.4 compared to operation of the SLPR without a reflector. The combined specular/diffuse solar collector was optimized for $\lambda < 400$ nm to meet the photophysical properties of CN_x. Solar hydrogen production rates of ≈ 97.1 -111.5 $\mu\text{mol}\cdot\text{h}^{-1}$ could be demonstrated. Solar hydrogen production rates were found to correlate with the incident solar irradiance. In subsequent long-term experiments, the influence of naturally occurring fluctuations in sunlight^[3,4] will be investigated and correlated to the observed solar hydrogen production rate.

References:

- [1] A. Rajagopal *et al.*, *Sustain. Energy Fuels* **2020**, *4*, 6085–6095, DOI: doi.org/g6rpdq.
- [2] P. Li *et al.*, *Beilstein J. Org. Chem.* **2024**, *20*, 74–91, DOI: doi.org/mgjt.
- [3] J. K. B. Bishop *et al.*, *J. Geophys. Res. Ocean.* **1991**, *96*, 16839–16858, DOI: doi.org/fxfxj4.
- [4] E. A. Smith *et al.*, *Clim. Change* **1983**, *5*, 211–235, DOI: doi.org/brw2bg.

Water-soluble ionic carbon nitrides for enhanced photocatalysis and other catalytic applications

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In addition to conventional (non-ionic) carbon nitrides, water-soluble ionic carbon nitrides represent a novel class of poly(heptazine imide) (PHI) materials that enable photocatalysis under quasi-homogeneous conditions. Their superior performance has been demonstrated in photocatalytic hydrogen peroxide (H_2O_2) production. A key advantage of these materials lies in their reversible solubility: by simply adjusting the ionic strength of the medium, the dissolved photocatalyst can be easily recovered and redissolved without any loss of activity or selectivity [1-3].

Recently, we synthesized water-soluble PHI materials incorporating various alkali metal ions, paving the way for a rational design approaching to enhance both photocatalytic activity and stability. The photophysical properties of these materials were investigated using ultrafast time-resolved spectroscopy and correlated with their photocatalytic efficiency in H_2O_2 production.

Additionally, we found that water-soluble ionic carbon nitrides serve as highly effective stabilizers for ultrafine gold nanoparticles (Au NPs) with diameters of 2–3 nm. The stabilized nanoparticles exhibit remarkable dispersibility and exceptional stability even in solutions with high ionic strength. Their catalytic performance was demonstrated in the selective reduction of 4-nitrophenol to 4-aminophenol using NaBH_4 as a model reaction, where they outperform even benchmark “naked” Au NPs stabilized by an excess of NaBH_4 [4].

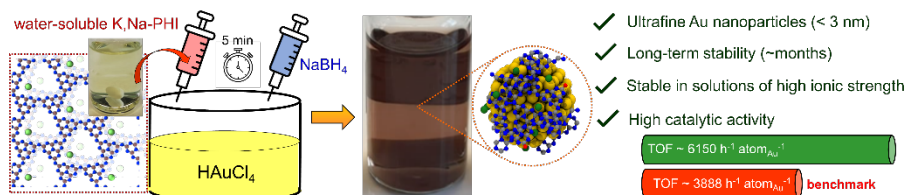


Fig. 1. Concept of effective stabilization of ultrafine Au nanoparticles using water-soluble ionic carbon nitride.

References

- [1] I. Krivtsov, D. Mitoraj, C. Adler, M. Ilkaeva, M. Sardo, L. Mafra, C. Neumann, A. Turchanin, C. Li, B. Dietzek, R. Leiter, J. Biskupek, U. Kaiser, C. Im, B. Kirchhoff, T. Jacob, R. Beranek, *Angew. Chem. Int. Ed.* 59 (2020) 487.
- [2] C. Li, E. Hofmeister, I. Krivtsov, D. Mitoraj, C. Adler, R. Beranek, B. Dietzek, *ChemSusChem*. 14 (2021) 10.
- [3] C. Li, Christiane Adler, I. Krivtsov, Dariusz Mitoraj, R. Leiter, U. Kaiser, R. Beranek, B. Dietzek, *Chem. Commun.* 57 (2021) 10739.
- [4] Mohamed M. Elnagar, Johannes Liessem, Changbin Im, Dariusz Mitoraj, Ludwig A. Kibler, Christof Neumann, Andrey Turchanin, Robert Leiter, Ute Kaiser, Timo Jacob, Igor Krivtsov and Radim Beranek, *Nanoscale*, 15 (2023), 19268

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A Photocatalytically Active Rotaxane Mimicking Photosystem I

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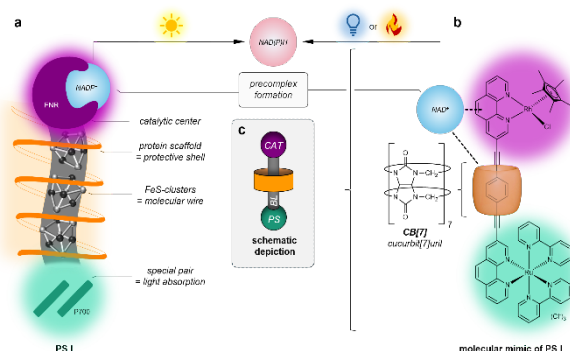
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In synthetic settings, the prevention of catalyst deactivation from chemical changes to its molecular structure during active operation is the primary concern and remains elusive.^[1] Inspired by membrane and protein integration of the natural photosynthetic apparatus of green plants ensuring structural integrity of key components, we report a photocatalytically active rotaxane mimicking photosystem I. In our Ru-Rh dyad system the two metal centers are connected by sensitive alkyne-units. By strategically burying the bridging ligand in a macrocycle cavity, i.e. in cucurbit[7]uril, the heterodinuclear rotaxane photocatalyst preserves both, structural integrity and activity of its components. Superior, long-term photocatalytic activity under enzyme-like H-bond-driven substrate preorganization at the catalytic center. These results underscore the pivotal function of rationally engineered interplay between supramolecular assemblies in catalysis and open new catalytic paradigms for advanced and sustainable supramolecular methodologies, with direct applications in artificial photosynthesis and light-driven water splitting.^[2]

Figure 1: (a) Simplified representation of PS I, showing the special pair used for light absorption (cyan), followed by the molecular wire (FeS4 clusters & ferredoxin) connecting the special pair with the ferredoxin-NADP+ reductase (FNR) serving as catalyst (CAT, purple). The molecular wire is shielded in a protective protein shell (orange helix). The FNR forms a precomplex with NADP+ in its enzymatic pocket before conversion to NADPH takes place. (b) Chemical depiction of the herein presented PS I-mimicking rotaxane, showing the NAD+ precomplex formation in its artificial binding pocket. Catalytic conversion of NAD+ to NADH can be obtained either by photocatalysis or thermal catalysis. (c) Schematic depiction of the investigated rotaxane used in this study.



[1] Zedler, L., et al. Outpacing conventional nicotinamide hydrogenation catalysis by a strongly communicating heterodinuclear photocatalyst. *Nat Commun* 13, 2538 (2022).

[2] Müßler, M. et al. A Photocatalytically Active Rotaxane Mimicking Photosystem I. *ChemRxiv* (2025). doi:10.26434/chemrxiv-2025-1nsr5.

From UV to Visible: Strategic Ligand Modification in Heteroleptic Copper(I)-Bibenzimidazole Complexes for Advanced Photophysical Properties.

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Copper, an earth-abundant and cost-effective alternative to precious metals, offers tunable redox and luminescence properties, making it an ideal candidate for photochemical applications. In this study, we focused on the synthesis, structural characterization, and photophysical studies of novel heteroleptic Cu(I) complexes through strategic ligand modifications, including π -system extension as well as N, N'-propylene-protection in bbim, significant bathochromic shifts in the absorption spectra were achieved, enhancing visible-light utilization. Here, we introduce a synthetic method for attaching phenylacetylene substituents to bbim derivatives via Negishi coupling. The Cu complexes were obtained in high yields via a one-pot, two-step process, and X-ray crystallography confirmed their structural integrity and hydrogen-bonding interactions. The absorption spectra exhibited a bathochromic shift due to the extended π -system extending up to 450 nm, enabling visible-light absorption. Overall, these findings demonstrate the potential of π -extended diimine ligands for the design of efficient Cu(I)-based photosensitizers.

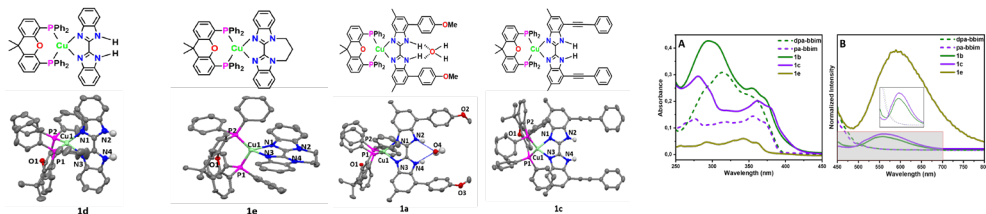


Figure 1: X-ray structure of different Cu(I) complexes, UV-vis and emission spectroscopic data.

[1] Huang, T. H., Hu, Q. L., Zhao, F. Z., Zheng, D., Liu, Q., Wu, T. C., & Chen, J. (2020). Journal of Luminescence, 227, 117530.

[2] Zhang, Y., Schulz, M., Wächtler, M., Karnahl, M. & Dietzek, B Coord. Chem. Rev. 356, 127–146 (2018).

Covalent Integration of Mo₃S₇ Clusters into Phenanthroline-Grafted Polyampholyte Copolymers for Photocatalytic Hydrogen Evolution

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Abstract:

Creating durable hybrid photocatalysts requires combining the molecular precision of cluster catalysts with the structural robustness of polymeric supports.^[1] A polyampholyte graft copolymer based on polydehydroalanine- *g* -methoxy polyethylene glycol was functionalized with 1,10-phenanthroline units to serve as a scaffold for the covalent immobilization of Mo₃S₇ clusters. The cluster incorporation was achieved by reaction of the phenanthroline-functionalized polymer with Mo₃S₇ in the presence of tetramethylammonium counterions, followed by purification to afford a hybrid polymeric material. The structure and composition of the resulting material were confirmed by NMR, SEC, DLS, TGA, FTIR, XPS, and ICP-OES. The hybrid system was then evaluated for photocatalytic hydrogen evolution using eosin Y (EY) and Diiodo-BODIPY as photosensitizers under visible-light irradiation. Hydrogen formation was quantified by gas chromatography. Compared with the corresponding non-polymer system containing only Mo₃S₇ clusters and sensitizers, the polymer-bound material showed significantly enhanced hydrogen production and markedly improved operational stability. Notably, the solution retained its color and catalytic activity over extended irradiation times, whereas the bare system underwent rapid bleaching and deactivation. These results suggest that the polymer matrix effectively stabilizes both the catalyst and sensitizer, suppressing deactivation and enabling prolonged photocatalytic performance. This work highlights a modular strategy for the covalent integration of molecular clusters into functional polymer scaffolds for durable hybrid photocatalytic systems.

References:

[1] Ji, Z., Trickett, C., Pei, X., & Yaghi, O. M. (2018). Linking molybdenum–sulfur clusters for electrocatalytic hydrogen evolution. *Journal of the American Chemical Society*, 140(42), 13618-13622.

4CzIPN Photosensitizes the Light-Driven Hydrogen Evolution Reaction and NAD⁺ Reduction

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TADF compounds have found great application as photocatalyst in recent years. Their use as photosensitizers (PS), however, is still limited although they have a huge potential as abundant alternatives for traditional noble metal-based PSs, such as $[\text{Ru}(\text{bpy})_3]^{2+}$.^[1] We herein investigate the TADF compound 4CzIPN as a PS together with the catalyst cobaloxime ($\text{Co}(\text{dmgH})_2(\text{py})\text{Cl}$) in the photochemical hydrogen-evolution reaction (HER) and together with the catalyst PhenRhCp^* in the photochemical NAD^+ reduction. After optimization, we achieved turnover numbers (TONs) of over 5,000 for the HER and TONs of over 70 for the NAD^+ reduction. Stern-Volmer quenching experiments demonstrating that the quenching of the excited singlet state (S_1) of 4CzIPN by ammonium ascorbate is by far more dominant than the quenching of its excited triplet state (T_1). This work demonstrates that 4CzIPN can sensitize the cobaloxime-catalyzed light-driven HER and the PhenRhCp^* catalyzed reduction of NAD^+ to NADH with ammonium ascorbate as the SED and gives an excited insight into the quenching mechanism of TADF compounds as PSs.

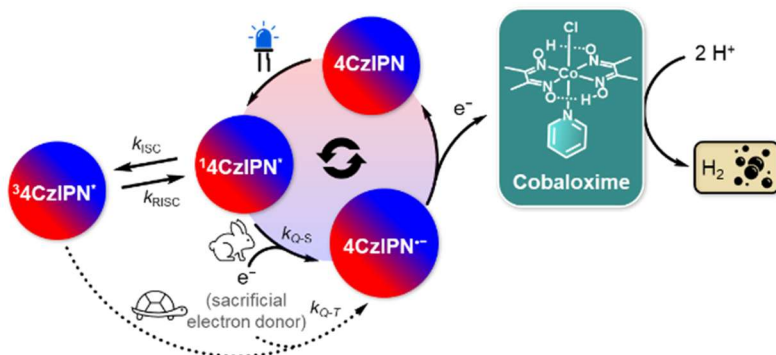


Figure 1: Overview of the hydrogen evolution reaction with 4CzIPN as the photosensitizer and Cobaloxime as the catalyst.

- [1] A. M. Polgar, Z. M. Hudson, "Thermally activated delayed fluorescence materials as organic photosensitizers" *Chem. Commun.* **2021**, 57, 10675–10688.

Soft-matter confinement modulates excited-state dynamics of Ru-photocatalysts for hydrogen evolution in aqueous media

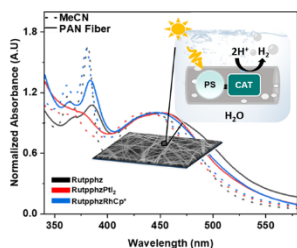
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In the face of anthropogenic climate change the hunt for sustainable, clean energy sources has led to the exploration of renewable energy technologies. Among these, solar energy represents the most abundant and universally accessible resource. Using molecular level approaches such as photo-electrochemical cells or photochemical molecular devices (PMDs), a direct solar to chemical energy conversion is possible. To enable a scale-up of such a well understood molecular systems, we report the incorporation of Ru-complexes into scalable electrospun polyacrylonitrile (PAN) soft-matter matrices.¹ We incorporated Ru-complexes linking the photosensitizer moiety Rutpphz (tpphz = tetrapyrido[3,2-a:2',3'-c:3'',2''h:2''',3'''-j]phenazine) with RhCp*Cl or PtI₂ (Cp* = pentamethylcyclopentadienyl) moieties as catalytic centers into electrospun, PAN nanofibers. In a homogeneous organic phase the dinuclear complex [(tbbpy)₂ Ru(tpphz)Rh(Cp*)Cl]Cl(PF₆)₂ (RutpphzRhCp*), demonstrated catalytic hydrogen production for up to 650 hours, while the related dinuclear complex [(tbbpy)₂ Ru(tpphz)PtI₂](PF₆)₂ (Ru-tpphzPtI₂) was reported with a turnover number (TON) of 520 for hydrogen production. The electrospinning of these complexes into PAN is an attractive tool for heterogenization, providing good scalability, numerous



active sites, porous structure, and high stability of the soft-matter. We thoroughly characterized these hybrid materials by means of: SEM, XPS, EDX, ATRIR, FT-Raman, O-PTIR, NMR, UV-Vis, diffuse reflectance and transient absorption and demonstrated their application for photocatalytic hydrogen evolution reactions (HER) in aqueous media.

- Tran, J. H.; Vashistha, N.; Edwards, A.; Mengele, A. K.; Koba, A.; Ullah, S.; Bauer, J.; Griebel, J.; Schmitt, M.; El-Mashtoly, S. F.; Popp, J.; Ziegenbalg, D.; Dietzek-Ivanšić, B.; Rau, S.; Anjass, M. Soft-Matter Confinement Modulates Excited-State Dynamics of Ru Photocatalysts for Hydrogen Evolution in Aqueous Media. *ACS Mater. Au* **2026**, acsmaterialsau.5c00212. <https://doi.org/10.1021/acsmaterialsau.5c00212>.

Immobilization of HER photodyad into polymer matrix results in enhancement of its turnover number and lifetime

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Tailored poly(dehydroalanine)-based (PDha) graft copolymers are excellent dispersing agents for the nonpolar HER photocatalysts insoluble in aqueous-organic media, which is frequently used for the light-driven HER [1-3]. However, due to insolubility of the studied HER photocatalysts in aqueous-organic media, it is practically difficult to evaluate the separate impact of the photocatalyst-polymer interactions on the performance of the photocatalyst. In this work, to evaluate separately the impact of the interactions between the polymer and the catalyst, the PDha-*g*-AMPS-*g*-mPEG₁₀₀₀ graft copolymer was used for electrostatic complexation of the Ru(tpphz)PtI₂ hydrogen-evolving photodyad [4-5]. The HERs were carried in the H₂O-MeCN-TEA solvent mixture in which both the molecular dyad and the graft copolymer were soluble. The hydrogen-evolving performance of the molecular Ru(tpphz)PtI₂ and hybrid Ru(tpphz)PtI₂@PDha-*g*-AMPS-*g*-mPEG₁₀₀₀ photocatalysts, forming optically transparent solutions, were evaluated *in situ* using headspace GC for over 200 hours. The photodyad exhibited a two-fold increase in TON and noticeably prolonged lifetime before its reductive de-activation. The hybrid Ru(tpphz)PtI₂@PDha-*g*-AMPS-*g*-mPEG₁₀₀₀ photocatalysts was monitored *in situ* using steady- and transient-state UV-Vis absorption and Resonance Raman spectroscopic analyses and it was confirmed on the molecular level that the de-activation of the photodyad is indeed inhibited upon complexation by the graft copolymer. The oxidative re-activation of the complexed dyad showed that the graft copolymer matrix does not impede this process and that the hydrogen-evolving activity of the complexed dyad remains steady for multiple de-activation / re-activation cycles [6].

[1] D. Costabel et al., *ACS Appl. Mat. Interfaces*, **2023**, 15, 20833-20842, 10.1021/acsami.2c18529.

[2] A. Nabiyan et al., *Chem. Eur. J.*, **2021**, 27, 16924-16929, 10.1002/chem.202100091.

[3] D. Costabel et al., *Chem. Eur. J.*, **2020**, 27, 4081-4088, 10.1002/chem.202004326.

[4] M.G. Pfeffer et al., *Nat. Chem.*, **2022**, 14, 500-506, 10.1038/s41557-021-00860-6.

[5] S. Klingler et al., *Angew. Chem. Int. Ed.*, **2023**, e202306287, 10.1002/anie.202306287.

[6] Yu. Utievskiy et al., *ChemRxiv*, **2025**, preprint, 10.26434/chemrxiv-2025-tzphq.

Synthesis and PCET-Reactivity of a High-Valent Cu–F Species

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Despite considerable efforts, few reactions can incorporate fluoride directly into C(sp³)–H bonds.¹ One strategy for this transformation entails the formation of a high valent copper(III) fluoride species, a subsequent PCET step and a radical rebound.^{2,3} While efficient in capturing carbon centered radicals, the copper fluoride complex is less efficient in the preceding PCET step.² Contrasting this, the copper(III) hydroxide congener is more efficient in the PCET reaction.⁴ Conceivably, this is caused by higher oxidative asynchronicity of the PCET step in the copper fluoride case.^{3,4} To gain further insights into the underlying PCET processes – especially regarding asynchronous reaction pathways – a highly basic copper(II) fluoride complex bearing a potentially redox active carbazole moiety was devised. Reaction with mild oxidants produced a new thermally unstable species. Supported by DFT calculations this species was assigned to a high valent copper(III) fluoride species (Figure 1, left). Electrochemical investigations revealed a reversible redox event at unusually low potential (Figure 1, right). Further investigations of the PCET reaction by UV/Vis and EPR spectroscopies showed the competency of the copper(III) complex to abstract hydrogen atoms from phenols with BDE comparable of these of weak C–H bonds (Figure 1, center).

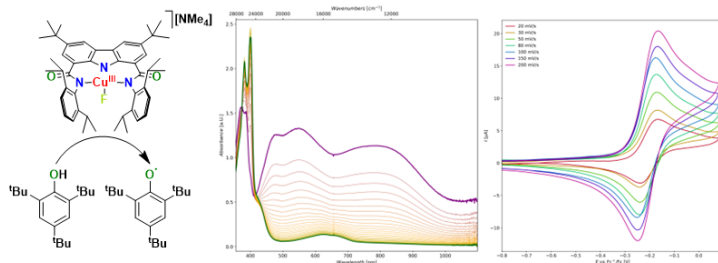


Figure 1: PCET reaction between the copper(III) fluoride complex and phenols (left) monitored by UV/Vis (center) and CV experiments showing Cu(II)/Cu(III) redox event (right).

[1] R. Ge *et al.*, Chem. Catal., **2024**, 4, 101009, 10.1016/j.checat.2024.101009.

[2] J.K. Bower *et al.*, J. Am. Chem. Soc., **2020**, 142, 8514, 10.1021/jacs.0c02583.

[3] H. Hintz *et al.*, Chem. Catal., **2023**, 3, 100491, j.checat.2022.100491.

[4] M. Mandal *et al.*, J. Am. Chem. Soc. **2019**, 141, 17236, 10.1021/jacs.9b08109.

Photocatalytic Proton Coupled Electron Transfer to Polycyclic Aromatic Compounds with Metalloporphyrin Hydride

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The hydrogenation of polycyclic aromatic hydrocarbons is challenging due to the thermodynamic requirements for breaking aromaticity. Birch reduction is still the most common synthetic route. Even photoredox catalysis with visible light requires multi-photon strategies.^[1] Light-driven proton-coupled electron transfer (PCET) is a potential strategy to overcome the thermodynamic limitations for the formation of weak element-hydrogen (E–H) bonds. Chirik and co-worker introduced photoactive iridium hydrides as catalysts for the photohydrogenation of anthracene.^[2] However, the catalyst requires high energy (blue) light and elevated H₂ pressures.

Herein, we report porphyrin-based iridium (III) hydrides (Figure 1) as photocatalysts for challenging hydrogenation reactions.^[3] The synthetic scope and mechanistic examinations will be discussed.

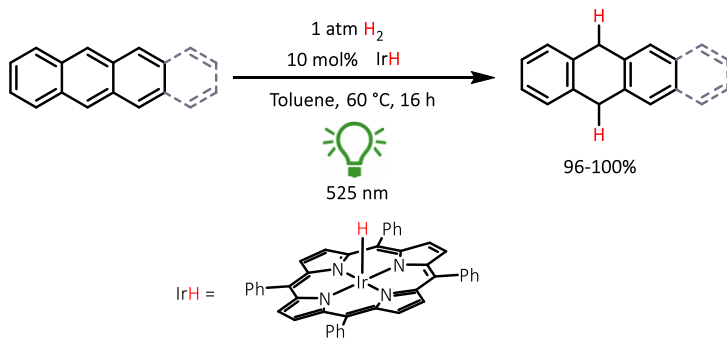


Figure 1: Photo-hydrogenation of polycyclic aromatic hydrocarbons.

- [1] A. Chatterjee and B. König, *Angew. Chem. Int. Ed.* **2019**, 58, 14289-14294.
- [2] Y. Park, S. Kim, L. Tian, H. Zhong, G. D. Scholes and P. J. Chirik; *Nat. Chem.* **2021**, 13, 969–967.
- [3] K. Oelschlegel, M. Heinz, S. Maji, R. Naumann, Y. F. S. Höhle, N. Alizadeh, M. Finger, M. Otte, K. Heinze, M. C. Holthausen, S. Schneider, *JACS Au* **2025**, 5, 4706–4713.

Development of a low-scaling multicomponent DFT algorithm

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The Born-Oppenheimer approximation (BOA) is one of the most fundamental approximations in quantum chemistry.^[1] However, in some molecular systems, nuclear quantum effects (NQE) such as anharmonicity in the zero-point energy or tunnelling can have a significant impact on structural and dynamic properties.^[2,3] To account for these in a more direct way, multicomponent methods have been developed.^[4-6] These aim at the efficient description of NQEs for selected light nuclei as wavefunctions, while keeping the remaining atoms as point charges. The most widely used variant of these methods is the Nuclear Electronic Orbital approach.^[7]

Our group is currently focused on the computational efficiency of NEO methods.^[8] These allow for a much wider scope of applications in organic and biomolecular compounds, where other post BOA methods would be too expensive to apply.

The presented poster will display elucidating examples, which emphasize the strength of NEO methods when it comes to the computation of delicate systems, where NQE's cannot be neglected. Furthermore, a critical comparison to commonly used canonical electronic structure methods such as VPT2 will be made to demonstrate the computational efficiency of NEO.

[1] M. Born, R. Oppenheimer, *Annalen der Physik*, **1927**, 389, 457–484, 10.1002/andp.19273892002.

[2] A. Pérez, M. E. Tuckerman, H. P. Hjalmarson, O. A. von Lilienfeld, *J. Am. Chem. Soc.*, **2010**, 132, 11510–11515, 10.1021/ja102004b.

[3] W. Fang, J. Chen, M. Rossi, Y. Feng, X.-Z. Li, A. Michaelides, *J. Phys. Chem. Lett.*, **2016**, 7, 2125–2131, 10.1021/acs.jpclett.6b00777.

[4] I. L. Thomas, *Phys. Rev.*, **1969**, 185, 90–94, 10.1103/PhysRev.185.90.

[5] M. Tachikawa, *Chem. Phys. Lett.*, **2002**, 360, 494–500, 10.1016/S0009-2614(02)00881-3.

[6] H. Nakai, *Int. J. Quantum. Chem.*, **2007**, 107, 2849–2869, 10.1002/qua.21379.

[7] S. P. Webb, T. Iordanov, S. Hammes-Schiffer, *J. Chem. Phys.*, **2002**, 117, 4106–4118, 10.1063/1.1494980.

[8] L. Hasecke, M. Breitenbach, M. Gimferrer, R. Oswald, R. A. Mata, *J. Phys. Chem. A*, **2025**, 129 (15), 3560–3566, 10.1021/acs.jpca.5c00382.

The self-consistent tangent nudged elastic band method

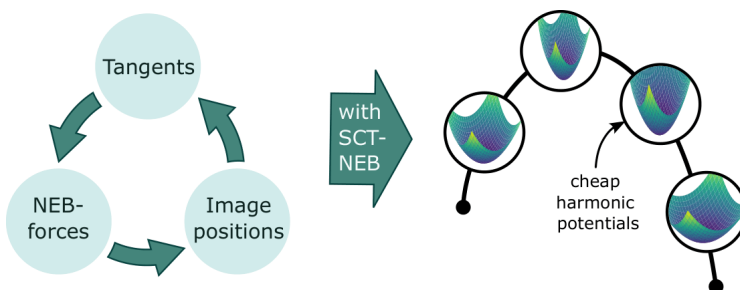
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Locating the reaction pathway, or minimum energy path, on the potential energy surface is a high-dimensional problem, for which multiple methods have been developed. One popular method is the Nudged Elastic Band (NEB) approach^[1], which approximates the reaction path as a series of images leading from the reactant to the product structure. These images are optimized while also considering the tangent direction of the reaction path, as well as an artificial spring force that connects them. The efficiency and accuracy of this optimization process depend on the chosen step predictor. By introducing the self-consistent tangent NEB (SCT-NEB) approach it became possible to significantly reduce the number of iterations required by the NEB to produce a reaction pathway. The SCT-NEB method uses approximated Hessians to propagate the images in between full NEB steps. These micro-iterations lead to a faster convergence by replacing expensive gradient calculations with cheap movement on the approximated surface.

Figure 1:



Visualization of the SCT-NEB method using harmonic potentials.

[1] H. Jónsson, G. Mills, K. W. Jacobsen in Classical and Quantum Dynamics in Condensed Phase Simulations, WORLD SCIENTIFIC, **1998**, pp. 385–404, 10.1142/9789812839664_0016.

Mixed Oxy-Hydride Materials as PCET Reagents

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Proton-coupled electron transfer (PCET) reactions are crucial in chemical energy conversion, which involves converting electric energy into bond energy and vice versa. In these reactions, electrons generated during the oxygen evolution reaction are used to reduce small molecules such as protons, and CO₂. While PCET reactions at molecular complexes have been investigated intensively for energy conversion reactions, extensive literature on water splitting by materials was focused on electron transfer ET rather than PCET at the interface of surface species.^[1] Initial research of PCET reactions at the interface of solid materials and solutions focused on carbon and oxide materials with hydroxy (*M*–OH) groups that form oxo (*MO*) surface species upon oxidation. Materials with hydridic H-atoms have been rarely investigated so far, although such surface *M*–H species are key intermediates in energy conversion reactions, e.g., HER (hydrogen evolution reaction), or the hydrogenation of (polar) double bonds.^[2]

This prompted us to investigate perovskite-type oxides (*ABO*₃) where oxide ions are substituted by hydride anions as PCET reagents. The material BaTiO_{3-x}H_x is synthesized in topotactical solid state synthesis with varying amounts of hydride anions. The anionic sublattice is comprised of both O²⁻ and H⁻ anions around Ti cations (Fig. 1) existing in a mixed IV/III oxidation state.^[3] The material has been characterized thoroughly and initial studies in PCET show that these oxy-hydrides are able to transfer an H-atom to typical HAT reagents such as TEMPO.

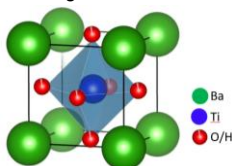


Figure 1. Crystal structure of BaTiO_{2.80}H_{0.20} showing cubic structure.

[1] a) S. Ardo, G. J. Meyer, *Chem. Soc. Rev.* **2009**, 38, 115-164, 10.1039/B804321N; b) Roubelakis, M. M.; Bediako, D. K.; Dogutan, D. K.; Nocera, *Energy Environ. Sci.* **2012**, 5, 7737–7740. [2] J.N. Schrauben, et al., *Science*, **2012**, 336, 1298-1301, 10.1126/science.1220234. [3] C. Eklöf-Österberg., et. al., *Journal of Phys. Chem. C.* **2019**, 123 (4), 2019-2030, 10.1021/acs.jpcc.8b08451.

Interplay of Proton-Coupled Electron Transfer and Enzyme Dynamics in Pyruvate Oxidase

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Pyruvate oxidases (POXs) are key enzymes in the aerobic energy metabolism of bacteria that lack a respiratory chain. These homotetrameric, dual-cofactor enzymes utilize thiamine diphosphate (ThDP) and flavin adenine dinucleotide (FAD) to catalyze the oxidative decarboxylation of pyruvate^{1,2}, employing molecular oxygen as the terminal electron acceptor and generating hydrogen peroxide². In the presence of inorganic phosphate, the reaction yields acetyl phosphate, which is used for ATP generation³. During catalysis, two electrons and at least one proton are transferred from ThDP to FAD across a distance of over 10 Å—an energetically demanding process due to solvent reorganization and the associated energetic penalty^{1,4}.

To elucidate how this long-range electron transfer is facilitated, crystallographic analysis using a stable substrate-ThDP analog revealed that previously unresolved C-terminal residues bind to the active site, displacing numerous solvent molecules while also potentially serving as an electron-transfer way station.

Using X-ray crystallography, and kinetic steady-state and pre-steady-state analyses, we define the structural basis for the dynamic nature of the C-terminus and its role in proton-coupled electron transfer during the catalytic cycle of pyruvate oxidase.

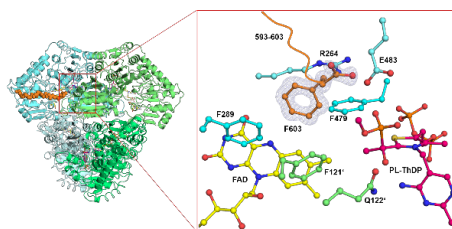


Figure 1: Crystallographic snapshot of the active site of POX with a stable ThDP analog. Previously unresolved C-terminal ten residues are resolved and positioned within the substrate entry channel, with the terminal residue F603 extending into the active site and displacing solvent molecules.

¹Muller and Schulz, *Journal of molecular biology*, **1994**, 237(3), 315-335, <https://doi.org/10.1006/jmbi.1994.1233>.

²Sedewitz et al., *Journal of bacteriology*, **1984**, 160(1) 273-278, <https://doi.org/10.1128/jb.160.1.273-278.1984>.

³Sedewitz et al., *Journal of bacteriology*, **1984**, 160(1), 462-465, <https://doi.org/10.1128/jb.160.1.462-465.1984>.

⁴Tittmann et al., *Biochemistry*, **2000**, 39(35), 10747-10754, <https://doi.org/10.1021/bi0004089>.

Dinitrogen derived Electrochemical Acetonitrile Release from a Rhenium PNP-Pincer complex

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Reductive N_2 splitting into nitrido complexes is a promising strategy for nitrogen fixation beyond ammonia.^[1,2] Electrochemically driven approaches are still in their infancy and recently gained more attention. In the last years, our group introduced rhenium pincer platforms that facilitate the electrochemically driven reductive splitting of dinitrogen.^[3-6] In addition, synthetic strategies were developed to generate nitriles from N_2 through nitride alkylation and subsequent chemical redox steps.^[7]

In this contribution, we present the transfer of this synthetic approach to the electrochemical redox regime. The formation of acetonitrile is demonstrated by electrolysis of an N_2 derived rhenium aldimido complex (Figure 1). The mechanism will be discussed based on electroanalytical examinations.

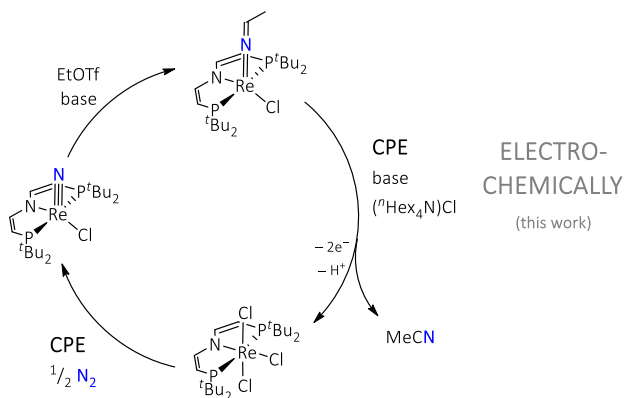


Figure 1: (Electro-)chemical conversion of Dinitrogen to Acetonitrile.

- [1] S. J. K. Forrest *et al.*, *Chem. Rev.*, **2021**, 121, 6522-6587.
- [2] S. Kim *et al.*, *Chem. Rev.*, **2020**, 120, 5637-5681.
- [3] B. M. Lindley *et al.*, *J. Am. Chem. Soc.*, **2018**, 140, 7922-7935.
- [4] R. S. van Alten *et al.*, *Eur. J. Inorg. Chem.*, **2020**, 1402-1410.
- [5] L. Alig *et al.*, *Angew. Chem. Int. Ed.*, **2022**, 61, e202113340.
- [6] M. Fritz *et al.*, *Angew. Chem. Int. Ed.*, **2022**, 61, e202205922.
- [7] I. Klopsch *et al.*, *Angew. Chem. Int. Ed.*, **2016**, 55, 4786-4789.

Main-Group Metal Porphyrin Complexes for Targeted C–H Activation

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The activation of strong, non-polar C–H bonds remains a significant challenge due to their high bond dissociation free energies and low polarity and is typically enabled by transition metal complexes.^[1] In this work, redox-stable main-group metal porphyrin systems based on the Zn/Al/Sn triad are explored as platforms for (electrochemical) C–H bond activation. The design strategy combines redox-active porphyrin ligands with redox-inert, Lewis acidic metal centres to access complexes exhibiting high O–H bond dissociation free energies (BDFEs), a key parameter governing the targeted reactivity. In this context, a series of porphyrin ligands with systematically varied *meso*-substituents and electronic properties was employed to synthesize the corresponding (PP)M–(OH)_x complexes [M = Zn²⁺, Al³⁺, Sn⁴⁺; x = 1, 2; y = 0–2]. Distinct synthetic routes had to be developed for the preparation of the aluminium and tin complexes, followed by comprehensive structural and electronic characterization.^[2] Current investigations focus on establishing a detailed understanding of thermochemical trends within this series, with the aim of enabling targeted reactivity. The results obtained thus far already provide fundamental insights into the influence of ligand substitution and metal identity on bond strengths and reactivity, establishing these main-group metal porphyrin complexes as promising platforms for probing C–H bond activation.

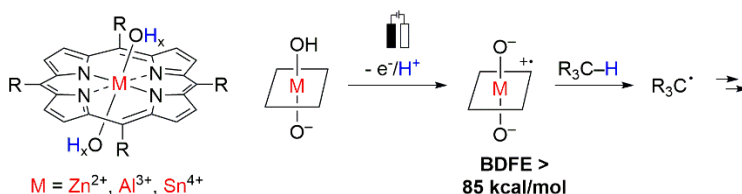


Figure 1: Main-group metal porphyrin hydroxo complexes targeted for the activation of C–H bonds.

[1]: For a recent review see: Larrosa et al., *Chem. Rev.* **2023**, 123, 7692.

[2]: Unpublished results.

Molecular Beam Studies on Methanol Partial Oxidation on Zinc Oxide

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The PCET reaction dynamics of methanol partial oxidation on ZnO are investigated by introducing methanol and molecular oxygen in molecular beams, with subsequent detection of the product formaldehyde using ion imaging techniques. In this context, the interaction between O₂ and ZnO in the absence of methanol is examined using state-resolved ionization of a molecular beam of O₂ before and after collision with the surface. State-resolved ionization is performed with a recently developed REMPI scheme (resonance enhanced multi photon ionization).^[1] We observe that the processes of direct scattering and trapped desorption leads to molecules with populations in different spin states.

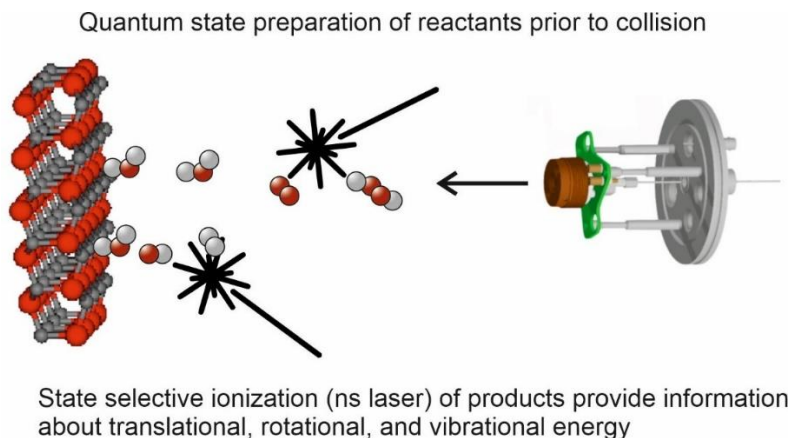


Figure 1: State-resolved molecular beam surface scattering on ZnO.

[1] I. Kallos *et al.*, J. Chem. Phys., **2025**, 162, 051103,
<https://doi.org/10.1063/5.0251383>.

Studying Hydrogen-Bound States of Hydrogenases under Turnover Conditions by Parahydrogen-Enhanced NMR

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Understanding the mechanistic principles underlying fundamental natural processes such as hydrogen conversion may guide the design of more efficient and selective synthetic catalysts systems.^[1] Mechanistic pathways are frequently governed by low-concentrated transient species that elude direct detection and are intrinsically challenging to analyze with conventional analytical techniques.^[2] This is particularly pronounced for hydrogenase catalysis and the characterization of diamagnetic EPR-silent hydrogen-bound species of the active site that rely on high-resolution diffraction data (XRD) or nuclear resonance vibrational spectroscopy (NRVS) for structural information.^[3] While ¹H NMR spectroscopy is ideally suited for studying hydrogenases –both substrate (H⁺/H₂) and product (H₂/H⁺) can be detected – its inherently low sensitivity has limited its application. Recently, the use of parahydrogen has overcome this limitation, enabling the characterization of two previously undetected on-cycle species in [Fe]-hydrogenase catalysis.^[4] Additionally, we extended this methodology to symmetric dihydride complexes resembling the reactivity of nitrogenase enzymes.^[5] This study extends this methodology to another class of hydrogenases, demonstrating its exceptional sensitivity in studying hydrogen-bound intermediates under turnover conditions.

- [1] L. Sun, C. Duboc, K. Shen, *ACS Catalysis* **2022**, 12, 9159–9170.
- [2] A. Haryanto *et al.*, *J Energy Chem* **2024**, 90, 632–651.
- [3] a) H. Ogata *et al.*, *Nature* **2015**, 520, 571–574; b) H. Ogata *et al.*, *Nat. Commun.* **2015**, 6, 7890.
- [4] L. Kaltschnee *et al.*, *Nat. Catal.* **2024**, 7, 1417–1429.
- [5] J. F. Matz *et al.*, *J. Am. Chem. Soc.* **2026**, 148, 7181–7188.

Catalytic dinitrogen activation using molybdenum porphyrins

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The fixation of atmospheric dinitrogen is a key industrial process for the production of fertilizers and all other nitrogenous products. In recent years, pincer complexes were extensively studied as catalysts for the Nitrogen Reduction Reaction (NRR).^[1,2] Despite the widespread use of metalloporphyrins as catalysts for reductive transformations of small molecules, such as CO₂ and O₂,^[3] their application as NRR catalysts is vastly underrepresented, with only report of by Miller, Holland, and co-workers.^[4]

Here, we report of the activation and fixation of dinitrogen by a molybdenum tetratolylporphyrin (TTP) complex. Catalytic ammonia generation was obtained with the PCET reagent Sml₂/ethyleneglycole. The solvent dependent redox chemistry and ground state investigation of the [Mo^{IV}X₂(TTP)] precursor complexes will be presented.

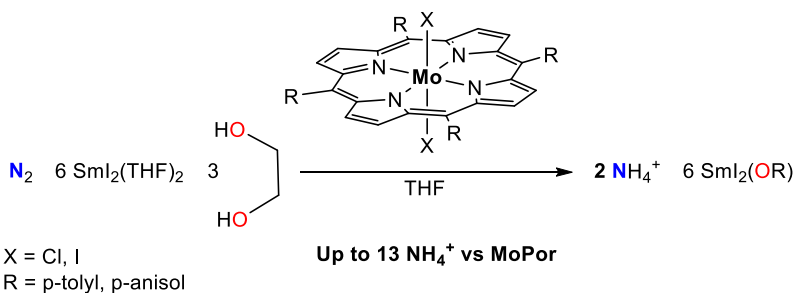


Figure 1: Catalytic NRR using [Mo(X)₂(Por)] in THF.

- [1] K. Arashiba *et al.*, *Nat. Chem.*, **2011**, 3, 120-125.
- [2] M. J. Chalkley *et al.*, *Chem. Rev.*, **2020**, 120, 5582-5636.
- [3] R. Zhang *et al.*, *ChemSusChem*, **2021**, 14, 293-302.
- [4] A. S. Hegg *et al.*, *Faraday Discuss.*, **2023**, 243, 429-449.

Reversible Long-range PCET in Ribonucleotide Reductases

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Ribonucleotide reductase (RNR) is an essential enzyme in deoxyribonucleotide biosynthesis. RNR function depends on tightly regulated conformational changes and assembly dynamics. In *Escherichia coli*, RNR consists of two homodimeric subunits, α_2 and β_2 , which form a transient ~250 kDa complex in the enzymatically active state. Despite decades of study, the structure of the native tetrameric complex remains unresolved due to the transient nature of subunit interaction and the coexistence of active and inactive states in equilibrium. In this study, we employ ¹³C Electron-Nuclear Double Resonance (ENDOR) spectroscopy to investigate interaction between redox-active tyrosines across the α/β Interface. Additionally, we employ state-of-the-art cryo-EM to capture snapshots of distinct functional states of the individual subunits and the complex in the native enzyme. These structural snapshots might provide mechanistic insights into RNR activity and regulation, potentially opening new avenues for the development of antibiotic and anticancer therapeutics.

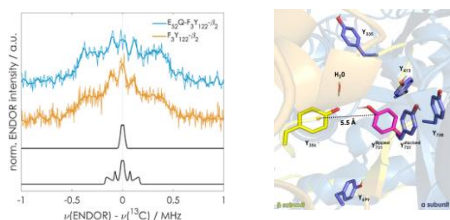


Figure 1: ¹³C Mims ENDOR spectra for ¹³C-Y- α_2 + (E₅₂Q-)F₃Y₁₂₂- β_2 or F₃Y₁₂₂- β_2 with GDP/TTP as substrate/effector at pH 7.6 agrees with the proposal of a colinear PCET between Y₃₅₆ and Y₇₃₁ enabled by a conformational change of Y₇₃₁

References:

- [1] A. Meyer *et al*, JACS, **2022**, 144, 11270, 10.1021/jacs.2c02906.
- [2] F. Hecker *et al*, JACS, **2021**, 143, 7237, 10.1021/jacs.1c01359.
- [3] S. Dai *et al*, Nature **2019**, 573, 609, 10.1038/s41586-019-1581-9.

Graphene-Based Nanoreactor for Nanoscale Spectroscopic Investigation of Water Oxidation on ZnO

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Advancing nanoscale spectroscopic analysis of catalytic water oxidation on ZnO surfaces as well as its control via electrostatic gating requires innovative experimental platforms [1]. This work introduces a graphene-based nanoreactor engineered to enable such investigations under controlled electrochemical conditions. The device (Figure 1a) features suspended graphene electrodes separated by a thin hexagonal boron nitride (hBN) dielectric, creating a confined reaction chamber where ZnO nanoparticles interact with water molecules. This setup allows simultaneous electrostatic gating of the catalytic interface and optical access for scattering-type scanning near-field optical microscopy (s-SNOM), facilitating in situ monitoring of catalytic intermediates through nanoscale infrared spectroscopy. Fabrication involved electron-beam lithography and reactive ion etching to define microchannels on a Si/SiO₂ substrate, followed by deterministic transfer of graphene/hBN heterostructures to realize fully suspended nanoreactor regions. The optimized thin hBN improves mechanical stability while maintaining optical and electrostatic functionality. Alongside initial near-field characterization of the suspended device, ongoing work focuses on electrolyte inclusion and operando near-field studies. Complementary electrical measurements on thin ZnO films configured as back-gated field-effect transistors demonstrate gate-dependent modulation of drain current, confirming tunable surface charge density and effective control over catalytic interfaces. This platform thus lays the groundwork for precise nanoscale exploration of catalytic water oxidation mechanisms on ZnO.

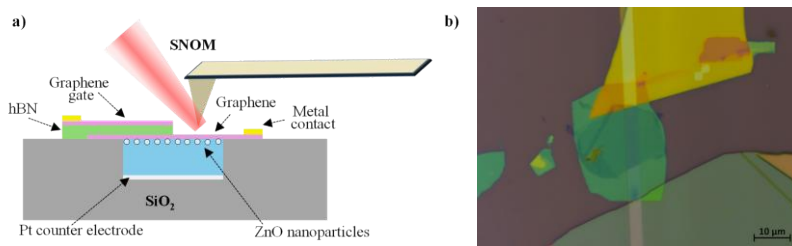


Figure 1: a) Nanoreactor architecture, (b) suspended graphene/hBN on microchannel.

[1] C. Yang *et al.*, Chem. Rev. 2025, 125, 1, 223–293,
<https://doi.org/10.1021/acs.chemrev.4c00327>

Charge, Shape and Size effects of Cages on their Host-Guest Chemistry

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Supramolecular cages are known to influence chemical reactivity and catalysis by providing confined environments and electrostatic interactions that can protect reactive species or result in new selectivities.¹ Here, nearly isostructural supramolecular tetrahedral M₄L₄ cages with different overall charges were synthesized (Fig 1. compounds **1** to **4**). Further, literature known cages with different geometries and charges (tetrahedral, cubic, and octahedral) have been prepared (Fig 1. compounds **5** to **8**). In parallel, a range of guest molecules have been synthesized (Fig 2). Host–guest encapsulation studies conducted with the mentioned cages and complexes and alcohols are presented here. In addition, we show how counterion exchange strategies result in a tunable cage solubility.

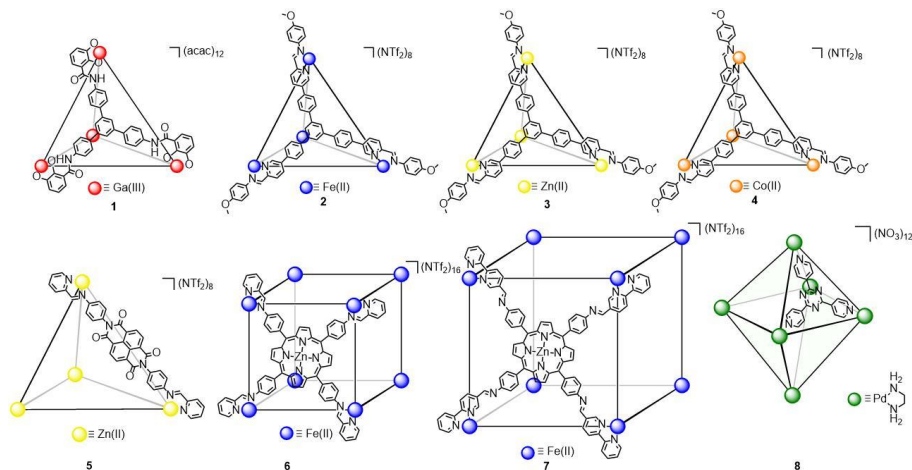


Figure 1: Structures of the supramolecular cage compounds investigated in this study.

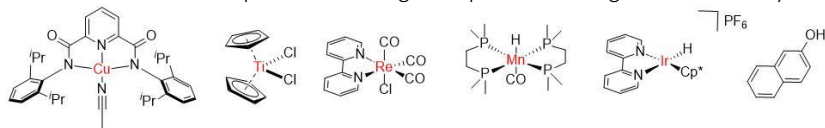


Figure 2: Selection of guest compounds investigated in this study.

[1] F. Huang *et al.* Chem. Rev. **2015**, *15*, 115. DOI: 10.1021/acs.chemrev.5b00352.

Beyond a Passive Solvent: Unveiling the Remarkable Photocatalytic Activity and Thermal Promotion of γ -Valerolactone in Sustainable Diphenylmethane Oxidation

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The aerobic oxidation of diphenylmethane (DPM) to benzophenone is a vital industrial process, but the classical methods lead to the formation of large volumes of toxic and corrosive wastes and often require high temperature when molecular oxygen is the sole oxidant. In this study we present spray flame-synthesized perovskite LaCoO_3 and spinel Mn_3O_4 as promising catalysts as well as a highly efficient, green alternative γ -valerolactone (GVL), a biomass-derived solvent, which acts as an active promoter for benzylic $\text{C}(\text{sp}^3)\text{-H}$ bond activation. Experimental data reveals a profound "solvent effect": traditional solvents like acetonitrile yield minimal conversion, whereas GVL enables significant activity under both thermal and photocatalytic conditions. Most notably, the system demonstrates exceptional photocatalytic activity at room temperature (25°C), achieving 43% conversion with 100% selectivity for benzophenone under UV light (365 nm), nearly triple the efficiency of acetonitrile (15.7%). Mechanistic studies, including radical scavenging and EPR spectroscopy, confirm a radical pathway where GVL may participate by forming radicals that initiate the reaction chain. This work establishes GVL as a powerful, biodegradable promoter for mild and sustainable benzylic oxidation.

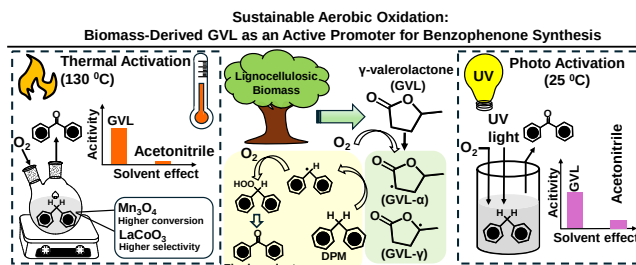


Figure 1: Schematic representation of sustainable aerobic oxidation of diphenylmethane to benzophenone.

[1] X. Wu *et al.*, *Angew. Chem. Int. Ed.* **2024**, 63, e202409826, DOI:

<https://doi.org/10.1002/anie.202409826>.

[2] A. Wang *et al.*, *Green Chem.*, **2024**, 26, 353, DOI:

<https://doi.org/10.1039/D3GC03639A>.

Unifying Scaling Relations and Multiple Reaction Mechanisms for Screening Transition Metal-Doped Co₃O₄ for OER

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Accelerating the discovery of oxygen-evolution reaction (OER) catalysts requires high-throughput screening strategies combining descriptor-based frameworks with dedicated mechanistic analyses.^[1-3] In this study, we present a unified methodology using the example of doped Co₃O₄ in the OER by developing a mechanistically resolved, potential-dependent volcano approach that accounts for the uncertainty of adsorption free energies when analyzing activity trends. We evaluate the influence of different dopants (Cr, Mn, Fe, Ni, Cu, and V) on the OER activity by selectively substituting octahedral Co sites on the (001) facet of Co₃O₄ using density functional theory calculations (DFT). We identify Cr, Fe, Ni, and V as promising dopants as they exhibit increased OER activity compared to undoped Co₃O₄, while Cr shows the strongest promoting effect among all dopants considered in this study. We compare our theoretical predictions with two different series of synthesized Co₃O₄ nanoparticle catalysts and find good agreement regarding the qualitative trends of OER activity. To validate the strong promoting effect of Cr, we synthesize surface-enriched, Cr-doped Co₃O₄ nanoparticles, which confirms the theoretical prediction of increased OER activity. The theoretical model developed in this work is a transferable framework that can be equally applied to other materials and electrocatalytic processes for quantifying dopant effects by considering uncertainty and promoting effects when analyzing activity trends.

[1] K. Dhaka, K. S. Exner, *J. Catal.* **2025**, 443, 115970. DOI: [10.1016/j.jcat.2025.115970](https://doi.org/10.1016/j.jcat.2025.115970)

[2] K. Dhaka, S. Kenmoe, A. Fängerlings, R. Pentcheva, K. Tschulik, K. S. Exner, *ChemCatChem* **2025**, 17, e00992. DOI: [10.1002/cctc.202500992](https://doi.org/10.1002/cctc.202500992)

[3] M. Usama, S. Razzaq, C. Hättig, S. N. Steinmann, K. S. Exner, *Nat. Com.* **2025**, 6137. DOI: [10.5281/zenodo.15650140](https://doi.org/10.5281/zenodo.15650140)

ETHYLENE GLYCOL PARTIAL OXIDATION ON Co_3O_4 AND Au SURFACES: AB INITIO MOLECULAR DYNAMICS SIMULATIONS

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The oxidation of 2-propanol to acetone at the Co_3O_4 (001)/ H_2O interface has been recently studied using ab initio molecular dynamics to understand the roles of temperature, surface structure, and electrochemical environment [1]. In the same vein, we now study the case of a more complex molecule, namely ethylene glycol, on the same metal oxide to understand its oxidation process. Ethylene glycol oxidation can yield six value-added products: glycolaldehyde, glycolic acid, glyoxylic acid, glyoxal, oxalic acid and formic acid. We investigate the influence of surface termination, solute coverage, temperature, and water dissociation on reaction pathways, including scenarios involving solvated ethylene glycol molecules and KOH-induced alkaline environments.

Our simulations reveal that the Co^{3+} -terminated (B-termination) Co_3O_4 surface is significantly more reactive than the Co^{2+} -terminated (A-termination) surface, consistently favoring two-electron oxidation products such as glycolaldehyde under alkali-free conditions. Strong alkalinity is required to drive four-electron oxidation toward glycolate and to promote C–C bond cleavage leading to C_1 products such as formaldehyde and formate. Water plays an active role beyond solvation. It dissociates on cobalt oxide surfaces and competes with ethylene glycol for active sites while enabling proton transfer via the Grotthuss mechanism. Defect engineering further enhances selectivity toward C_2 products, in agreement with experimental observations.

On Au (111), ethylene glycol oxidation proceeds more easily than on Co_3O_4 , yielding four-electron products even in the absence of alkaline media, though higher pH remains necessary for further oxidation. Overall, our results establish a unified mechanistic picture of thermal and electrochemical ethylene glycol oxidation, demonstrating that catalyst surface structure, alkalinity, and defect engineering are key factors for tuning product distribution.

[1] Omranpoor, A. H., Kox, T., Spohr, E., & Kenmoe, S. (2022). Influence of temperature, surface composition and electrochemical environment on 2-propanol decomposition at the Co_3O_4 (001)/ H_2O interface. *Applied Surface Science Advances*, 12, 100319

Partial selective oxidation of 2-Propanol on $\text{Co}_3\text{O}_4(111)$ and V-doped $\text{Co}_3\text{O}_4(111)$ model catalyst: effects of hydroxyls and dopants

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Partial oxidation of alcohols is gaining considerable attention as a promising reaction system for important processes in technological applications. In recent studies, we investigated the mechanisms of selective 2-propanol decomposition over model $\text{Co}_3\text{O}_4(111)/\text{Au}(111)$ and $\text{Co}_3\text{O}_4(111)$ containing different amounts and forms of vanadium oxide. We address the evolution of the reaction paths, intermediates and the desired products acetone and propene under reaction conditions and establish detailed correlations with the microscopic structure of the catalyst. The specific focus of this study lies at the understanding of the role of water as well as possible reaction mechanisms of competing reaction routes.

Specifically, our findings revealed that by pretreatment of $\text{Co}_3\text{O}_4(111)$ catalysts with H_2O at elevated temperatures (573 K) it becomes possible to substantially enhance the formation rate of acetone and its surface precursor propoxy species, whereas water deposition in the low temperature range rather suppresses the reaction. This result is in line with the observations obtained on the powdered Co_3O_4 -based catalysts investigated under technologically relevant conditions. The IRAS and STM results suggest that the origin of the reactivity enhancement upon high temperature treatment with water is related to formation of isolated O_3H -groups.

Additionally, we report on the recent progress in development of V-doped $\text{Co}_3\text{O}_4(111)$ and mixed $\text{VO}_x\text{-Co}_3\text{O}_4(111)$ oxides. Three types of V-containing structures were identified: V atoms embedded into the Co_3O_4 lattice, two-dimensional (2D) and three-dimensional (3D) VO_x islands whose relative abundance strongly depends on the amount of deposited V. V atoms in different oxidation state were identified, including V^{3+} , V^{4+} and V^{5+} involved in vanadyl ($\text{V}^{5+}=\text{O}$) groups by employing CO as a probe molecule for adsorption sites. The latter species were shown to participate in dissociation of 2-propanol to the propoxy reaction intermediate, likely serving as H acceptor. At low V coverage, acetone forms on $\text{Co}_3\text{O}_4(111)$, while increasing V amounts promote an alternative pathway forming propene through C–O bond scission, confirmed by detection of surface intermediates and gas-phase propene above 430 K.

Surface OH Dynamics and 2-Propoxide Formation Pathways during 2-Propanol Oxidation over Co_3O_4 : An Operando ME-DRIFTS Study

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The oxidation mechanism of 2-propanol (iPrOH) on oxide catalysts is believed to include the formation of 2-propoxide (iPrOx) as a key intermediate¹. This species can occur either by generating an OH group on the surface or by forming and releasing H_2O . Isolated OH groups have been shown to play an important role in 2-propanol dehydrogenation on Co_3O_4 model catalysts. In this work, the mechanism of 2-propanol oxidation over powder Co_3O_4 is further investigated using *operando* modulated DRIFT spectroscopy combined with phase-sensitive detection analysis (ME-DRIFTS-PSD)². Infrared measurements at 120 °C showed the formation of several species during the oxidation of iPrOH on Co_3O_4 . This temperature corresponds to an unstable low-temperature channel characterized by high iPrOH conversion and high acetone selectivity. The spectra revealed bands assigned to carboxylates and acetone ($1200\text{--}1720\text{ cm}^{-1}$), iPrOx ($940\text{--}1170\text{ cm}^{-1}$), and two types of surface OH groups (3630 and 3575 cm^{-1} ; α and β , respectively). ME-DRIFTS-PSD analysis showed that the OH- α band is anti-correlated with the iPrOx bands, indicating that its formation derives from the deprotonation of iPrOH to iPrOx. On the other hand, OH- β band show no intensity change over time and no modulation, suggesting that its formation is unrelated to any adsorbate. Similar findings were observed at higher temperatures. Therefore, these results show that the selective oxidation of iPrOH involves the activation of distinct surface OH sites, paving the way for new mechanistic scenarios and new catalyst formulations to improve catalytic performances.

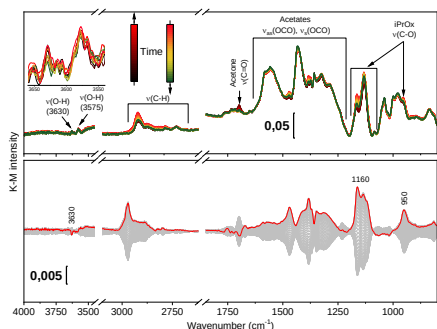


Figure 1: *Operando* DRIFTS spectra in the time-domain (top) and phase-domain (bottom). The color bars indicate iPrOH coverage over time. The red line in the phase-resolved spectra represents the spectrum of the in-phase angle at $\phi = -115^\circ$ ($t \approx 19.2\text{s}$).

[1] Anke, S. *et al.*, *ACS Catal.*, **2019**, 9, 5974–5985, doi.org/10.1021/acscatal.9b01048.

[2] Baurecht, D. *et al.*, *Rev. Sci. Instrum.*, **2001**, 72, 3782, doi.org/10.1063/1.1400152.

Electrocatalytic Oxidation of Ethylene Glycol on NiSe-Functionalized Electrodes

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The electrochemical oxidation of ethylene glycol has attracted considerable attention due to its potential applications in fuel cells and sustainable energy technologies. In this work, nickel selenide (NiSe) materials were studied as catalysts for ethylene glycol oxidation in alkaline media. The materials were prepared via electrodeposition, enabling controlled formation of the active phase and its interaction with the electrode surface. The obtained systems were characterized using Raman spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDX). Raman spectroscopy provided insight into reaction intermediates and surface species, while XRD confirmed the crystalline structure of NiSe. SEM analysis revealed the morphology of the deposited material, and EDX enabled determination of elemental composition and distribution. Electrochemical measurements demonstrated that NiSe exhibited enhanced catalytic activity, including higher current densities and improved oxidation behavior. These findings highlight the potential of NiSe as an efficient electrocatalyst for ethylene glycol oxidation.

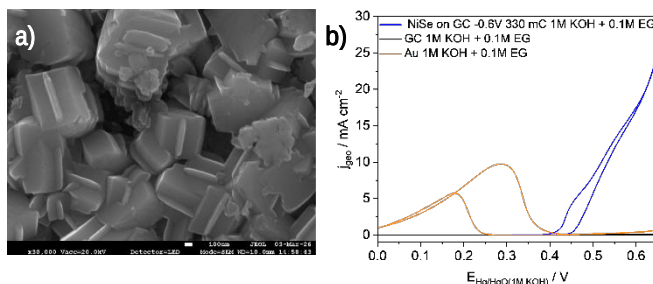


Figure 1: a) SEM image of electrodeposited NiSe, b) ethylene glycol oxidation on glassy carbon (GC), gold and NiSe modified GCE electrodes.

[1] F. Hiege. *Electrochemical and Spectroscopic Characterization of Nickel Selenides-based OER Electrocatalysts*; Ruhr-Universität Bochum, 2025.

Electrochemical Oxidation of Ethylene Glycol on Cobalt-based Oxides: Mechanistic Studies and the Role of the Catalyst Material

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The electrocatalytic oxidation of alcohols is a promising alternative as the anode reaction in the production of green hydrogen as it proceeds at significantly lower potentials than the sluggish oxygen evolution reaction.^[1] The oxidation of ethylene glycol further provides valuable products like glycolic acid which find use in the synthesis of biodegradable polymers.^[2] While cobalt-oxide based materials are of increasing interest due to their abundance compared to the commonly investigated gold catalysts, little is known about the mechanism of the ethylene glycol oxidation on such materials. In our work, we investigated the electrooxidation of ethylene glycol on two different Co-based catalysts, namely LaCoO₃ perovskite and Co₃O₄ spinel nanoparticles. The two materials show a distinct difference in electrochemical behavior with vastly different Tafel slopes suggesting different rate limiting steps. In addition to this their product selectivity determined by HPLC differs significantly with the Co₃O₄ spinel material producing a mixture of glycolate and formate while electrocatalytic oxidation on LaCoO₃ yielded nearly exclusively formate. Further electrochemical studies and product analysis were conducted to understand the reaction pathway for the oxidation of ethylene glycol to its different products. Investigations focused on oxidizing the reaction intermediates of ethylene glycol on Co₃O₄ allowed us to rationalize the different behavior of cobalt-based electrocatalysts compared to gold. All in all, our findings lay a foundation to understand how the oxidation of ethylene glycol proceeds mechanistically and how the catalyst may influence product distributions.

[1] S. Najafshirvari et al., Chemistry **2021**, 27, 16809, <https://doi.org/10.1002/chem.202102868>.

[2] J. Qi et al. , Curr. Opin. Electrochem., **2022**, 32, 100929, <https://doi.org/10.1016/j.coelec.2021.100929>.

Photothermal Promotion of Liquid-Phase Ethylene Glycol Oxidation over Non-Noble Co_3O_4 Catalysts

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Selective oxidation of ethylene glycol (EG) is a key reaction for biomass valorization, enabling the production of value-added chemicals such as glycolic acid (GA) and formic acid (FA). Enhancing activity and selectivity using earth-abundant catalysts remains a central challenge. Photothermal catalysis, which combines thermal activation with photoexcited charge carriers, offers a promising strategy to accelerate oxidation reactions beyond purely thermocatalytic pathways. In this work, we investigate the photothermal oxidation of EG over visible-light-responsive Co_3O_4 nanoparticles. Under alkaline conditions at 130 °C, irradiation with a 450 nm LED enhanced EG conversion by up to 26% compared to dark conditions, while maintaining constant reaction temperature, thereby excluding thermal heating effects. The enhancement showed clear light-intensity dependence and was also observed under 365 nm illumination, whereas 660 nm irradiation produced no improvement, confirming the necessity of bandgap excitation. Kinetic analysis revealed a reduction in apparent activation energy by 4.5 kJ mol⁻¹ under illumination. Only minor selectivity shifts were detected, indicating that photoexcitation primarily accelerates oxidation without significantly promoting detrimental C–C bond cleavage. Overall, these results demonstrate a synergistic photo-thermocatalytic effect and highlight the potential of photothermal strategies for efficient liquid-phase selective oxidation using non-noble metal oxides. Ongoing mechanistic studies aim to elucidate the role of photogenerated holes in substrate oxidation and electrons in O_2 activation, particularly their involvement in $\text{Co}^{3+}/\text{Co}^{2+}$ redox cycling.

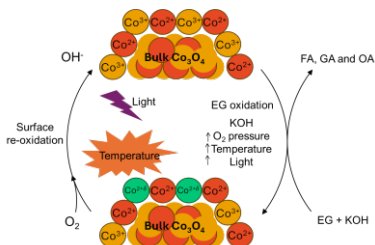


Figure 1: Scheme of photothermal catalytic Ethylene Glycol Oxidation over Co_3O_4 Catalysts.

[1] C. Leiva-Leroy, Y. Jiang *et al.*, ChemRxiv. 12 January 2026. DOI: 10.26434/chemrxiv-2025-bdf6c-v2 [2] C. Leiva-Leroy *et al.*, Angew Chem Int Ed Engl, 2025, e19188, DOI: 10.1002/anie.202519188

OER-Relevant Surface Hydroxyl Structure on Doped Co_3O_4 Nanoparticles Probed by Phase-Sensitive Sum Frequency Generation

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Abstract text: The oxygen evolution reaction (OER) is a major kinetic bottleneck in electrochemical water splitting. Spinel Co_3O_4 is a promising OER catalyst whose activity can be tuned by doping. However, how doping modifies the surface hydroxyl (OH) structure where OER elementary steps occur remains poorly understood. Vibrational sum frequency generation (vSFG) spectroscopy has been widely used to study surfaces and interfaces due to its high sensitivity and surface specificity. Here, we used phase-sensitive vSFG spectroscopy to identify the orientation, type, and relative population of surface OH species on undoped, Mn-doped, and V-doped Co_3O_4 nanoparticles. Phase-resolved $\text{Im}\chi^{(2)}$ spectra reveal two H-up OH resonances: bidentate OH centered at $3526\text{--}3585\text{ cm}^{-1}$ and monodentate OH centered at $3736\text{--}3770\text{ cm}^{-1}$. Mn doping markedly increases both signals, indicating a higher population of strongly bound OH species, whereas V doping causes only moderate changes. Electrochemical measurements show that Mn-doped Co_3O_4 exhibits reduced OER activity, consistent with stable bonded OH structures that hinder OH^- transport and delay CoOOH formation. In contrast, V-doped Co_3O_4 shows improved OER activity, consistent with less and weakly bounded OH configurations that facilitate proton-coupled electron transfer. Notably, the relative population ratio of bidentate to monodentate OH follows the same trend as the OER activity. This further suggests that bidentate OH species may be more favorable for OER than monodentate OH. These results manifest vSFG as a powerful molecular-level probe of surface OH structure on complex oxide electrocatalysts and suggest that dopant-controlled hydroxyl configurations are a key factor for OER activity.

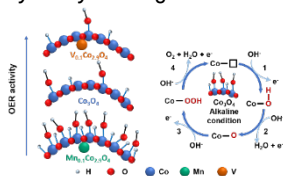


Figure 1. Schematic illustration of dopant-dependent surface hydroxyl configurations on Co_3O_4 nanoparticles and their correlation with OER activity.

[1] F. Yan *et al.*, *Improving Characterization of Nanoparticulate Films Using Surface-Specific Vibrational Spectroscopy*, ChemRxiv, 2025.

Probing the Reversibility of Pre-OER Activation of Doped Co_3O_4 via Transient Operando UV-Vis Spectroelectrochemistry

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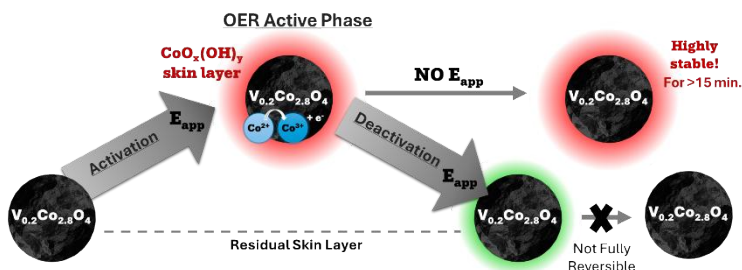
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The development of efficient water-splitting technologies is limited by the sluggish kinetics of the Oxygen Evolution Reaction (OER). While earth-abundant Co_3O_4 nanoparticles (NPs) are promising OER pre-catalysts, they undergo a structural reconstruction under working conditions to become the real working catalyst [1]. Although this process is critical for activation, the fundamental questions regarding the exact mechanism of this transformation, its stability, and the extent of its reversibility upon removal of the driving force remain unclear.

In our work, we employ time-resolved operando UV-Vis Spectroelectrochemistry (SEC) to track the dynamical behavior of high-performing V-doped Co_3O_4 NPs. Our prior research identified two distinct regions in pre-OER activation: oxidized- Co^{3+} formation, followed by the formation of catalytically active $\text{CoO}_x(\text{OH})_y$ skin layer at higher applied potentials (E_{app}) [2]. To assess the stability of activated states after pre-OER activation, we monitored their preferences via two different paths: spontaneous relaxation and under control. Under open circuit conditions, the skin layer exhibited surprisingly remarkable stability (>15 min). Even when forcing back under control with back- E_{app} , it only partially disappeared with incomplete Co^{3+} reduction. These findings reveal that the pre-OER activation is not a completely reversible process, leaving a permanent impact on the catalyst's surface. These mechanistic insights offer a pathway to rationally design of enhanced-activity and stable OER catalysts.



[1] T. Wiegmann et al. ACS Catal., **2022**, 12, 6, 3256, 10.1021/acscatal.1c05169

[2] L. Kampermann et al. ACS Catal., **2025**, 15, 18391, 10.1021/acscatal.5c03900

Cooperative Co-Fe Effect on the OER Activity of CoFe₂O₄ (100), (001) and (111) surfaces

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Water splitting, a key method for green hydrogen production, is limited by the sluggish anodic half process - the oxygen evolution reaction (OER) [1]. This necessitates finding efficient and affordable electrocatalysts which can reduce the overpotential. Using density functional theory calculations with an on-site Hubbard U term, we study the OER activity of the CoFe₂O₄ (CFO) (001), (100), and (111) surfaces, exploring a wide range of potential active sites and the effect of solvation. The lowest overpotential of 0.20 V is found for an octahedral Co at the A-layer termination of the (100) surface, which contains both Fe and Co. This is attributed to the stabilization of the *OOH intermediate by binding both to the Co^{Oct} and to a neighbouring Fe^{Tet} site [2]. Upon including implicit solvation, the octahedral Fe site on B-layer termination of the Fe-rich (001) surface becomes the most active, with an overpotential of 0.37 V. Remarkably, the sites with highest catalytic activity are found to retain more bulk-like oxidation states. Our results show that bonding configurations that break the OER scaling relationship lead to overpotentials beyond the top of the volcano and open new routes to designing catalysts for water splitting.

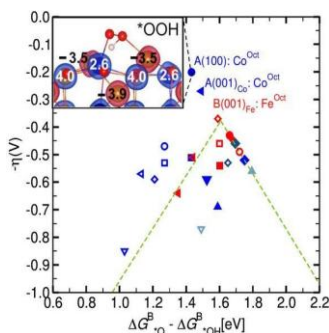


Figure 1: Volcano plot of $-\eta$ as a function of the difference of binding energies of *O and *OH for the CoFe₂O₄ (001) and (100) surfaces. Cooperative Co-Fe interactions stabilize adsorbate geometries that deviate from monodentate binding typically assumed in the scaling relationship and help reach overpotentials beyond the top of the volcano.

[1] J. Rossmeisl *et al.*, J. Electroanal. Chem., **2007**, 607, 83–89, <https://doi.org/10.1016/j.jelechem.2006.11.008>

[2] S. Rafiezadeh *et al.*, ChemCatChem, **2025**, e01290, <https://doi.org/10.1002/cctc.202501290>

Subsurface V-dopant-driven Charge Redistribution Promotes the OER Activity of the $\text{Co}_3\text{O}_4(001)$ Surface

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A fundamental understanding of how atomic-scale surface modifications govern catalytic activity is essential for the rational design of high-performance electrocatalysts for sustainable energy conversion. Here, we present a DFT+*U* investigation of the effect of Mn and V doping on the oxygen evolution reaction (OER) activity of $\text{Co}_3\text{O}_4(001)$, examining both A- and B-surface terminations. Mn incorporated at surface octahedral sites has a detrimental effect on OER performance. In contrast, V-doping exhibits pronounced termination-dependent behavior. At the B-terminated surface, V^{5+} at a surface octahedral site reduces the overpotential at Co_{oct} from 0.48 V to 0.43 V. Remarkably, at the A-termination, subsurface V^{4+} inverts the trend of Co_{oct} site being more active by dramatically lowering the overpotential at the Co_{tet} site from 0.74 V to 0.18 V. Across all studied reaction sites, deprotonation of $^*\text{OH}$ to $^*\text{O}$ is the potential-determining step (PDS). This exceptional enhancement of activity of Co_{tet} originates from a V^{4+} -induced charge redistribution that modifies a surface $\text{Co}^{3+}(\text{IS})$ to Co^{2+} , weakening $^*\text{OH}$ binding and lowering the PDS by 0.56 eV. These findings show that selective cation doping as a powerful strategy to tune the electrocatalyst performance.

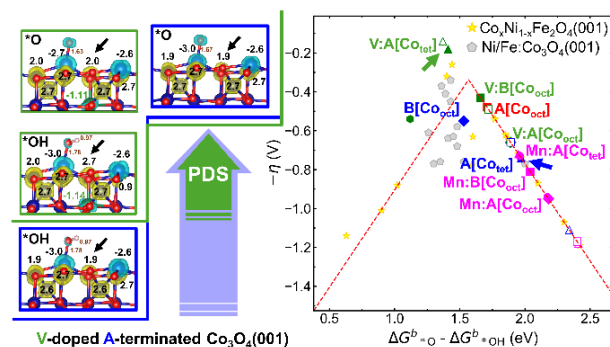


Figure 1: Volcano plot of $-\eta$ vs $\Delta G^b_{*O} - \Delta G^b_{*OH}$ for pristine, Mn-, and V-doped $\text{Co}_3\text{O}_4(001)$, along with side views of the spin densities of $^*\text{OH}$ and $^*\text{O}$ intermediates, highlighting the superior OER activity of the V-doped A-layer at the Co_{tet} site.

Defect-Driven Surface Transformations in Co-Based Spinel Catalysts: Linking Active Site Evolution to Activity and Selectivity in OER and Alcohol Oxidation

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This project investigates how surface transformations in Co-based spinel catalysts govern activity, stability, and selectivity in both the oxygen evolution reaction (OER) and electrochemical alcohol oxidation. Focusing on Co-Ni, Co-V, and mixed Co-M (M = Fe, Mn, Cr), it examines the influence of composition, defects, particle shape, and surface orientation on catalytic performance. A correlative, multimodal approach, combining electrochemical methods with advanced techniques such as XPS, XAS, TEM, APT, EBSD, SECCM, EC-AFM, and in situ Raman spectroscopy, enables operando insights into structural, compositional, and oxidation state changes. The results reveal that catalytic behaviour is governed by dynamic surface transformations and the formation of active oxyhydroxide phases (e.g., CoOOH). Defects, dopants, and surface facets modulate these processes, influencing active site evolution and deactivation pathways. This work establishes unified structure–activity–selectivity relationships and provides design principles for optimizing Co-based catalysts.

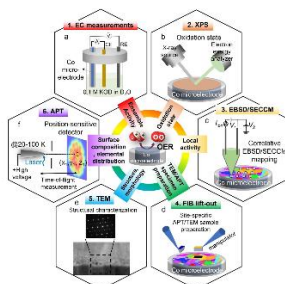


Figure 1: Pictorial Representation of the Correlative Microscopy Approach

[1] Bala Krishnan, M. Corva, P. Hosseini, M. Heidelmann, U. Hagemann, E. Batsa Tetteh, W. Schuhmann, K. Tschulik, T. Li, *Angew. Chem. Int. Ed.*, 2023, 62, e202305982.

[2] C. Luan, M. Corva, **U. Hagemann**, H. Wang, **M. Heidelmann**, K. Tschulik, T. Li, *ACS Catal.*, 2023, 13, 1400-1411

Operando X-ray Diffraction Studies of Co Oxide Model Catalysts during Oxygen Evolution Reaction and Alcohol Oxidation

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Overcoming the slow kinetics of the anodic oxygen evolution reaction (OER) is a key challenge for the sustainable production of green hydrogen via electrolysis.

Transition-metal oxides such as Co_3O_4 are among the best precious-metal-free electrode materials for the anodic OER in alkaline electrolysis [1]. Moreover, these spinel-type transition metal oxides are an important class of catalysts for the selective oxidation of organic compounds in the liquid phase. Here, we present *operando* surface X-ray diffraction (SXRD) studies of OER model catalysts, consisting of thin epitaxial $\text{Co}_3\text{O}_4(111)$ films electrodeposited on $\text{Au}(111)$ substrates. Previous studies have shown reversible changes in the oxide's structure, in particular the formation of a sub-nm $\text{CoO}_x(\text{OH})_y$ skin layer in the pre-OER potential range [1,2]. Combined *operando* SXRD and electrochemical impedance spectroscopy as well as *operando* X-ray absorption spectroscopy measurements demonstrated that thermal annealing leads to a defect-free $\text{Co}_3\text{O}_4(111)$ surface and completely suppresses the skin layer formation. Potential-induced surface restructuring consequently only occurs in the presence of surface defects. The presence of this skin layer promotes oxygen evolution at low overpotentials but results in higher Tafel slopes. As a result, defect-free $\text{Co}_3\text{O}_4(111)$ surfaces are more active at high current densities than defective Co_3O_4 surfaces that undergo surface restructuring [3]. Furthermore, studies of ethylene glycol (EG) oxidation on Co_3O_4 films revealed similar structural changes, even though they appear to be less pronounced under alcohol oxidation conditions, especially at higher EG concentrations.

We acknowledge financial support by the Deutsche Forschungsgemeinschaft via special research area TRR 247, project B10 (project no. 388390466).

[1] E. M. Davis *et al.*, J. Am. Chem. Soc., **2024**, 146, 13770, 10.1021/jacs.3c13595.

[2] C. Qiu *et al.*, ChemCatChem, **2024**, 16, e202400988, 10.1002/cctc.202400988.

[3] Scharf *et al.*, ACS Catal., **2026**, 10.1021/acscatal.5c08785.

The Impact of Manganese Incorporation and Morphology on the Activity of Cobalt Spinel Catalysts in Oxygen Evolution Reactions

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Co-based catalysts have shown promising activity towards electrochemical oxygen evolution reaction (OER) and chemical water oxidation using ceric ammonium nitrate (CAN test).^[1] While pure Mn oxides have relatively low activity in OER, higher OER performances of mixed phases of Mn- and Co-based oxides has been reported in the past.^[2] In our work, we investigated the correlation between Mn incorporation up to 20% Mn into Co-spinel catalyst with two distinct morphologies (spheres and platelets) and their activity in the CAN test and OER. The $\text{Co}_{3-x}\text{Mn}_x\text{O}_4$ catalysts were synthesized via co-precipitation and subsequent thermal decomposition. Rietveld refinement revealed an increase of the lattice parameter, indicating Mn incorporation (Fig. 1a). At higher Mn contents a separation into two cubic spinel phases was observed. Regarding OER (Fig. 1b), a trend emerged independent from spinel morphology: both series exhibited enhanced activity for low Mn contents (~2.5% Mn) due to a decrease in overpotentials, whereas higher Mn contents led to a decline in activity. In contrast, the morphology played a more dominant role in the CAN test (Fig. 1c): While the activity of the spherical series decreases as the Mn content increases, the activity of the platelet series fluctuates. The results likely stem from an opposing effect of the catalyst's mesostructure on its specific surface area and its electric conductivity.^[3]

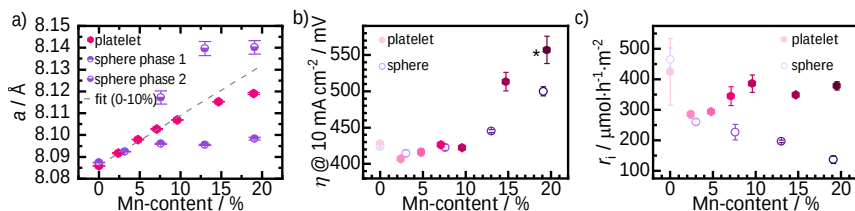


Figure 1: a) Lattice parameter of the synthesized Co/Mn-spinels. b) Overpotential η at 10 mA cm^{-2} (BET surface area normalized). c) Initial rate r_i (BET surface area normalized).

[1] A. Rabe *et al.*, Chem. Eur. J., **2021**, 27, 17038-17048, DOI:

10.1002/chem.202102400.

[2] K. R. Park *et al.*, Catalysts, **2019**, 9, 564, DOI: 10.3390/catal9060564.

[3] J. Heese-Gärtlein *et al.*, Chem. Eur. J., **2020**, 26, 12256-12267, DOI:

10.1002/chem.201905090.

Nanocubes and Cuboctahedra: Entropic Stabilization versus Thermal Segregation in Rock Salt- and Spinel-Type Multinary Oxides from Spray-Flame Synthesis

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Multinary oxides with ≥ 5 cations, often termed high-entropy oxides (HEOs), are attractive for energy applications for their compositional tunability. HEOs are frequently associated with entropy-driven stabilization, where high temperature and configurational entropy offset mixing enthalpies. Preserving entropy-stabilized structures requires rapid cooling, making synthesis challenging, especially for nanomaterials. To investigate whether spray-flame synthesis (SFS), providing flame temperatures >2300 K and cooling rates up to 106 K/s, meets these requirements and to critically assess the entropy stabilization concept, three model systems were synthesized: the rock salt-type $\text{Co}_{0.2}\text{Cu}_{0.2}\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2}\text{O}$ (RS1) and two spinels featuring tetrahedral and octahedral sites, constraining the effective entropy, the known $(\text{Co}_{0.2}\text{Cu}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})_3\text{O}_4$ (SP1) and the novel seven-cation $(\text{Co}_{0.2}\text{Cu}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.1}\text{Mg}_{0.05}\text{Al}_{0.05})_3\text{O}_4$ (SP2). All samples formed faceted nanocubes and cuboctahedra (~ 10 nm), a morphology rarely observed for materials from gas-phase syntheses. Hot-stage X-ray diffraction revealed entropy-stabilization for RS1: the single-phase rock salt transiently segregated CuO, and re-formed a high-entropy stabilized solid solution above 1120 K. In contrast, as-synthesized SP1 contained segregated NiO, whereas as-synthesized SP2 was phase-pure; upon heating, NiO dissolved into the spinel lattice while CuO segregated continuously and segregation of CuO was observed for SP2. The $\text{Ni}^{2+}/\text{Cu}^{2+}$ substitution reflects site competition while its incorporation in the as-synthesized products as observed for SP2 highlights that SFS can access phases otherwise unstable at room temperature. Spray-flame synthesis proves to be a powerful synthesis route: It provides direct access to high-temperature single-phase states at the nanoscale without post-annealing, thereby preventing grain coarsening, preserving high surface area, and yielding faceted morphologies. Taken together, these features highlight the outstanding potential of spray-flame synthesis for designing compositionally complex oxides with unique morphologies.

OER Activity of Co-Based Catalysts: From Molecular Catalysts to Heterogeneous Spinel

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Water electrolysis is a key technology for sustainable hydrogen production, but its efficiency is limited by the slow kinetics of the oxygen evolution reaction (OER).[1] Developing efficient and stable electrocatalysts is therefore essential.[2] In this work, spinel-type cobalt oxide Co₃O₄ nanocubes with controlled transition-metal doping were synthesized using a hydrothermal method to systematically investigate how composition and surface structure influence OER activity. By introducing different dopant cations and comparing their catalytic performance, clear correlations between electronic structure, surface composition, and electrocatalytic behavior were identified.[3] Certain dopants (e.g. Cr) significantly enhanced OER activity, approaching the performance of benchmark catalysts, while others (e.g. Mn) reduced catalytic efficiency. Additional thermal treatment of the pristine Cr-doped sample revealed dopant segregation effects at the particle surface, further influencing catalytic activity. These results highlight the importance of both bulk and surface composition in determining the activity of cobalt-based OER catalysts and provide insights into the rational design of nanostructured electrocatalysts for water electrolysis. Moreover, Molecular catalysts based on Co-oxo complexes represent structural motifs of the spinel catalysts. Co-oxo complexes were synthesized, characterized and showed OER activity, with possible formation of CoO_x(OH)_y deposits as active species during OER.

[1] H. M.A. Amin, M.A. Sani, A. El Arrassi, S. Saddeler, S. Schulz, K. Tschulik, *ChemCatChem* **2025**, 17, e01234

[2] C. Placke-Yan, G. Bendt, S. Salamon, J. Landers, H. Wende, U. Hagemann, S. Schulz, *Materials Adv.* **2024**, 5, 3482-3489

[3] C. Placke-Yan, H.M. Amin, G. Bendt, U. Hagemann, S. Schulz, *ChemRxiv*, **2025**, 2025, 1016

[4] S. Karwasara, X. Ma, H. M.A. Amin, T. Fockenberg, G. Kanu, C. Wölper, S. Disch, S. Schulz, *Inorg. Chem.* **2026**, accepted

MatInf RDMS for Materials Data Integration in CRC/TRR 247

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The development of a Research Data Management System (RDMS) for CRC projects presents significant challenges, particularly in terms of providing a reliable infrastructure for geographically distributed research teams and ensuring flexibility in handling heterogeneous research data. Within the INF project of CRC/TRR 247, not only a fault-tolerant hardware infrastructure has been established, but also an extensible, open-source RDMS for inorganic materials science has been developed [1]. A distinctive feature of the proposed system is its configurable user-defined data type system, which can be flexibly adapted to the specific requirements of materials research. The stepwise extension of the system with services responsible for processing specific types of research data enables structured storage and analysis, while supporting a gradual transition from a document-oriented paradigm to a fact-centric approach [2]. This paradigm facilitates the effective integration of heterogeneous information (Fig. 1), thereby enabling advanced multidimensional analysis of materials science data.

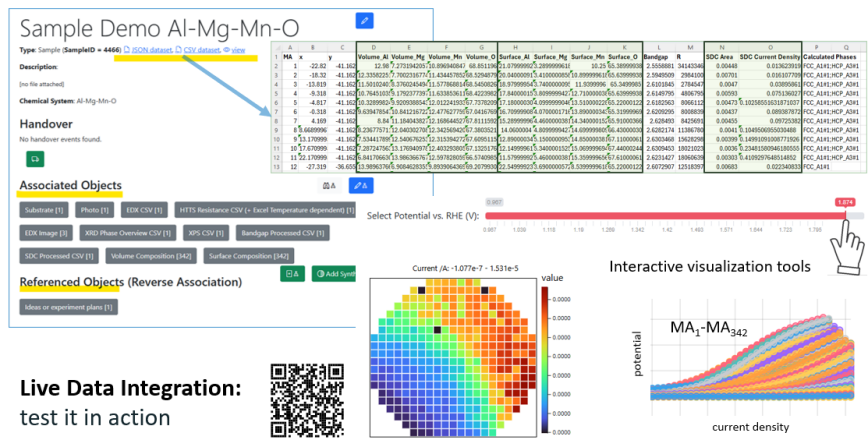


Figure 1: Data integration in CRC/TRR 247 as the sample-oriented workflow outcome.

[1] V. Dudarev, L. Banko, A. Ludwig, *npj Comput Mater*, **2025**, 11, 116, DOI: 10.1038/s41524-025-01618-1.
[2] V. Dudarev, A. Ludwig, *J Cheminform*, **2026**, DOI: 10.1186/s13321-026-01180-y.

Optimized flavin triplet sensitization by ring contraction – A photophysical study

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Ring-contracted flavins represent a newly developed class of organic triplet sensitizers with great promise as synthetic tools. Compared to unmodified flavins, they exhibit higher triplet-state energies, enabling a broader range of substrates.[1] We investigated the influence of substitution at the aromatic ring (see Figure 1) on the photophysical properties of ring-contracted flavins using a combination of steady-state and time-resolved methods, including femtosecond transient absorption (TA).

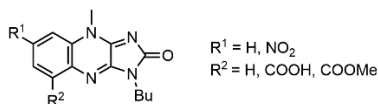


Figure 1: Structure of the studied ring-contracted flavins.

Our TA measurements show the formation of a triplet state with time constants of 700 ps or longer, depending on the derivative. As the triplet state's lifetime was too long to be determined within the 1 ns range of our TA experiment, we performed cryogenic measurements to reveal phosphorescence lifetimes on the order of seconds at 77 K. We find that introducing an ester substituent to the flavin increases the triplet formation yield as compared to the unsubstituted ring-contracted flavin. Addition of a nitro group significantly changes the properties of the triplet state compared to the ester-substituted flavin: the triplet energy is lowered and the lifetime is shortened.

We plan to extend our studies from photophysics to photochemistry of ring-contracted flavins, including challenging triplet-sensitized ring-closure reactions in salicylate derivatives. We will measure and improve reaction quantum yields for different ring-contracted flavin variants and for optimized excitation schemes.

[1] A. Rehpenn *et al.*, *Angew. Chem. Int. Ed.*, **2024**, 63, e202318590, 10.1002/anie.202318590

Enantioselective $[6\pi]$ -Photocyclization via Chromophore Activation by Chiral Lewis Acids

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Chiral, AlBr_3 -activated 1,3,2-oxazaborolidines have been employed as photocatalysts to enable the enantioselective $[6\pi]$ cyclization of 3-[(1,1'-biphenyl)-2-yl]-2-methylcyclopent-2-enones. A total number of 21 tetracyclic products were obtained as single diastereomers in 78-99% *ee* and 39-83% yield upon variation of the terminal phenyl ring in the substrate. A strong bathochromic shift of the substrate's absorption upon coordination to the Lewis acid enables the selective excitation of the catalyst-substrate complex at suitable wavelengths, which allows for catalyst loadings as low as 2.5 mol% while retaining excellent enantioselectivity. DFT calculations provide evidence for a two-point binding motif, where the carbonyl oxygen atom of the substrate is coordinated to the Lewis-acidic boron atom of the oxazaborolidine, while hydrogen bonding between a methylene proton and the oxygen atom of the heterocycle locks the orientation of the substrate relative to the chiral catalyst. This induces a helical conformation which is responsible for enantioface differentiation in the cyclization of the substrate.

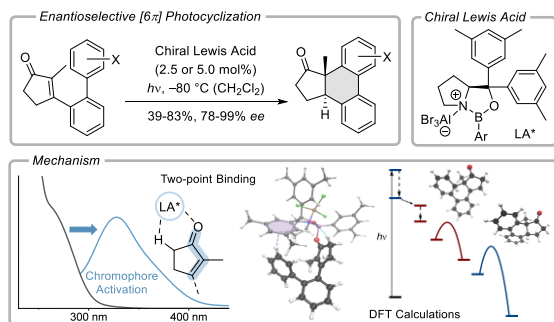


Figure 1: Graphical Abstract

[1] D. Grünwald, C. Mohan Jayakumari, N. Jeremias, J. Zuber, C. J. Stein, T. Bach, *J. Am. Chem. Soc.* **2025**, *147*, 46525, DOI: 10.1021/jacs.5c17390.

Solvent-Selective Photoinduced Transformations of Pyridine–BCl₃ Lewis Complexes

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Lewis acid–base adducts play a central role in catalysis, yet their excited-state reactivity is poorly understood. We investigate the photochemistry of pyridine–BCl₃ under protic and aprotic conditions using in situ multinuclear NMR and computations. In contrast to pyridinium systems, which typically undergo ring contraction in protic media [1], pyridine–BCl₃ shows inverse solvent selectivity. In methanol, UV irradiation induces chloride abstraction to form a pyridine–BCl₂⁺ cation with chloride counterion, consistent with boronium-type species [2,3]. In acetonitrile, however, a distinct pathway leads to ring contraction and formation of a BCl₂-coordinated cyclopentene derivative in the presence of trace water, resembling related solvent-dependent Lewis adduct and pyridinium chemistry [4,5]. NMR spectroscopy and computations confirm the structures and reveal strong solvation effects governing the reactivity [6,7]. These results demonstrate that subtle changes in solvation can invert photochemical pathways in Lewis acid–base systems.

[1] T. Damiano et al., *Org. Biomol. Chem.*, 2007, DOI: 10.1039/b706244n:

[2] S. Coffie et al., *Angew. Chem. Int. Ed.*, 2015, DOI: 10.1002/anie.201508653

[3] D. P. Schwinger et al., *J. Am. Chem. Soc.*, 2022, DOI: 10.1021/jacs.2c06683

[4] R. Ling and P. S. Mariano, *J. Org. Chem.*, 1998, DOI: 10.1021/jo980855i

[5] R. Ueno et al., *Nat. Commun.*, 2025, DOI: 10.1038/s41467-025-57527-w

[6] C. Feldmeier et al., *J. Magn. Reson.*, 2013, DOI: 10.1016/j.jmr.2013.04.011

[7] P. Erdmann and L. Greb, *Angew. Chem. Int. Ed.*, 2022, DOI: 10.1002/anie.202403356

Bifunctional Chiral Phosphoric Acids as Sensitisers for Enantioselective Dearomative [2+2] Photocycloadditions

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The dearomative [2+2] photocycloaddition represents a powerful synthetic strategy for transforming planar, (hetero)aromatic precursors into complex, three-dimensional molecular scaffolds. Achieving enantiocontrol over the up to four generated stereogenic centers is challenging due to the high reactivity of photoexcited states. To address this limitation, we incorporate sensitising moieties directly into the catalyst structure. Efficient energy transfer in this system occurs only when the substrate is preorganized in the chiral pocket of the catalyst at the moment of excitation.^[1] Building on this concept, we are developing a method for the dearomative [2+2] cycloaddition of *N*-protected indole-2-carboxylic acids. While structurally related molecules have been reported to undergo racemic reactions by sensitisation, an organocatalytic approach to enantioenriched products remains elusive.^[2] As a catalyst platform, we envision a C₂-symmetric chiral phosphoric acid bearing two thioxanthone moieties, which serve both as photosensitisers and as steric bulk.^[1]

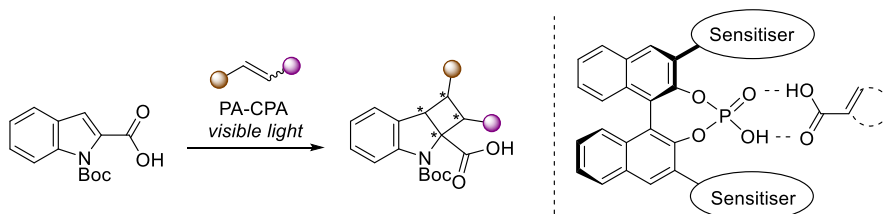


Figure 1: General reaction scheme (left) and the catalyst-substrate complex, stabilized by hydrogen-bonding interactions with the carboxylic acid (right).; (PA-CPA = photochemically active chiral phosphoric acid)

[1] F. Pecho *et al.*, *Chem. Eur. J.* **2020**, *26*, 5190 – 5194, 10.1002/chem.202000720.

[2] M. Oderinde *et al.*, *J. Org. Chem.* **2021**, *86*, 1730–1747, 10.1021/acs.joc.0c02547.

Mechanistic and Computational Insights into Enantioselective Photocatalysis with Lewis Acid–Activated Oxazaborolidines

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In recent years, photocatalytic transformations have emerged as powerful tools in asymmetric synthesis [1], offering new ways to control reactivity and selectivity through light-induced processes. However, understanding and predicting the enantioselectivity in catalyzed reactions remains highly challenging due to the complex interplay between excited-state dynamics, non-equilibrium effects, and stereochemical control.

This work aims to establish a computational workflow for modeling the enantioselectivity of photocatalytic processes mediated by chiral oxazaborolidine catalysts activated by the Lewis acid AlBr_3 [2]. We focus on combining ground-state electronic-structure methods with conformer sampling [3] and an analysis of non-covalent interactions in the chiral environment to describe how substrate binding and Lewis-acid activation shapes the corresponding stereochemical outcome. The proposed protocol is designed to predict enantioselectivity trends across different catalyst–substrate combinations and to provide mechanistic insight into the origin of chiral induction in these systems.

In parallel, we outline how these theoretical approaches can be coupled with transient absorption spectroscopy experiments, using calculated excited-state energetics and spectral signatures to support the assignment of experimental transients and to identify key intermediates along the photocatalytic pathway. By integrating predictive computations with time-resolved spectroscopy, this contribution aspires to deliver a general framework for elucidating mechanisms and guiding the rational, in-silico optimization of enantioselective photocatalytic reactions.

[1] F. Liu, X. Peng, J. Yu, X. Huang, *Org. Chem. Front.*, 12, 16 (**2025**) 4608–4634.

[2] S. Stegbauer, C. Jادل, T. Bach, *Chemical Science*, 13, 40 (**2022**) 11856–11862.

[3] P. Pracht, S. Grimme, C. Bannwarth, F. Bohle, S. Ehlert, G. Feldmann, J. Gorges, M. Müller, T. Neudecker, C. Plett, S. Spicher, P. Steinbach, P.A. Wesolowski, F. Zeller, *J. Chem. Phys.*, 160, 11 (**2024**) 114110.

Interrogating Open-Shell Intermediates with Time-Resolved EPR

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Many photoinduced reactions involve transient species with unpaired electrons like triplet states or radicals [1]. Common time-resolved spectroscopic techniques like transient absorption (TA) spectroscopy or time-correlated single photon counting (TCSPC) monitor the reaction dynamics of either all components involved in the reaction or only of bright states, respectively. In contrast to that, electron paramagnetic resonance (EPR) spectroscopy allows for selective observation of single reactive intermediates making use of their unpaired electron spins. Especially time-resolved EPR spectroscopy (TR-EPR) can provide valuable insights into the reaction and spin dynamics of even short-lived intermediates [2].

This contribution introduces two customized EPR spectrometers to monitor dynamics in direct detection mode (DD-TR-EPR) [3] and the ultrawide single sideband phase sensitive detection (U-PSD-EPR) which was recently introduced by Guo *et al.* [4], respectively. It reintroduces PSD into TR-EPR enabling the complete observation of the intermediates starting from their laser-induced creation until reaching their thermal equilibrium which is heavily complicated in DD-TR-EPR if possible, at all.

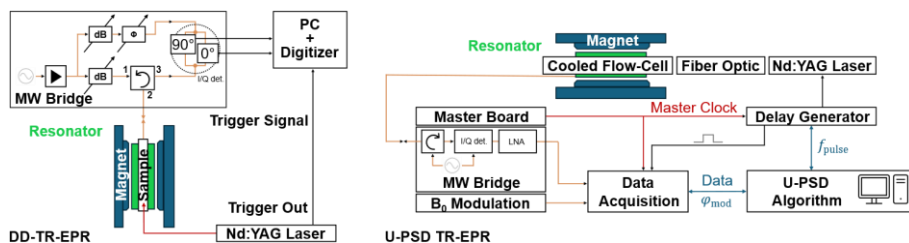


Figure 1: The DD (left) and U-PSD approach (right) in TR-EPR. Customization of the microwave bridge and reimplementing of the data acquisition of a commercial EPR spectrometer enables the recording of TR-EPR spectra of CIDEP signals. U-PSD EPR is realized via synchronization of laser and data acquisition to the master clock of a commercial table-top EPR spectrometer utilizing the U-PSD algorithm as published by Guo *et al.*

[1] J. Rehbein *et al.*, *Nature*, **2024**, 632, 550-556, 10.1038/s41586-024-07622-7

[2] S. Weber, *eMagRes*, **2017**, 6, 255-270, 10.1002/9780470034590.emrstm1509

[3] S. I. Weissman *et al.*, *J. Magn. Reson.*, **1976**, 24, 167-169, 10.1016/0022-2364(76)90243-2

[4] X. Guo *et al.*, *Rev. Sci. Instrum.*, **2023**, 94, 084101, 10.1063/5.0143480

Exploring Substituent Effects on Triplet Sensitization with Ring-contracted Flavins

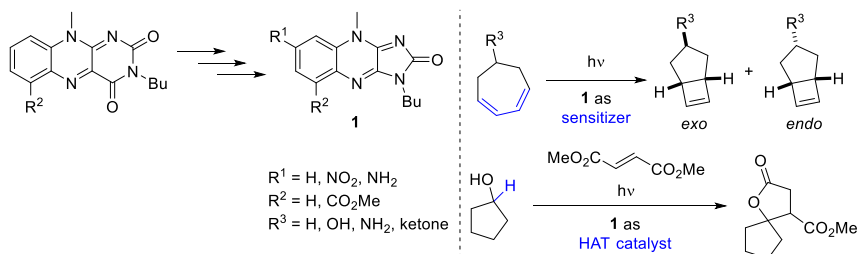
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Flavin catalysts can be used in a wide range of applications in photochemistry [1]. The addition of hydroxide base to flavin catalysts induces a sequence of reactions that leads to a new class of ring-contracted analogues [2]. Compared to the parent compound (–)-riboflavin, these ring-contracted flavins exhibit substantially higher triplet energies, amongst other improved photophysical parameters. This property makes them promising catalysts for triplet sensitization with an envisioned broadened substrate scope. A series of ring-contracted flavins (**1**) bearing different substituents on the aromatic core was synthesized and investigated by spectroscopic techniques. We chose the sensitization of cycloheptadiene as a test reaction for triplet energy transfer, since it leads to synthetically interesting bicycloheptene products. Our ongoing studies aim at elucidating the influence of catalyst substitution on the efficiency and diastereoselectivity of the catalytic reaction. In an orthogonal reaction, ring-contracted flavins are also active hydrogen atom transfer (HAT) catalysts, which we confirmed by the formation of spirocyclic lactones derived from cyclopentanol.



Future studies aim for a holistic understanding of the influence of catalyst substitution on photophysical properties and, ultimately, catalytic efficiency.

[1] V. Srivastava et al., *RSC Adv.* **2021**, *11*, 14251–14259, 10.1039/D1RA00925G.

[2] A. Rehpenn et al., *Angew. Chem. Int. Ed.* **2024**, *63*, e202318590, 10.1002/anie.202318590.

Rewriting Copper Catalysis: Chlorosulfonylation of Alkenes through a Cu(II)/Cu(III) Pathway

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Photocatalytic atom transfer radical addition (ATRA) reactions [1] are typically associated with a Cu(I)/Cu(II) redox cycle. In contrast, the copper complex bearing the rigid dpc (3,6-di-*tert*-butyl-1,8-di(pyridin-2-yl)-9*H*-carbazole) ligand [2] enforces a planar geometry that suppresses flattening distortion [3]. Using the chlorosulfonylation of alkenes as a model reaction, we demonstrate that oxidation of the Cu(dpc)OAc complex can initiate and sustain the catalytic cycle. Preassembly of the Cu(II) complex with a sulfonyl reagent allows light-driven formation of a Cu(III) species accompanied by generation of a sulfonyl radical, which is then trapped by the olefin, generating a radical species. Subsequent single-electron transfer regenerates the Cu(II) complex and forms a carbocation that undergoes nucleophilic addition by the chloride ion, giving the desired ATRA product. These results reveal a Cu(II)/Cu(III) photocatalytic manifold for ATRA-type transformations.

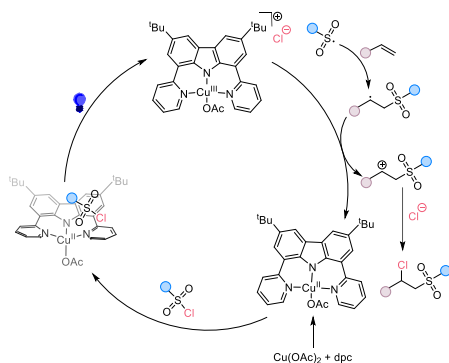


Figure 1: Proposed Cu(II)/Cu(III) reaction mechanism for Chlorosulfonylation.

[1] M. S. Kharasch *et al.*, *Science* **1945**, 102, 128, 10.1126/science.102.2640.128

[2] N. Sinha *et al.*, *Angew. Chem. Int. Ed.* **2021**, 60, 23722–23728,
10.1002/anie.202106398

[3] M. Iwamura *et al.*, *Acc. Chem. Res.* **2015**, 48, 782–791, 10.1021/ar500353h

Copper (II)-Photocatalyzed Radical Anellation of Nitroalkanes with Alkenes or Alkynes for the Synthesis of Isoxazoles and Isoxazolines

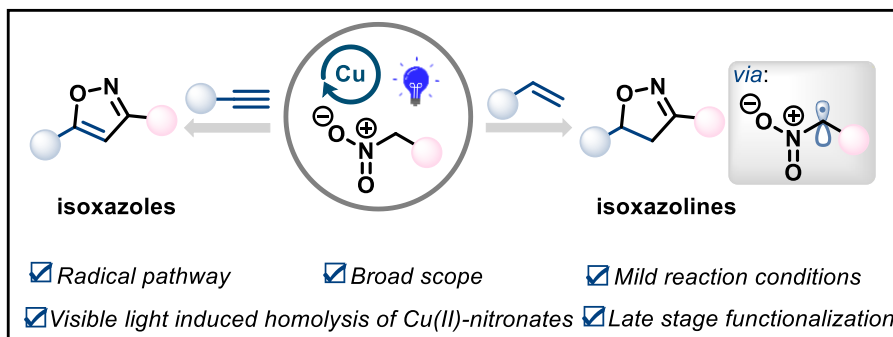
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The synthesis of heterocyclic compounds, particularly isoxazoline and isoxazole, has garnered significant attention due to their versatile pharmacological properties and synthetic utility.¹ Classical approaches for the synthesis of heterocycles are 1,3-dipolar cycloadditions.² So, hereby we report the visible light-mediated copper (II)-catalyzed one-step synthesis of isoxazoles and isoxazolines from readily available ethyl nitroacetate or phenyl nitromethane. The developed protocol eliminates the need for substrate preactivation or additives and offers an extensive scope of activated and unactivated alkenes and alkynes as coupling partners. Key intermediates for this formal [3+2]-cycloaddition are α -nitro radicals generated via photoinduced single electron oxidation of nitronates, contrasting the generation of such radicals via Cu(I)-photocatalysis by a reductive pathway, which shows a different reaction pattern in the coupling with alkenes.



References:

- [1] (a) L. Brunton, B. A. Chabner and B. Knollman, Goodman and Gilman's The Pharmacological Basis of Therapeutics, McGraw Hill, New York, 12th edn, **2011**; (b) K. A. Kumar, M. Govindaraju, N. Renuka and G. V. Kumar, J. Chem. Pharm. Res., **2015**, 7, 250; (c) F. Hu and M. Szostak, Adv. Synth. Catal., **2015**, 357, 2583; (d) J. Sperry and B. Wright, Curr. Opin. Drug Discovery Dev., **2005**, 8, 723.
- [2] (a) T. M. V. Pinho e Melo, Curr. Org. Chem., **2005**, 9, 925; (b) M. W. Davies, R. A. J. Wybrow, C. N. Johnson and J. P. A. Harrity, Chem. Commun., **2001**, 1558; (d) F. Himo, T. Lovell, R. Hilgraf, V. V. Rostovtsev, L. Noodleman, K. B. Sharpless and V. V. Fokin, J. Am. Chem. Soc., **2005**, 127, 210.

Eosin Y Disproportionation Promoted Alkene Hydrofunctionalizations in Fluorinated Assemblies

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Alkenes are one of the most versatile functional groups in organic synthesis due to the π -character of the double bond. Over the past decade, photoredox catalysis has emerged as a powerful tool for functionalizing alkenes using milder conditions. However, it often necessitates the use of photocatalysts with strong oxidizing potential. Remarkably, the developed methods are limited to alkenes with an oxidation potential of less than 2 V, which excludes most unconjugated alkenes.^[1] In this context, fluorinated alcohols, (R_fOH) thanks to fluorine's exceptional physicochemical properties,^[2] can modulate the physical properties of photocatalysts due to their strong hydrogen-bonding affinity. Recently, our group observed the disproportionation of Eosin Y (EY) to $EH^\bullet$ and $EH_3^\bullet$ in the presence of fluorinated solvents during photocatalytic polyene cyclizations. This clearly demonstrates the indispensable nature of the interaction between EY and R_fOH , since direct oxidation of the alkene ($E_{ox} \approx 2$ V vs SCE) by excited EY ($E_{Red} (^3EH_2^*/EH_2^{\bullet-}) = 0.83$ V vs SCE) is chemically impossible.^[3] Herein, we present our work on developing mild and selective hydrofunctionalization beyond the limits of alkenes' photooxidation.

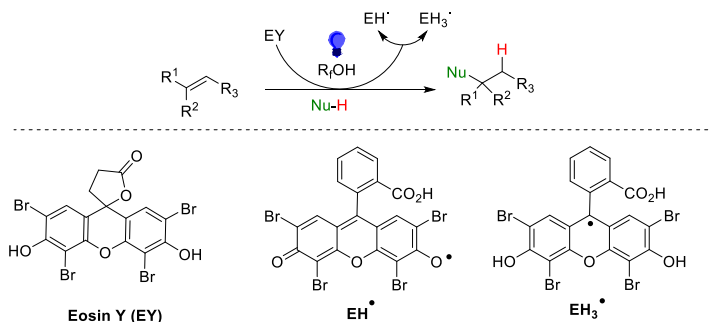


Figure 1: Eosin Y Disproportionation Promoted Alkene Hydrofunctionalization in Fluorinated Assemblies.

[1] (a) D.-G. Yu, *et al.*, Chem. Soc. Rev. **2025**, 54, 6726, <https://doi.org/10.1039/d5cs00181a>; (b) T. Ritter *et al.*, J. Am. Chem. Soc. **2025**, 147, 4736, <https://doi.org/10.1021/jacs.4c18185>. [2] J. Xiao *et al.*, Chem. Rec. **2020**, 20, 142. [3] T. Gulder *et al.*, **2025** <https://doi.org/10.26434/chemrxiv-2025-hx8h0>

1,2- Aminosulfonylation of Alkenes via a Photoexcited Cu(I)- Substrate Complex: A Three Component Coupling Approach

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Copper photocatalysis has emerged as a mild and energy efficient alternative for different atom transfer radical addition (ATRA) type of processes, creating plethora of possibilities for simple procedures to construct intricate molecular structures.¹ We report a Cu(I)-photocatalyzed three-component coupling process to achieve regioselective, vicinal 1,2-aminosulfonylations of alkenes. The critical aspect of this methodology is found in the utilization of in situ generated photoactive Cu(I)- amine substrate complexes,² which facilitate the formal oxidation of Cu(I) to Cu(III) in a stepwise manner. In this way, the conceivable two-component chlorosulfonylation of alkenes is effectively suppressed, allowing the combination of styrene derivatives, sulfonyl chlorides, and amines. Furthermore, this protocol can be used to facilitate late-stage functionalization, thereby enabling the diversification of biomolecules.³

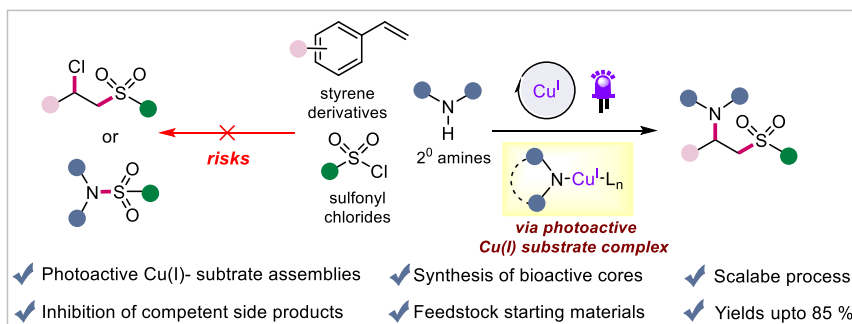


Figure 1: Schematic approach for 1,2-Aminosulfonylation of Alkenes

[1] Engl, S.; Reiser, O. Copper-Photocatalyzed ATRA Reactions: Concepts, Applications, and Opportunities. *Chem. Soc. Rev.* **2022**, 51, 5287–5299.

[2] Bissember, A. C.; Lundgren, R. J.; Creutz, S. E.; Peters, J. C.; Fu, G. C. Transition-Metal-Catalyzed Alkylations of Amines with Alkyl Halides: Photoinduced, Copper-Catalyzed Couplings of Carbazoles. *Angew. Chem., Int. Ed.* **2013**, 52, 5129–5133.

[3] Syu, J.-F.; Gopula, B.; Jian, J.-H.; Li, W.-S.; Kuo, T.-S.; Wu, P.-Y.; Henschke, J. P.; Hsieh, M.-C.; Tsai, M.-K.; Wu, H.-L. Asymmetric Synthesis of β -Aryl β -Imido Sulfones Using Rhodium Catalysts with Chiral Diene Ligands: Synthesis of Apremilast. *Org. Lett.* **2019**, 21, 4614–4618.

From Sparse Experimental Data to Reaction Discovery: Machine Learning in AD-HoC Nickel Cross-Couplings

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Machine learning has emerged as a promising tool for advancing experiment optimization, but experimental datasets remain challenging: they are expensive to generate, often sparse and biased, and intrinsically noisy. Consequently, many machine learning studies rely either on nearly noise-free theoretical data or on highly curated databases from experiments that are often limited in chemical space and accuracy. Here, we investigate the potential of machine learning for predicting yields in AD-HoC nickel cross-couplings under photoredox conditions [1]. The reaction space is characterized by broad chemical diversity and high dimensionality with over $19 \cdot 10^6$ possible combinations of reactants. To navigate this space effectively and enable yield prediction with machine learning, we develop and apply a genetic algorithm to identify an informative subset of reactions for model training. The resulting models were then applied to virtual high-throughput screening of the whole chemical space to identify regions of high reaction yield, model uncertainty, and untested combinations. Comparison to expert predictions reveals insights into biases and limits of both machine learning algorithms and human intuition and shows how to overcome bottlenecks in real-world chemical optimization, enabling navigation of vast chemical spaces.

[1] I. Ghosh *et al.*, *Nature*, **2023**, 619, 87-93, 10.1038/s41586-023-06087-4.

The Synergy of EPR Spectroscopy and Computational Chemistry toward Unveiling Open-Shell Intermediates in Photocatalysis

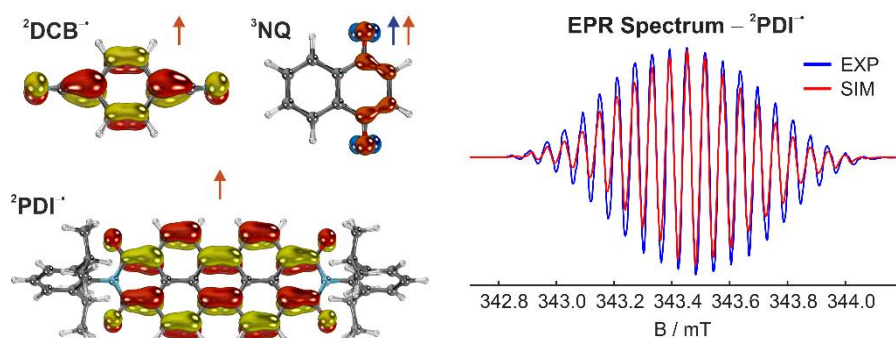
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Open-shell intermediates relevant to photocatalysis, such as radicals and triplet states, are unveiled through the combined use of electron paramagnetic resonance (EPR) spectroscopy and computational methods. Visible-light-induced single-electron transfer generates long-living 1,4-dicyanobenzene (DCB) and perylene diimide (PDI) radical anions from their neutral precursors. Their electronic structures are resolved via hyperfine interactions of the unpaired electron with H and N nuclei across the π -system. Spin-Hamiltonian simulations further bridge experiment and theory, providing quantitative agreement between observed and calculated EPR spectra. In parallel, the reactive $n\pi^*$ and $\pi\pi^*$ triplet states of 1,4-naphthoquinone (NQ) are identified using DFT and multiconfigurational approaches. Hydrogen-bond stabilization of both the ground and excited states of NQ in water facilitates photosensitization and the redox-neutral Friedel–Crafts acylation of NQ.^[1]

Finally, recent advances in the development of us-ns time-resolved EPR are highlighted for probing the formation and fate of highly reactive paramagnetic species in photocatalytic processes (see our instrumentation poster as well).



- [1] T. Mandal, R. Sharma, **E. Mendez-Vega**, J. Rehbein, B. König, *Nat Commun*, 2026, 17, 1813, <https://doi.org/10.1038/s41467-026-69343-x>.

Photocatalytic denitrative homo- and cross-coupling of nitroalkanes towards the synthesis of alkenes

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Abstract text: Alkenes serve as fundamental motifs across natural products and synthetic molecules, yet efficient, mild, and versatile olefination strategies remain in demand. Nitroalkanes, renowned for their broad reactivity as nucleophiles or corresponding radicals,¹ still offer untapped potential in photocatalysis. Here, we report a unified, photocatalyzed generation of α -nitroalkyl radicals through oxidation of simple, non-prefunctionalized nitronates, followed by a radical addition to another nitronate (formal homo- or cross-coupling) with subsequent double denitration to furnish alkenes. This transformation leverages both the pro-nucleophilic and pro-electrophilic nature of nitroalkanes, challenging the classic *McMurry*-type coupling protocol, as well as alkene metathesis. Moreover, the synthetic manifold is scalable and demonstrates its applicability through the synthesis of medicinally relevant Combretastatin. Additionally, we report a second pathway for nitroalkanes, as they undergo a cross-coupling reaction with malonate radicals under photocatalysis *via* a heteroleptic Cu(I)-catalyst.² A novel charge-transfer mechanism furnishes the generation of two radicals, that are subsequently coupled selectively allowing the formation of Knoevenagel-type alkene products.

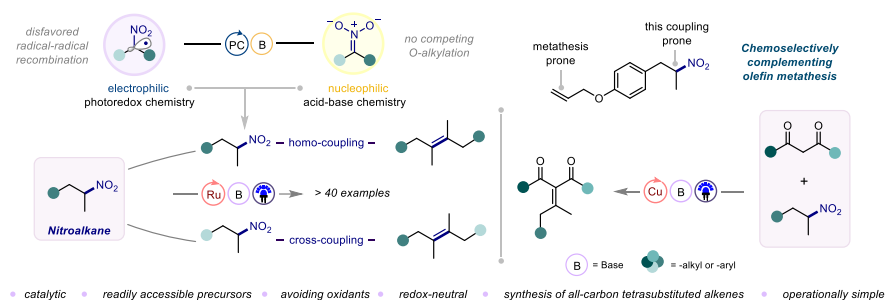


Figure 1: Photocatalytic homo- and cross-coupling of nitroalkanes (left), Photocatalytic cross-coupling of nitroalkanes and malonates (right).

[1] N. Kornblum *et al.*, *J. Am. Chem. Soc.* **1971**, 93, 4316-4318, <https://doi.org/10.1021/ja00746a051>. [2] T. Mandal, M. Ghosh *et al.*, *Nat Catal* **2025**, 8, 607–622. <https://doi.org/10.1038/s41929-025-01357-y>.

Lumi's Delight - A Comic Book

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Lumi's Delight - a scientific Comic Book for young readers aged 6-10 years and all adults young at heart!



Lumi is an educational comic that follows Lumi, a curious ray of sunlight, on its journey from the Sun to Earth. Along the way, Lumi explores how daylight interacts with the natural world, visiting a variety of ecosystems and learning how light influences life on our planet. The comic introduces both young readers and adults to the science of light and its essential role in biological processes, such as photosynthesis and circadian rhythms. Lumi meets plants, animals, and even microorganisms, uncovering the connections between sunlight and the rhythms of life on Earth. The aim of the comic is to inspire curiosity about natural phenomena, foster scientific literacy, and raise awareness about the importance of daylight in our daily lives. The book is available for free in several languages. (<https://tscnlab.github.io/LumisDelight/>)

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