

4th International Conference
on **Proton-Coupled Electron Transfer**

June 5-9, 2023 | Port Aventura, Spain



**CHEMICAL
REVIEWS**

**ACS APPLIED
ENERGY MATERIALS**



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1. Welcome to PCET 2023

It is a real pleasure to welcome you to the 4th International Conference on Proton-Coupled Electron Transfer. This conference follows successful meetings in France (2011), Sweden (2014) and the United States of America (2018). Each of these meetings has brought together researchers from various sub-disciplines of the field and provided a venue for these scientists to share their latest results and engage in discussion on emerging and exciting work in the area of PCET. The program in this 4th PCET meeting reflects the growing diversity and expansion of this interdisciplinary field covering organic, enzymatic, catalytic, theoretical and materials chemistry.

It is exciting to welcome so many experts in the field as well as the newcomers to their first-ever PCET conference. It is my hope that the scientific presentations will cultivate enthusiastic discussion in formal and informal settings, and that this gathering of researchers from around the world will lead to continued advancements in the field of proton-coupled electron transfer.

This conference would not have been possible without the hard work and contributions of many people. I want to thank the members of the International Advisory Board, especially Jillian Dempsey, the organizer of PCET2018, for their guidance in the development of this edition's program.

Anna M. Beiler and Carlos Garcia Bellido have done tremendous work as members of the Local Host Committee helping in all aspects of the conference including logistics, and will continue working tirelessly this week to ensure the success of the meeting. I also want to thank the team at ICIQ including Anna Lopez Grau, Judit Martinez, and Laia Plana Mendoza for their support. Also, I thank our sponsors that have generously provided financial support for this meeting.

Most of all, I want to thank all of you for making the journey to PortAventura in Tarragona to participate in this meeting. If there is anything we can do to help make your experience a more positive one, please do not hesitate to ask.

Most sincerely,

Antoni Llobet

2. Meeting and Venue Information

Wireless Connection

ConventionCenter

Events2023

Inappropriate Behavior

PCET2018 will provide a welcoming and inclusive environment for all attendees. Scientific debate is highly encouraged and should be carried out in a manner that is respectful to all attendees. Inappropriate behavior—including harassment (including sexual harassment), property destruction, or violation of laws—will not be tolerated. Inappropriate, suggestive, offensive, and/or unwelcome comments related to an attendee or guest's gender, gender identity or expression, race, religion, ethnicity, age, or disability are expressly forbidden. Any attendee who feels they have been subjected to comments or acts that violate this Inappropriate Behavior act should promptly report their concerns to the conference chair. All matters will be handled discretely.

Recording Policy

All presentations at PCET2018 are off the record. No audio or video recording is permitted, and photography of slides and posters is strictly forbidden. No scientific content reported at this meeting should be shared via social media, blogs, or in scientific publications without written permission from the presenters. Attendees are welcome to take photographs at social events and share their enthusiasm for the meeting via social media following the above policies.

Group Photo

The group photo will take place Wednesday, June 7, directly before lunch.

Map of Resort



HABITACIONES ROOMS

- 1 Aruba (101-128)
- 2 Barbados (201-242)
- 3 Curaçao (301-342)
- 4 Dominica (401-428)
- 5 La Española (501-542)
- 6 Franciscita (601-628)
- 7 Club San Juan (701-729) Premium Rooms
- 8 Guadalupe (801-842)
- 9 Haití (901-928)
- 10 isla Margarita (1001-1042)
- 11 Jamaica (1101-1142)
- 12 St. Kitts (1201-1242)
- 13 Long Island (1301-1342)
- 14 Martinica (1401-1428)

RESTAURANTES RESTAURANTS

- 15 Puerto Viejo
- 16 La Piazza
- 17 El Tinglado
- 18 Buffet el Bohío
- 19 Salsa Café
- 20 Mango Bongo
- 21 La Bodeguita del Medio

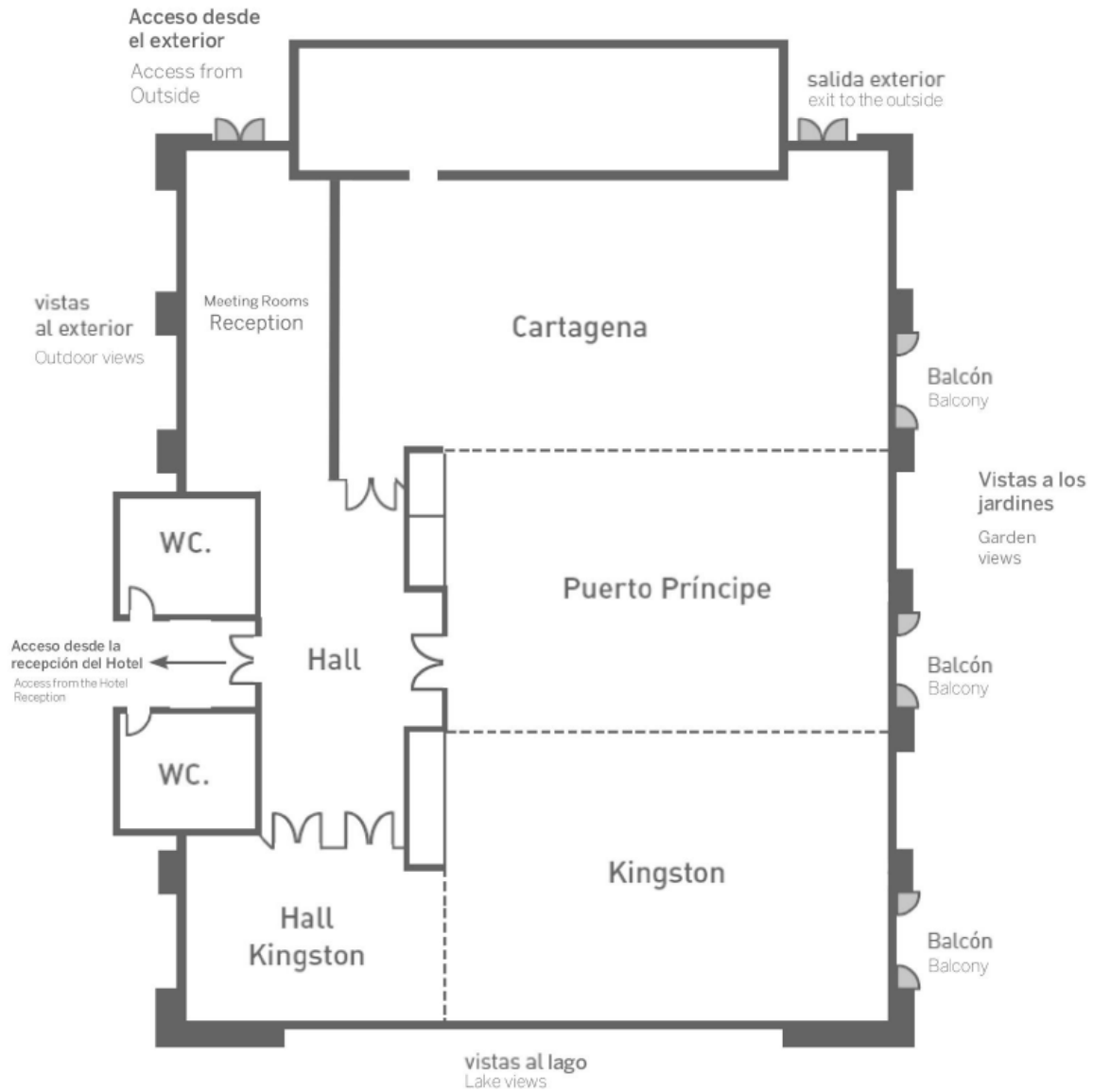
SALAS DE REUNIÓN MEETING ROOMS

- 23 La Habana

OTROS SERVICIOS OTHER SERVICES

- 24 Fitness Center & Spa
- 25 Voley Playa / Beach Volleyball
- 26 Piscinas / Swimming Pool
- 27 Mini Football

Map of Meeting Area



Location Details

If you are staying at Hotel Caribe, check in for the room in the *Hotel Caribe lobby*. **Breakfast** is included with the room reservation and will be served in *Buffet el Bohío*, located downstairs directly beneath the meeting space.

All conference events will take place in the meeting area *La Habana* (see resort map). **Lunch** is included in the conference registration and will be served in *Buffet el Bohío*, located downstairs directly beneath the meeting space.

Conference check-in will be in the hall outside *Kingston Room*.

All talks will take place in the *Kingston Room*.

Refreshment breaks and poster sessions will be held in *Puerto Principe*.

Dinner is not included in the conference package. For those staying at Hotel Caribe, you have the option to reserve spots at the on-site restaurants through the hotel app (a reservation is needed). Feel free to explore other restaurants in the beach town of Salou, or visit Tarragona's historic Part Alta for dinner. Salou can be reached by foot (15-30 minutes) or by car or taxi (<10 minutes). Tarragona is a 12-minute train ride or a 20-minute car or taxi trip. Don't hesitate to ask the Organizing Committee or local attendees from ICIQ for recommendations!

Excursion Details

If you have signed up for the excursion to the Poblet Monastery, please meet outside in front of the Hotel Caribe lobby at 15:15h on Wednesday, June 7. The bus will board promptly at **15:30h**.

If you have signed up for the conference dinner, please arrive at the Carbonic Restaurant in Salou by **20:00h** on Wednesday evening. The address is: Carrer Major, 55, Salou. It can be reached by walking (15 min), car, or taxi. If you would like to walk from the conference center, please meet outside in front of the Hotel Caribe lobby at 19:30h.

3. Block Schedule

	Monday 5 th June	Tuesday 6 th June	Wednesday 7 th June	Thursday 8 th June	Friday 9 th June	
9.00 h		Oliver Wenger & Murielle Delley	James Mayer	Sven Stripp	Gerald Meyer	9.00 h
		Andrea Sartorel	Veronica Augustyn	Moritz Senger	Poster flash talks	
10.00 h		Wenjing Song		John W. Peters	Ana Moore	10.00 h
		Alexander Miller	Véronique Balland	Holger Dau	Closing Ceremony	
11.00 h		Ellen Matson		Coffee Break	Coffee Break	11.00 h
		Coffee Break	Poster session B	Ming-Tian Zhang		
12.00 h		Jonas Peters		Matthew Chambers		12.00 h
		Helena Roithmeyer	Yogesh Surendranath	Sven Schneider		
13.00 h		Timothy Warren	Cyrille Costentin	Ally Aukauloo		13.00 h
		Marcos Gil-Sepulcre	Sascha Ott			
14.00 h		Lunch	Lunch	Lunch		14.00 h
		Vincent Artero		Pablo Garrido Barrios		
15.00 h		Sergio Gonell	Free time	Inke Siewert		15.00 h
		Ana M. Geer		Stephan Kupfer		
16.00 h		Marc Robert		Ludovic Troian Gautier		16.00 h
		Noémie Elgrishi		Jia-Wei Wang		
17.00 h		Victor Mougel	Visit to Poblet Monastery	Coffee Break	Poster flash talks 1-2	17.00 h
		Poster session A		Ivana Ivanovic		
18.00 h				Gregorio Guisado-Barros		18.00 h
				Javier Concepcion		
19.00 h						19.00 h
20.00 h			Event Dinner			20.00 h
21.00 h						21.00 h
22.00 h						22.00 h
23.00 h						23.00 h

Invited speakers

Short talk

Poster session

Poster flash talks

*In every poster session there will be a wine / coffee break

4. Detailed Schedule

Monday, June 6, 2023

11:00 — 18:00h	Conference Check-in and Registration
15:15 — 15:30h	Welcoming Remarks by Antoni Llobet (Institute of Chemical Research in Catalonia (ICIQ), Spain)
15:30 — 15:50h	Leif Hammarström (Uppsala University, Sweden) “Free-Energy Dependence of PCET Reaction Rates”
15:50 — 16:00h	Questions and Discussion
16:00 — 16:20h	Sharon Hammes-Schiffer (Yale University, USA) “Hydrogen Tunneling and Excited Vibronic States in Proton-Coupled Electron Transfer”
16:20 — 16:30h	Questions and Discussion
16:30 — 16:40h	Martin Srnec (Czech Academy of Sciences, Czech Republic) “Off-Diagonal Thermodynamics And Its Effect On H-Atom Abstraction Reactivity”
16:40 — 16:45h	Questions and Discussion
16:45 — 16:55h	Matthew Kessinger (University of North Carolina at Chapel Hill, USA) “Reorganization Energies for Interfacial PCET to a Molecular Water Oxidation Catalyst”
16:55 — 17:00h	Questions and Discussion
17:00 — 17:20h	Shane Ardo (University of California Irvine, USA) “Marcus Analysis of Excited-State Proton-Transfer Reactions, and Resulting Applications”
17:20 — 17:30h	Questions and Discussion
17:30 — 17:50h	Cecilia Tommos (Texas A&M University, USA) “Understanding The Thermodynamics and Pcet of Tyrosine and Tryptophan Protein Residues”
17:50 — 18:00h	Questions and Discussion

Tuesday, June 7, 2023

8:00 — 8:45h	Breakfast
9:00 — 9:20h	Murielle Delley / Oliver Wenger (University of Basel, Switzerland) “H-Transfer Reactions with Inorganic Materials and Metal Complexes”
9:20 — 9:30h	Questions and Discussion
9:30 — 9:40h	Andrea Sartorel (University of Padova, Italy) “Photoelectrochemical C-H Activation with Dyes Enabling Proton-Coupled Electron Transfer”
9:40 — 9:45h	Questions and Discussion
9:45 — 9:55h	Wenjing Song (Chinese Academy of Sciences, China) “Atomic Dispersed Metal Catalyzed Selective Hydrogenation Via Proton Coupled Electron Transfer”
9:55 — 10:00h	Questions and Discussion
10:00 — 10:20h	Alexander Miller (University of North Carolina at Chapel Hill, USA) “Mechanistic Insight into Metal Hydride Photochemistry Guides Solar Fuels Catalyst Design”
10:20 — 10:30h	Questions and Discussion
10:30 — 10:50h	Ellen Matson (University of Rochester, USA) “Net H-atom Uptake and Transfer at Polyoxovanadate-Alkoxide Surfaces”
10:50 — 11:00h	Questions and Discussion
11:00 — 11:30h	Coffee Break
11:30 — 11:50h	Jonas Peters (California Institute of Technology, USA) “PCET pathways to catalytic, electrocatalytic, and photo(electro)catalytic nitrogen fixation”
11:50 — 12:00h	Questions and Discussion
12:00 — 12:10h	Helena Roithmeyer (University of Zurich, Switzerland) “Heterogenized Electrocatalytic Ammonia Oxidation with a Supramolecular Host-guest System”
12:10 — 12:15h	Questions and Discussion
12:15 — 12:35h	Timothy Warren (Michigan State University, USA) “Electrocatalytic Ammonia Oxidation by Earth-Abundant Metal Complexes”

12:35 — 12:45h	Questions and Discussion
12:45 — 12:55h	Marcos Gil Sepulcre (Max Planck Institute for Chemical Energy Conversion, Germany) “Water Oxidation Catalysis Using Ruthenium Coordination Oligomers Anchored through Ch- π Interactions”
12:55 — 13:00h	Questions and Discussion
13:00 — 14:30h	Lunch
14:30 — 14:50h	Vincent Artero (Université Grenoble Alpes, CNRS, CEA, France) “Proton Relays in Molecular Electrocatalysis: How Do They Allow for Reversible Behavior?”
14:50 — 15:00h	Questions and Discussion
15:00 — 15:10h	Sergio Gonell (Institute of Advanced Materials (INAM). Universitat Jaume I, Spain) “Protonation Steps in Iridium and Cobalt Organometallic Piano-Stool Complexes for CO ₂ Electroreduction”
15:10 — 15:15h	Questions and Discussion
15:15 — 15:25h	Ana M. Geer (Universidad de Zaragoza, Spain) “Electrocatalytic CO ₂ Reduction by Piperazine-bridged Multinuclear Cobalt Complexes”
15:25 — 15:30h	Questions and Discussion
15:30 — 15:50h	Marc Robert (Université Paris Cité, CNRS, France) “Cascade PCET to CO ₂ with 6 Electrons and 6 Protons Using Molecular Cobalt Catalyst”
15:50 — 16:00h	Questions and Discussion
16:00 — 16:10h	Noémie Elgrishi (Louisiana State University, USA) “Controlling Proton and Electron Transfers to Oxyanions for Water Purification”
16:10 — 16:15h	Questions and Discussion
16:15 — 16:35h	Victor Mougél (ETH Zurich, Switzerland) “From On-Demand Redox Potential Modulation to Catalytic Applications: New Avenues for Synthetic Iron-Sulfur Clusters”
16:35 — 16:45h	Questions and Discussion
16:45 — 18:15h	Poster Session A

Wednesday, June 7, 2023

8:00 — 8:45h	Breakfast
9:00 — 9:20h	James Mayer (Yale University, USA) “PCET Chemistry of Hydrogen at Semiconductor and Metal Interfaces”
9:20 — 9:30h	Questions and Discussion
9:30 — 9:50h	Veronica Augustyn (NC State University, USA) “Aqueous Electrochemistry of Hydrous Transition Metal Oxides”
9:50 — 10:00h	Questions and Discussion
10:00 — 10:20h	Véronique Balland (Université Paris Cité, France) “Proton-insertion Coupled Electron Transfer at TiO ₂ Nanostructured Electrodes”
10:20 — 10:30h	Questions and Discussion
10:30 — 12:00h	Poster Session B
12:00 — 12:20h	Yogi Surendranath (Massachusetts Institute of Technology, USA) “Understanding Interfacial Proton and Hydride Transfer”
12:20 — 12:30h	Questions and Discussion
12:30 — 12:50h	Cyrille Costentin (Univ Grenoble Alpes, DCM, CNRS, France) “Proton Coupled Electron Transfer Molecular Catalysts. Principles and Applications”
12:50 — 13:00h	Questions and Discussion
13:00 — 13:20h	Sascha Ott (Uppsala University, Sweden) “Cation-Coupled Electron Hopping Transport And Redox Conductivity In Metal-Organic Frameworks”
13:20 — 13:30h	Questions and Discussion
13:30 — 15:00h	Lunch
15:30 — 19:00h	Excursion to El Monestir de Poblet
20:00 — 22:00h	Conference Dinner at Restaurant Carbónic

Thursday, June 8, 2023

8:00 — 8:45h	Breakfast
9:00 — 9:20h	Sven Stripp (Technische Universität Berlin, Germany) “The Unexpected Complexity of PCET in Biological Proton Reduction”
9:20 — 9:30h	Questions and Discussion
9:30 — 9:40h	Moritz Senger (Uppsala University, Sweden) “PCET Reactions in Non-Light Active Enzymes Triggered By Light”
9:40 — 9:45h	Questions and Discussion
9:45 — 10:05h	John W. Peters (The University of Oklahoma, USA) “The Parameters That Define Flavin-Based Electron Bifurcation”
10:05 — 10:15h	Questions and Discussion
10:15 — 10:35h	Holger Dau (Freie Univ. Berlin, Germany) “The Electron-Proton Bottleneck of Photosynthetic Oxygen Evolution”
10:35 — 10:45h	Questions and Discussion
10:45 — 11:15h	Coffee Break
11:15 — 11:35h	Ming-Tian Zhang (Tsinghua University, China) “Energetics of Proton-Coupled Electron Transfer in M-(μ -OH)-M (M = Cu, Ni) Complexes “
11:35 — 11:45h	Questions and Discussion
11:45 — 11:55h	Matthew Chambers (Louisiana State University, USA) “Insights into Light-Initiated Net Hydrogen Atom Transfers to Early Transition Metal Oxos”
11:55 — 12:00h	Questions and Discussion
12:00 — 12:20h	Sven Schneider (University of Göttingen, Germany) “Nitrogen Fixation Strategies guided by PCET”
12:20 — 12:30h	Questions and Discussion
12:30 — 12:50h	Ally Aukaloo (Université Paris-Saclay, CNRS, France) “Porphyrins Decorated with Urea Functions for CO ₂ Activation and Reduction”
12:50 — 13:00h	Questions and Discussion
13:00 — 14:30h	Lunch

14:30 — 14:40h	Pablo Garrido-Barros (University of Granada, Spain) “Harnessing Light for Photocatalytic PCET Using Molecular Mediators”
14:40 — 14:45h	Questions and Discussion
14:45 — 15:05h	Inke Siewert (Georg-August-Universität Göttingen, Germany) “Hydrogenation of C=O Bonds in CO ² , Ketones, and Aldehydes by Electrons and Protons”
15:05 — 15:15h	Questions and Discussion
15:15 — 15:25h	Stephan Kupfer (Friedrich Schiller University Jena, Germany) “Tailor-made Electron Transfer Pathways in Photocatalysis— a Quantum Chemical Perspective”
15:25 — 15:30h	Questions and Discussion
15:30 — 15:40h	Ludovic Troian-Gautier (Université catholique de Louvain, Belgium) “Electron Photo-Accumulation in Ir(III) Photosensitizers for Proton and Carbon Dioxide Reduction”
15:40 — 15:45h	Questions and Discussion
15:45 — 15:55h	Jiawei Wang (Institute of Chemical Research in Catalonia (ICIQ), Spain) “Homoleptic Al(III) Photosensitizers for Durable CO ₂ Photoreduction”
15:55 — 16:00h	Questions and Discussion
16:00 — 16:30h	Coffee Break
16:30 — 16:45h	Poster Flash Talks 1 & 2
16:45 — 17:05h	Ivana Ivanović-Burmazović (Ludwig-Maximilian-Universität München, Germany) “Excited-State PCET Chemistry Under High-Pressure Measured By Time-Resolved Femto- And Nanosecond Transient Absorption Spectroscopy”
17:05 — 17:15h	Questions and Discussion
17:15 — 17:25h	Gregorio Guisado-Barrios (Universidad de Zaragoza- CSIC, Spain) “Acceptorless Dehydrogenation of N-heterocycles Catalyzed by a Single Iridium(III) Metal Complex Assisted by Visible Light”
17:25 — 17:30h	Questions and Discussion

- 17:30 — 17:50h **Javier J. Concepcion** (Brookhaven National Laboratory, USA)
“CO Insertion into a Ru-H bond: the Role of Formyl Intermediates in
the Interconversion between Three Isomers”
- 17:50 — 18:00h Questions and Discussion

Friday, June 9, 2023

8:00 — 8:45h	Breakfast
9:00 — 9:20h	Gerald Meyer (University of North Carolina at Chapel Hill, USA) “PCET Reactivity of Formyl Complexes and Organic Hydrides within CHASE”
9:20 — 9:30h	Questions and Discussion
9:30 — 10:00h	Poster Flash Talks 3 – 6
10:00 — 10:20h	Ana Moore (Arizona State University, USA) “Multiproton Coupled Electron Transfer Thermodynamics and Dynamics”
10:20 – 10:30h	Questions and Discussion
10:30 — 11:00h	Closing Ceremony
11:00 — 11:30h	Refreshments

5. Oral Presentation Abstracts

FREE-ENERGY DEPENDENCE OF PCET REACTION RATES

Leif HAMMARSTRÖM

Address: Department of Chemistry – Ångström Laboratory, Uppsala University, Box 523, SE75120 Uppsala, Sweden. Leif.hammarstrom@kemi.uu.se

Theories for proton transfer (PT) and proton-coupled electron transfer (PCET) predict a free-energy dependence of the rate constant that is analogous to that for electron transfer (ET), *i.e.* of the form given by eq. 1.^[1,2] Here, the driving force ($-\Delta G^\circ$) and reorganization energy (λ) will be different for the three types of reactions, even when the same reactants are involved. This offers a useful way to distinguish and deliberately control the different concerted and step-wise mechanisms of PCET reactions. We recently illustrated the possibilities to change mechanisms in mechanistic zone diagrams^[3], which generalize our experimental results with small organic molecules^[4,5], model proteins^[6,7] and metal hydrides^[8-10], and the presentation will discuss some recent examples. We argue that these guidelines are useful to designing efficient catalysts for PCET transformations.

In spite of the success of PCET theories, the quadratic free-energy dependence of eq. 1 had until recently not been experimentally demonstrated. Instead, almost all studies show a linear dependence of $\ln k$ vs. $-\Delta G^\circ_{\text{PCET}}$ over up to more than 1 eV change in $-\Delta G^\circ_{\text{PCET}}$. Therefore, the recent demonstration of the Inverted region behavior for concerted PCET was of fundamental importance.^[11] In addition, several studies have reported different free-energy dependencies of k_{PCET} for the same reaction when acid/base or oxidant/reductant was varied, *i.e.* different Bronsted slopes. This has led to suggestions of “asynchronous” PCET, which is not consistent with tunneling of electron and proton from a joint transition state.^[3,10] It is interesting to examine the origin of the different Bronsted slopes, and why they appear in some systems while others show a perfectly symmetric dependence on $\Delta G^\circ_{\text{PT}}$ and $\Delta G^\circ_{\text{PCET}}$.

Acknowledgements: I am grateful for rewarding collaboration with Sascha Ott, Starla Glover, Cecilia Tommos, Sharon Hammes-Schiffer, James Mayer and their groups, whose individual names are given in the references.

References:

- [1] Cukier, R.I.; Nocera, D.G. *Ann. Rev. Phys. Chem.* **1998**, *49*, 337.
- [2] Hammes-Schiffer, S. *Acc. Chem. Res.* **2001**, *34*, 273.
- [3] Tyburski, R.; Liu, T. Glover, S.D.; Hammarström, L. *J. Am. Chem. Soc.* **2021**, *143*, 560.
- [4] Nilsen-Moe, A.; Rosichini, A.; Glover, S.D.; Hammarström, L. *J. Am. Chem. Soc.* **2022**, *144*, 7308.
- [5] Tyburski, R.; Hammarström, L. *Chem. Sci.* **2022**, *13*, 290.
- [6] Nilsen-Moe, A.; Reinhardt, C.R.; Glover, S.D.; Liang, L.; Hammes-Schiffer, S.; Hammarström, L.; Tommos, C. *J. Am. Chem. Soc.* **2020**, *142*, 11550.
- [7] Nilsen-Moe, A.; Reinhardt, C.R. Huang, P.; Agarwala, H.; Lopes, R.; Lasagna, M.; Glover, S.D.; Hammes-Schiffer, S.; Tommos, C; Hammarström, L. *in preparation*.
- [8] Bourrez, M.; Steinmetz, R.; Ott, S.; Gloaguen, F.; Hammarström, L. *Nature Chem.* **2015**, *7*, 140.
- [9] Liu, T.; Guo, M.; Orthaber, A.; Lomoth, R.; Lundberg, M.; Ott, S.; Hammarström, L. *Nature Chem.* **2018**, *10*, 881.
- [10] Liu, T.; Tyburski, R.; Wang, S.; Fernández-Terán, R.; Ott, S.; Hammarström, L. *J. Am. Chem. Soc.* **2019**, *141*, 17245.
- [11] Parada, G.A.; Goldsmith, Z.K.; Kolmar, S.; Pettersson Rimgard, B.; Mercado, B.Q.; Hammarström, L.; Hammes-Schiffer, S.; Mayer, J.M. *Science* **2019**, *364*, 471.

HYDROGEN TUNNELING AND EXCITED VIBRONIC STATES IN PROTON-COUPLED ELECTRON TRANSFER

Sharon Hammes-Schiffer¹

¹ *Department of Chemistry, Yale University, New Haven, CT 06520, United States.*

E-mail: sharon.hammes-schiffer@yale.edu

Proton-coupled electron transfer (PCET) reactions play a vital role in a wide range of chemical and biological processes. This talk will summarize the main concepts from our PCET theory and will present recent applications to catalysis and energy conversion. Our general theoretical formulation for PCET^[1,2] includes the quantum mechanical effects of the electrons and transferring protons, as well as the motions of the donor-acceptor modes and solvent or protein environment. This PCET theory enables the calculation of rate constants, current densities, and kinetic isotope effects for comparison to experiment. This theoretical framework also enables the study of the nonequilibrium dynamics of PCET processes. Applications to electrochemical, photochemical, and biologically relevant PCET will be presented, with emphasis on the roles of hydrogen tunneling, excited vibronic states, reorganization, electrostatics, and conformational motions. Inverted region behavior for PCET and the recently discovered proton-coupled energy transfer mechanism^[3] will also be discussed. The fundamental insights obtained from these theoretical studies are guiding the design of more effective catalysts and energy conversion devices.

References:

- [1] Soudackov, A.; Hammes-Schiffer, S. *J. Chem. Phys.* **1999**, 111, 4672; *J. Chem. Phys.* **2000**, 113, 2385.
- [2] Hammes-Schiffer, S. *J. Am. Chem. Soc.* **2015**, 137, 8860.
- [3] Rimgard, B. P.; Tao, Z. Parada, G. A.; Cotter, L. F.; Hammes-Schiffer, S.; Mayer, J. M.; Hammarström, L. *Science* **2022**, 377, 742.

OFF-DIAGONAL THERMODYNAMICS AND ITS EFFECT ON H-ATOM ABSTRACTION REACTIVITY

Martin Srnec,¹ Mauricio Maldonado-Domínguez,¹ Daniel Bím¹

¹ Address: J. Heyrovský Institute of Physical Chemistry, Czech Academy of Sciences.

We formulated an original and unique theoretical framework aiming at the prediction of C-H bond activation reactivity.^[1,2] In its current form, it features two thermodynamic factors that we named asynchronicity and frustration that together modulate coupled proton-electron transfer reactivity. Only after addition of these two factors to the classical well-documented effect known as linear free energy relationship (LFER capturing the effect of reaction energy on the barrier) a complete thermodynamic basis for the control of reactivity/selectivity is formed. Asynchronicity lowers the reaction barrier (increasing the reaction rate) so that a more asynchronous reaction gets faster, whereas frustration acts on the barrier in the opposite way so that a more frustrated reaction gets slower. In principle, each of the two factors and their combination enable changing the preference of which C-H-bond is likely to be activated that would be otherwise driven by LFER, which favors the weakest C-H bonds in molecules. To demonstrate the power of the approach, we will show and discuss H-atom abstraction reactivity of several transition-metal complexes and organic radicals.

• **Acknowledgements:** The financial support of the Grant Agency of the Czech Republic (Grant No. 21-10383S)

References:

- [1] Bím, D.; Maldonado-Domínguez, M.; Rulíšek, L.; Srnec, M. *Proc.Nat. Sci. Acad. U.S.A.*, **2018**, 115, E10287-E10294.
[2] Maldonado-Domínguez, M.; Srnec, M. *Inorg. Chem.*, **2022**, 61, 18811–18822.

Reorganization Energies for Interfacial PCET to a Molecular Water Oxidation Catalyst

Matthew KESSINGER,¹ Alexander SOUDACKOV,² Kai, CUI², Jeremiah, XU¹, Sharon HAMMES-SCHIFFER², Gerald MEYER¹

¹ Address: University of North Carolina at Chapel Hill, Chapel Hill North Carolina, USA, 27514
kessm05@email.unc.edu

² Address: Yale University, New Haven, Connecticut, USA, 06520

Proton-coupled electron transfer (PCET) reactions are vital steps in the fuel-forming reactions of artificial photosynthesis. In these systems several independent reactions occur in concert to generate chemical fuels. Of these reactions, water oxidation at electrode-electrolyte interfaces to yield electrons and protons remains a lasting challenge. Therefore, understanding how various reaction conditions, such as solution pH, buffer identity and concentration, and electric field strength, impact the kinetic parameters of interfacial PCET reactions is crucial for designing effective artificial photosynthetic schemes. Here, we have investigated the interfacial PCET reaction between a model water oxidation catalyst bound to the surface of a conductive metal oxide electrode and an aqueous electrolyte.^[1] Pulsed laser excitation of the catalyst triggered the interfacial PCET reaction of interest, and the resulting kinetics were collected as a function of free energy change. Analysis of this data within the framework of Marcus-Gerischer theory provided the reorganization energy for the PCET reaction. We found that the PCET reorganization energy was independent with respect to both electric field strength and solution pH. However, the PCET rate constant exhibited a weak dependence on the solution pH from pH 3-7. These findings and more are discussed in the context of artificial photosynthesis with an eye toward future applications in solar fuels synthesis.

References:

[1] Kessinger, M.; Soudackov, A.; Schneider, J.; Bangle, R.; Hammes-Schiffer, S.; Meyer, G. *Journal of the American Chemical Society*, **2022**, *144*, 20514.

MARCUS ANALYSIS OF EXCITED-STATE PROTON-TRANSFER REACTIONS, AND RESULTING APPLICATIONS

Cassidy N. Feltenberger,¹ Shirley Chang,¹ Dennis Tang,¹ Gabriel S. Phun,¹ Annette Böhme,² Rohit Bhide,¹ Harry A. Atwater,² Shane Ardo^{1,3,4}

¹ Department of Chemistry, ³ Department of Chemical & Biomolecular Engineering, ⁴ Department of Materials Science & Engineering, University of California Irvine, Irvine, CA 92697 USA, ardo@uci.edu
² Department of Applied Physics and Materials Science, California Institute of Technology, Pasadena, CA 91125, USA

Marcus's landmark prediction that activation free energy exhibits a parabolic dependence on standard thermodynamic driving force can be derived using Fermi's (Second) Golden Rule.^[1] Fermi's Golden Rule is based on perturbation theory, and therefore it assumes *weak* electronic coupling. Notwithstanding, over a half-century of experiments have shown that Marcus theory holds for reactions that involve significant nuclear transfer along the reaction coordinate, such as proton-coupled electron-transfer reactions,^[2] many times where *strong* electronic coupling is presumed. This conundrum remains at the forefront of chemical kinetics research.

In an effort to bridge this knowledge gap, we synthesized several new organic photoacids that were specifically designed to assist us in evaluating whether the behavior of excited-state proton-transfer (ESPT) reactions is consistent with classical Marcus theory. Photoacids, and analogous photobases, constitute a class of molecules that upon absorption of light undergoes a reversible change in acidity, i.e. pK_a . Using the weak aqueous photoacid 5-aminonaphthalene-1-sulfonate ($pK_a^* \approx 12$), we demonstrated dynamic ESPT quenching by glycine, proline, phosphate, trifluoroethoxide, and hydroxide.^[3] Using the strong aqueous photoacid 9-hydroxyphenanthrene-3,10-disulfonate ($pK_a^* \approx 2$), we demonstrated dynamic ESPT quenching by formate, (bi)carbonate, acetate, chloroacetate, and water. These data collectively support the existence of Marcus normal region behavior.

While these photochemical studies are fundamentally interesting, also appealing is the ease by which important information is gleaned using readily available steady-state photoluminescence spectroscopy. Moreover, use of confocal microscopy to map dye fluorescence in three dimensions reports on nanoscale activity of aqueous protonic species, including the first direct measurements of pOH in a gas diffusion electrode driving electrochemical CO_2 reduction at $>0.1\text{ A/cm}^2$.^[4] Collectively, our efforts form the foundational framework to increase spatial resolution for quantitative measurements of local species activities in complex microenvironments, and to assess the suitability of models for reactions that involve substantial nuclear transfer.

• **Acknowledgements:** This material is based on work performed by the Liquid Sunlight Alliance, which is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Fuels from Sunlight Hub under Award DE-SC0021266, and the U.S. National Science Foundation under Award 2102665.

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UNDERSTANDING THE THERMODYNAMICS AND PCET OF TYROSINE AND TRYPTOPHAN PROTEIN RESIDUES

Cecilia TOMMOS

Department of Biochemistry & Biophysics, Texas A&M University, College Station, Texas, USA
tommos@tamu.edu

Redox proteins use metallocofactors, a few universal organic molecules, and four types of amino acids (tyrosine (Y), tryptophan (W), cysteine and glycine) to perform electron transfer (ET) and proton-coupled electron transfer (PCET) reactions.^[1] Redox proteins participate in a myriad of metabolic pathways and are essential for most, if not all, living organisms. Within the context of protein ET/PCET, the amino acids listed above serve as one-electron, or radical, redox mediators. Amino-acid radicals are notoriously difficult to study and, consequently, detailed mechanistic insights into one of nature's essential redox tools was missing. This lack of knowledge motivated us to develop a rigorous approach to systematically map the fundamental properties of protein Y and W redox reactions.

We have made, and continue to develop, a family of well-structured model proteins specifically designed to study Y and W oxidation-reduction (Fig. 1).^[1] These so called α_3X proteins have a single redox-active residue (X_{32}) buried inside a 65-residue protein scaffold (α_3). Previous work has shown that the α_3X proteins remain stable and well-structured across a broad pH range and that residue X_{32} can be uniquely and reversibly oxidized and reduced. We have assembled a unique "thermodynamic ladder" for Y, W and a series of non-canonical Y_{32}^* residues containing reversible E° values obtained at near identical protein and solution conditions.^[1] This data set was expanded to include full Pourbaix (E° vs. pH) diagrams for the α_3X proteins shown in Fig. 1, top and middle rows. In collaboration with the Hammarström and Hammes-Schiffer groups, PCET kinetics and mechanisms associated with X_{32} oxidation in α_3Y ,^[2] α_3W ,^[3] 2MP- α_3C and 4MP- α_3C (Nilsen-Moe *et al.* manuscript in preparation) have been characterized in detail. We have also gained insights on how the protein controls the lifetime of the very long-lived X_{32}^\bullet radicals.

We are currently expanding the α_3X system to include a series of non-canonical W_{32}^* residues (Fig. 1, bottom row). Rigorously determined $\Delta E^\circ(W_{32}^* - W_{32})$ values will be obtained to serve as benchmarking data to refine and broaden the scope of the computational protocol described in Reinhardt *et al.* *JPC B* 2021 for the residues shown in Fig. 1, top row. We also work to develop α_3XX proteins ($X = Y, W$ and/or non-canonical Y/W residues) to study Y/W-based multistep ET/PCET.

Acknowledgements: National Institutes of Health award R01 GM19079

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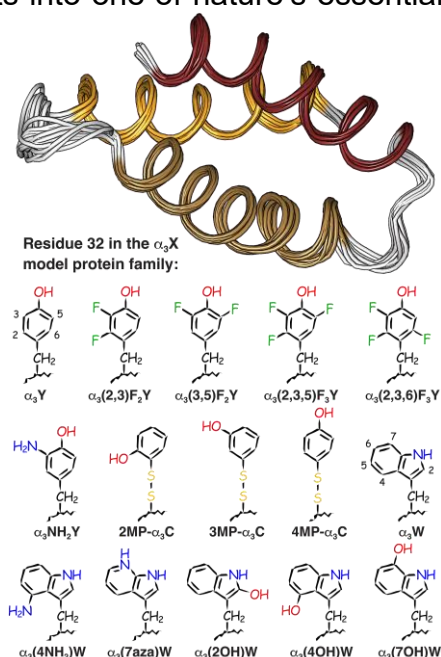


Figure 1. The α_3X proteins are based on an α -helical scaffold (α_3) with a single redox-active residue at interior position 32 (X_{32}). Site 32 is occupied by Y_{32} (in the α_3Y protein), W_{32} (in α_3W), $2,3F_2Y_{32}$ (in $\alpha_3(2,3F_2)Y$) and so forth for the displayed residues. The top ribbon diagram displays the 32-member NMR ensemble of structures representing the α_3W protein in solution.

H-TRANSFER REACTIONS WITH INORGANIC MATERIALS AND METAL COMPLEXES

Murielle F. DELLEY, Oliver S. WENGER

Department of Chemistry, University of Basel, St. Johannis-Ring 19, 4056 Basel, Switzerland

Heterogeneous catalysis is essential to most industrial chemical processes. However, these processes are often not efficient or selective enough, and typically use rare and expensive noble metals as catalysts. Improving the sustainability of current processes will rely on the development of new controls in catalysis and of abundant materials as catalysts. Earth-abundant transition metal phosphides and sulfides have recently emerged as promising materials for the catalysis of H-transfer reactions, such as hydrotreating and water splitting.^[1-4] This highlights the catalytic potential of transition metal phosphides and sulfides, but this potential has not been exploited much yet due to a limited understanding of their interfacial chemistry. This talk will discuss our current efforts in expanding the catalytic universe of transition metal phosphides and sulfides, and in developing new control elements to tune catalytic properties by chemical surface modification and electric fields.

Photoredox and energy transfer catalysis have become popular in organic synthesis, but understanding the photochemical reactivity on a fundamental level is often challenging. The second part of the talk will focus on different types of photoreactions, for which a basic mechanistic understanding seemed particularly desirable for the development of more rational approaches to photocatalysis. In recent work, an iridium(III) hydride complex was found to undergo photo-triggered hydrogen atom transfer (HAT) to olefins,^[5] which represents a fundamentally different type of photoreactivity compared to the single electron transfer (SET) behavior seen for most transition metal complexes. Newly emerging concepts in photocatalysis are based on the consecutive absorption of multiple photons per substrate turnover,^[6] to accumulate the energy of two photons for particularly challenging reactions.

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PHOTOELECTROCHEMICAL C-H ACTIVATION WITH DYES ENABLING PROTON-COUPLED ELECTRON TRANSFER

Yunshuo YANG,¹ Giulia VOLPATO,¹ Elena ROSSIN,¹ Catia NICOLETTI,¹ Ruggero BONETTO,¹ Elena COLUSSO,¹ Luca DELL'AMICO,¹ Serena BERARDI,² Elisabetta COLLINI,¹ Stefano CARAMORI,² Stefano AGNOLI,¹ Andrea SARTOREL¹

¹ Address: Department of Chemical Sciences University of Padova (Italy) andrea.sartorel@unipd.it

² Department of Chemical and Pharmaceutical Sciences, University of Ferrara (Italy)

Dye-sensitized photoelectrochemical cells are an appealing technology for exploiting solar light towards the activation of small molecules. The most investigated process has long been light driven water splitting into hydrogen and oxygen;^[1] more recently, oxidation of organic compounds has emerged as an alternative anodic route, in particular for the oxidation of alcohols.^[2] In this work, we have developed dye-sensitized photoelectrodes for the oxidative activation of C-H bonds, which is considered a Holy Grail in organic reactivity. The key feature is the use of a quinacridone organic dye that operates through a proton-coupled electron transfer, converting the N-H group into a N centered radical, capable of hydrogen atom abstraction from allylic and benzylic C-H groups. The reactivity in terms of photocurrent response is indeed correlated to the Bond Dissociation Free Energy of the N-H bond in the quinacridone dye (80.5 Kcalmol⁻¹) and of the C-H bonds in the organic substrates (Figure 1). This work provides a mechanistically oriented strategy to the design of dye-sensitized photoelectrodes for selective organic transformations.

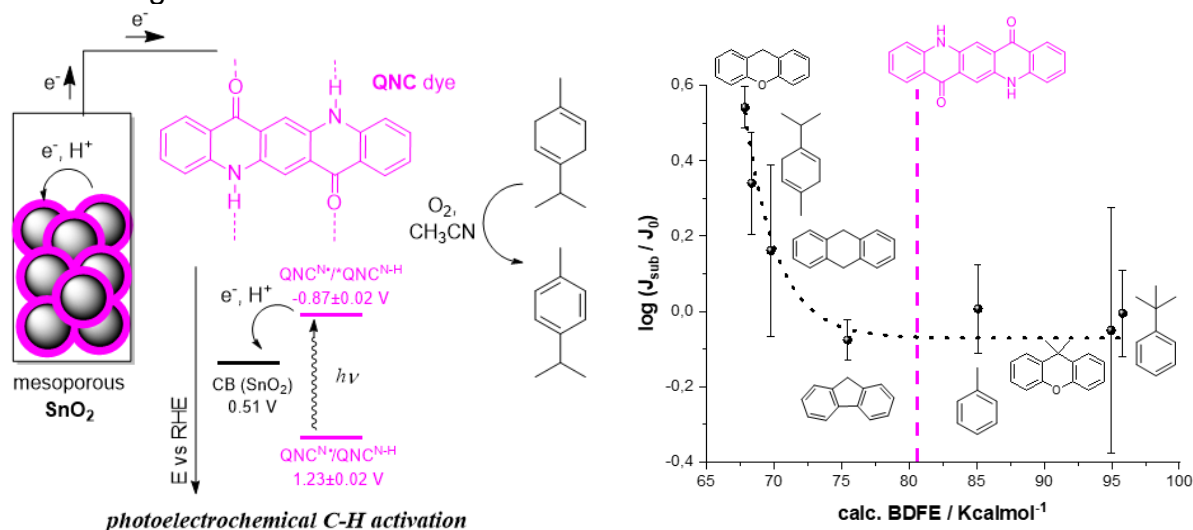


Figure 1. Photoelectrochemical C-H activation through quinacridone dye-sensitized SnO₂ electrodes (left) and photocurrent response in terms of the Bond Dissociation Free Energy of N-H in quinacridone and of C-H in organic substrates (right).

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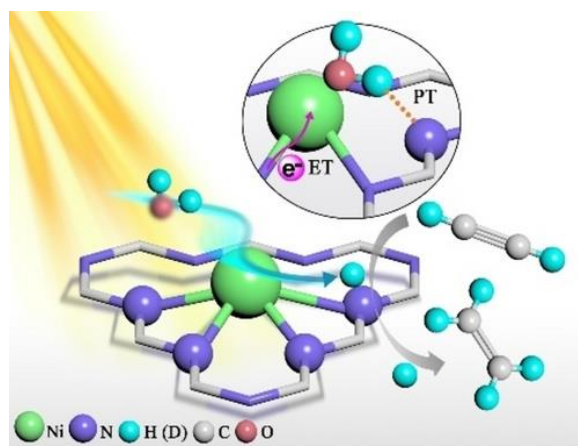
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ATOMIC DISPERSED METAL CATALYZED SELECTIVE HYDROGENATION via PROTON COUPLED ELECTRON TRANSFER

Wenjing SONG, Tongtong JIA, Jikun LI, Chuncheng CHEN, Jincai ZHAO

Address: Key Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China
Email: wsongunc@iccas.ac.cn

The use of water as a source of hydrogen is attractive for selective hydrogenation reactions, where hydrogen liberation is a crucial step.^[1-2] Our study describes the selective hydrogenation catalyzed by the (carbon nitride) pyridinic nitrogen ligated Ni^{2+} ($\text{N}_x\text{-Ni}^{2+}$).^[3-4] Upon excitation, the electron transfer from carbon nitride to Ni^{2+} is coupled to heterolysis of the adsorbed water, transferring proton to a non-coordinated nitrogen: $\text{N}_x\text{-Ni}^{2+} + \text{e}^- + \text{H}^+ \rightarrow \text{N}_{x-1}\text{-Ni}^{+}\cdots\text{NH}^+$. The active intermediates ($\text{N}_{x-1}\text{-Ni}^{+}\cdots\text{NH}^+$) hydrogenates alkyne substrates, likely following the proton coupled electron transfer that bypasses the hydride transfer. The sequential two (photo-induced) electron-proton transfer affords alkene with high selectivity. This reaction paradigm offers a facile method for synthesizing valuable deuterated alkene products with high deuterium incorporation using D_2O and unlabeled alkynes. It is expected that analogue PCET mechanism would promote the hydrogenation/valorization of various unsaturated functionalities, with efficient and selective conversion relying on well-managed electron/proton transfer/migration.



Scheme 1. Illustration of the photo-induced proton coupled electron transfer over (carbon nitride) pyridinic nitrogen ligated Ni^{2+} that liberates hydrogen from water for semi-hydrogenation of alkenes.

Acknowledgements

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MECHANISTIC INSIGHT INTO METAL HYDRIDE PHOTOCHEMISTRY GUIDES SOLAR FUELS CATALYST DESIGN

Alexander MILLER¹

¹ Department of Chemistry
University of North Carolina at Chapel Hill
Chapel Hill, NC 27516
ajmm@email.unc.edu

Transition metal hydride complexes are featured intermediates in biological, organometallic, and energy conversion catalysis. Photoexcitation of such metal hydride intermediates can initiate a myriad of possible reactions (**Figure 1A**).^[1] If the appropriate photoinitiated proton-coupled electron transfer (PCET) reaction can be enforced, visible light can be used to reduce kinetic barriers, lower electrochemical overpotential, or unveil entirely new reaction products. Coupling photochemical fuel formation with electrochemical regeneration of the hydride reveals opportunities for solar fuels catalysis. Mechanistic studies of metal hydride photochemistry will be described in the context of developing *molecular photoelectrocatalysts*,^[2] single-component catalysts that both harvest visible light and mediate chemical bond formation (**Figure 1B**). Thermodynamic analyses are paired with time-resolved kinetic studies to elucidate the molecular-level mechanistic details of the PCET pathways that lead to H₂ evolution and hydrogen transfer reactions. Comparisons with traditional multi-component semiconductor/electrocatalyst solar fuels approaches will be discussed.

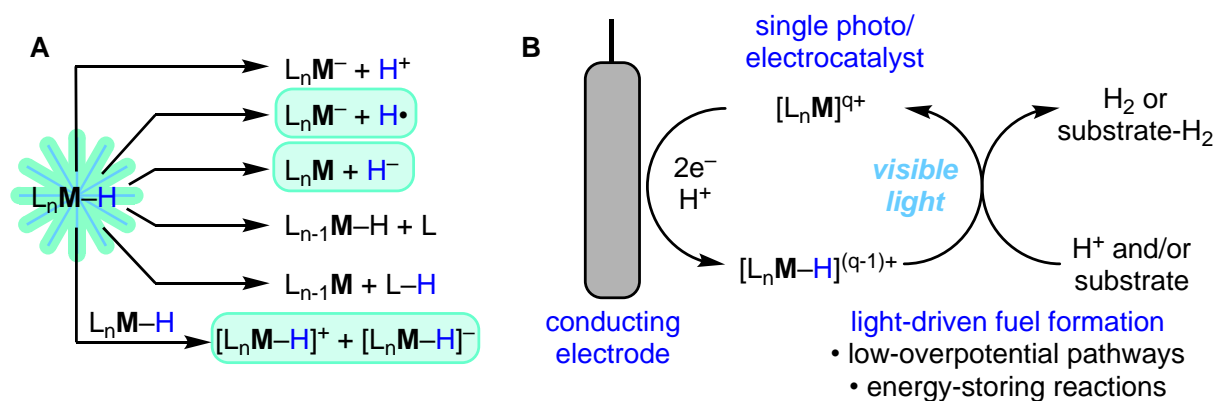


Figure 1. (A) Possible photochemical pathways of transition metal monohydride complexes. (B) General scheme for single-component molecular photoelectrocatalysis.

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Net H-atom uptake and transfer at polyoxovanadate-alkoxide surfaces

Eric SCHREIBER¹ and Ellen M. MATSON¹

¹ *Department of Chemistry, University of Rochester, Rochester NY 14627 USA
e-mail: matson@chem.rochester.edu*

The rich electrochemical properties of transition metal oxides have positioned these materials as valuable materials for emergent energy-related technologies. In all these applications, a defining feature of active materials is their ability to accept and transfer H-atom equivalents (i.e. proton/electron pairs) via proton-coupled electron transfer (PCET). Challenges associated with understanding these surface mediated chemical transformations with atomic resolution has resulted in the study of polyoxometalate clusters as molecular models. In this talk, I will describe my group's efforts in understanding net H-atom uptake at the surface of reduced variants of the Lindqvist-type polyoxovanadate-alkoxide cluster, $[V_6O_{19-n}(OMe)_n]^n$. In the case of these low-valent vanadium oxide assemblies, nucleophilic bridging sites are kinetically inhibited by functionalization of the cluster surface with organic ligands. This molecular modification enables selective H-atom uptake at terminal oxide sites. The impact of reaction site and cluster electronics on reaction driving force of PCET is explored. Additional work described will contrast the kinetics of PCET at terminal oxide sites to the reactivity observed at bridging oxides in POV-alkoxide clusters.

PCET pathways to catalytic, electrocatalytic, and photo(electro)catalytic nitrogen fixation

Jonas Peters

*Division of Chemistry and Chemical Engineering, California Institute of Technology (Caltech),
1200 E California Blvd, Pasadena, CA-91125 USA*

Nitrogen reduction to ammonia is a requisite transformation for life and there is growing interest in developing sustainable technologies for ammonia synthesis using renewably sourced energy. Such approaches can lead to distributed on-demand fertilizer production and may enable ammonia to be used as a zero-carbon alternative fuel. Our group has had an ongoing interest in the study of well-defined synthetic catalysts that mediate nitrogen reduction (N_2R) to ammonia (and hydrazine). We are especially interested in the operative mechanisms by which such catalysis occurs. Most recently, we have been pursuing the idea that proton-coupled electron transfer (PCET) pathways for N_2R can be more thermally efficient than step-wise ET/PT pathways and have tested this hypothesis via the development of electrochemical PCET (ePCET) mediators that enable electrocatalytic N_2R (and other reductive transformations) to be driven at potentials sufficiently anodic that the competing hydrogen evolution reaction (HER) is mitigated. Relatedly, we are pursuing novel catalysts and conditions for photodriven N_2R , and systems that enable (photo)electrochemical N_2R . Here, visible light rather than temperature, pressure, or electrochemical potential, provides the primary driving force needed for catalytic ammonia generation.

HETEROGENIZED ELECTROCATALYTIC AMMONIA OXIDATION WITH A SUPRAMOLECULAR HOST-GUEST SYSTEM

Helena ROITHMEYER,¹ S. David TILLEY¹

¹ Address: Department of Chemistry, University of Zürich, Winterthurerstrasse 190, 8057, Zurich, Switzerland

Surface-anchored host molecules allow for the binding of catalytically active guest complexes. The heterogenization of ammonia oxidation electrocatalysts via surface-bound host-guest (HG) complexes combines high stability and high performance. For that purpose, a tailored HG system with the ability to oxidize ammonia in both organic and aqueous solutions was designed. The backbone of the Ru(bpy-NMe₂)(tpada)(Cl)](PF₆) (where bpy-NMe₂ is 4,4'-bis(dimethylamino)-2,2'-bipyridyl, tpada is 4'-(adamantan-1-yl)-2,2':6',2''-terpyridine) (Figure 1) catalyst features an adamantyl motif as the binding group, which showed high binding constants with β -cyclodextrin in solution ($K = 1580.7 \pm 6\%$) as determined by ¹H NMR titration. Strong binding affinities were also observable when the catalyst was absorbed on a mesoporous ITO (mITO) surface functionalized with a phosphonated derivative of β -cyclodextrin. We compared our newly designed catalyst to our previously developed naphthylene-substituted catalyst [Ru(bpy-NMe₂)(tpnp)(Cl)](PF₆)^[1] (where

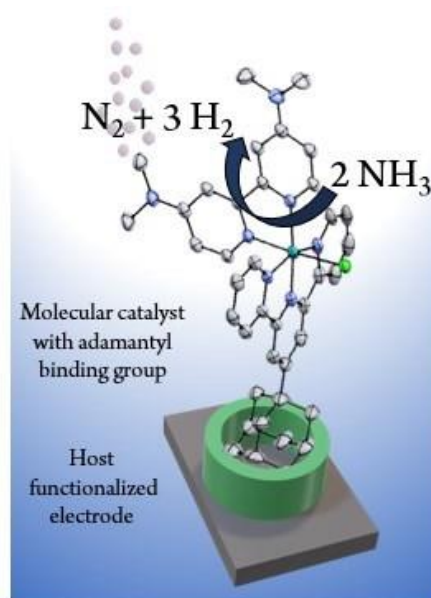


Figure 1: Heterogenized ammonia oxidation with a tailored surface bound host-guest system.

tpnp is 4'-(naphthalen-2-yl)-2,2':6',2''-terpyridine) for its stability, endurance and recyclability during catalysis. Both guests are able to oxidize ammonia in both organic and aqueous solutions and are stable on the order of hours. The host-bound electrode can be refunctionalized multiple times after catalysis without a reduction in the performance of the functionalized electrode. We found that guest **1** exhibits a higher surface loading, higher currents and significantly higher stability towards basic conditions.

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Electrocatalytic Ammonia Oxidation by Earth-Abundant Metal Complexes

Md. Estak AHMED,¹ Pokhraj GHOSH,¹ Danushka EKANAYAKE,¹ Fatimah ASULTAN,¹ and Timothy H. WARREN¹

¹ Address: Department of Chemistry, Michigan State University, East Lansing, MI 48824, United States
warre155@msu.edu

Owing to its high energy density and established global production and distribution networks, ammonia (NH₃) is an appealing fuel, particularly when synthesized by green methods. On a per-hydrogen atom basis, ammonia contains nearly the same chemical energy as hydrogen (H₂). Thus, sustainable catalysts that electrocatalytically oxidize ammonia for fuel cells or on-demand hydrogen production with only nitrogen (N₂) as a byproduct are highly desirable.

We describe electrocatalytic ammonia oxidation using molecular systems based on Earth-abundant copper^[1] and iron. Each approach focuses on enabling the conversion of NH₃ to masked forms of the amidyl radical •NH₂ via PCET. Copper(I) β-diketiminato catalysts [Cu^I] enable ammonia oxidation via deprotonation of oxidized copper(II) ammine complexes {[Cu^{II}]-NH₃}⁺ to form copper(II) amide species [Cu^{II}]-NH₂. The significant unpaired electron density on the amide N atom in [Cu^{II}]-NH₂ facilitates N-N coupling to dicopper(I) hydrazine species [Cu^I]-NH₂NH₂-[Cu^I]. While experimental studies reveal that ferrocenium (Fc⁺) can stoichiometrically oxidize NH₃, a combination of mechanistic and computational studies suggests that outersphere oxidation of H-bonded ammonia dimers or trimers [NH₃]_x (x = 2 or 3) occurs. To encourage H-bonding near the Fc⁺ center, we synthesized a family of ferrocene complexes that feature pendant pyridine bases that serve as efficient electrocatalysts for ammonia oxidation. We hypothesize that a pendant pyridyl base engages in H-bonding to ammonia that facilitates PCET of the H-bonded ammonia molecules to give an amidyl radical (•NH₂) stabilized by a protonated pyridinium base en route to hydrazine (H₂N-NH₂) that undergoes facile oxidation to nitrogen (N₂).

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Water oxidation catalysis using ruthenium coordination oligomers anchored through CH- π interactions

M. Gil-Sepulcre,^{1,2} O. Rüdiger,² S. DeBeer,² A.Llobet^{1,*}

¹Institute of Chemical Research of Catalonia (ICIQ), The Barcelona Institute of Science and Technology (BIST), Tarragona, Spain.

²Max Planck Institute for Chemical Energy Conversion, 45470 Mülheim an der Ruhr, Germany

e-mail: marcos.gil-sepulcre@cec.mpg.de

The search for environmentally benign renewable energy sources as alternatives to the combustion of fossil fuels is a key target considering the continuously increasing energy demands and the consequences of the associated greenhouse gas emissions.^{[1],[2]} Within this context, artificial photosynthesis is one of the most promising solutions. In particular, water splitting with sunlight ($h\nu$ -WS), where sunlight drives the water oxidation to dioxygen (WO) and proton reduction (PR) to hydrogen is one of the most promising approaches.^[3] To achieve the design of an efficient and robust artificial device, a catalyst is needed for both processes.

Here, we prepared a new family of Ru-based oligomeric catalysts that can be anchored on the surfaces of graphitic materials through CH- π interactions between the auxiliary ligands bonded to Ru center and the hexagonal rings of the graphitic surfaces. A combination of spectroscopic, microscopic and electrochemical techniques allows an exquisite molecular control of the anchoring and the catalytic process. The resulting hybrid materials achieved current densities in the range of 0.2-0.3 A/cm² at neutral pH values, and remarkable long-term stabilities for more than 12 hours towards oxidation of water to dioxygen (Figure 1).^{[4],[5]} The present work provides the basis for the design of robust and efficient hybrid molecular electroanode materials based on Ru complexes.

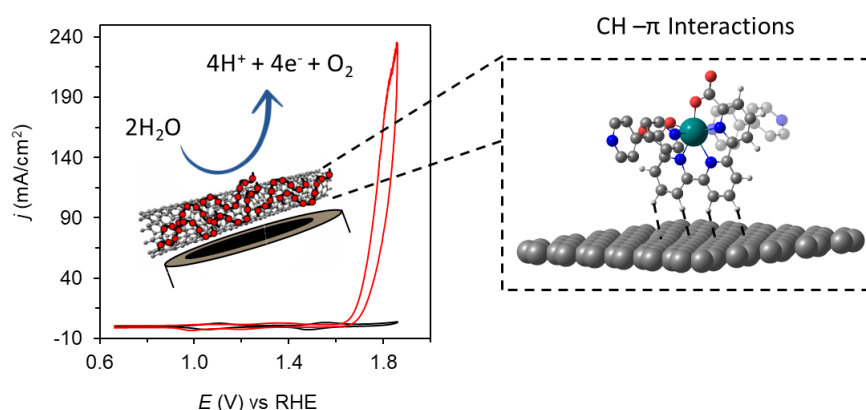


Figure 1: CV of molecular Ru-based hybrid electroanodes at pH 7, and the DFT calculated structure of a single Ru unit anchored by CH- π interactions on a graphitic surface.

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PROTON RELAYS IN MOLECULAR ELECTROCATALYSIS: HOW DO THEY ALLOW FOR REVERSIBLE BEHAVIOR?

Vincent ARTERO,¹

¹ *Laboratoire de Chimie et Biologie des Métaux, Université Grenoble Alpes, CNRS, CEA, Grenoble, France ; e-mail: vincent.artero@cea.fr*

Catalysis in hydrogenases and other metallenzymes 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 for H₂ evolution [²] and oxidation [³]. Specifically, catalytic platforms with installed proton relays display bidirectional [⁴] and, in rare cases, reversible catalysis [^{3a}]. In this presentation we will show how a detailed molecular electrochemistry study can help understanding and quantifying the role of the protons relays related to these remarkable behaviors.^[5]

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PROTONATION STEPS IN IRIIDIUM AND COBALT ORGANOMETALLIC PIANO-STOOL COMPLEXES FOR CO₂ ELECTROREDUCTION

Sergio GONELL,¹ Eduardo PERIS¹

¹ Address: Institute of Advanced Materials (INAM). Universitat Jaume I. Av. Vicente Sos Baynat s/n., 12071 Castelló (Spain)

sgonell@uji.es

The development of new strategies for the conversion of carbon dioxide into fuels relies on deep understanding of the different proton-coupled electron transfer steps in the catalytic process. Molecular catalysts are promising candidates because their activity and selectivity can be tuned using ligand design strategies, and because detailed mechanistic studies can be used to guide catalyst optimization.

Iridium and cobalt piano-stool complexes based cyclopentadienyl ligands in combination with different type of bidentate ligands are promising candidates for the proton-coupled electroreduction of CO₂.^[1,2,3] In this contribution, we will present the silver-free synthesis of isostructural iridium and cobalt solvento, piano-stool complexes based on a pentamethylcyclopentadienyl ligand and a bis-N-heterocyclic carbene ligand (methylenabis(N-methylimidazol-2-ylidene), Figure 1). Cyclic voltammetry has enabled to establish similarities and differences between their proton-coupled electron transfer steps. The highly donating nature of the bis-carbene ligand gives rise to a different behavior with respect their analogues bearing bidentate ligands with different donor atoms. Isolation of intermediates and DFT calculations have provided mechanistic insight in CO₂ electroreduction.

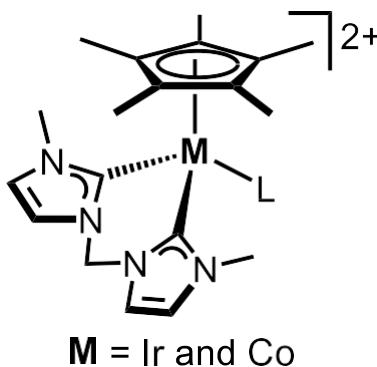


Figure 1. Complexes focus of this study

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ELECTROCATALYTIC CO₂ REDUCTION BY PIPERAZINE-BRIDGED MULTINUCLEAR COBALT COMPLEXES

Ana M. GEER,¹ Luis TARIFA,¹ José A. LOPEZ,¹ Cristina TEJEL,¹ Dennis G. H. HETTERSCHIED,²

¹ Address: Departamento de Química Inorgánica, Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), CSIC-Universidad de Zaragoza, Pedro Cerbuna 12, 50009 Zaragoza, Spain, anageer@unizar.es

² Address: Leiden Institute of Chemistry, Leiden University, RA, Leiden 2300, The Netherlands.

The development of renewable alternatives to fossil-based energy is arguably the most critical scientific challenge of this century. The increasing demand for sustainable energy sources has led to the investigation of electrocatalytic CO₂ reduction as a potential solution for carbon capture and conversion into value-added products.^[1] For this promising area to emerge, we need to develop new robust and efficient catalytic materials. In particular, molecular electrocatalysis offers the advantage of using catalysts with tunable structures, which leads to a level of understanding and control of reactivity that is difficult to achieve with heterogeneous catalysts.^[2-3] In this study, we describe the electrocatalytic CO₂ reduction potential of piperazine-bridged multinuclear cobalt complexes. A family of cobalt complexes with piperazine cores with varying electronic properties, such as the tetranuclear **PyFurPip-Co4**, have been prepared and their electrochemical properties studied in detail (Figure 1).

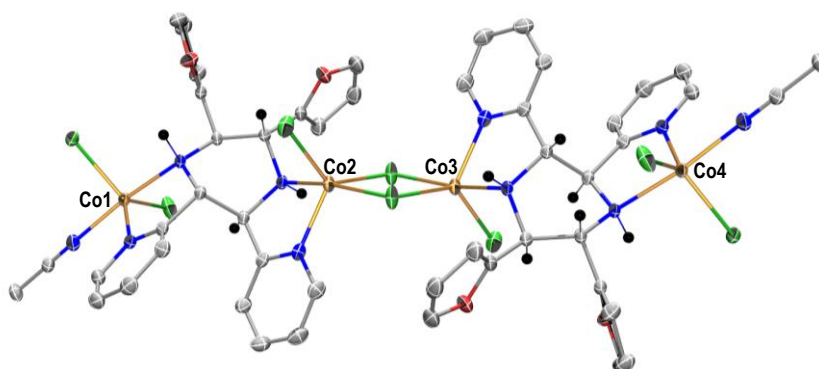


Figure 1. ORTEP view of complex **PyFurPip-Co4** used in this study. Displacement ellipsoids are drawn at the 50% probability level.

Furthermore, the influence of the electronic and geometric properties of the complexes on the CO₂ reduction performance was explored. This study highlights the potential of piperazine-bridged multinuclear cobalt complexes as electrocatalysts for CO₂ reduction and highlights the importance of understanding the relationship between catalyst structure, stability, and activity for the development of efficient and sustainable energy solutions.

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CASCADE PCET TO CO₂ WITH 6 ELECTRONS AND 6 PROTONS USING MOLECULAR COBALT CATALYST

Marc Robert^{1,2}

¹ *Université Paris Cité, CNRS, Laboratoire d'Electrochimie Moléculaire, F-75013 Paris, France,
robert@u-paris.fr*

² *Institut Universitaire de France (IUF), F-75005 Paris, France*

Molecular catalysts can be employed to achieve multi PCET reactions to carbon dioxide, with main objective the production of useful organic compounds and fuels - *renewable fuels* - in which solar energy would be stored. They may in particular provide excellent selectivity. Recently, we have found that Co phthalocyanine adsorbed at carbon nanotubes can convert CO₂ to CO, and then CO to CH₃OH, opening the path to a cascade process for the production of methanol. Upon combining electrochemical and spectroscopic studies (IR, XAS), we have uncovered the reasons for such remarkable reactivity.

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CONTROLLING PROTON AND ELECTRON TRANSFERS TO OXYANIONS FOR WATER PURIFICATION

Callie STERN,¹ Devin MECHE,¹ Vanessa HULSE,¹ Katy KNECHT,¹ Noémie ELGRISHI¹

¹ Address: 232 Choppin Hall, Louisiana State University, Baton Rouge, LA, 70803, noemie@lsu.edu

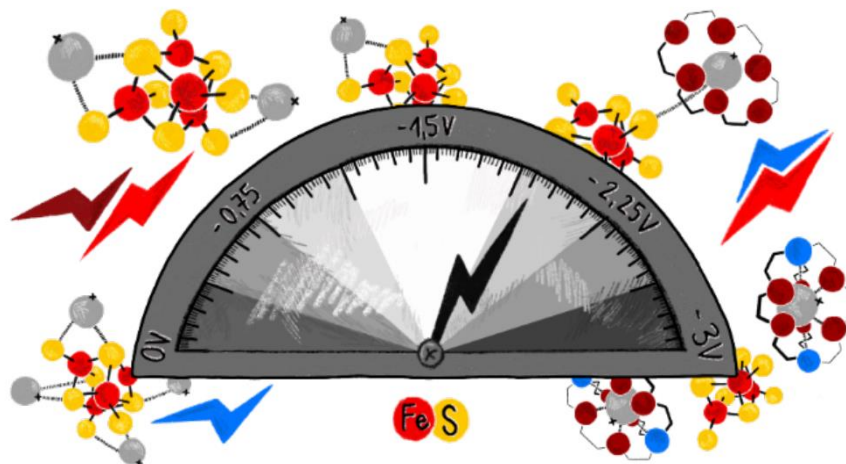
Research efforts in the energy storage community have highlighted the fundamental role of proton-coupled electron transfer (PCET) processes. Problematics of energy-efficiency and facilitating PCET processes are also fundamental to electrochemical water purification methods. Our group works on energy-efficient remediation of toxic oxyanions from contaminated water and industrial waste streams. Oxyanions are a class of negatively charged molecules composed of an atom surrounded by oxygens and include for example chromate, arsenate, perchlorate, nitrite, phosphate, and sulfate. We use electrochemical and spectroscopic methods to explore the PCET processes required to affect the chemistry of these oxyanions for water purification or chemical recovery. Recent work of the group will be presented on understanding and controlling the movement of protons and electrons for water denitrification and for hexavalent chromium reduction. Results on facilitating these transformations using molecular electrocatalysts will be presented to improve the energy-efficiency of the electrochemical processes. The mechanism will be described, along with the pivotal role of buffers in these electrocatalytic processes.

FROM ON-DEMAND REDOX POTENTIAL MODULATION TO CATALYTIC APPLICATIONS: NEW AVENUES FOR SYNTHETIC IRON-SULFUR CLUSTERS

Victor Mougel,¹ Subal Dey,¹ Liam Grunwald,¹ Fabio Masero¹

¹ Department of Chemistry and Applied Biosciences, ETH Zurich, Vladimir-Prelog-Weg 2, 8093 Zürich, Switzerland

Cubane-type iron-sulfur clusters are some of nature's most ancient and versatile cofactors. However, seemingly simple, their main function is electron transfer, that can be coupled to proton transfers. While being ubiquitous in enzymatic systems, a few significant functions remained to be modeled using synthetic molecular mimics. In this talk, we will introduce the use of synthetic Fe₄S₄ clusters acting as concerted proton electron transfer (CPET) mediators for electrocatalytic metal hydride generation, exploited in the context of CO₂ reduction.^[1] Further exploring bio-inspired strategies for electron transfers and storage, we will report here the preparation of the first complete redox series of Fe₄S₄ complexes² that covers all oxidation states accessible by one-electron transformations of the individual Fe-atoms ([Fe₄S₄]⁴⁺-[Fe₄S₄]⁰).^[2] The redox potential of Fe₄S₄ cubanes is often conceived as a static parameter, which fails to explain some of Nature's more elaborate electron transfer mechanisms, particularly conformationally gated ones.^[3] Further replicating the modulation of electric fields in enzymatic systems with our synthetic models, we will present here the case of a synthetic Fe₄S₄(SR)₄ model complex exhibiting dynamic redox potentials on-demand. This can be used to control the occurrence of formerly "uphill" electron transfers similar to these observed in Fe₄S₄-containing ATPases, archerases.



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PCET CHEMISTRY OF HYDROGEN AT SEMICONDUCTOR AND METAL INTERFACES

James MAYER

Chemistry Department, Yale University, P.O. Box 208107, New Haven, CT 06520-8107
james.mayer@yale.edu

Hydrogen is often present at reactive surfaces and solid-solution interfaces, and it is a key component of many catalytic and electrocatalytic processes. Examples of the PCET reactions shown below will be described, for colloidal nanoparticles of gold, cerium oxide,^[1,2] and iridium oxide, and for nickel oxide electrodes.^[3,4] Connections among these reactions, and between PCET electrocatalysis and heterogeneous catalysis, will be developed.^[5,6]

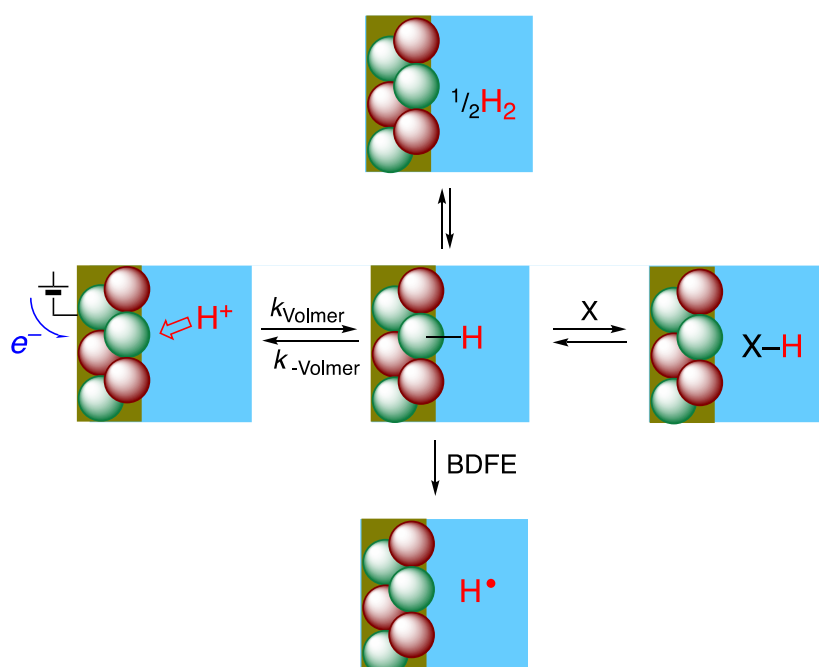


Figure 1. PCET reactions at a solid-solution interface.

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Aqueous Electrochemistry of Hydrated Transition Metal Oxides

Veronica Augustyn

*Dept. of Materials Science and Engineering, NC State University, Raleigh, NC 27596,
vaugust@ncsu.edu*

Technological interest in electrode materials with long-term stability in aqueous electrolytes is motivated by the urgent need for large scale, safe, and low cost electrochemical energy storage and conversion. Transition metal oxides are an important class of redox-active electrode materials for aqueous electrochemical technologies. In aqueous electrolytes, many transition metal oxides will interact with water molecules and protons to form hydrated oxides, materials where the distinction between the solid and liquid phase becomes “nebulous.” I will share results from our group that attempt to answer several fundamental questions on the behavior of hydrated transition metal oxides in aqueous electrolytes: (1) Where does the electric double layer end and intercalation begin? (2) Do inserted protons transport along confined structural water networks? and (3) Is proton insertion coincidental or necessary to catalyze the hydrogen evolution reaction? Together, the results inform the understanding of the ion and proton insertion kinetics and surface catalytic activity of hydrated transition metal oxides in aqueous electrolytes.

Proton-insertion coupled electron transfer at TiO₂ nanostructured electrodes

Véronique BALLAND¹

¹ Address: Université Paris Cité, Laboratoire d'Electrochimie Moléculaire, 75013 Paris, France,
veronique.balland@u-paris.fr

Titanium dioxide (TiO₂) is a wide band-gap n-type semiconductor with versatile functionalities, widespread used as electrode or photoelectrode material in a variety of energy conversion and storage applications. In the field of energy conversion, its photoinduced charge separation properties make it exploited for the photolysis or photoelectrolysis of water, or to produce electricity in dye-sensitized solar cells.^[1,2] In view of energy storage, its use relies on its intrinsic redox activity and its ability to be electrochemically reduced when biased to a sufficiently reducing potential, a reversible process that is accompanied by the (de)insertion of small cations such as Li⁺ in order to compensate locally for the injected negative charge. TiO₂ is thus used as anode material in Li-ion batteries,^[3] where its robustness but also its ease of processing at the nanoscale and its polymorphism allows fundamental studies of the electron-cation coupled charge storage mechanisms.

Here, I will present a less known facet of the electrochemical reactivity of TiO₂, associated to the reversible mass storage of the electron-proton couple. I will first trace the discovery of this proton-insertion coupled electron transfer (PICET) reactivity in mild buffered aqueous electrolytes,^[4] and highlight its specificities by discussing the influence of extrinsic parameters such as the electrolyte composition,^[5,6] as well as intrinsic parameters such as the crystallinity of TiO₂.^[7] Finally, I will discuss the influence that bulk electron-proton storage in TiO₂ can have on a proton-coupled electrochemical reduction catalysis operating at the surface of TiO₂, such as the reduction of dioxygen by a manganese porphyrin, thus highlighting the possible interplay between charge storage and energy conversion.^[8]

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Understanding Interfacial Proton and Hydride Transfer

Noah B. Lewis,¹ Hai-Xu Wang,¹ Ryan P. Bisbey,¹ Wei Lun Toh,¹ Bryan Y. Tang,¹ Karl S. Westendorff,¹ Alexander V. Soudackov,² Yogesh Surendranath¹

¹ *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States; yogi@mit.edu*

² *Department of Chemistry, Yale University, New Haven, Connecticut 06520, United States*

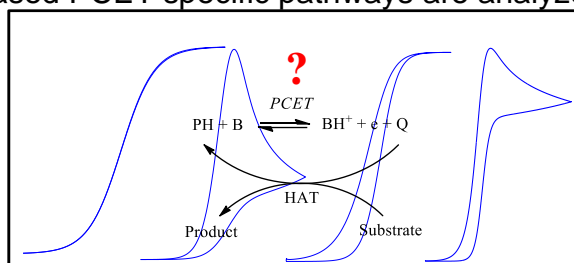
Proton and hydride transfers are complementary and critical elementary steps in energy conversion and catalysis. These reactions can be driven electrochemically via either outer-sphere electron transfer to a soluble molecular active site or can proceed via inner-sphere charge transfer directly at surface active sites on an electrode. While the former has been the subject of extensive investigations at the molecular level, relatively little is known about the latter, termed interfacial PCET (I-PCET) and hydride transfer (I-HyT). For I-PCET, we have constructed molecularly well-defined hosts of I-PCET on carbon electrode surfaces and used these systems to uncover the intrinsic pH dependent kinetics of this reaction. We find that a simple mechanistic model with contributions from hydronium, water, and hydroxide captures kinetic trends across 14 pH units and 3 order of magnitude in rate. For I-HyT, we employ chemo-selective molecular hydride acceptors to reveal that metal surfaces can catalyze the direct reduction of H₂ to hydrides. Whereas molecular hydricity is defined by the molecular structure of the donor, we find that surface hydricity can be tuned by over 40 kcal/mol by varying the applied potential. These studies highlight the key distinctions between outer-sphere and interfacial PCET and hydride transfer and provide a foundation for designing new reactions and (electro)catalysts.

PROTON COUPLED ELECTRON TRANSFER MOLECULAR CATALYSTS. PRINCIPLES AND APPLICATIONS

Cyrille COSTENTIN¹

¹ Univ Grenoble Alpes, DCM, CNRS, 38000 Grenoble, France.
cyrille.costentin@univ-grenoble-alpes.fr

Proton Coupled Electron Transfer (PCET) molecular catalysts will be presented in the framework of cyclic voltammetry (CV). Formal kinetic analysis of the various responses expected in the case of PCET catalysts following either stepwise or concerted pathways will be described. Both buffered solution and non-buffered aqueous media are considered. In the first case we show that, besides possible limitation by buffer diffusion, the PCET sequence may be rate limiting. CV wave shape, position and intensity are discussed in terms of thermodynamic and kinetic penalties associated to each mechanism. In the second case, we show that a non-classical *pseudo*-canonical cyclic voltammogram with hysteresis due to hydronium production is obtained for a Nernstian PCET catalyst with water as proton acceptor. Thermodynamic and kinetic penalties resulting from water based PCET specific pathways are analyzed.



Then, we use this framework investigate the electrochemical catalysis of alcohol oxidation in water with a PCET catalyst, N-hydroxyphthalimide. We have found that the rate constant for benzyl alcohol oxidation is independent of *pH* strongly suggesting a true hydrogen atom transfer (HAT) as rate determining step. When water is the proton acceptor to generate the active form of the catalyst, i.e. N-oxyl PINO radical, the catalytic process follows a stepwise PTET pathway which kinetics partially limits the catalytic current. ^[1-2]

Finally, recent results showing the role of PCET to generate a free coordination site on a molecular catalyst enabling small molecule activation (namely N_2O) will be discussed. ^[3]

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CATION-COUPLED ELECTRON HOPPING TRANSPORT AND REDOX CONDUCTIVITY IN METAL-ORGANIC FRAMEWORKS

Jingguo LI,¹ Ben A JOHNSON,¹ Sascha OTT¹

¹ Department of Chemistry – Ångström Laboratory, Box 523, 75120 Uppsala, Sweden

Electron hopping through metal-organic frameworks is coupled to the physical translocation of charge-balancing counter cations. This process is usually characterized by an apparent diffusion coefficient (D_e^{app}), which is a composite metric that includes components from electron and cation diffusion migration.^[1] To further our understanding of charge transport in MOFs, we take inspiration from proton-coupled electron transfer (PCET) systems. In this presentation, we will draw analogies between the two systems, and show how solvent polarity and the nature of the cation will determine the extent of ion-pairing in MOFs, which in turn governs transport kinetics (Figure 1a). Depending on such external parameters, different microscopic transport mechanisms may be operating in the same MOF.^[2] Furthermore, we will demonstrate that MOFs with electronically isolated redox active sites are redox conductors. This implies that conductivity is maximal at an applied potential that corresponds to the mid-point potential of the redox active unit, and decreases rapidly upon deviating from this value. For the first time, we will demonstrate redox conductivity in MOFs by characteristic bell-shaped conductivity curves as a function of applied potential (blue and green in Figure 1b).^[3]

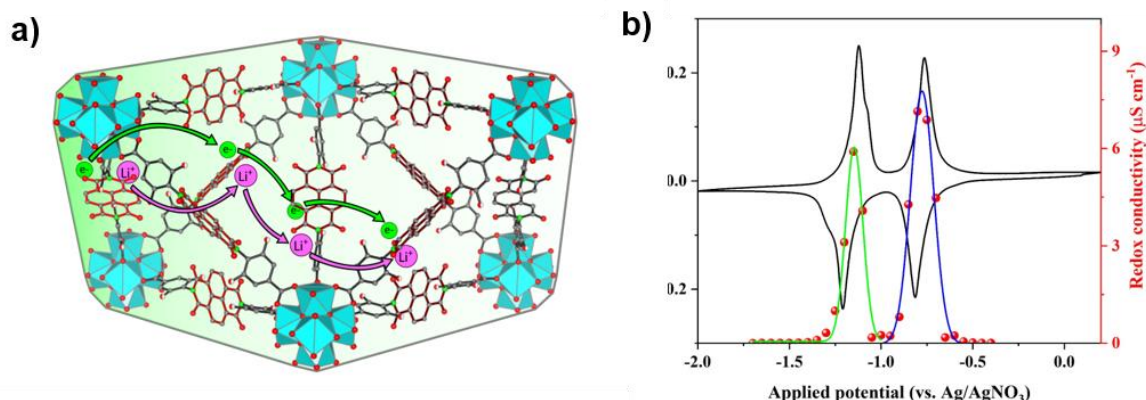


Figure 1. a) Schematic representation of cation-coupled electron hopping transport through a metal-organic framework. b) Cyclic voltammogram (black) of a MOF composed of redox active naphthaleindiimide (NDI) linkers, and the corresponding conductivity curves (in blue and green). Bell-shaped curves that are characteristic of redox conductivity are demonstrated for the first time.

• Acknowledgements

Financial support from the Swedish Energy Agency (P42029-2), the Knut & Alice Wallenberg Foundation (KAW 2019.0071), and the Olle Engkvists Foundation (212-0147) is gratefully acknowledged.

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The Unexpected Complexity of PCET in Biological Proton Reduction

Sven T. Stripp,¹

¹ *Biophysical Chemistry, Technische Universität Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany*

[FeFe]-hydrogenases are highly efficient H₂ oxidation and proton reduction (H₂ evolution) catalysts. Under ambient conditions, turnover rates of up to 10 kHz have been reported, most notably at negligible electric overpotential ($E_0 = -420$ mV vs. SHE).[1] [FeFe]-hydrogenases bind an unique active site cofactor, composed of a [4Fe-4S] cluster covalently bound to a diiron site. The later is modified with 3–4 CO ligands, 2–3 CN ligands, and an azadithiolate ligand that is in hydrogen-bonding contact with the second coordination sphere of the cofactor.[2]

High resolution crystal structures have revealed the structure of several [FeFe]-hydrogenases and cofactor states; however, the mechanism of hydrogen turnover remains elusive.

Based on the infrared signature of the active site cofactor[3], I will introduce different redox species and discuss their role in catalysis. We found that reduction of the cofactor is coupled to proton transfer and forms an apical hydride species (aH⁻) that reacts with a second proton to H₂. [4] Surprisingly, a second PCET event occurs upon reduction of the [4Fe-4S] cluster. I will discuss how reduction and protonation of the [4Fe-4S] cluster impedes “overreduction” of the diiron site and the successive formation of a bridging hydride species (μH^-) that is an off-cycle intermediate.[5] Our findings have important implications for the design of biomimetic catalysts than can be used in fuel cells.[6]

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PCET REACTIONS IN NON-LIGHT ACTIVE ENZYMES TRIGGERED BY LIGHT

Moritz SENER,¹ Princess CABOTAJE,¹ Mira GAMACHE,¹ Henrik LAND,¹ Gustav BERGGREN¹

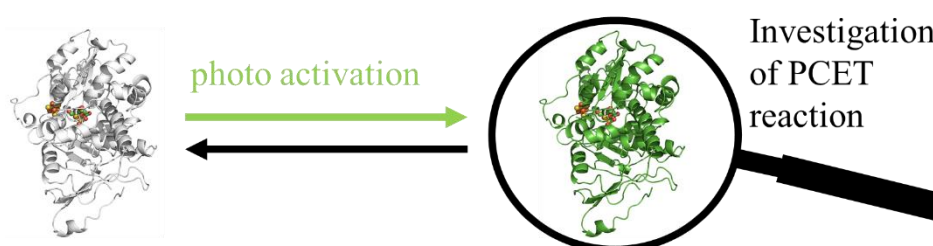
¹ Uppsala University, Department of Chemistry - Ångström Laboratory, Molecular Biomimetics;
Biophysical and Bioinorganic Chemistry

moritz.senger@kemi.uu.se

[FeFe]-Hydrogenases are metallo enzymes that catalyse bidirectional H₂ turnover ($2e^- + 2H^+ \leftrightarrow H_2$) raising interest for their application in a hydrogen economy. Catalysis takes place at a cofactor composed of a [4Fe4S]-cluster and an unusual diiron site that is common for all [FeFe]-Hydrogenases. The most studied group of [FeFe]-Hydrogenases (Group A) facilitate bidirectional and reversible catalysis at high turnover numbers and protons are transferred to the active site via a conserved Proton Transfer Pathway (PTP) composed of amino acid residues and water molecule. Studies on the reaction mechanism are usually triggered chemically or electrochemically. Here I artificially activate [FeFe]-hydrogenases photochemically via an organic redox dye to reveal the molecular events of:

- reduction triggered proton transfer to the active site via the PTP ^[1]
- PCET steps in the catalytic cycle of different [FeFe]-hydrogenases featuring alternative second coordination spheres of the cofactor ^[2]
- potential H₂ sensing function in sensory [FeFe]-hydrogenases ^[3]
- whole cell semi-artificial photosynthesis ^[4]

More general, our results demonstrate how artificial photo activation can be used as a tool to investigate PCET reactions in non-light active enzymes.



Scheme 1. Artificial photo activation to investigate PCET reactions in non-light active enzymes.

References:

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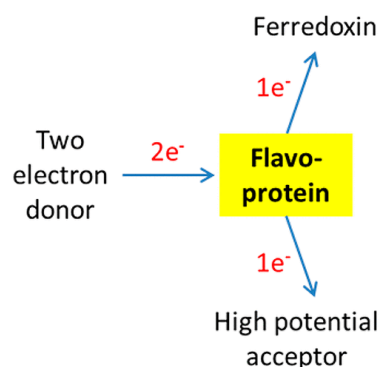
THE PARAMETERS THAT DEFINE FLAVIN-BASED ELECTRON BIFURCATION

John W. Peters¹, David N. Beratan², and Carolyn E. Lubner³

¹ Department of Chemistry and Biochemistry, The University of Oklahoma, Norman, OK 73019, jw.peters@ou.edu

² Department of Physics, Duke University, Durham, NC 27708 & Department of Chemistry, Duke University, Durham, NC 27708, ³ Biosciences Center, National Renewable Energy Laboratory, Golden, CO 80401

The term “Electron Bifurcation” (EB) has its origins as a component of the “Chemiosmotic Hypothesis” in the explanation of the functioning of what is coined the “Q cycle”. The basics of the “Chemiosmotic Hypothesis” is that the electron transport chain (ETC) couples the negative change in free energy from exergonic electron transfer reactions, from both mobile and fixed electron carriers, to drive the formation of a proton/ion gradient. The potential energy of the proton/ion gradient is then harnessed to drive the formation of chemical energy in the form of ATP which is the unifying form of energy for life processes. The elegant interconversion between potential energy species provides the basis for defining biological energy conservation fundamental to life. Phenomena satisfying this criterion were not recognized again for nearly forty years when about a decade ago, EB re-emerged in the context of anaerobic metabolism. Several examples of flavin-based electron bifurcating enzymes have been described that involve the coupling of the oxidation of a two-electron donor such as the organic cofactor NAD(P)H coupled intimately to one electron reductions of a high potential acceptor and the low potential electron carrier ferredoxin (right)^[1]. In anaerobic metabolism, where free energy cannot be squandered without dire consequences to cell viability, EB provides a high-fidelity mechanism to promote efficient energy conservation. Recent work from our research laboratories and others have provided the basis for defining the basic tenants that define flavin-based bifurcation. We suggest these tenants include 1) a bifurcating center capable of brokering both single and pairwise electron transfer reactions, 2) an energetic intermediate is required capable of driving a reduction reaction more negative than the average reduction potential of the two redox transitions of the bifurcating center, 3) a fixed and defined stoichiometry of 1:1 electrons transferred along different energetic paths, and 4) an energy landscape or specific mechanism that circumvents energy-wasting short-circuiting reactions^[2]. The talk will discuss the elegant enzyme architectures and the interesting physical properties and mechanistic features they have evolved to satisfy these criteria.



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The electron-proton bottleneck of photosynthetic oxygen evolution

Paul Greife^{1#}, Matthias Schönborn^{1#}, Matteo Capone^{2,3#}, Ricardo Assunção¹, Daniele Narzi³, Leonardo Guidoni^{3*}, Holger Dau^{1*}

[#]These three authors contributed equally. ^{*}Corresponding authors.

¹Dept. of Physics, Freie Univ. Berlin, Germany;

²Dept. of Information Engineering, Computer Science and Mathematics, Univ. of L'Aquila, Italy;

³Dept. of Physical and Chemical Sciences, Univ. of L'Aquila, Italy;

Today's oxygen-rich atmosphere results from photosynthetic O₂-production during water-splitting at the protein-bound manganese cluster of photosystem II. Formation of the O₂ molecule starts from a state with four accumulated electron holes, the S₄ state, postulated half a century ago and remaining enigmatic ever since. Here we resolve this missing key element in photosynthetic O₂-formation and its crucial mechanistic role. We tracked 230,000 excitation cycles of dark-adapted photosystems with microsecond infrared spectroscopy. Combining these results with computational chemistry reveals that first a crucial proton vacancy is created through gated sidechain deprotonation. Subsequently, a reactive oxygen radical is formed in an astonishing single-electron multi-proton transfer event. This is the slowest step in photosynthetic O₂-formation, with moderate energetic barrier and remarkable entropic slowdown. We identify the enigmatic S₄ as the oxygen-radical state; its formation is followed by fast O-O bonding and O₂-release. In conjunction with previous breakthroughs in experimental and computational investigations, a compelling atomistic picture of photosynthetic O₂-formation emerges. Our results provide insight into a biological process that has probably operated in the same unique way for three billion years and are expected to support the knowledge-based design of artificial water-splitting systems.[1]

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Energetics of Proton-Coupled Electron Transfer in M-(μ -OH)-M (M = Cu, Ni) Complexes

Ming-Tian Zhang

Center of Basic Molecular Science, Department of Chemistry, Tsinghua University, Beijing 100084, China

A series of hydroxo-bridged dicopper/dinickel complexes has been used to target reactive copper species relevant to proposed intermediates in catalytic hydrocarbon oxidations by particulate methane monooxygenase. The redox potentials and pKa values of M-(μ -OH)-M (M = Cu, Fe) complexes were determined and the bond dissociation energy of the O-H bond in M^{II}-(μ -OH)-M^{II}, M^{II}-(μ -OH)-M^{III}, and M^{III}-(μ -OH)-M^{III} were also determined according to pKa and $E_{1/2}$ in acetonitrile solution. We'll also discuss the effect of structure (including metal, substituent on the ligand, charge ...) on the energetics of the PCET reactions, as well as the kinetics of the reaction between M-(μ -O)-M and C-H substrates.

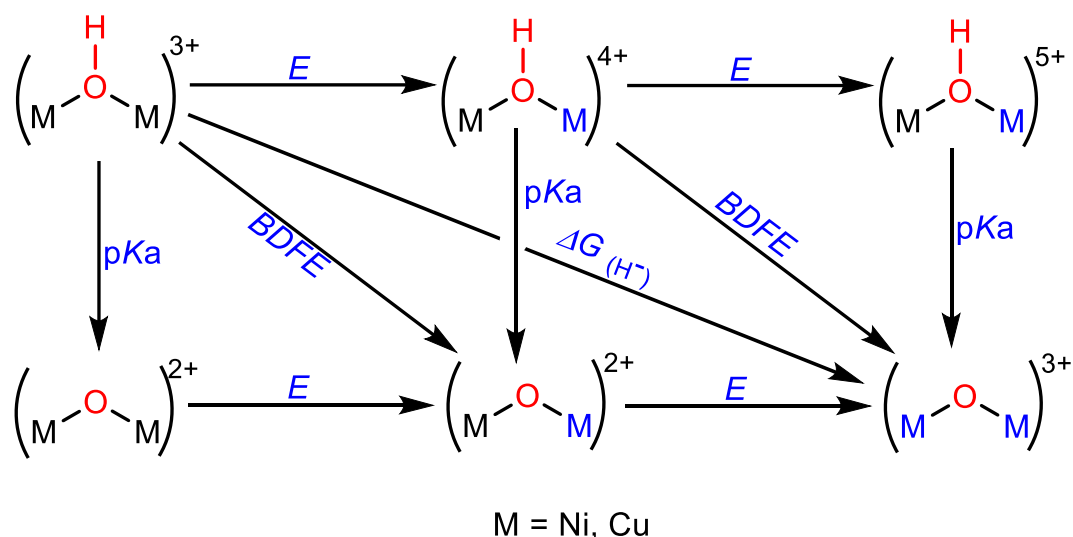


Figure 1. Energetics of PCET reactions in M-(μ -OH)-M (M = Cu, Ni) Complexes

Insights into Light-Initiated Net Hydrogen Atom Transfers to Early Transition Metal Oxos

Courtney L. Baumberger,¹ Dinushini Siddhharatchi,¹ Saeed Fosshat,¹ Victoria Z. Valley,¹ Victor Rodriguez-Ortiz,¹ Frank R. Fronczek,¹ Matthew B. Chambers¹

¹Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803-1804, United States. chambers@lsu.edu

Biological cofactors, such as cytochrome P450, employ metal oxos to activate C–H bonds under ambient conditions via hydrogen atom transfer.^[1] A unique aspect of cytochrome P450 is that the high valent intermediate that accepts the H atom has a radical cation delocalized in the π -system of the ancillary ligand to accept an electron while the oxo accepts the proton.^[1,2] By separating the acceptor sites and allowing the π -system to act as the electron acceptor as opposed to the metal center, we hypothesized that this lowered the activation barriers gating HAT by attenuating the inner sphere reorganization energy for ET. To mimic this synthetically, we explored stable early transition metal oxos that, upon a LMCT, possess the zwitterionic structure of compound I in the excited state. Using group VI dioxos of the form $\text{MO}_2\text{X}_2(\text{bpy})$, $\text{M}=\text{Mo}$, W , we observe facile HAT from alkanes upon excitation (Figure 1).^[3] The reactivity of variants in corroboration with TDDFT suggests that a $\text{bpy} \rightarrow \text{M}$ LMCT is necessary for HAT reactivity. This presentation will elaborate on mechanistic insights, impacts of product selectivity after HAT, and photocatalytic activity and stability.

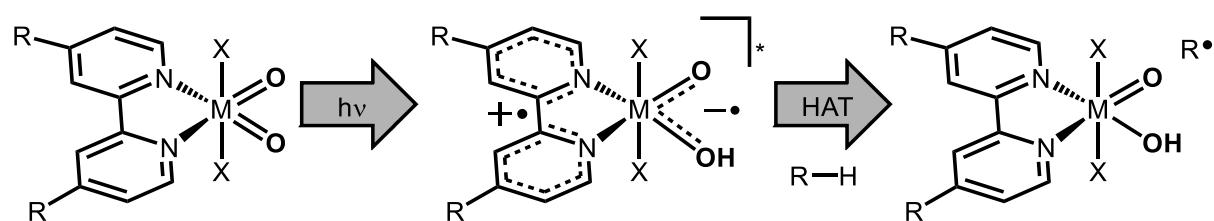


Figure 1. Representation of LMCT and subsequent net HAT upon excitation of $\text{MO}_2\text{X}_2(\text{bpy})$ complexes, $\text{M}=\text{Mo}$ and W .

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Nitrogen Fixation Strategies guided by PCET

Sven Schneider

Address: University of Göttingen, Institute for Inorganic Chemistry, Tammannstr. 4, 37077 Göttingen, Germany, sven.schneider@chemie.uni-goettingen.de

Nitrogen fixation at ambient conditions has made remarkable progress in recent years, while the direct catalytic transformation of N_2 to nitrogenous organic products, such as amines, nitriles or nitro compounds, remain unknown.

Reductive splitting of dinitrogen into transition metal nitride complexes represents a potential entry towards N_2 fixation beyond ammonia (Figure 1),^[1] and can also be driven electrochemically or photochemically.^[2] In this contribution, synthetic strategies will be discussed that are guided by the N–H PCET thermochemistry vs. organic electrophiles to control the selectivity for NH_3 vs. NR_xH_{3-x} formation.

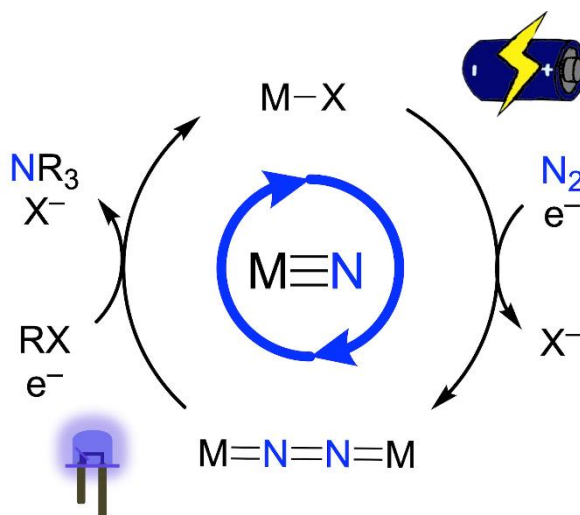


Figure 1. Nitrogen fixation to ammonia or organic products via reductive N_2 splitting.

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Porphyrins Decorated with Urea Functions for CO₂ Activation and Reduction

Chanjuan Zhang,¹ Eva Pugliese,¹ Winfried Leibl,² Marie Sircoglou,¹ Philipp Gotico,² Zakaria Halime,¹ Ally Aukauloo^{1,2}

¹ Université Paris-Saclay, CNRS, Institut de chimie moléculaire et des matériaux d'Orsay, 91405, Orsay, France, ally.aukauloo@universite-paris-saclay.fr

² Service de Bioénergétique, Biologie Structurale et Mécanismes (SB2SM), CEA/DRF/JOLIOT, Université Paris-Saclay, 91191, Gif-sur-Yvette, France

Biomimetic multipoint hydrogen bonding stabilization using urea functions at an iron porphyrin catalyst boosted the CO₂ reduction to CO with a consequent drop in the overpotential while maintaining high turnover frequencies. Entrapped water molecules within the molecular urea clefts were found to be the source of protons.^[1] Adapting the 3D topological layout of an iron porphyrin catalyst bearing urea groups in the second coordination sphere can induce a switch from higher affinity for CO₂ binding to faster reaction rate for the CO₂ electrocatalytic reduction to CO with a noticeable change in the kinetic isotope (H/D) effect.^[2] When coupled to a photosensitizer the exceptionally high performance for CO₂-to-CO photocatalytic reduction displayed by the iron-porphyrin with urea groups in the second coordination sphere is the result of the interaction CO₂ with the catalyst prior the occurrence of the second electron uptake in the catalytic cycle.^[3] The cooperativity between the two metal centres held by a urea linker was evidenced for both homo- and heterobimetallic analogues leading to a significant enhancement of the catalytic performances of the heterogeneous CO₂-to-CO electrocatalytic reduction in water.^[4]

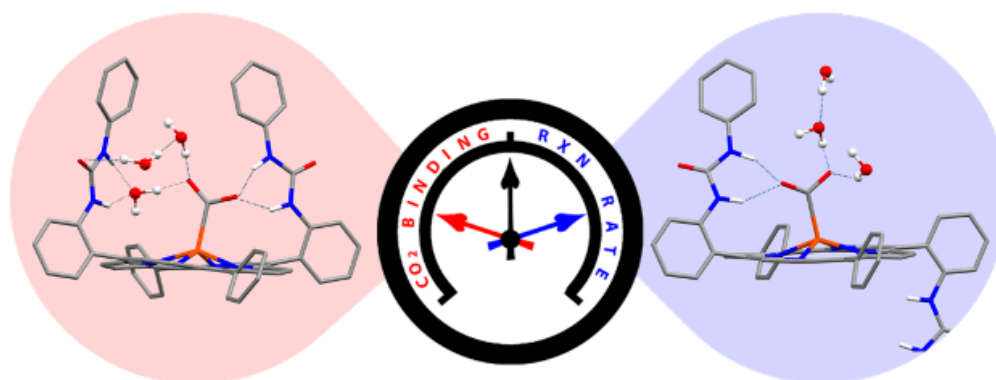


Figure 1. Atropisomeric control for the CO₂ capture and activation

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HARNESSING LIGHT FOR PHOTOCATALYTIC PCET USING MOLECULAR MEDIATORS

Pablo GARRIDO BARROS,¹

¹ Address: Department of Inorganic Chemistry, University of Granada, Granada, 18071, Spain.
pgarridobarros@ugr.es

Proton-coupled electron transfer (PCET) steps have become central to the development of new technologies for renewable energy conversion and sustainable chemical synthesis.^[1,2] Their kinetic advantage relative to stepwise proton and electron transfers, translating into a higher energy efficiency, is key to a number of biological processes and has inspired new chemical methodologies. When applied to reductive transformations, they can facilitate the synthesis of value-added chemicals and fuels from unsaturated organic substrates or small molecules such as N₂ or CO₂ respectively. However, the highly reducing conditions that these substrates typically require to form the new X–H bonds, recombination of protons and electrons to generate H₂ is usually thermodynamically and kinetically favorable. While the challenge remains to generate selective, and broadly applicable PCET donors that are stable to spontaneous H₂ evolution, last years have witnessed the development of both stoichiometric and catalytic reductive PCET reagents.^[3] Photocatalytic systems, which can harness light to generate strong excited-state PCET donors, are especially attractive as a means for direct solar energy utilization.^[4] This talk will focus on the development of molecular platforms for photocatalytic PCET relevant to energy conversion towards the synthesis of renewable fuels and chemicals.

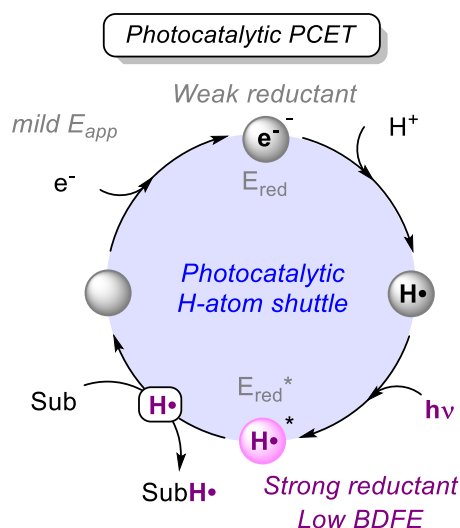


Figure 1. Photocatalytic strategy for proton coupled electron transfer using a molecular mediator.

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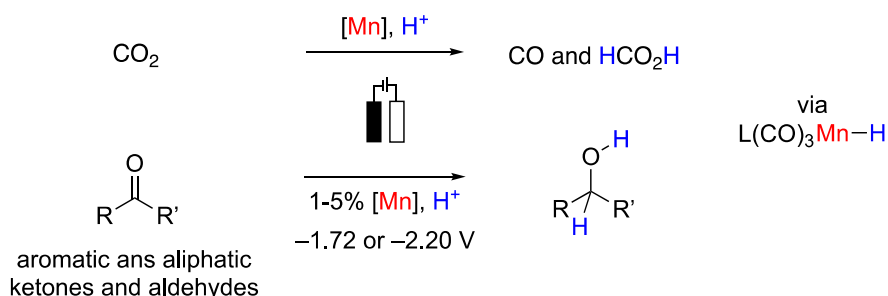
Hydrogenation of C=O Bonds in CO₂, Ketones, and Aldehydes by Electrons and Protons

Inke SIEWERT, Igor Fokin, Kai-Thorben Kuessner

¹ Address: Georg-August-Universität Göttingen, Germany, inke.siewert@chemie.uni-goettingen.de

Hydrogenation reactions are fundamental functional group transformations in chemical synthesis. Initially, research on hydrogenation reactions focused on the use of noble metal complexes based on Ru, Rh, Ir, Pd, Pt and remarkable achievements have been made using such complexes. However, recently the focus shifted towards the use of non-precious metal catalysts, as these metals exhibit a higher availability in earth's crust.^[1] In the first instance, the direct reduction of C=O bonds with H₂ seems to be a very atom and redox economic approach. However, the reaction protocols for base-metal catalyzed hydrogenation reactions require often harsh reaction conditions and high H₂ pressure to activate H₂ and each ton of H₂ that is formed *via* steam reforming produces about 12 tons of CO₂.^[2]

We developed an electrochemical approach utilizing electrons and protons for the catalytic hydrogenation of polar double bonds, such as C=O in CO₂, ketones, and aldehydes.^[3] In a proof of principle study we demonstrated that *in-situ* generated Mn hydride species hydrogenate CO₂ forming formic acid. This protocol was later expanded to aromatic, and aliphatic ketones as well as aldehydes. The method is selective for C=O bonds over the thermodynamically favored hydrogenation of C=C bonds. The competing hydrogen evolution reaction was suppressed successfully, and the reactions proceed with high Faraday efficiencies. In-depth mechanistic studies gave valuable insights for catalyst improvement.



Scheme 1. Schematic presentation of the hydrogenation of C=O bonds by H⁺ and e⁻.

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TAILOR-MADE ELECTRON TRANSFER PATHWAYS IN PHOTOCATALYSIS – A QUANTUM CHEMICAL PERSPECTIVE

Georgina E. SHILLITO,¹ Guangjun YANG,¹ Stephan KUPFER¹

¹ Address: Institute of Physical Chemistry, Friedrich Schiller University Jena, Helmholtzweg 4, 07743 Jena, Germany. stephan.kupfer@uni-jena.de

Solar energy conversion is among the most promising approaches to transform our energy sector towards sustainability. In this context, photocatalysis allows the conversion of sunlight into chemical energy such as molecular hydrogen. Typically, both the light-harvesting unit as well as the catalytic centres in (supra)molecular photocatalysts heavily rely on precious 4d and 5d transition metals due to their favourable photophysical and electrochemical properties, alongside thermal, light and pH stability. Thus, the broadscale application of such systems is limited by the scarce availability of these metals. Unfortunately, utilizing earth-abundant 3d metal-based photosensitizers, e.g. Fe(II) complexes, suffers from excited-state lifetimes in the ps regime limiting the photocatalytic ability.^[1,2]

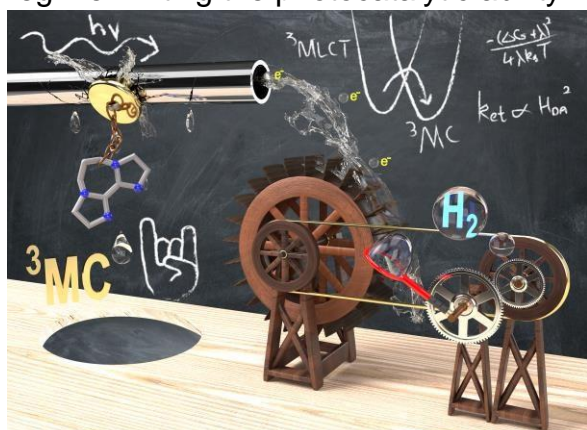


Figure 1. Assessing and tuning excited-state electron transfer channels within the semi-classical Marcus picture for molecular photocatalysts using quantum chemistry.^[4,7]

electron transfer kinetics in photocatalysts in the frame of H₂ generation.^[5] To this aim, the driving forces, electronic couplings as well as the reaction coordinates connecting the diabatic states involved in the light-driven process of interest are elucidated by means of our lately introduced external optimizer pysisyphus.^[7]

Here, we tailor the accessibility of prominent – yet undesirable – excited-state deactivation channels via the so-called metal-centred states. Based on the reliable description of photophysical and photochemical processes investigated using state-of-the-art multiconfigurational methods and cost-efficient time-dependent density functional theory,^[3] we present selected aspects of our theory-driven design concepts to drive the desired electron and energy transfer processes associated with catalytic turn-over.^[4] In particular, we focus on simulating competitive intramolecular energy and

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Electron Photo-Accumulation in Ir(III) Photosensitizers for Proton and Carbon Dioxide Reduction

Simon DE KREIJGER,¹ Renato N. SAMPAIO,² Benjamin ELIAS,¹ Ludovic TROIAN-GAUTIER¹

¹ *Université catholique de Louvain, 1 Place Louis Pasteur, 1348 Louvain-la-Neuve.*

Ludovic.Troian@uclouvain.be

² *University of North Carolina at Chapel Hill, 123 South Road, Chapel Hill, North Carolina*

In view of developing novel sustainable energy supply as an alternative or complement to fossil fuels, different technologies have been explored for the conversion of sunlight into useful energy sources. Among them, the sunlight-triggered hydrogen evolution reaction (HER) represents a promising solution to worldwide consumption of fossil fuels as hydrogen is an energy-dense and carbon-free fuel. This HER usually operates via a photoinduced electron transfer (PET) from a photosensitizer (PS) to a catalytic centre, where hydrogen is produced. Current challenges in the field are related to the development of more robust hydrogen evolving catalysts and photosensitizers that absorb a wider range of the solar spectrum as well as a deeper engagement of researchers towards the development of active repair strategies.

In here, we will present our recent effort to develop novel Ir(III) photosensitizers with increased visible light absorption and that are able to store up to four electrons on one ligand. The excited-state behavior and photo-induced electron properties were investigated by nanosecond transient absorption experiments which highlighted that multiple subsequent reduction could be performed using visible light irradiation. Finally, these newly developed photosensitizers were evaluated for proton and CO₂ reduction using well-established catalysts and compared to prototypical iridium(III) photosensitizers unable to photo-accumulate electrons.

Homoleptic Al(III) Photosensitizers for Durable CO₂ Photoreduction

Jia-Wei Wang,¹ Zhi-Mei Luo¹, Antoni Llobet¹

¹ Institute of Chemical Research in Catalonia (ICIQ), Avda. Països Catalans, 16 43007 Tarragona.
jwang@iciq.es

Exploiting noble-metal-free systems for high-performance photocatalytic CO₂ reduction still presents a key challenge, partially due to the long-standing difficulties in developing potent and durable earth-abundant photosensitizers. Therefore, based on the very cheap aluminum metal, we have deployed a systematic series of homoleptic Al(III) photosensitizers featuring 2-pyridylpyrrolide ligands for CO₂ photoreduction.^[1] The combined studies of steady-state and time-resolved spectroscopy as well as quantum chemical calculations demonstrate that in anerobic CH₃CN solution at room temperature, visible light excitation of the Al(III) photosensitizers leads to efficient population of singlet excited states with nanosecond-scale lifetimes and notable emission quantum yields (10~40%). The results of transient absorption spectroscopy further identified the presence of emissive singlet and unexpectedly non-emissive triplet excited states. More importantly, the introduction of methyl groups at the pyrrolide rings can greatly improve the visible-light absorption, reducing power and durability of the Al(III) photosensitizers. With an Fe(II)-quaterpyridine catalyst, the most methylated Al(III) photosensitizer achieves an apparent quantum efficiency of 2.8% at 450 nm for selective (> 99%) CO₂-to-CO conversion, which is nearly 28 times that of the unmethylated one (0.1%) under identical conditions. The optimal system realizes a maximum turnover number of 10250 and higher robustness than the systems with Ru(II) and Cu(I) benchmark photosensitizers. Quenching experiments using fluorescence spectroscopy elucidate that the photo-induced electron transfer in the Al(III)-sensitized system follows a reductive quenching pathway. In the follow-up work, we have further utilized time-resolved X-ray absorption spectroscopy to monitor the electron transfer kinetics in the Al(III)-Fe(II)-based system and the formation time of the active Fe(I) species.

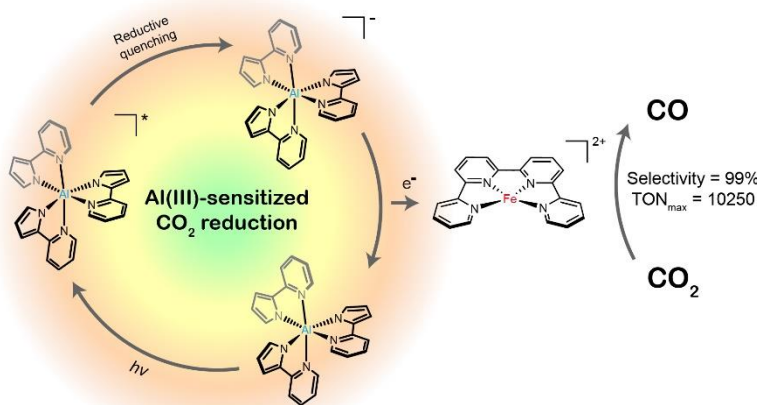


Figure 1. Scheme for the Al(III)-Fe(II) system for CO₂ reduction to CO.

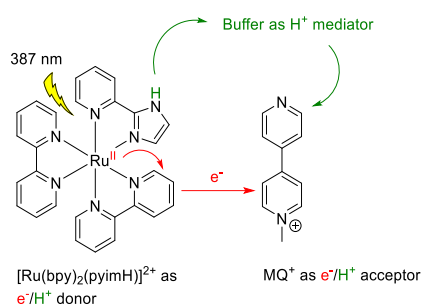
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Excited-state PCET chemistry under high-pressure measured by time-resolved femto- and nanosecond transient absorption spectroscopy

Daniel Langford,¹ Robin Rohr,² Stefan Bauroth,¹ Achim Zahl,² Alicja Franke,^{2,3} Ivana Ivanović-Burmazović,^{2,3} and Dirk M. Guldi¹

¹Department of Chemistry and Pharmacy & Interdisciplinary Center for Molecular Materials (ICMM), Physical Chemistry I, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstrasse 3, 91058 Erlangen, Germany, ²Department of Chemistry and Pharmacy, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstrasse 1, 91058 Erlangen, Germany, ³Department of Chemistry, Ludwig-Maximilians-Universität München, Butenandtstraße 5-13, Haus D, 81377 München, Germany
Ivana.Ivanovic-Burmazovic@cup.uni-muenchen.de



Scheme 1. Excited-state PCET investigated under elevated

well as the concept of using pressure to modulate PCET mechanisms. By means of TAS we visualized altering ratio of rate constants for PT and ET steps upon concentration and/or pressure increase (up to 120 MPa) resulting in changeover from a stepwise to concerted mechanism. Pressure studies of photoinduced redox processes under such conditions revealed a value of activation volume, $\Delta V^\ddagger = -3.3 \pm 3.0 \text{ cm}^3 \text{ mol}^{-1}$, that is close to zero, as expected for a concerted mechanism. At low [MQ⁺], the absorbance changes attributed to PT and following ET are well separated for pressures up to 60 MPa. This goes hand-in-hand with $\Delta V^\ddagger = -14.5 \pm 0.5 \text{ cm}^3 \text{ mol}^{-1}$, in line with the occurrence of pure ET, where the volume of the transition state is usually smaller than that of the reactants.^[2]

We have elucidated the mechanism of excited-state PCET (**Scheme 1**),^[1] based on pressure-dependent measurements by femto-/nano-second resolved transient absorption spectroscopy (TAS) with a home-made high-pressure cell for detection (**Figure 1**). Our rather unique study of excited-state PCET under high-pressures, enabled us to demonstrate the power of variable pressure measurements in the excited-state chemistry to distinguish between stepwise and concerted PCET processes, as well as the

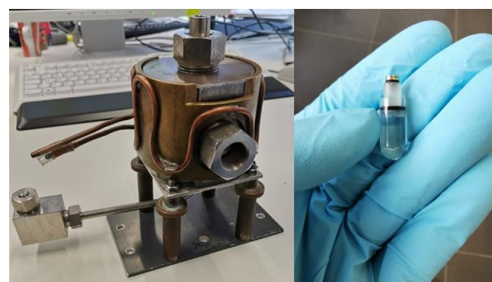


Figure 1. Left: Home-made pressure cell using water as a pressurizing medium. The pump/probe pulses pass the cell through the optical windows at the front and backside. The top screw enables access to the sample chamber. Right: Cylindrical cuvette (inner diameter: 4 mm) sealed with a moveable piston used for high-

• **Acknowledgement:** We acknowledge a financial support by DFG through the project GU 517/23-1 | IV 80/12-1.

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ACCEPTORLESS DEHYDROGENATION OF N-HETEROCYCLES CATALYZED BY A SINGLE IRIIDIUM(III) METAL COMPLEX ASSISTED BY VISIBLE LIGHT

Gregorio GUISADO-BARRIOS,^{*1} Carmen MEJUTO,² Laura IBAÑEZ-IBÁÑEZ,² José A. MATA,^{*2}

¹ Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), Universidad de Zaragoza- CSIC, 50009, Zaragoza, Spain, E-mail: gguisado@unizar.es

² Instituto de Materiales Avanzados (INAM), Centro de Innovación en Química Avanzada (ORFEO-CINQA), Universitat Jaume I, 12071 Castellón, Spain

The acceptorless dehydrogenation of tetrahydroquinolines (THQs) has recently received considerable attention, not only because it avoids the use of stoichiometric oxidants in these organic reactions, but also owed to their prospective use in alternative energy technologies as Liquid Organic Hydrogen Carriers (LOHCs) for hydrogen storage in the liquid form.^[1]

Still, the development of effective catalysts for hydrogen-storage has proven difficult since they must fulfill a series of technical specifications in practical terms. One of the most limiting factors is hydrogen's discharge temperature from carrier (90-300°C). In contrast, visible light irradiation can provide energy inputs thermally inaccessible. Effective photocatalytic systems for the acceptorless dehydrogenation of N-heterocycles have been recently reported.^[2] However, despite their success, they rely on a ruthenium-based photosensitizer $[\text{Ru}(\text{bpy})_3]^{2+}$ and a cobalt complex $[\text{Co}(\text{dmgH})_2\text{PyCl}]$ (dmgH = dimethylglyoximate). Additionally, a third iridium catalysts $[\{\text{Ir}(\text{Cp}^*)(\text{Cl})\}_2(\text{thbpy})]$ bearing (thbpy = 4,4',6,6'-tetrahydroxy-2,2'-bipyrimidine) is required to efficiently catalyze the reverse process (i.e. hydrogenation of N-heterocycles). Herein, the availability of a single effective catalyst for both transformations is highly desirable.

Thus, the synthesis and catalytic performance of a standalone iridium complex towards the visible light assisted acceptorless dehydrogenation of N-heterocycles and the thermal reverse reaction will be presented in this contribution (Figure 1).^[3]

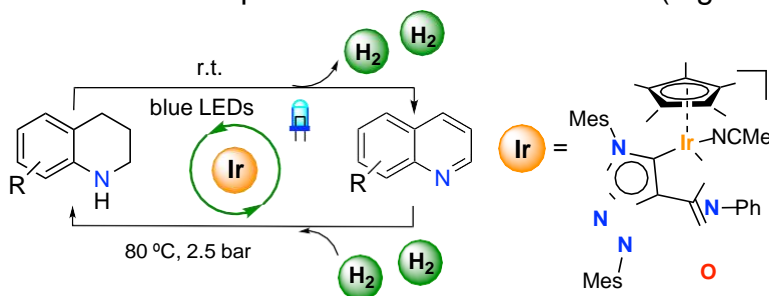


Figure 1. (De)hydrogenation of N-heterocycles catalyzed by a Ir(III) metal complex.

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CO insertion into a Ru-H bond: the role of formyl intermediates in the interconversion between three isomers

Javier J. Concepcion, Sai P. Desai, Andressa Vidal Muller, Chiara Cappuccino, Mehmed Z. Ertem

Address: Chemistry Division, Brookhaven National Laboratory, Upton, NY 11973, USA

Metal hydrides play a pivotal role in mediating key elementary steps leading to the formation of CO₂ reduction products. A detailed understanding of the hydride transfer step will enable efficient conversion of CO₂ to formic acid, methanol, and other value-added chemicals. The thermodynamics for the hydride transfer (thermodynamic hydricity) between donor (e.g., a metal-hydride) and acceptor (e.g., CO₂) determines if the hydride transfer is viable or not. A series of Ru hydride isomers with N-heterocyclic carbene (NHC) ligands will be presented. The thermodynamic hydricity within this series changes by ~10 kcal/mol. Such a change is difficult to achieve with introduction of electron-donating and/or electron-withdrawing groups. The interconversion between isomers takes place through formyl intermediates generated by insertion of CO into a Ru-H bond. To our knowledge, this is the first experimental demonstration of this process. Understanding the reactivity of metal formyl intermediates might enable the identification of homogeneous catalysts that operate at lower temperatures, pressures, and/or overpotentials. The reaction of the more hydridic Ru-NHC hydrides with CO₂ is significantly faster than for other Ru hydrides with similar hydricities. This is a clear demonstration of the *trans* effect of the carbene ligand on the rate of hydride transfer (kinetic hydricity).

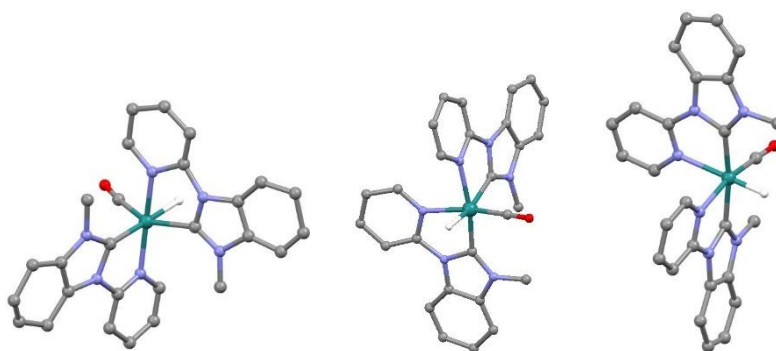


Figure 1. X-ray structures of the isomeric Ru-NHC hydrides.

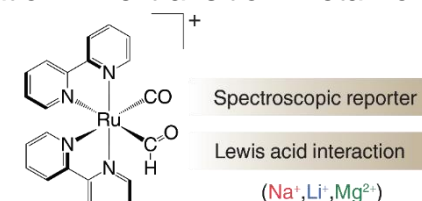
• **Acknowledgements:** This work was supported by the U.S. Department of Energy, Office of Science, Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, under contract DE-SC0012704.

PCET REACTIVITY OF FORMYL COMPLEXES AND ORGANIC HYDRIDES WITHIN CHASE

Jake Sirlin,¹ Andressa Muller,² Alexander Deetz,¹ Mehmed Ertem,² Javier Concepcion,^{2*} Renato Sampaio^{1*} and Gerald Meyer¹

¹Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill NC USA 27599
gimeyer@email.unc.edu ²Chemistry Division, Brookhaven National Laboratory, Upton, NY USA 11973

The **Center for Hybrid Approaches in Solar Energy to Liquid Fuels**, called CHASE, is advancing the quest for liquid fuels generated from water and carbon dioxide feedstocks with sunlight as the only energy source.^[1] To realize this quest, CHASE utilizes hybrid photoelectrodes based on molecular catalysts integrated with semiconductors for water oxidation and CO₂ reduction.^[2,3] In ongoing CHASE studies it has become evident that a more detailed understanding of the PCET reactivity of transition metal formyl complexes and organic hydrides could one day enable the catalytic reduction of CO₂ to a liquid fuel like methanol. This will be the focus of this presentation. The transition metal formyl complex **Ru-CHO** has emerged as a particularly useful reactant for fundamental PCET studies and for catalysis applications.^[3] The infrared stretch of the carbonyl reports on the electron density at the metal center, Scheme 1. The formyl oxygen atom formed Lewis acid-base adducts with Na⁺, Li⁺, and Mg²⁺ in acetonitrile solutions that had a dramatic impact on



Scheme 1. Formyl Complex **Ru-CHO**.

the reactivity. For example, **Ru-CHO** displayed rapid decarbonylation reactivity to form mainly the hydride [Ru(bpy)₂(CO)(H)]⁺ and CO, yet in the presence of Li⁺ only 17% had reacted after ten days. The electrochemical and spectroscopic properties of the **Ru-CHO**...Mg²⁺ adduct differed most significantly from **Ru-CHO** and were consistent with computational studies that revealed a carbene like structure that reacted further to yield methanol. Reactivity studies of **Ru-CHO** with renewable *dihydrobenzimidazole organic hydrides* enabled identification of conditions where conversion to the hydroxymethyl complex [Ru(bpy)₂(CO)(CH₂OH)]⁺ **Ru-CH₂OH** was quantitative. This conversion involves formal hydride and proton transfer that may proceed by distinct mechanistic pathways to form **Ru-CH₂OH**. Computational and experimental studies designed to elucidate the underlying mechanism(s) of these fundamental transformations will be presented. Taken together the results show that a remarkable breadth of metal formyl and organic hydride PCET reactivity can be accessed with renewable reagents in the quest for liquid solar fuels.

Acknowledgements

This material is based upon work solely supported as part of the Center for Hybrid Approaches in Solar Energy to Liquid Fuels (CHASE), an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0021173.

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MULTIPROTON COUPLED ELECTRON TRANSFER THERMODYNAMICS AND DYNAMICS

E. Odella,¹ W. Guerra,¹ M. Secor,² E. Gonzalez,¹ R. Dominguez,¹ D. Heredia,¹ E. Reyes,¹ K. Knappenberger,¹ Y. Yoneda,³ J. Shee,³ E. Arsenault,³ M. Head-Gordon,³ G. Fleming,³ S. Hammes-Schiffer,² G. Moore,¹ T. Moore,¹ and A. Moore¹

¹ School of Molecular Sciences Arizona State University, Tempe, Arizona 85287-1604
amoore@asu.edu

² Department of Chemistry, Yale University, New Haven, Connecticut 06520-8107

³ Department of Chemistry, University of California Berkeley, Berkeley California 94720

Inspired by the PCET process in photosystem II involving Tyr_z-His190, a benzimidazole-phenol (BIP) system has been used to illustrate an E1PT process involving one-electron oxidation of the phenol accompanied by transfer of its proton to the attached benzimidazole.^[1] With amino- and other-substituted BIPs, one-electron, two-proton PCET reactions take place (an E2PT process). Aiming at long-range proton translocation, constructs consisting of a phenol, a Grotthuss-type hydrogen-bonded network based on a polybenzimidazole framework (bridge), and a terminal proton acceptor (TPA) were studied. Translocation of protons up to ~16 Å occurs by an E4PT process.^[2] In polybenzimidazoles there is a decrease in the redox potential of the phenoxyl radical/phenol couple by 60 mV per benzimidazole unit. Substitution of benzimidazoles by electron-withdrawing substituents reduces this drop, evidencing that benzimidazole-based bridges are non-innocent participants in the PCET processes.^[3] An E1PT process photochemically initiated was studied with a BIP covalently attached to a triphenylfluorophenylporphyrin (BIPPF₁₅). Two-dimensional electronic-vibrational spectroscopy (2DEV) showed that PCET takes place on two-time scales: 1) an ultrafast process from the unrelaxed S₁ state, and 2) a slower process on the time scale of a few hundred ps arising from the relaxed S₁ state. The ultrafast process enables the observation of the initial F-C state evolving to full charge separation on the 120 fs time scale via the development of a dipole moment resulting from a dihedral twisting between the BIP and the macrocycle.^[4] With the BIP of BIPPF₁₅ substituted by a pyridine derivative TPA, the dynamics of a photoinduced E2PT process were explored. It was found that following porphyrin excitation, proton arrival to the TPA and electron arrival to the porphyrin are concerted within 24 fs.^[5] To increase the driving force of the PCET process, a dyad consisting of a porphyrin fluorinated at the *beta*-positions and a BIP (BIPPF₂₃) was prepared; its photophysical properties will be presented.

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6. Poster Presentation Details

All posters will be displayed in the Puerto Principe room, next to the conference sessions. Posters can be hung as early as Monday but must be removed by 13:00h on Wednesday, preferably after the 2nd poster session.

The poster abstracts in the following section are numbered P1, P2, etc and correspond to the posterboard where they should be hung. The first official poster session is on **Tuesday, June 6, from 16:45 pm to 18:15h**. During this session, posters 1 – 28 will be presented. The second official poster session is on **Wednesday, June 7, from 10:30 to 12:00h**, during which time posters 29 – 55 will be presented.

Please note that you can present your poster in both sessions, but it will only be judged in the official session. Three poster prizes sponsored by the Royal Society of Chemistry will be awarded to outstanding poster presentations, and 6 posters will be selected for flash talks.

7. Poster Presentation Abstracts

P1. The Role of Benzothiadiazole Unit in Organic Polymers on Photocatalytic Hydrogen Production

Martin Axelsson,¹ Ziyang Xia², Sicong Wang¹, Ming Cheng², Haining Tian¹

¹ Address: Department of Chemistry Ångström, Uppsala University, Sweden, martin.axelsson@kemi.uu.se

² Address: Institute for Energy Research, Jiangsu University, China

Organic polymers based on donor-acceptor structure are a promising class of efficient photocatalysts for solar fuel production. Among these polymers, poly(9,9-dioctylfluorene-alt-1,2,3-benzothiadiazole) (PFBT) with fluorene donor and benzothiadiazole acceptor units has been shown good photocatalytic activity for hydrogen evolution when it is prepared into polymer dots (Pdots) in water^[1]. The current understanding in the field is that residual Palladium from the coupling reaction in the synthesis is the main catalytic site for the reaction^[2-3]. However, in this study we prove that a key catalytic intermediate is the reaction between the reduced polymer and protons on the acceptor site benzothiadiazole (BT). We have previously shown that a molecule based on BT can act as a catalyst for the HER on its own, after a protonation step^[4]. Moreover, a model compound 1,2,3-benzothiadiazole di-9,9'-dioctylfluorene (BTDF) is synthesized to investigate the mechanism for protonation and its kinetics of benzothiadiazole in presence of an organic acid by cyclic voltammetry. We experimentally show that benzothiadiazole in BTDF can rapidly react with protons with a simulated value of $0.1 - 5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ which should play a crucial role in the following photocatalytic step.

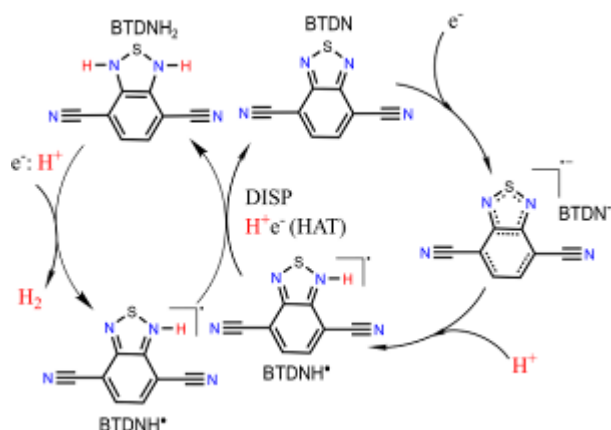
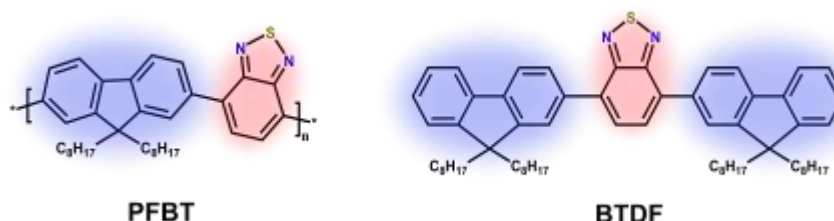


Figure 2 : The catalytic cycle of BTDN^[4]



Scheme 1 : The Chemical structure of PFBT and BTDF

References:

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P2. Gatekeeping effect of ancillary ligand in a PCET triad

Benedikt Bagemihl[‡], Andrea Pannwitz[‡], Sven Rau[‡]

[‡]Institute for Inorganic Chemistry 1, Albert-Einstein-Allee 11, 89081 Ulm

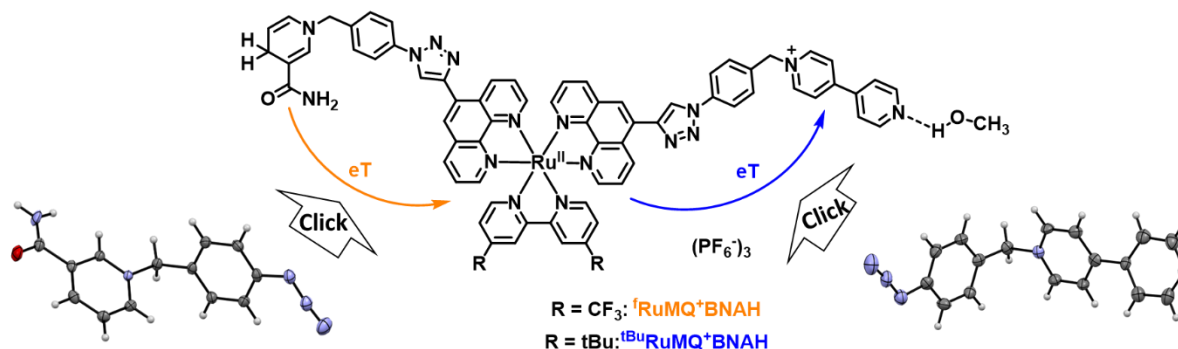


Figure 3: Structure and schematic electron transfer in our PCET triads

We present two donor-photosensitizer-acceptor triads composed of N-benzyl nicotinamide (BNAH) as an electron donor, a ruthenium(II) photosensitizer as central unit and 4,4'-bipyridine (Monoquat, MQ⁺) connected via Click Chemistry.^[1] BNAH has been used as a one-electron sacrificial electron donor in catalysis but can in principle work as a two electron/ one-proton (hydride) donor.^[2] MQ⁺ as an electron acceptor can also take up both a proton and an electron, as shown previously.^[3] The combination of these two interesting building blocks in our modular triads shows charge transfer yielding different final states depending on the substitution on the ancillary ligand on the central photosensitizer. Interestingly, lifetimes of charge separated states for both triads are long in the order of ms. Herein, we analyze the electron transfer in our triads by ns-time-resolved transient absorption and emission spectroscopy and conclude on the properties of the triazole and the ancillary ligands on the PS in these architectures as well as the detailed mechanism of PCET at the proton coupled electron acceptor.

P3. THE MOLECULAR QUEST: DEVELOPMENT OF TRUE MOLECULAR WATER OXIDATION CATALYSTS

Marcos GIL-SEPULCRE, Julia BEERHUES, Pablo DURAND, Mercè MARTIN-SABÍ,
Daniel SÁNCHEZ-RESA, Aranya SARKAR, Paula TRIS-MARZO, Antoni LLOBET

*Institut Català d'Investigació Química (ICIQ), Barcelona Institute of Science and Technology (BIST),
Tarragona, Spain
ptris@iciq.es*

Sunlight-driven water splitting to form hydrogen, a clean fuel, and oxygen is a promising approach to support the transition from fossil fuels to sustainable energy sources. Yet, developing a powerful catalytic system for the thermodynamically uphill water oxidation remains an obstacle.

In our research group, we develop metal complex catalysts to face this challenge. Those molecular catalysts have the advantage of having a well-defined active center. This allows the investigation of catalytic mechanisms, which lead to rational catalyst design, e.g. directed adjustment of the ligand.

However, it is important to understand the deactivation pathways and characterize rigorously the molecular catalysts to guarantee their true catalytic activity in water oxidation. Principles and basic checks are provided to ensure molecular first-row transition metal complex catalysis.

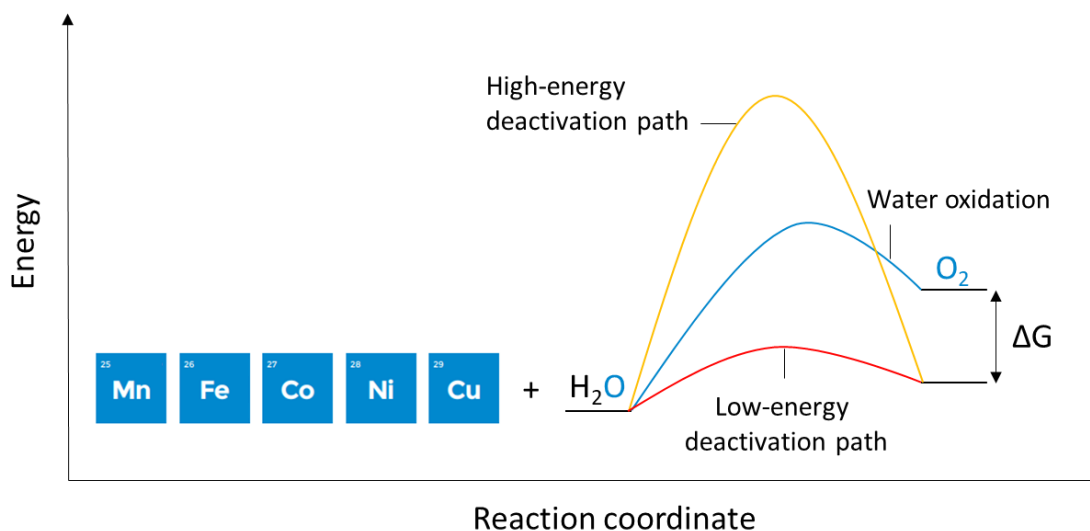


Figure 1. Energy diagram for water oxidation and the competing deactivating oxidation.

References:

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P4. Solar Hydrogen Evolution through Ammonia Oxidation using Hybrid Ruthenium-based Electroanodes

Anna M. Beiler, Alisa Denisiuk, Josep A. Gutiérrez-Orgaz, Wenhui Li, Jan Holub, Francisco-Javier Sánchez-Baygual, Marcos Gil-Sepulcre, Mehmed Z. Ertem, Dooshaye Moonshiram, Emilio Palomares and Antoni Llobet

(a) Institute of Chemical Research of Catalonia (ICIQ). (b) Chemistry Division, Energy & Photon Sciences Directorate, Brookhaven National Laboratory, Upton, NY, USA (c) Instituto Madrileño de Estudios Avanzados en Nanociencia (IMDEA-Nanociencia). Calle Faraday 9, 28049 Madrid (Spain)

Molecular catalysts can promote ammonia oxidation, turning ammonia into a promising candidate as a carbon-free fuel or as a hydrogen carrier.^[1] We investigate ammonia oxidation using carbon paper anodes functionalized with the oligomer {[Ru(II)(bda- κ -N₂O₂)(4,4'-bpy)]₁₀(4,4'-bpy)}, **Rubda-10@CP** (Figure 1).^[2] Electrochemical studies demonstrate that the Ru-based anode catalyzes NH₃ oxidation to N₂ and H₂ in a 1:3 ratio at an applied potential of 0.1 V vs. Fc^{+/0} in propylene carbonate, with turnover numbers > 7000. Additionally, we show the first example of a heterogenized solar-driven ammonia splitting process using these anodes in a PV-EC cell with no external applied bias producing N₂ and H₂ in a 1:2.9 ratio.^[3]

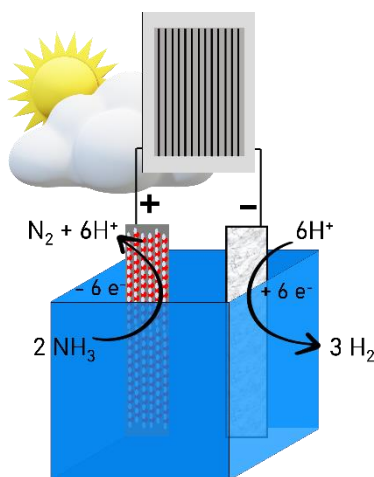


Figure 1. A single perovskite cell can split ammonia to N₂ and H₂ in an electrochemical cell using a carbon anode functionalized with a molecularly-defined ruthenium-based oligomer and a platinum counterelectrode.

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P5. Exploring Polyoxometalate Catalyzed Water Oxidation, Computationally

Maria BESORA¹

¹ Department of Physical and Inorganic Chemistry, Faculty of Chemistry, Universitat Rovira i Virgili. C/ Marcel·lí Domingo, 1, 43007 Tarragona, Catalonia, Spain.

Water splitting is a promising strategy to transition from fossil to greener fuels, with hydrogen as energy vector. However, water oxidation has associated high overpotentials. To address this challenge, the development of improved water oxidation catalysts (WOCs) is necessary, and different catalysts with improved capabilities are reported every year.^[1] Polyoxometalates (POMs) have emerged as interesting WOCs as they are a special type of molecular catalysts, constituted by metal oxide fragments and with controlled and discrete structure. There is special interest on developing WOCs based on earth-abundant metals, which offer ecological, social, and economic benefits. Therefore, POMs based on earth-abundant metals like iron^[2] or cobalt^[3] are specially interesting, such as $[\text{Fe}^{\text{III}}_4(\text{H}_2\text{O})_2(\text{B}-\alpha\text{-PW}_9\text{O}_{34})_2]^{6-}$ and $[\text{Co}^{\text{II}}_4(\text{H}_2\text{O})_2(\text{B}-\alpha\text{-PW}_9\text{O}_{34})_2]^{10-}$, among others. Computational chemistry is a powerful tool for analyzing catalytic systems in detail, postulating or rejecting reaction mechanisms, increasing the knowledge on the active species, and designing improved catalysts. The results and conclusions of computational studies on polyoxometallate catalytic systems will be discussed, see Figure 1.

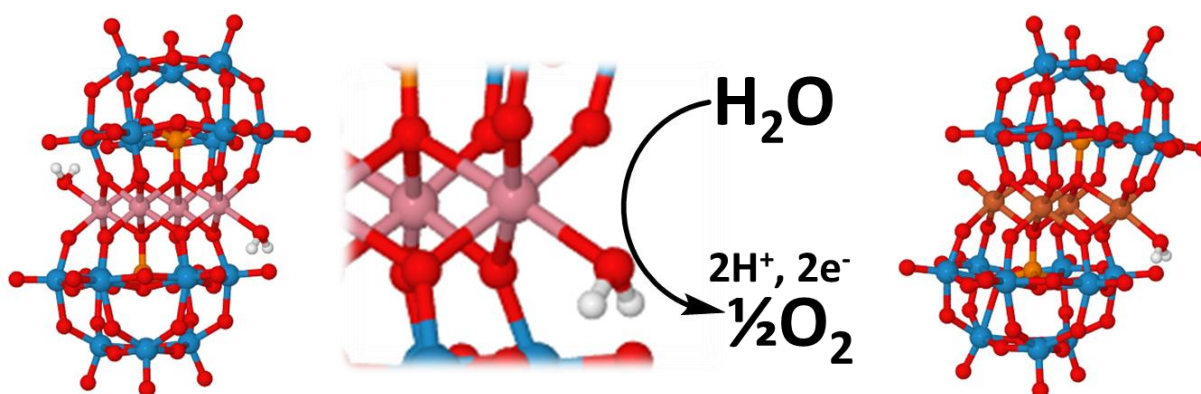


Figure 1

References:

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P6. INVESTIGATION OF BIMETALLIC CYCLAM COMPLEXES AS POTENTIAL CATALYSTS FOR CO₂ REDUCTION

Sarah BIMMERMANN¹ and Ulf- Peter APFEL,^{1,2}

¹ *Inorganic Chemistry I, Ruhr-Universität Bochum, Universitätsstraße 150, 44801 Bochum, Germany, sarah.bimmermann@rub.de*

² *Department of Electrosynthesis, Fraunhofer UMSICHT, Osterfelder Straße 3, 46047 Oberhausen, Germany*

The utilization of CO₂ as a sustainable carbon source is an urgent topic for the chemical value chain. In this perspective, transition metal complexes often play a crucial role to function as catalyst for the electrochemical and photochemical CO₂ reduction. A widely investigated ligand type within this research is the macrocycle cyclam with its four N-donor atoms.^[1] While the corresponding nickel complex is an efficient and selective CO₂ reduction electrocatalyst, the cobalt analogue is capable to produce CO via the photocatalytic approach.^[2,3] To figure out important key factors, which have a positive effect on the catalysis, ligand modification is an important research topic. Apart from modifications of the cyclam molecule itself, two cyclam molecules can be coupled by different linker units.^[4,5] The resulting ligands allow the simultaneous coordination of two metal ions, where the metal-metal distance can be altered by the use of different linkers, expecting an enhanced CO₂ reduction referring to the bimetallic active centers present in CODHs. Within this work, two cyclam molecules were coupled by either a *para*- or a *meta*-xylene linker and the corresponding homobimetallic nickel and cobalt complexes were tested as potential catalysts for the electrochemical or photochemical CO₂ reduction.

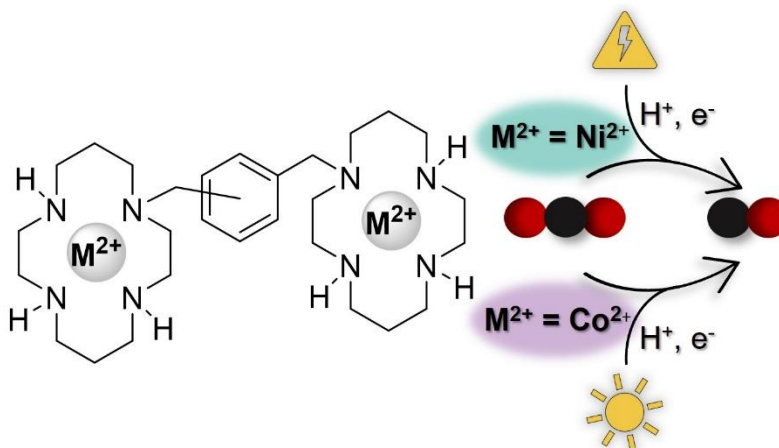


Figure 1. General structure and idea of the application of a bimetallic cyclam complex for the electrochemical and photochemical CO₂ reduction.

References:

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P7. THREE ELECTRONS PHOTOACCUMULATION ON AN HYBRID POLYOXOMETALATE AND CATALYTIC APPLICATION

Weixian Wang,¹ Guillaume Izzet,¹ Anna Proust,¹ Sébastien Blanchard,¹

¹ Address: Institut Parisien de Chimie Moléculaire, Sorbonne Université, CNRS, Paris, France
sebastien.blanchard@sorbonne-universite.fr

Polyoxometalates (POMs) are oxoclusters of early transition metals in their highest oxidation state (Mo^{VI} , W^{VI} , V^{V} ,...). They display a wide diversity of structures, and some of them present quite interesting photophysical properties.^[1] In our team, we have specialized in the functionalization of POMs surfaces with organic function, generating hybrid organic-inorganic molecules.^[2]

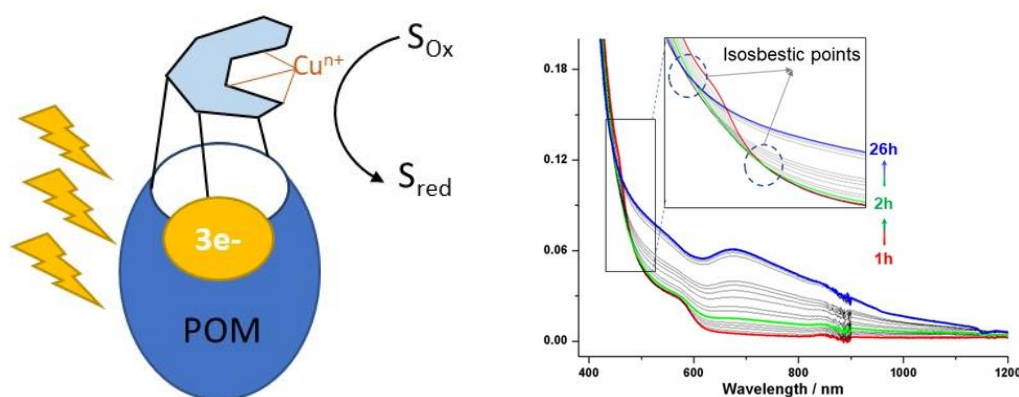


Figure 1 : Schematic representation of the hybrid POM and UV-visible follow up of charge photoaccumulation

In this presentation, I will describe the synthesis of a new hybrid bearing a copper complex and its photophysical properties. This system is able to store, under visible light irradiation, up to three electrons. Moreover, its ability to release these electrons has been studied: photocatalytic generation of CF_3 radicals has been established, and the importance of a covalent link between the POM and the copper complex for efficient electron transfer was demonstrated.^[3]

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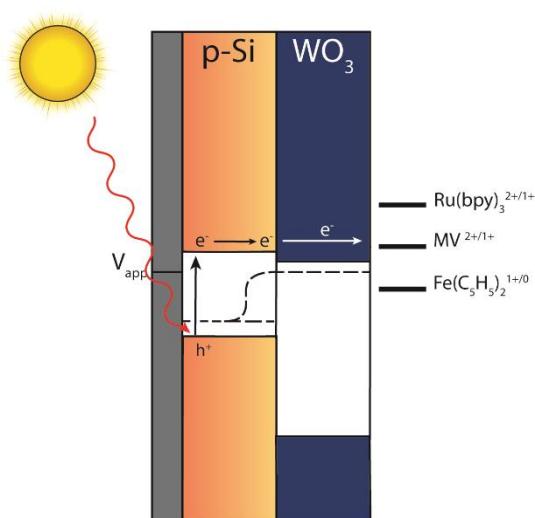
P8. Understanding Interfacial Band Structure of WO₃ – Coated Silicon Hybrid Photocathodes

Alexandria R. C. Bredar¹, Hannah R. M. Margavio², Carrie Donley¹, Jillian L. Dempsey¹, Gregory N. Parsons²

¹University of North Carolina at Chapel Hill, Chapel Hill, NC 27599

²North Carolina State University, Raleigh, NC 27606
abredar@email.unc.edu

Si / WO₃ hybrid photoelectrodes were synthesized via W metal atomic layer deposition (ALD), followed by high temperature oxidation to generate WO₃. Two oxidation temperatures (400 °C and 600 °C) are compared to understand the role of defect states towards the investigated (photo)electrochemical processes. X-ray photoelectron spectroscopy (XPS), grazing incidence X-ray diffraction (GIXRD), and scanning transmission electron microscopy (STEM) data were collected to characterize the phase, crystallinity, and purity of WO₃ films. STEM data were also coupled with electron energy loss spectroscopy (mono-EELS) and ultraviolet photoelectron spectroscopy (UPS) to characterize the Si / WO₃ interface and measure the band gap and valence band position of WO₃. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were used to assess electron transfer properties of the (photo)electrodes, with [Ru(bpy)₃]²⁺, [Co(bpy)₃]³⁺, and [Fe(C₅H₅)₂]²⁺ as homogeneous redox probes to map redox processes driven by conduction band states and potential defect states within the band gap that are electrochemically active. The performance of these photocathodes will help us better understand how to engineer the interface of Si wafers with protecting layers to make more robust electrodes. The role of protons on the photovoltage, from annealing with H₂ and/or by adding acid to the electrolyte is investigated.



P9. INVESTIGATING PROTON-COUPLED ELECTRON TRANSFER PROCESSES OF AN NADH ANALOGUE

Rima CHARAF¹, Leif HAMMARSTRÖM¹

¹ Address: Department of Chemistry – Ångström Laboratory, Uppsala University, Uppsala, Sweden
rima.charaf@kemi.uu.se

The mechanistic study of proton-coupled electron transfer processes^[1,2] is necessary to gain insight into a variety of fields, mainly related to energy conversion. Of particular interest is the investigation of the conditions which allow for concerted proton-coupled electron transfer, where electron and proton transfer in a single step, avoiding the formation of high-energy intermediates. In this work, the NADH analogue BNAH (1-benzyl-1,4-dihydronicotinamide)^[3,4] is put into the condition in which concerted PCET is favored. This is done by selecting an oxidant and a base that, alone, do not provide enough driving force for the respective stepwise mechanisms to take place, but, together, they can lead the system through the concerted pathway. Since addition of base is needed for a possible transfer of proton coupled with the transfer of electron, rate constants measured with and without the addition of an external base are used to gain insight into the mechanism. These studies open the way to following investigations on two-electrons/one-proton transfer, which NADH undergoes in many biological redox processes.

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P10. INVESTIGATIONS INTO THE REACTIVITY OF TRANSITION METAL COMPLEXES WITH REDOX-ACTIVE LIGANDS FOR PROTON COUPLED ELECTRON TRANSFER

Bronte CHARETTE and Alan HEYDUK

*Department of Chemistry, University of California at Irvine, Irvine, California 92677-2025, United States
brontec@illinois.edu*

Thermochemical and kinetic studies were conducted to determine the impact of the metal ion on the ligand-centered hydrogen atom transfer (HAT) reactivity for a family of Group 10 metal complexes containing a tridentate pincer ligand derived from bis(2-mercapto-*p*-tolyl)amine, [SNS]H₃.^[1,2] Equilibrium measurements determined from spectrophotometric titrations were used to determine the bond dissociation free energy (BDFE) of these complexes. These values were corroborated using the pK_a (N-H) and E° in the Bordwell equation as well as from kinetic data (k_1/k_{-1}). These studies have shown that changing the metal center has a measurable influence on the BDFE and the HAT reactivity for this series. Additionally, a new nickel(II) complex, [ON(H)O]Ni(PPh₃) [ON(H)O]²⁻ = bis(3,5-di-*tert*-butyl-2-phenoxy)amine), bearing a protonated redox-active ligand was investigated for its ability to serve as a hydrogen-atom (H•) and hydride (H⁻) donor.^[3] Bond dissociation free energy (BDFE) and hydricity (ΔG°_{H-}) measurements benchmark the thermodynamic propensity of this complex to participate in ligand-centered H• and H⁻ transfer reactions. The products of both (H•) and hydride (H⁻) reveal interesting nickel products with unusual geometries.

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P11. New, Rapid, and Accurate Experimental Method for Thermodynamic Hydricity Measurement Using Electrocatalytic Hydrogen Reduction Reaction

Hye Won CHUNG,¹ Hai-Xu WANG,¹ Yogesh SURENDRANATH¹

¹ Address: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, USA.
Email: hyewonc@mit.edu

Hydride transfer (HT) is a key elementary step in various chemical transformations, and thermodynamic hydricity (ΔG_{H^-}), the free energy for $HA \rightarrow H^- + A^+$, is an important parameter for reaction design. Nevertheless, most ΔG_{H^-} values are obtained computationally due to experimental challenges. For example, the “hydride transfer” and “H₂ heterolysis” methods often suffer from lengthy detection time (up to months) and limited scope due to intrinsically slow kinetics of HT and the need for prior estimation of unknown hydricity. Alternatively, the “potential-pK_a” method has lower accuracy due to generation of unstable intermediates.

Herein, we report a new, rapid, and accurate method based on the electrocatalytic hydrogen reduction reaction (HRR) which interconverts H₂ and hydrides.^[1] The reversible nature of HRR allows the determination of ΔG_{H^-} of HA from open circuit potential (E_{OCP}) measurement together with the Nernst equation (**Figure 1**). By using a Pt electrocatalyst, this method offers high accuracy (± 0.2 kcal/mol) without compromising detection time (typically <30 min), and the wide accessible potential range obviates prior estimations of unknown hydricity. It can be applicable to previously under-explored solvents such as THF. This novel electrochemical method allows an easy access to experimental ΔG_{H^-} values which can provide valuable mechanistic insights for future HT applications.

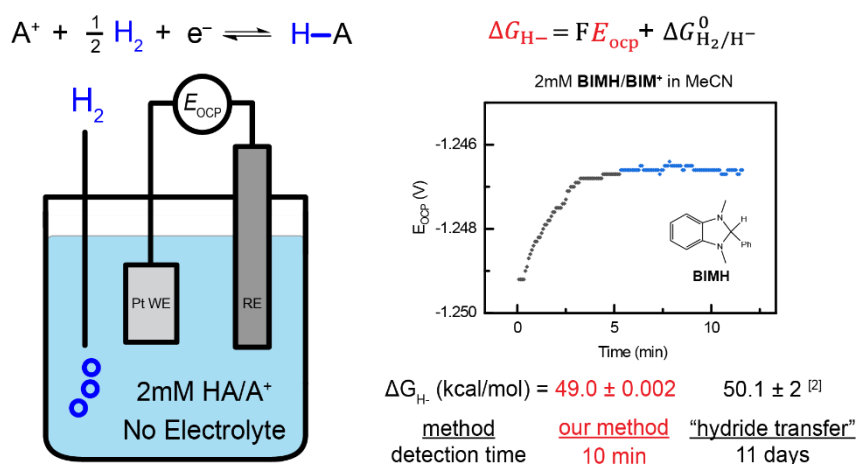


Figure 1. Experimentation and theory of our electrochemical method for thermodynamic hydricity measurement based on the hydrogen reduction reaction.

• **Acknowledgements** We gratefully acknowledge Alexander Miller, Allison Smith, Ksenija Glusac, Sebastian Sena, Morris Bullock, and Rein Kirss for collaboration.

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P12. Photo active nickel complexes mediates trifluoromethylation and cross coupling reactions.

Shubham Deolka,^a Janet Bahri,^a Govindarajan Ramadoss,^a Eugene Khaskin,^a Julia R. Khusnutdinova^a

^a Coordination Chemistry and Catalysis Unit, Okinawa Institute of Science and Technology Graduate University; Japan.

e-mail: Shubham.Deolka2@oist.jp

Our group's longstanding interest is in the development of new ligand platform for selective bond activation. We focused our attention on naphthyridine as a versatile fragment for building up both binucleating and mononucleating ligands. While studying coordination chemistry of naphthyridines with Ni, we eventually discovered that, simple and substituted naphthyridines tend to form mononuclear Ni complexes.^[1] when bis-trifluoromethyl Ni precursor was used. Moreover, these complexes could be easily oxidized by air to give rare examples of aerobically formed, stable Ni(III) bis-trifluoromethyl complexes. Furthermore, we then studied their reactivity in light-induced homolysis confirmed by radical trap studies. This led to the development of several versatile synthetic protocols for Ni-catalyzed, photoinduced C-H bond trifluoromethylation using either the Umemoto reagent or a combination of Langlois reagent with an oxidant in the presence of blue LED light at room temperature. A number of electron-rich simple arenes or heterocycles (pyrroles, indoles) could be trifluoromethylated under these conditions. This is a rare example of photoinduced catalytic trifluoromethylation of C-H bonds in which only Ni catalyst is used in the absence of precious metal-containing photoredox catalysts.^[2]

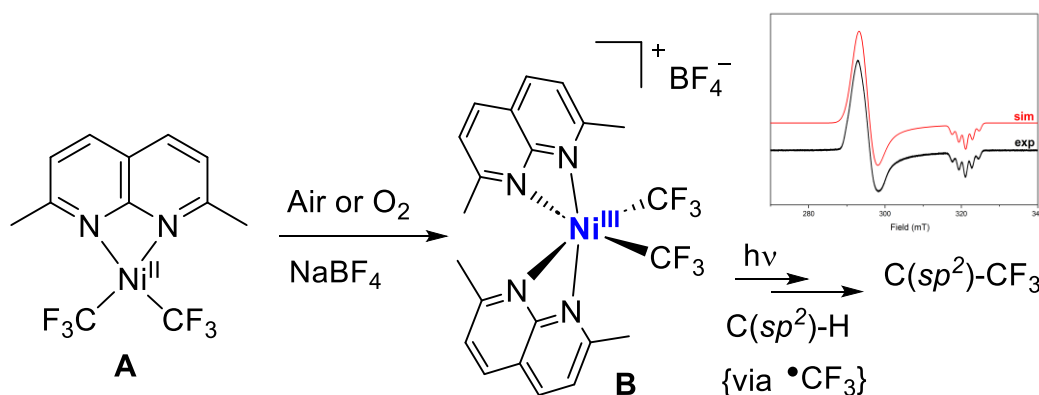


Figure 1. (a) Schematic representation of metal-metal cooperation for small molecule activation. (b) High valent Ni(III) catalyze trifluoromethylation reactions.

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P13. BOOSTING N₂ REDUCTION AND AMMONIA OXIDATION REACTION BY EARTH-ABUNDANT MOLECULAR CATALYSTS

Dependu DOLUI,¹ Jérémy DE FREITAS¹ and Prof. Marc ROBERT¹

¹Laboratoire d'Electrochimie Moléculaire, Université Paris Cité, CNRS, F-75006, Paris, France
E-mail: dependu.dolui@u-paris.fr

Photo-electrochemical N₂ activation is a promising sustainable technology for renewable energy generation and storage [1]. Use of earth-abundant N₂ and water makes it a more attractive and futuristic resource [2]. However, very low efficiency and poor selectivity restricted their large-scale applications. [3-4] Conversely, ammonia is an attractive, clean fuel and alternate storage pathway for green energy hydrogen. In the current industrial model, the Haber-Bosch process becomes highly energy-demanding and a prime suspect for global warming. [5] Thus, it is necessary for the hour to generate ammonia from green renewable energy and resurrect the magic of the ammonia to complete the N-cycle. In this project, we can develop NH₃ implementing photo-electrochemical conditions using a series of earth-abundant metal complexes at ambient pressure and temperature conditions. Also, we succeeded in generating N₂ from the ammonia oxidation (AO) reaction. This study is one of the prime examples for the upgradation of an existing earth-abundant molecular catalyst for next-generation fuel creation and sustainable storage of Hydrogen energy.

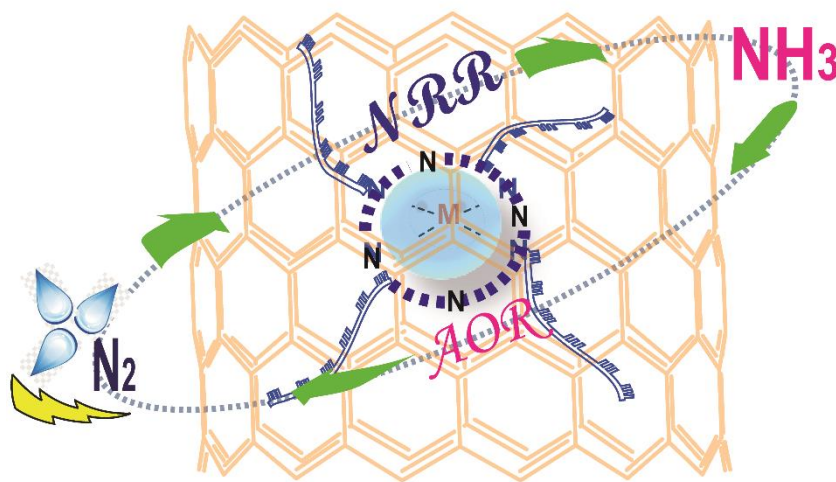


Figure 4: Selective NRR and AOR by molecular catalyst supported with carbon materials.

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P14. COMPUTATIONAL EXPLORATION OF METAL-FREE PORPHYRIN DERIVATIVES FOR SUSTAINABLE PHOTOCATALYTIC HYDROGEN GENERATION

Ouissam El Bakouri,¹ Lluís Blancafort¹

¹ *Institute of Computational Chemistry and Catalysis and Department of Chemistry, University of Girona, C/ M. Aurèlia Capmany, 69, 17003 Girona, Catalonia, Spain*
ouissam.bakouri@udg.edu

Photocatalysis has emerged as a promising avenue for generating clean energy by utilizing simpler molecules as photocatalysts, mimicking enzyme processes. However, traditional metal-based catalysts face challenges such as high cost, limited availability, and potential toxicity, which have spurred the exploration of metal-free alternatives for sustainable electrocatalysis. Porphyrin derivatives, known for their versatile and tunable properties, have garnered significant attention as potential candidates for renewable energy research. In addition, gaining deep insights into the fundamental mechanisms that govern the electrocatalytic activity of these porphyrin derivatives is important, paving the way for developing highly efficient and sustainable photocatalysts for clean energy generation. In the literature, many studies involving free-metal porphyrin species exhibit promising electrocatalytic activity for hydrogen generation in acid media, with a favorable pathway involving a sequential series of steps: reduction, protonation, reduction, and protonation.^{[1][2]} Yet, in only a few there is a proper equilibrium between sustainability and efficiency. In this study, we delve into the impact of electronic structure on the electrocatalytic activity of various porphyrin derivatives for hydrogen evolution and photoreduction reactions. We specifically target those more sustainable, employing cutting-edge quantum chemical calculations.

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P15. TOWARDS AN ELECTROCATALYTIC CASCADE SEQUENCE FOR THE REDUCTION OF CO₂ TO METHANOL

Sergio FERNÁNDEZ,¹ Eric A. ASSAF,² Nilay HAZARI³, Mehmed Z. ERTEM, Alexander J. M. MILLER¹

¹ Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290, United States, ² Department of Chemistry, Yale University, P.O. Box 208107, New Haven, Connecticut 06520, United States, ³ Chemistry Division, Energy & Photon Sciences, Brookhaven National Laboratory, Upton, New York 11973, United States

Multicatalyst cascades are a promising strategy for the electrocatalytic reduction of CO₂ to liquid fuels.^[1] For example, cascades based on catalytic thermal hydrogenation have been reported for the conversion of CO₂ into methanol.^[2] Proton- coupled electron transfer reduction strategies offer an intriguing alternative, however, in which (photo)electrochemical catalysis could mediate the transfer of 6H⁺ and 6e⁻ under mild reaction conditions. The design, optimization, and mechanistic study of an electrochemical – thermal cascade sequence for the reduction of CO₂ to CH₃OH going through formate as one of the key reaction intermediates is presented. The first reaction of the sequence consists of electrochemical CO₂ reduction to formate using [Cp*Ir(bpy)Cl]⁺ (Cat₁) in ⁱPrOH solution. The electrolysis solution is treated with trifluoromethanesulfonic acid (Cat₂) to thermally drive the Fischer esterification of formate to isopropyl formate at room temperature. Finally, (H-PNP)Ir(H)₃ (Cat₃) is employed as a transfer hydrogenation catalyst to convert isopropyl formate to methanol. This process uses ⁱPrOH as both the hydride and proton donor (*i. e.* H₂ equivalents) giving acetone as byproduct which a candidate for electrochemical reduction to regenerate ⁱPrOH. Opportunities and challenges associated with realizing a fully integrated catalytic cascade will be discussed.

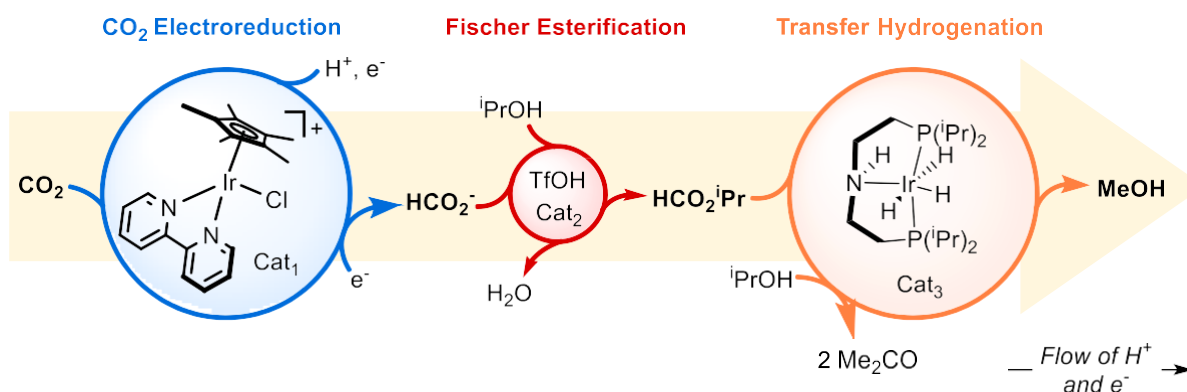


Figure 1. Proposed CO₂-to-MeOH multicatalyst cascade.

• Acknowledgements

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P16. THEORETICAL ELECTROCATALYTIC CO₂ REDUCTION REACTION USING A HOMOGENEOUS NON-NOBLE METAL COMPLEX

Gabriela GARCIA,¹ Ataulpa BRAGA,²

¹ Department of Fundamental Chemistry, Institute of Chemistry of the University of São Paulo (IQ-USP), São Paulo, Brazil. E-mail: ggarcia@iq.usp.br ² Department of Fundamental Chemistry, Institute of Chemistry of the University of São Paulo (IQ-USP), São Paulo, Brazil.

Inspired by the work of Ratnadip De *et al* [1], a manganese complex with corrole ligand was used as the catalyst (Figure 1) for the theoretical calculations of CO₂ electroreduction's reaction path to form acetic acid. Based on this, a reaction mechanism was proposed, through computational methods, as a proof of concept to this type of reaction (Figure 2). The calculations were carried out with unrestricted B3LYP functional and Def2-SVP basis set. Since this is an open shell system, all structures were optimized with different multiplicities, resulting that they all are more stable as triplets or quartets, varying according to how many electrons they gain on each step. No spin contamination was found in any structure.

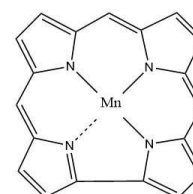


Figure 1. Catalyst

It was verified that the electroreduction of the initial Mn (III) (R1) to Mn (II) (I1) forms a species that can activate a carbon dioxide molecule from saturated atmosphere. As it follows, the intermediate I2 receives a proton from water (20% in acetonitrile solution), leaving the carbon more electrophilic. When receiving another electron, I3 becomes able to bind a second CO₂ molecule, forming the carbon-carbon bond, which is the most interesting step for this work, since its goal is to form C₂+ products. On the following ones, the reaction undergoes successive proton coupled electron transfers, that in the end will release acetic acid and restore the initial catalyst.

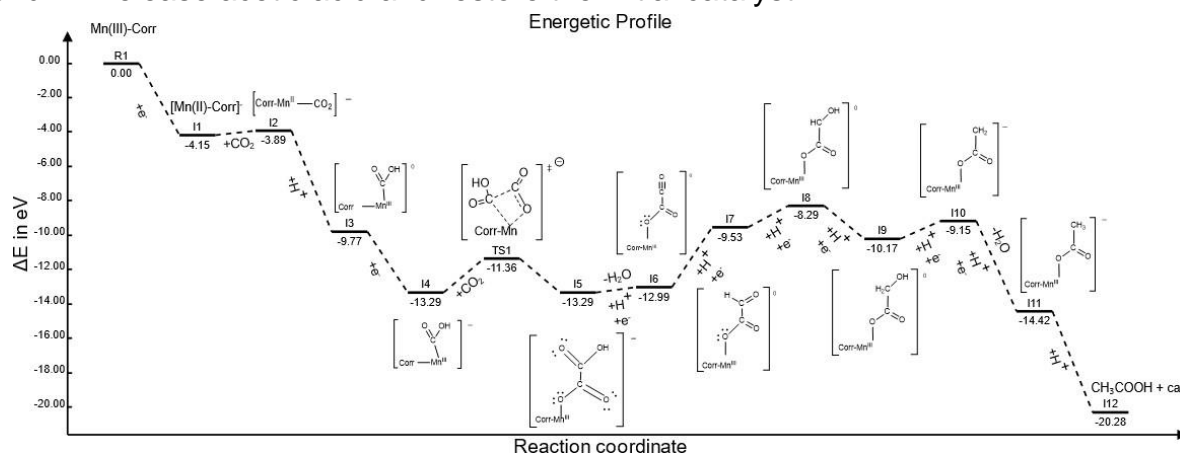


Figure 2. Energetic Profile

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P17. Oxygen- and Hydrogen-Atom Transfer Reactivity of Tungsten Oxide Colloids

Noah J. Gibson,¹ Giovanni A. Parada,^{1,2} James M. Mayer¹

¹ Address: Department of Chemistry, Yale University, New Haven, Connecticut 06520-8107, United States.
(noah.gibson@yale.edu)

² Current address: Department of Chemistry, The College of New Jersey, New Jersey 08628, United States.

Oxygen-atom transfer, hydrogen atom transfer, and proton-coupled electron transfer (OAT/HAT) are fundamental redox reactions performed by enzymes, molecules, and solid interfaces.^[1-5] Greater understanding of these reactions at solid/liquid interfaces is important for the development of efficient and selective metal oxide catalysts and electrocatalysts. Herein, we report a novel synthesis of colloidal, oleyl amine-capped (*h*-WO_{3-x}) nanocrystals (NCs) and their physical characterization. These colloids are a valuable model system for exploring HAT and OAT reactions. *h*-WO_x is naturally sub-stoichiometric in oxygen and can readily intercalate hydrogen to form tungsten “blues” or “bronzes”.^[6-7] Our approach utilizes stoichiometric reactions in non-aqueous solvents with reagents that heavily favor the transfer of a hydrogen or oxygen atom. The *h*-WO_{3-x} NCs can be reduced by photolysis or by chemical reductants, which can be monitored spectroscopically. Titrations find that upwards of 20% of the total tungsten per NC can be reduced. Preliminary reactions with OAT, HAT, and ET reagents show disparate reactivity that changes with the average redox state of the NC. This presents an opportunity to examine OAT and HAT reactions at oxide/solution interfaces which could have important implications for the design of future catalysts.

• **Acknowledgements** This research was supported by funding from the National Science Foundation under CHE-1609434 and CHE1904813. N.J.G. acknowledges support from a National Science Foundation Graduate Research Fellowship.

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P18. TRANSFERRING HOMOGENEOUS WATER SPLITTING CATALYSTS TO THE SURFACE OF ELECTRODES

Carolina GIMBERT-SURIÑACH,¹ Sergi GRAU,² Marta VENTOSA,² Navid JAMEEI MOGHADDAM,² Axel GUINART,¹ Adelina VALLRIBERA,¹ Roser PLEIXATS,¹ Albert GRANADOS,¹ Antoni LLOBET²

¹Departament de Química and Centro de Innovación en Química Avanzada (ORFEO-CINQA), Universitat Autònoma de Barcelona, 08193 Cerdanyola del Vallès, Spain, carolina.gimbert@uab.cat

²Institute of Chemical Research of Catalonia (ICIQ-BIST), 43007 Tarragona, Spain

Light induced water splitting (hv-WS) is an attractive way of generating green hydrogen and involves the synchronization of (i) light absorption, (ii) charge separation and (iii) chemical reactions that are triggered by hydrogen evolution catalysts (HEC) and water oxidation catalysts (WOC), which often involve proton coupled electron transfer (PCET) processes.^[1] hv-WS is a broad field that will only be successfully implemented with joint efforts of many disciplines, ranging from fundamental inorganic and organic chemistry to material science, electrochemistry, nanotechnology, photonics or engineering. In this poster, examples of homogeneous catalytic systems based on molecular structures that are active HEC will be presented (Figure 1, left).^[2-3] With the aim of transferring the high catalytic activity of selected homogeneous HEC and WOC to the surface of electrodes three different strategies have been designed (Figure 1, right): (a) supramolecular interactions between the catalyst and the conductive support^[4,5] and embedding of the catalyst into (b) organic semiconductors^[6] or (c) SiO₂ or TiO₂ matrixes. Advances towards each strategy will be presented in the context of the construction of a hv-WS device.

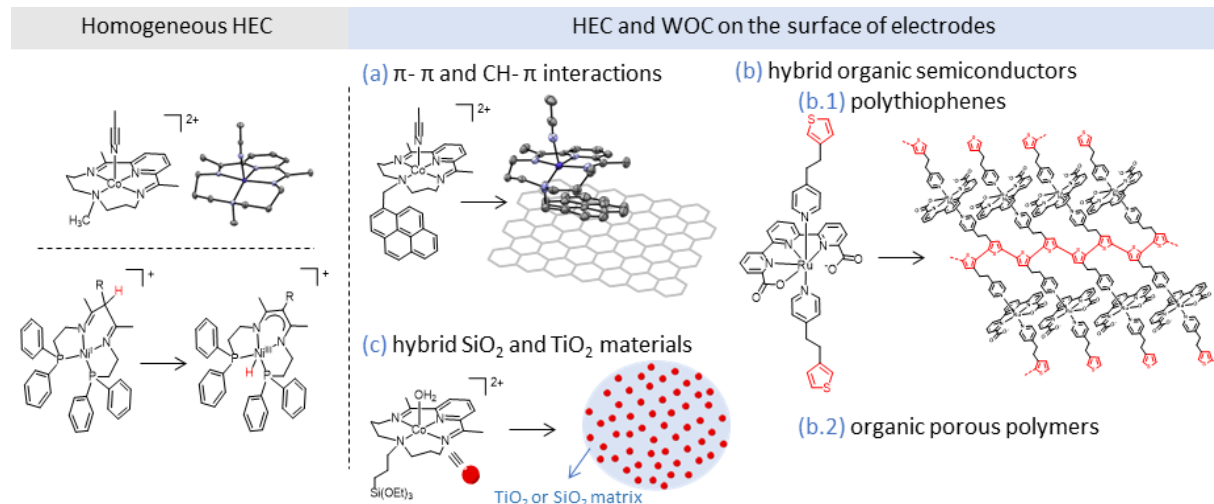


Figure 1. Left) Homogeneous HEC. Right) Strategies towards heterogenization of molecular HEC and WOC.

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P19. PROTON DEPENDENT ELECTROCHEMISTRY OF BORONATE ESTER OF N-ACETYL-D-NEURAMINIC ACID

Saurav Kumar GUIN,¹ Tobias KRÄMER,¹ Eithne DEMPSEY¹

¹ *Department of Chemistry, Maynooth University, Maynooth, Co. Kildare, Ireland*
Email: SauravKumar.Guin@mu.ie; sauravkrugin@yahoo.co.in

N-acetyl-D-neuraminic acid (Neu5Ac) is an important member in the family of sialic acids. It is endogenously produced in higher vertebrates and it participates in a variety of physiological activities in humans including neurocognitive development of the human brain, alteration of gut-microbiota of gut-brain axis at an early stage of life and neuroprotective mechanism for some neurodegenerative diseases at later stages of life.^[1] Therefore, European Commission has approved its regulatory inclusion as nutrition additives in commercial food products. On the other hand, It is also a potential biomarker for the diagnosis and risk stratification of acute coronary syndrome and development of cancers. Therefore, Neu5Ac assay in commercial food, biological and clinical matrices is of interest.

The assay of Neu5Ac in various samples of interest often suffers from the interference of sugars and sugar alcohols. The density functional theory based calculations along with the cyclic voltammetry, square wave voltammetry and Fourier-transformed alternating current voltammetry studies of an electroactive boronate ester of Neu5Ac revealed a significantly different proton coupled electrochemistry compared to boronate esters of other sugars. Eventually, this phenomenon led us to develop a simple and rapid assay of Neu5Ac in aqueous buffer solution even in the presence of very high concentrations of sugars and sugar-alcohols.

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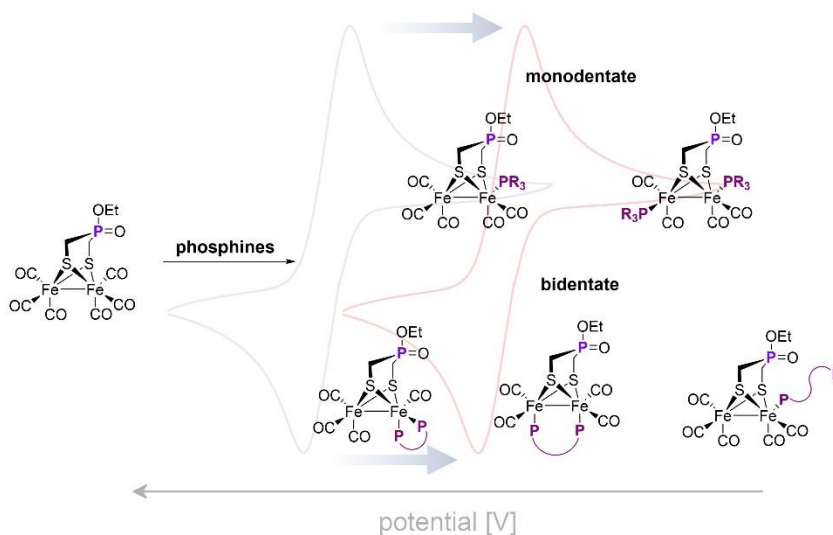
P20. PHOSPHINE-SUBSTITUTED DIIRON PHOSPHADITHIOLATE COMPLEXES

Tatiana GUSEVA,¹ Daniel SIEGMUND,² Philipp GERSCHEL,¹ Ulf-Peter APFEL^{1,2}

¹ Address: Inorganic Chemistry I, Ruhr-Universität Bochum, Universitätsstraße 150, 44801 Bochum, Germany; Tatiana.Guseva@ruhr-uni-bochum.de

² Address: Department of Electrosynthesis, Fraunhofer UMSICHT, Osterfelder Straße 3, 46047 Oberhausen, Germany

The H-cluster of the redox enzymes known as [FeFe] hydrogenases plays a crucial role in the H₂ production. It contains a secondary amine group, serving as proton-transferring shuttle between the active site and the protein's proton channel.^[1] Despite the intensive research regarding the function of [FeFe] hydrogenases, the exact states of the subsite and the course of the actual catalytic cycle are still controversial. To elucidate the catalytic processes of the H-cluster such as proton-coupled electron transfer or pure electron transfer and the states that are formed under these conditions, various mimics were synthesized and analyzed using numerous spectroscopic techniques.^[1] A recently synthesized model of the active site comprises a higher homologue of nitrogen, i.e. phosphorus, in the dithiolate linker, which opens up new paths for investigation of the H₂ production.^[2] We further investigated the influence on the electronic properties of the iron centers by introducing phosphines as ligands, which can lead to different reactions compared to these of the native H-cluster. The obtained complexes were characterized by IR spectroscopy and X-ray diffractometry as well as electrochemical investigation, showing differences depending on the phosphines introduced and their number.



Scheme 1. Schematic overview of the different phosphine bond modes obtained and the influence on the electrochemical behavior.

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P21. Electrochemistry in “gas-phase” heterogeneous catalysis? Ethylene oxidation to vinyl acetate as a case study

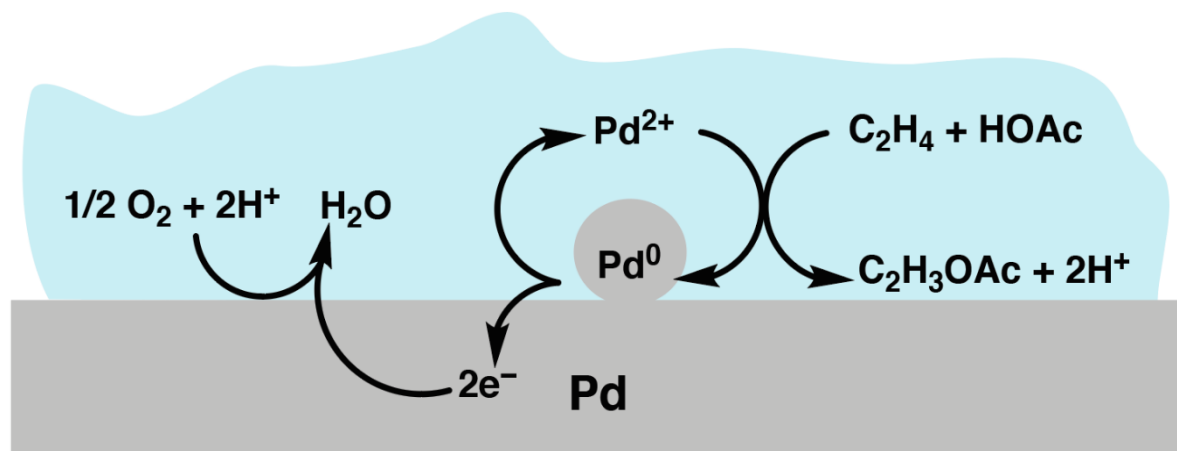
Deiaa HARRAZ,^{1*} Kunal LODAYA,^{1*} Bryan TANG,¹ Yogesh SURENDRANATH¹

* Denotes equal contribution

¹ Address: Massachusetts Institute of Technology, 77 Massachusetts Ave, Cambridge, MA 02139
dharraz@mit.edu

Electrochemical mechanisms have recently been shown to be operative in many examples of thermochemical redox catalysis, via coupling of electrochemical half-reactions on metallic catalyst particles.^[1,2] These studies have been limited to liquid phase catalysis where electrochemical measurements can be easily made. However, in many gas-phase reactions where heterogeneous catalysts are employed, thin liquid films can form on the catalyst surface.^[3] These thin liquid films provide a medium for ionic conduction at the catalyst surface, thus possibly enabling such electrochemical mechanisms to be operative in nominally gas-phase heterogeneous catalysis. To understand how electrochemical potential influences catalysis in such systems, we develop a method for potentiometric measurements to be made at such hydrated surface/gas interfaces, and apply it to study palladium-catalyzed vinyl acetate synthesis via oxidation of ethylene in presence of acetic acid vapor. The electrochemical potential of the catalyst is a potent descriptor for the reaction, as the product formation rate depends on the rate of palladium corrosion. We identify additives that modulate the catalyst potential and rate in the liquid phase, and show that these additives analogously modulate the gas-phase catalyst potential. These results highlight how electrochemical analysis can inform mechanism and guide catalyst design for nominally gas-phase catalysis.

Figure 1. Proposed scheme for band-mediated vinyl acetate synthesis in acetic acid liquid film on a palladium surface.



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P22. CONCERTED PCET TO A GRAPHITE ADSORBED METALLOPORPHYRIN OCCURS BY BAND TO BOND ELECTRON REDISTRIBUTION

Phillips Hutchison¹, Corey J. Kaminsky^{2,3}, Yogesh Surendranath², and Sharon Hammes-Schiffer¹

¹Department of Chemistry, Yale University, New Haven, CT 06520, United States. Email: phillips.hutchison@yale.edu

²Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, United States,

³ExxonMobil Technology & Engineering Co., Annandale, NJ 08801 United States.

Proton-coupled electron transfer (PCET) underlies many electrocatalytic transformations that are critical for a renewable energy economy. Mechanistic pictures for how PCET occurs at both homogeneous and heterogeneous electrocatalysts have been established, but the corresponding pictures for surface immobilized catalysts are less clear. Recent work has shown that a cobalt tetraphenylporphyrin non-specifically adsorbed to graphite (CoTPP-CH) catalyzes hydrogen evolution across the entire pH range through a concerted PCET mechanism characteristic of heterogeneous behavior.^[1] Using density functional theory, we investigated PCET at the adsorbed CoTPP using cluster and periodic models representing different modes of adsorption.^[2] Our calculations establish that protonation of the Co(II)TPP is accompanied by abstraction of an electron from the graphitic surface to form a Co(III)-hydride, thereby circumventing Co(II/I) redox. Moreover, as the electrode surface charges due to applied potential, the adsorbed molecule experiences the same electrostatic polarization as the graphitic surface, regardless of the adsorption mode. A combination of experimental and computational data leads to a mechanistic picture wherein proton donors are attracted to the CoTPP by polarizing the interface, resulting in the redistribution of electrons from band states to bond states. These insights have broad implications for electrocatalysis by chemically modified electrodes and surface immobilized catalysts.

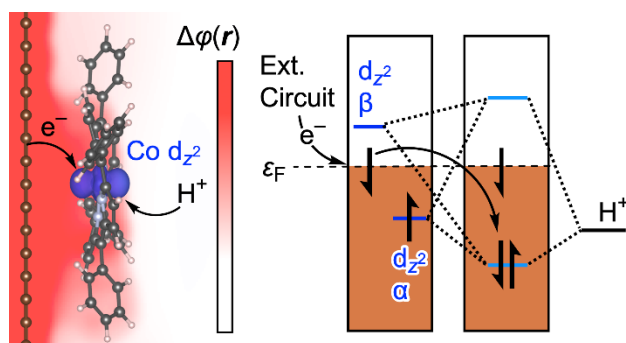


Figure 1. Left: Polarization of the electrochemical interface attracts protons to the non-specifically adsorbed CoTPP-CH. Right: Interaction of the H^+ with the singly occupied Co d_{z^2} results in a bonding interaction below the Fermi level that abstracts an electron from the graphitic surface. The electron taken from the Fermi level is in turn replaced by an electron from the external circuit.

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P23. PHOTOELECTROCHEMICAL CELL FOR SOLAR DRIVEN CARBON DIOXIDE REDUCTION

Hichem ICHOU¹, Stéphane DIRING¹, Thamer ALOUI³, Debashrita SARKAR², Nicolas BARREAU³, Marc ROBERT^{2,4} and Fabrice ODOBEL¹

¹CEISAM Laboratory, 44322 Nantes, France

²Université Paris Cité, CNRS, Laboratoire d'Electrochimie Moléculaire, F-75013 Paris, France

³Nantes Université, CNRS, Institut des Matériaux Jean Rouxel, IMN, 44322 Nantes, France.

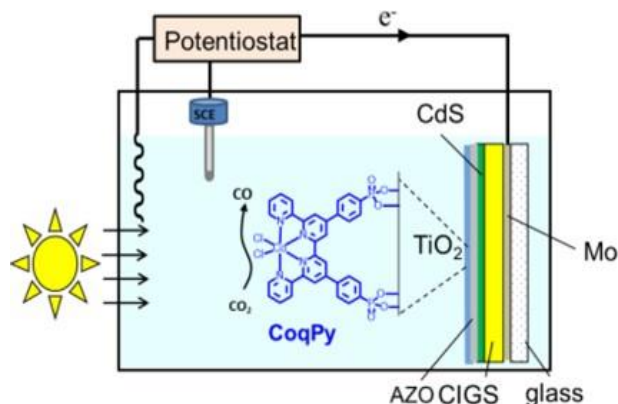
⁴Institut Universitaire de France (IUF), F-75005 Paris, France.

hichem.ichou@univ-nantes.fr, <https://ceisam.univ-nantes.fr/>

Keywords: Artificial photosynthesis, CO₂ reduction, Molecular catalysis, PEC, Co complex

Summary: Artificial photosynthesis could have the potential to play an important role as sustainable energy source for human activity. In order to convert solar energy into storable chemical fuels, photoelectrochemical cell (PEC) is one of the most attractive solutions.¹ Copper/indium/gallium di(sulfide/selenide) (CIGS) semiconductor is particularly well suited for the development of photocathodes for the solar driven reduction of CO₂ to various products, including e.g. CO.² This material has been chosen due to its high absorption coefficient, tunable band gap and importantly because its conduction band is high enough in energy to reduce CO₂ to CO when combined to an appropriate catalyst, in our case a cobalt quaterpyridine (CoqPy) complex (Figure 1). Based on our preliminary previous results,² the focus of this study is to optimize the surface area and the composition of the TiO₂ upper layer to enhance the photocurrent density. The potential and the limitations of the porous TiO₂ layer for this purpose will be discussed as well.³

Figure 1. Schematic representation of the photo-electrochemical half-cell for CO₂ reduction.



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P24. Determining Factors required to Favor Concerted Proton-Coupled Electron Transfer in Tungsten Hydride Complexes

Diane Isaacs,¹ Jillian Dempsey¹

¹ Address: Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290, United States, dpisaacs@live.unc.edu

The search to find storable renewable fuels hastens as global energy demands increase. Many fuel forming reactions depend upon metal hydride complexes that undergo proton-coupled electron transfer (PCET) reactions. Typically, metal hydride complexes operate through one of the stepwise PCET pathways where the electron and the proton transfer in sequential steps. There are few metal hydride complexes that are known to operate through the concerted proton-electron transfer (CPET) pathway. It is hypothesized that the CPET pathway is less accessed because it is not always kinetically feasible.^[1] However, the CPET pathway has the potential to avoid the high energy intermediates associated with the stepwise pathways. More fundamental knowledge is required to determine what factor(s) control the PCET mechanism for metal hydride complexes and how we can design catalysts for fuel forming reactions to be more efficient by operating through the CPET pathway. One of the first metal hydride complexes known to undergo the CPET pathway was $\text{CpW}(\text{CO})_3\text{H}$ (Cp = cyclopentadienyl), studied by the Hammarström group.^[2] However, when one CO ligand is swapped for a $\text{P}(\text{Me})_3$ ligand, $\text{CpW}(\text{CO})_2\text{P}(\text{Me})_3\text{H}$, the CPET pathway is no longer the major pathway for PCET.^[3] The reason for this change in mechanism by switching one ligand is hypothesized to be steric bulk or reorganization energy,^[2, 4] but more in depth research is required to validate one or both of these hypotheses. Ongoing work seeks to build on this knowledge by examining a series of phosphine ligands (L) on $\text{CpW}(\text{CO})_2\text{LH}$ complexes to investigate how steric bulk, electronics, and reorganization energy change the PCET mechanism. The PCET mechanism of each of the new analogs will be determined by studying each complex utilizing stopped-flow rapid mixing coupled with optical spectroscopy. Once the PCET mechanism for each complex has been determined, relationships with steric bulk and reorganization energy will be analyzed to identify any correlations between these factors and the PCET mechanism.

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P25. Proton-Coupled Electron Transfer at Electrode–Electrolyte Interfaces

Megan JACKSON, Jaeyoung LEE, Devon LEIMKUHL, Kenneth CHUA

University of North Carolina at Chapel Hill, Chapel Hill, NC 27517 USA

Proton-coupled electron transfer (PCET) reactions are essential to a wide range of reactions that take place directly at electrode surfaces. This poster summarizes the group's work investigating interfacial PCET processes. In part 1, we discuss the essential role of protons in a self-assembled organic charge storage material. In part 2, we discuss routes towards incorporating proton relays into electrodes for faster PCET steps in electrocatalysis. In part 3, we present steps towards systematically tuning E° for metal–H bond formation at specific electrode active sites.

P26. MONITORING SPECTRAL CHANGES OF REDOX ENZYMEENABLED BY ELECTRIC CURRENT

Arpitha KABBINALE¹, Per BÖRJESSON², Richard NEUTZE³

¹ Address: University of Gothenburg, Arpitha.kabbinale@gu.se

² Address: University of Gothenburg, ³ Address: University of Gothenburg

Most of the bioenergetic processes such as photosynthesis, cellular respiration are controlled by electron transfer. Proteins involved in these processes undergo conformational changes to accept/donate the electrons^[1]. To understand the mechanism, it is important to characterise the protein structural changes associated with their different redox states. Cyclic voltammetry experiments proved that redox potential of enzymes can be altered in the presence different electrode-electrolyte system^[2]. In the current research we used cytochrome C, heme containing protein that participate in electron transport chain. We built an inhouse electrode device (Figure 1) with platinum electrodes placed inside the rectangular glass capillary. Then we passed 4 mg/ml protein solution in sodium phosphate buffer in the presence of 4,4-bipyridine and sodium perchlorate. Absorption spectra of cytochrome C were then collected (Figure 2) using microspec. We started the experiment by collecting the absorption spectra of cytochrome C at its oxidised state. Then we provided 2V potential to electrode and collected reduced spectra at different time points which were similar to that of previously obtained reduced spectra in the presence of reduced agent. Electric current induces the changes in protein's redox states. Combining the electrochemistry and structural biology techniques creates a new path to determine the protein structures at their different redox states by tuning the potential of the system.

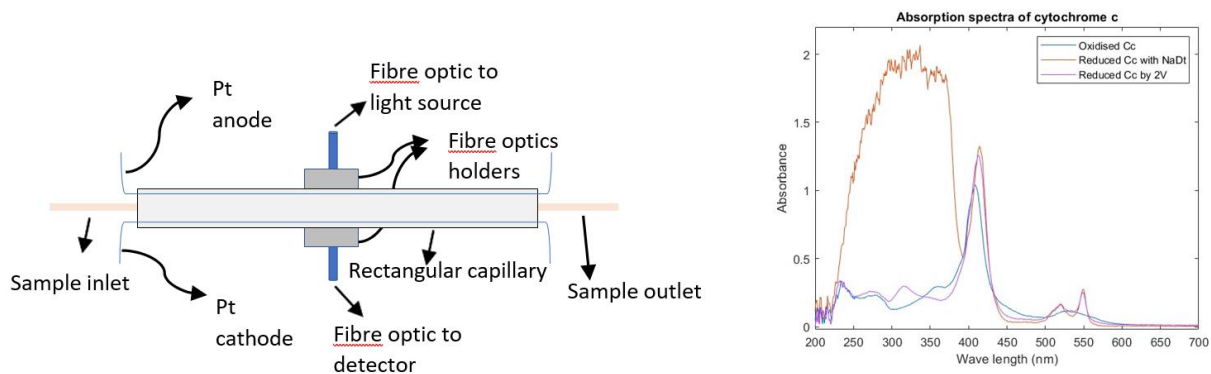


Figure 1. Platinum electrode device; **Figure 2.** Absorption Spectra of cytochrome C

Work to be done: 1. Design and construction of electrode device to increase the rate of reaction and to toggle between oxidised and reduced states of different proteins. 2. Testing with different buffers and electron mediators in which proteins and their crystals are stable. 3. Designing and constructing an electrode device that can support crystallography data collection.

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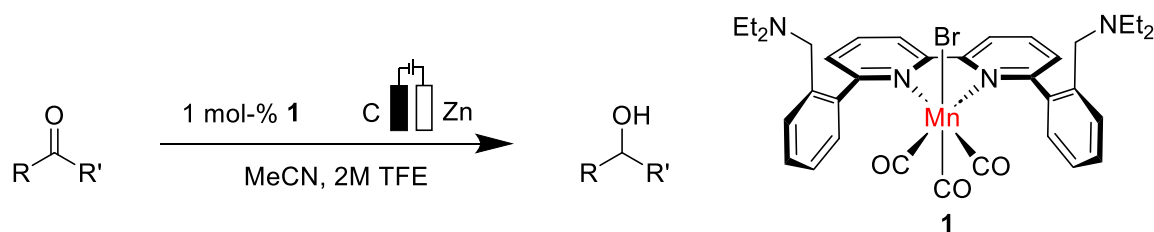
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P27. ELECTROCHEMICAL HYDROGENATION OF CARBONYL COMPOUNDS WITH A MANGANESE CATALYST

Kai-Thorben KUESSNER¹, Igor FOKIN¹, Inke SIEWERT¹

¹ Georg-August Universität, Tammannstraße 4, Göttingen/D, kai-thorben.kuessner@uni-goettingen.de

Hydrogenation reactions are a key step in many synthetic strategies for bulk and fine chemicals and thus have been investigated in detail over the last decades. Recently, also first row transition metal catalysts have been developed to accomplish such conversions.^[1] However thermal reductions oftentimes require high pressures of H₂ and elevated temperatures.^[2] Electrochemistry has recently re-emerged as a tool in synthetic chemistry to harness energy from renewable sources for more sustainable synthesis.^[3] Merging organometallic catalysis and electrochemistry is a promising strategy to direct the selectivity toward the specific target and represents an alternative approach to form catalytically active intermediates. Targeting hydrogenation reactions, we explored the electrochemical formation of the crucial metal hydride by reduction and protonation of the metal centre and established a dinuclear Mn-complex and phenol as a proton source for the chemoselective electrochemical hydrogenation of polar C=O-bonds over C=C-bonds.^[4]



Scheme 1. Electrochemical hydrogenation of carbonyl compounds using a literature known complex.^[5,6]

Herein we present a protocol for the electrochemical hydrogenation of aldehydes and ketones using electrons and trifluoroethanol as a proton source.^[5] Catalysis was achieved using a Mn-complex with an internal proton relay, previously shown to be active in the CO₂-reduction.^[6] Investigations into the mechanism showed that the hydrogenation likely proceed *via* H⁻/H⁺-transfer with a manganese(I) or manganese (0) hydride species as crucial intermediate.

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P28. STRONG INTERACTION BETWEEN AN Fe(III) PORPHYRIN AND GRAPHITIC SURFACE FOR BOOSTING CO₂ ELECTRORETION

Zhi-Mei Luo,¹ Marco Nicaso,¹ Carles Bo,^{*1} Antoni Llobet^{*1}

¹ Institute of Chemical Research of Catalonia (ICIQ), Barcelona Institute of Science and Technology (BIST), 43007 Tarragona, Spain; zluo@iciq.es; mnicaso@iciq.es

The exploitation of effective strategies to anchor molecular catalysts on conductive substrate is desirable for improving the catalytic performances of molecular electrodes toward electrochemical reduction of CO₂. Herein we immobilize a biphenyl-functionalized iron porphyrin on the graphitic surfaces, expectedly via strong CH- π interactions. This hybrid material behaves as a molecular electrode that catalyzes CO₂ reduction to CO in water with a high turn-over frequency (159.2 s⁻¹ at -0.87 V vs. RHE) and near-unity Faradaic efficiencies, much superior to the molecular electrode with the parent iron tetraphenyl porphyrin. The control experiments coupled with computational studies clarify the nature of the involved interactions. This work demonstrates a facile method to make high-performance molecular electrodes for CO₂ electroreduction.

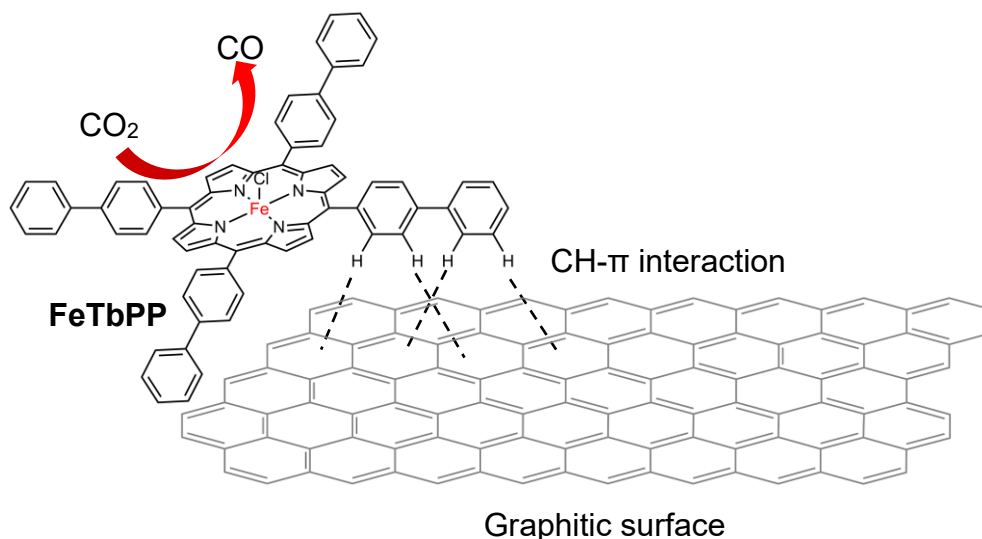


Figure 5. Scheme for anticipated CH- π interactions between an Fe porphyrin and graphitic substrate for CO₂ electroreduction.

P29. Graphite-Conjugated Acids Expose Mechanistic Basis for pH-Dependent Interfacial Proton Coupled Electron Transfer Kinetics

Noah B. LEWIS,^{1*} Ryan P. BISBEY,¹ Karl S. WESTENDORFF,¹ Alexander V. SOUDACKOV,² and Yogesh SURENDRANATH¹

¹ Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, USA

² Department of Chemistry, Yale University, New Haven, Connecticut, USA

*presenting author, Noah Lewis's, email: nblewis@mit.edu

The electrochemical PCET reactions critical to energy conversion and catalysis can be driven by outer-sphere electron transfer to soluble molecules (OS-PCET) or by interfacial polarization of surface-bound active sites (I-PCET). While pH-dependent kinetics of OS-PCET have been extensively studied with molecular precision, the inherent heterogeneity of surfaces has impeded molecular-level understanding of I-PCET. Employing graphite conjugated carboxylic acids as molecularly defined I-PCET hosts, we isolate the intrinsic pH-dependent kinetics of I-PCET across the entire pH range. We uncover a V-shaped kinetic profile with a rate minimum at pH 10 that rises log-linearly toward the pH extremes. Spanning three orders of magnitude, these I-PCET rates lack the pH-independent regions characteristic of OS-PCET. With these data we develop a mechanistic model for I-PCET, invoking rate-limiting CPET through pre-associated hydronium/water or water/hydroxide donor/acceptor pairs. This model captures the entire data set with only four adjustable parameters, each donor/acceptor couple's standard state rate constant and transfer coefficient. We find that I-PCET involving water/hydroxide is four-fold slower than hydronium/water, but both reactions display transfer coefficients of 0.7, denoting late transition states. These studies highlight key mechanistic distinctions between OS-PCET and I-PCET and provide a framework for understanding more complex I-PCET reactions critical to the clean energy transition.

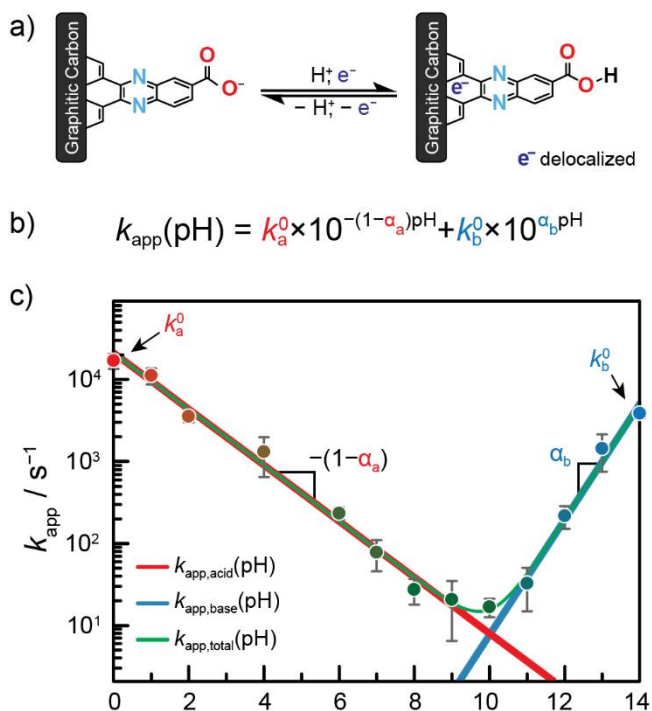


Figure 1: **a)** Structure of graphite conjugated carboxylic acids, displaying relevant PCET reaction; **b)** Derived rate law for apparent I-PCET rates involving the standard state rate constant (k^0) and transfer coefficient (α) of the hydronium/water couple dominating in acidic media (subscript “a”) and the water/hydroxide couple dominating in basic media (subscript “b”). **c)** V-shaped kinetic profile of I-PCET showing measured apparent rates as colored circles, and fits for the individual contributions of the acid dominating reaction ($k_{app,acid}$) and base dominating reaction ($k_{app,base}$) to the overall reaction ($k_{app,total}$).

P30. CATION AND CHARGE EFFECTS FOR MOLECULAR CO₂-TO-CO ELECTRO-REDUCTION IN A FLOW CELL

Chengyu LIU,¹ Dorian JOULIE,¹ Marc ROBERT^{1,2}

¹ Université Paris Cité, Laboratoire d'Electrochimie Moléculaire, CNRS, F-75006 Paris, France. Email : liu.chengyu@u-paris.fr

² Institut Universitaire de France (IUF), F-75005 Paris, France.

Electrochemical reduction of CO₂ into fuels is a critical step towards achieving global carbon-neutrality and solving the pressing energy crisis.^[1-3] Molecular flow cell systems have emerged as key players in this conversion process.^[1] In this study, we have applied two approaches to enhance the efficiency of these systems: 1) the use of electrolyte cation effect, which significantly improve the CO₂ reduction reaction (CO₂RR) activity and selectivity;^[2] 2) the application of catalyst charge effect, which greatly promotes the CO₂RR activity.^[3] Compared with our previous study, our results show that the CO₂RR activity, selectivity and stability have all been improved. Using a 0.5 M NaHCO₃ electrolyte, neutral cobalt phthalocyanine (CoPc) only reached a current density of 150 mA/cm² with a Faradaic efficiency (FE) above 95%. In contrast, the charged CoPc (CoPc²⁺, Figure 1 insert) was able to bear 500 mA/cm² with an FE > 95%. When CoPc²⁺ was used as the catalyst with Cs⁺ electrolyte, the system could even reach 600 mA/cm² with an FE of 96%. Importantly, under a high current density of 500 mA/cm², our optimized system maintained an FE above 95% for 15 min and 90% for over 30 min (Figure 1).

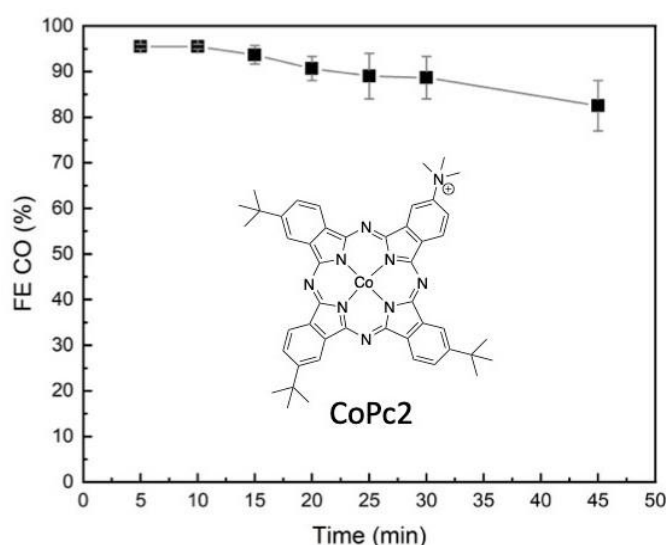


Figure 1. Faradaic efficiency of CO vs. electrolysis duration. Conditions: 500 mA/cm² current density, CoPc²⁺ (0.15 mg/cm²) as catalyst, 10 mL/min flow of 0.5 M CsHCO₃ electrolyte, 11 sccm flow of humidified CO₂. Insert: Chemical structure of CoPc²⁺.

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P31. Bio-inspired Active Site on a Coordination-adaptive Organosulfonate Ligand for Catalytic Water Oxidation

Tianqi LIU, Licheng SUN

Address: Department of Chemistry, School of Engineering Sciences in Chemistry Biotechnology and Health, KTH Royal Institute of Technology, 10044 Stockholm, Sweden. Email: tianqil@kth.se

Enzymes use adaptive frameworks to preorganize substrates, accommodate various structural and electronic demands of intermediates and accelerate related catalysis. Inspired by biological systems, a Ru-based molecular water oxidation catalyst containing a configurationally labile ligand [2,2':6',2''-terpyridine]-6,6''-disulfonate (tds²⁻) was designed to mimic enzymatic framework, in which the sulfonate coordination is highly flexible, and functions as both an electron donor to stabilize high-valent Ru and a proton acceptor to accelerate water dissociation, thus boosting the catalytic water oxidation performance thermodynamically and kinetically. The combination of single crystal X-ray analysis, various temperature NMR, electrochemical techniques and DFT calculations was utilized to investigate the fundamental role of the self-adaptive ligand, demonstrating that the on-demand configurational changes give rise to fast catalytic kinetics with a turnover frequency (TOF) over 2000 s⁻¹, which is comparable to oxygen evolving complex (OEC) in natural photosynthesis.

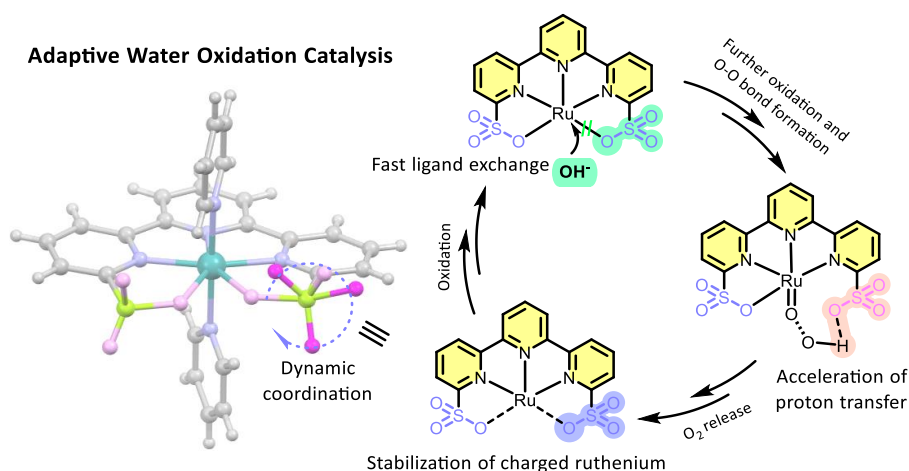


Figure 1. Proposed adaptive water oxidation pathways by Ru-tds.

• Acknowledgements

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P32. A VARIETY OF NON-SPECIFICALLY ADSORBED MACROCYCLES CAN EXPERIENCE MOLECULAR POLARIZATION

Vennela MANNAVA,¹ Yogesh SURENDRANATH²

¹ Address: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States; E-mail: vmannava@mit.edu

² Address: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

Molecularly modified electrodes (MMEs) have shown enhanced electrocatalytic behavior for various reactions beyond their individual constituents. While the molecular active sites in MMEs are generally assumed to operate through traditional redox-mediated pathways, recent studies have demonstrated that molecules covalently tethered to electrodes can experience electrochemical polarization and instead operate through concerted electrocatalytic pathways, by virtue of lying within the electrochemical double layer. This study addresses questions about the generalizability of molecular polarization phenomena in MMEs. We evaluate a series of macrocyclic electrocatalysts non-specifically adsorbed to carbon electrodes within carbon-Nafion films. The films all display hydrogen evolution reaction (HER) electrocatalysis with Nernstian scaling of onset across pH, including in basic conditions where redox-mediated HER is inaccessible, evincing the presence of molecular sites accessing polarized reactivity. Tafel analysis yields slopes around -120 mV/dec, further supporting the dominance of a polarized HER mechanism in these films. These results indicate that some fraction of macrocycles within each non-specifically adsorbed film is experiencing molecular polarization. By studying a variety of macrocycles, we begin to explore which molecular properties influence molecular polarization phenomena. This can help to define a new framework to evaluate the behavior of MMEs and motivate new design principles for enhanced MME electrocatalysis.

P33. ENABLING TRANSITION METAL HYDRIDE FORMATION VIA EXCITED-STATE PROTON-COUPLED ELECTRON TRANSFER

Ann Marie MAY,¹ Greg CURTIN², Elena JAKUBIKOVA², and Jillian DEMPSEY¹

¹ *Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3290;*
ammay6@live.unc.edu.

² *Department of Chemistry, North Carolina State University, Raleigh, NC 27695*

Photo-initiated PCET reactions that drive the formation of fuels from energy poor feedstocks are a promising strategy for artificial photosynthesis. My research explores the light-generated formation of transition metal hydride complexes, key reaction intermediates which undergo subsequent chemical transformations to produce targeted fuel products. Traditional approaches to enable this photoreactivity employ an external photosensitizer to absorb light and transfer an electron (or more rarely a proton) to a ground state catalyst, driving PCET to form a metal hydride bond. However, this strategy relies on multiple chemical species to drive catalysis, complicating their use and necessitating optimization of several components to achieve efficient photocatalysis. A more attractive alternative to this approach is to instead design a single transition metal complex capable of both absorbing light and undergoing chemical reactivity to form a metal hydride, eliminating the need for external photosensitizers. To accomplish this goal, this work employs transition metal complexes that exhibit ligand-to-metal charge transfer (LMCT) excited states. We postulate LMCT excited states increase the basicity at their metal centers upon photoexcitation and enable facile reduction and protonation to form a metal hydride. The optical properties and thermodynamic parameters that drive this photo-initiated PCET reactivity are being investigated, including formal reduction potentials and pK_a values. In addition, time-resolved absorption spectroscopies are employed to monitor accessible photo-initiated PCET reactivity and explore these reactions' mechanistic details.

P34. Circumventing Kinetic Barriers to Metal Hydride Formation Using Ligand-Cooperativity in PCET Reactions

Charlotte L. Montgomery, Leo Chevalier, Jillian L. Dempsey

¹University of North Carolina at Chapel Hill, Chapel Hill, NC (cmontgo@email.unc.edu)

The PCET reactions that form metal hydride complexes often have high kinetic barriers for direct metal protonation, which can lead to bottlenecks in catalytic processes. To circumvent kinetic barriers to metal-based protonation, acid-base functionality in the ligand backbone can be leveraged for kinetically accessible protonation sites. For example, the family of piano stool HER and CO₂ reduction precatalysts, [Co^{III}Cp(P₂^RN₂^{R'})(CH₃CN)]²⁺ (P₂^RN₂^{R'} = 1,5-di(R')-3,7-di(R)-1,5-diaza-3,7-diphosphacyclooctane), uses pendant proton relays on the P₂^RN₂^{R'} ligand to mediate cobalt hydride formation.^[1-2] However, the thermochemical and kinetic limits within the ligand-based PCET pathways are not well-elucidated experimentally.

Through a combination of electrochemical and spectroscopic techniques, three distinct PCET pathways to the metal hydride complex [HCo^{III}Cp(P₂^RN₂^{R'})]⁺, each proceeding via ligand-based intermediates, have been identified for [Co^{III}Cp(P₂^RN₂^{R'})(CH₃CN)]²⁺ complexes. This in-depth mechanistic and kinetic analysis showcases how the exogenous acid and P₂^RN₂^{R'} ligand design impact the mechanism and kinetics of hydride formation. The mechanism is primarily governed by acid strength, acid concentration, pendant amine pK_a, and timescale between electron transfer steps. Furthermore, proton transfer rate constants have been extracted in different mechanistic regimes, showing correlations with acid strength and cobalt oxidation state. Elucidation of these factors generate explicit design principles for efficient, selective, and durable catalysts for fuel production.

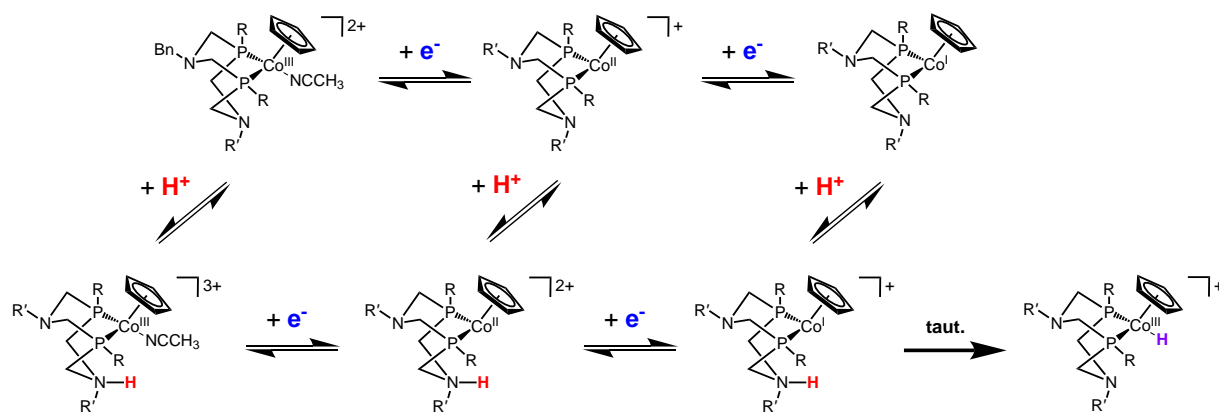


Figure 1. PCET pathways for ligand-based metal hydride formation for [Co^{III}Cp(P₂^RN₂^{R'})(CH₃CN)]⁺ complexes

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P35. Selective Oxidation Reactions by Fe-oxo Complexes on Solid Electrodes and in Artificial Metalloenzymes

Manijstha Mukherjee, Thomas R. Ward, Murielle F. Delley*

Department of Chemistry, University of Basel, Basel, Switzerland, CH 4056

Email: manijstha.mukherjee@unibas.ch

For decades, scientists have been striving to achieve stereo- and regio-selective oxidation of organic substrates under physiological conditions. In nature, heme monooxygenase enzymes utilize heme active sites to selectively oxidize organic substrates with molecular oxygen, using a high-valent Fe(IV)=O pi cation radical (Compound I) intermediate.¹ To emulate this process, a thiolate-ligated iron porphyrin (FePP) active site was previously developed on gold electrodes, which could catalyze hydroxylation and epoxidation using highly oxidizing species formed during the electrochemical oxygen reduction reaction (ORR).² To improve upon this electrochemical analogue, we sought to incorporate the FePP cofactor into a protein environment using streptavidin (Sav) as a scaffold, which is capable of anchoring biotinylated probes. Consequently, we created an artificial metalloenzyme (ArM) by anchoring a biotinylated FePP cofactor to Sav. This ArM, with thiolate ligation from the gold electrode, exhibited moderate activity for hydroxylation during electrochemical ORR. However, we discovered an exceptional activity towards 1 e⁻ oxidation of organic substrates using H₂O₂ as the oxidizing agent with this ArM, even in the absence of an electrode and therefore lacking specific axial ligation to the FePP. Through genetic optimization of Sav, we developed this artificial peroxidase to have the best-in-class catalytic efficiency. The specific environment in enzymes may create an electrostatic environment that allows for selective oxidation with chemical oxidants, such as in our case with H₂O₂. This raises the question of whether we could also use artificial electric fields/electrostatic environments, by polarization at an electrode surface, to achieve selective oxidation using chemical oxidants.

Enzymes achieve high selectivity for oxidation reactions due to their highly specialized electrostatic environments. Using oriented external electric fields (OEEF) as an artificial replacement of the enzymatic environment could provide a valuable tool for modifying the activity of a molecular catalyst. Indeed, detailed computational studies have shown that OEEFs can strongly influence the activity and selectivity of iron-oxo complexes for the oxidation of organic substrates.³ Despite significant theoretical progress, experimental verification of the impact of electric fields on catalysis in the field of selective hydroxylation has been limited. Our future plan is to conduct a thorough investigation of site-selective hydroxylation supported by an OEEF by exploring the vector properties of electric fields and comprehending their directional effects in greater detail. However, it is difficult to examine directional effects in homogeneous systems owing to the free rotation of catalysts, which nullifies the directionality of the OEEF. To overcome this challenge, we intend to immobilize our catalyst on an electrode. This work could pave the way for selective oxidation reactions by immobilized molecular catalysts that are tunable by external electric fields.

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P36. USING NON-CANONICAL TRYPTOPHAN RESIDUES TO STUDY AMINO-ACID BASED HIGH-POTENTIAL (PROTON COUPLED) ELECTRON TRANSFER

Marluci MULLER REBELATO,¹ Rosana LOPES,¹ Mauricio LASAGNA,¹ Cecilia TOMMOS¹

¹ Address: Texas A&M University, College Station, USA. E-mail: marluci.rebelato@gmail.com

Oxidoreductases use metallocofactors, organic molecules and four types of amino acids (tyrosine (Y), tryptophan (W), cysteine and glycine) to perform electron transfer (ET) and proton-coupled electron transfer (PCET) reactions. The four amino acids serve as one-electron (radical) redox mediators in biocatalytic and multistep ET/PCET processes. The Tommos group has created the so-called α_3X family of well-structured model proteins to study how the protein influences the PCET kinetics/mechanism of Y/W radical formation and the timescale/mechanism of radical decay. We are currently expanding the α_3X family with a series of proteins containing a noncanonical tryptophan residue. Incorporation was performed using a tryptophan auxotroph (*E. coli* strain ATCC 49980) cultivated on minimal medium containing the indole molecule of the amino acid of interest. Indole and nine substituted indole analogs were tested in the growth medium with successful expression of α_3W (from the indole-containing cultures) and four analogs yielding $\alpha_3(4\text{-amino})W$, $\alpha_3(4\text{-hydroxy})W$, $\alpha_3(7\text{-hydroxy})W$ and $\alpha_3(7\text{-aza})W$. The ATCC 49980 strain converts indole and the four substituted indoles to their corresponding amino acid and allows incorporation into the expressed α_3X scaffold. We are currently using CD and NMR spectroscopic methods to characterize the structural properties of the new α_3X proteins. Mechanistic studies will subsequently follow.

P37. ALD TiO₂ Films on Silicon Undergo PCET at Mild Potentials in Protic Organic Media

Hannah S. Nedzbala,¹ Dalaney Westbrook,¹ Hyuenwoo Yang,² Carrie L. Donley,³ Amar Kumbhar,³ Gregory N. Parsons², and James M. Mayer¹

¹ Address: Department of Chemistry, Yale University, New Haven, CT 06520-8107, USA,
hannah.nedzbala@yale.edu

² Address: Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina 27603, USA,

³ Address: Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599, USA

TiO₂ thin films are commonly used as a protective layer on semiconductors for use in photovoltaics, molecule-semiconductor hybrid (photo)electrodes, and more. While the oxidative stability of these films is well known, there are far fewer reports on the reductive behavior of TiO₂ coatings. This work will demonstrate that TiO₂ thin films on silicon can be (photo) electrochemically reduced in buffered acetonitrile at potentials relevant to the CO₂ reduction catalysis community. The reduction is proton coupled with a 1e⁻:1H⁺ stoichiometry, as demonstrated by Nernstian dependence of the Ti^{4+/3+} $E_{1/2}$ on the buffer pK_a. Experiments were conducted with and without illumination and a photovoltage of ~0.6 V was observed, which approaches the maximum attainable photovoltage for silicon. Characterization of the films before and after reduction indicate that the thin film restructures upon reduction to form islands, rendering ALD TiO₂ films a potentially poor choice as a support for immobilization of molecular catalysts. The potential of these reduced films to generate reactive HAT and hydride donor mediators useful to the CO₂ reduction community will be discussed.

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P38. SOLAR-DRIVEN H₂ EVOLUTION AND ALCOHOL OXIDATION

Vasilis NIKOLAOU,¹ Deborah ROMITO, Georgios CHARALAMBIDIS,² Stéphane DIRING¹, Athanassios G. COUTSOLELOS,² Fabrice ODOBEL¹

¹ Université de Nantes, CNRS, CEISAM UMR 6230, F-44000 Nantes, France.

vasileios.nikolaou@univ-nantes.fr

² Laboratory of Bioinorganic Chemistry, Department of Chemistry, University of Crete, Voutes Campus, 70013 Heraklion, Crete, Greece.

The prolonged and continually utilization of fossil fuels as primary energy source generated significant environmental complications, since their combustion is responsible for the exponential increase of greenhouse gas emissions.^[1] Hence, it is of great importance to establish cost-competitive, low-carbon technologies aiming to develop sustainable systems based on renewable sources.^[2] Green hydrogen (H₂) besides being a clean fuel is a chemical feedstock as well, which can be imperative for accomplishing multi-sector decarbonization.^[3] In the literature, there are plenty dye-sensitized photocatalytic systems (DSPs) utilized in H₂ evolution,^[4] which are composed of a photosensitizer (PS) and a catalyst (CAT) co-grafted onto n-type semiconductor (n-SC) nanoparticles (NPs) (**Figure 1**). Upon irradiation, the PS absorbs photons and injects electrons in the conduction band (CB) of the n-SC, which acts as electron relay between the PS and the CAT. Then, the reduced CAT performs the H₂ evolution and finally, the oxidized PS (PS⁺) is regenerated by an external sacrificial electron donor (SED). In this work we were able to discard the SED and perform concomitantly H⁺ reduction and alcohol oxidation by implementing a PS-CAT dyad instead of a single PS.

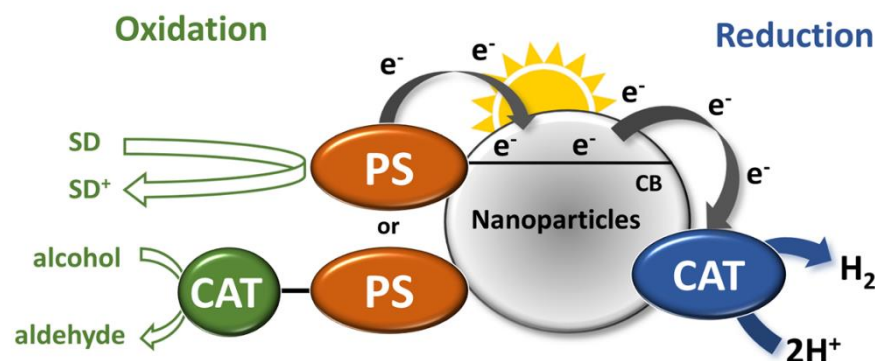


Figure 1. Overview of this work.

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P39. RATIONALIZING THE PHOTOINDUCED PCET REACTIVITY AND MULTIELECTRON STORAGE OF A DISULFIDE-DECORATED RHENIUM PHOTOSENSITIZER

Manuel OELSCHLEGEL,¹ Shao-An HUA,¹ Lucius SCHMID,² Oliver S. WENGER,²
Inke SIEWERT,¹ Franc MEYER¹

¹ Address: Georg-August University, Tammannstr. 4, 37077 Goettingen, DE

² Address: University of Basel, St.-Johanns-Ring 19, 4056 Basel, CH

m.oelschlegel@uni-goettingen.de

Artificial Photosynthesis is a promising concept to reduce our demand for fossil fuels and the impact of climate change on humankind. Solar energy is thereby converted to value-added products using catalytic systems.^[1,2]

Herein we present an organometallic rhenium complex capable of storing multiple electrons and protons in a light driven process and releasing those in a dark process. Use of a bipyridine ligand decorated with a disulfide functional group (Figure 1) allows for accommodation of two electrons and two protons, which can be released in a variety of (dark) reactions.^[3]

The PCET reactivity is rationalized using thermochemical measurements including cyclic voltammetry and non-aqueous pK_a determination. The square-scheme could be established and the ability to release the stored charges by means of hydride, H atom or proton transfer is demonstrated. With this knowledge in hand, the complex is employed in combined photoredox/HAT catalytic reactions.

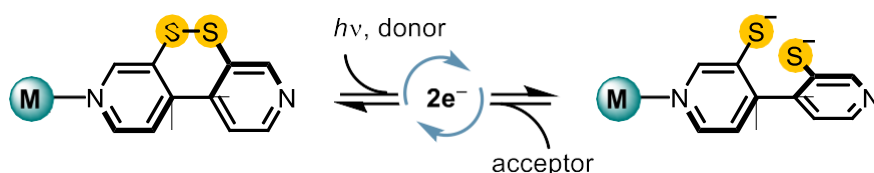


Figure 1. Key disulfide ligand used in this study and its reduced dithiolate form.

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P40. SEARCHING FOR PROTON-COUPLED ENERGY TRANSFER IN BIMOLECULAR SYSTEMS

Andrea ROSICHINI¹, Giorgio SCATTOLINI¹, Leif HAMMARSTRÖM¹

¹ Address: Department of Chemistry, Ångström Laboratory, Uppsala University, Uppsala, Sweden, andrea.rosichini@kemi.uu.se

A new type of proton-coupled process, in which proton transfer is coupled to excited state energy transfer, has been recently discovered and observed in a series of artificial molecular triads. This new mechanism has been called Proton-Coupled Energy Transfer (PCEnT)^[1].

The focus of this project is to investigate the possibility of PCEnT in bimolecular systems. Different molecules that undergo excited state intramolecular proton transfer (ESIPT) were chosen from literature as energy acceptors in combination with common singlet and triplet energy donors. The energies of donors and acceptors were tuned so that simple energy transfer would not be energetically accessible, but proton-coupled energy transfer would instead be possible. Each donor-acceptor pair was studied with multiple steady state and time resolved spectroscopic techniques, but PCEnT was not observed for any of them.

These results seem to indicate that other parameters, like electronic and vibronic coupling, most likely play a key role in the appearance of PCEnT in the original molecular triads that needs to be better understood in order to be able to design new systems in which PCEnT can be observed.

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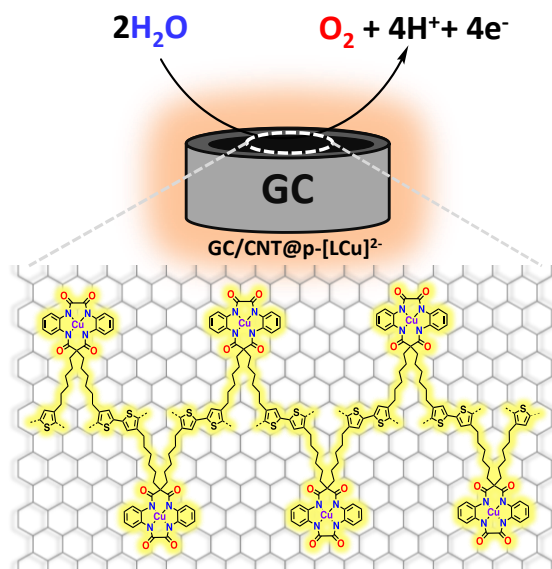
P41. Robust Molecular Anodes for Electrocatalytic Water Oxidation Based on Electropolymerized Molecular Cu Complexes

K. Ranu^{1, +}, S. Amthor¹⁺, C. G. Bellido¹, F. F. Salomon¹, M. Gil-Sepulcre^{1*}, A. Llobet^{1,2*}

¹ Institute of Chemical Research of Catalonia (ICIQ), Barcelona Institute of Science and Technology (BIST), Tarragona, Spain, Avinguda Països Catalans 16, 43007 Tarragona, Spain. ² Departament de Química, Universitat Autònoma de Barcelona, 08193 Cerdanyola del Vallès, Barcelona, Spain.

kranu@iciq.es cgbellido@iciq.es fsalomon@iciq.es

Artificial photosynthetic systems have gained attention to produce solar fuels in a sustainable way. Solar-driven water oxidation reaction (WOR) is an essential reaction to understand these systems. However, as this process is thermodynamically uphill, catalysts play important role to overcome the barrier. Towards this goal, d-block metals show unprecedented efficiency in different forms, from oxides to molecular systems.^[1] From past decades, several synthetic molecular water oxidation catalysts (WOCs) have been developed in order to get insight to the mechanism of O-O bond formation which involves multielectron and multiproton catalytic processes.^[2] Nonetheless, water oxidation reaction is still practically a big challenge. This work reports a Cu based molecular WOC based on TAML ligands [LCu]²⁻.^[3] This system has been modified with thiophene moieties that can polymerize on different graphitic surfaces^[4] under oxidative conditions. The versatility of this approach is to increase a loading of the catalyst as a film on heterogeneous surfaces. The resulting hybrid electroanode shows excellent performance to catalyze water to dioxygen at neutral pH achieving current density of 22 mA/cm² at 1.45 V vs NHE and working at an onset overpotential around 250 mV. Regarding the stability in long run, we achieved TONs in the range of 5000 during 24h in CPE with no apparent loss of activity and keeping its integrity as molecular catalyst.



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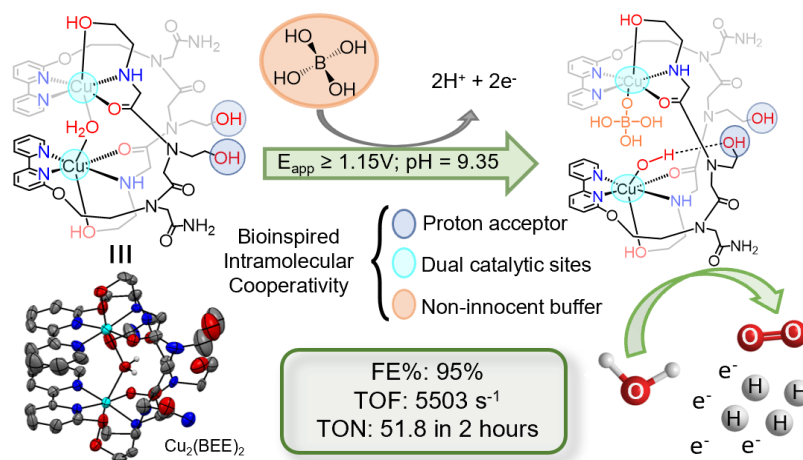
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P42. A DI-COPPER-PEPTOID AS A FAST ELECTROCATALYST FOR HOMOGENEOUS WATER OXIDATION

Guilin RUAN,¹ Pritam GHOSH,¹ Natalia FRIDMAN,¹ Galia MAAYAN¹

¹ Address: Schulich Faculty of Chemistry, Technion – Israel Institute of Technology Technion City, Haifa, 3200008, Israel, 13glruan@gmail.com / guilin@campus.technion.ac.il

Molecular catalysis enables precise structural design to mimic enzymes and/or to develop systems inspired by nature. To address slow kinetics and high overpotential of water oxidation, for example, numerous catalyst designs were inspired by photosystem II (PS-II), specifically the oxygen evolving complex (OEC).^[1] The cooperativity between OEC and its surrounding amino acids as well as related hydrogen bonding assist PCET process to occur for reducing energy barrier in transition states.^[2] However, a stable ligand scaffold with multiple functions for mimicking the secondary sphere effects of PS-II in a synthetic catalytic system is challenging. The Maayan's group previously demonstrated the ability of peptoids, N-substituted glycine oligomers, to stabilize intermediates and to form self-assembled di-copper-peptoid complexes.^[3-5] Capitalizing on these features, I will present a unique Cu-peptoid duplex, Cu₂(BEE)₂,^[6] that is a fast homogeneous electrocatalyst for water oxidation. Cu₂(BEE)₂ performs in controlled potential electrolysis with high Faradaic efficiency and with the highest turnover frequency as reported for Cu-based electrocatalysts. Extensive mechanistic studies suggest multiple PCET steps and the O-O bond formation during catalysis are facilitated by the ethanolic sidechains within the peptoid scaffold, forming intramolecular hydrogen bonds; and by the cooperativity between the two copper centers and borate as a non-innocent buffer.



Scheme 1. A scheme of contents including the molecular and crystal structures of Cu₂(BEE)₂, the participation of borate buffer during electron and proton transfers, and key parameters in this system for electrocatalytic homogeneous water oxidation.^[6]

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P43. HIGHLY EFFICIENT PHOTOCATALYTIC WATER OXIDATION PROCESS PERFORMED BY RU-COMPLEX COVALENTLY LOADED ON NOVEL CTFS.

Martina Salati,¹ Florian Dorchies,¹ Soranyel González-Carrero,² Jia-Wei Wang,¹ Marcos Gil-Sepulcre,^{1,3} Carlota Bozal-Ginesta,² Jan Holub,¹ Marta Ventosa,¹ James Durrant,² Antoni Llobet.¹

¹ Institute of Chemical Research of Catalonia (ICIQ), Tarragona, Spain

² Imperial College London (ICL), London, UK

³ Max-Planck Institute (MPI), Mülheim an der Ruhr, Germany

msalati@iciq.es

Light-induced water splitting ($h\nu$ -WS) for the production of hydrogen as solar fuel is considered a promising and sustainable strategy to deal with the current energy demand. An efficient system for WS involves a photoactive material able to separate and transfer the photogenerated charges, coupled with catalysts for hydrogen and oxygen evolution processes. Covalent triazine-based frameworks (CTFs) represent an interesting example of organic 2D materials recently emerged for their optimal and tunable characteristics (structural, optical, morphological).^[1,2] In this work, the synthesis, characterization and photocatalytic performance of a novel hybrid material are presented. This system is the first example of an efficient combination of highly active water oxidation catalyst (WOC), Ru-tda (where tda is terpyridine dicarboxylic acid), with CTFs, thanks to the covalent anchoring strategy.^[3,4] The hybrid material, namely RuCTF, performs as an excellent photocatalytic system, achieving an impressive TOF value of $1.9 \times 10^5 \text{ h}^{-1}$ and 4.5×10^5 TONs at pH 7, with sodium persulfate used as sacrificial electron acceptor. This system provides a promising and cheap alternative to metal-based semiconductors, that can ultimately lead to a more sustainable and low-cost production of clean energy.

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P44. PCET REACTIVITY OF (BPY)₃Mn(CO)₃-COOMe PROVIDES MECHANISTIC INSIGHT FOR THE ELECTROCHEMICAL REDUCTION OF CO₂ TO CO

Alison WANG,¹ Caroline SAOUMA¹

¹ Address: Department of Chemistry, University of Utah; 315 S 1400 E, RM 2020; Salt Lake City, UT, 84102, U.S.A. caroline.saouma@utah.edu

Proton-coupled electron transfer (PCET) plays an integral role in the reduction of CO₂ to CO. For example, in electrochemical reductions, a hydroxy carbonyl intermediate, M-COOH, is invoked, which then undergoes PCET to liberate water and form a M-CO intermediate; reduction of the latter results in loss of CO. Understanding this PCET step, and how to modulate the reactivity, is pertinent to advancing catalysis design. In most instances, a reduction-protonation sequence ensues, which results in catalytic currents at very cathodic potentials. By contrast, the protonation-reduction sequence occurs at more positive potentials and hence it is desirable to understand how to favor this mechanism. My poster will present research efforts in my group to understand the thermochemistry and reactivity of (bpy)Mn(CO)₃-COOMe. This serves as a model for (bpy)Mn(CO)₃-COOH, which is proposed as an intermediate for CO₂ reduction to CO. Both chemical and electrochemical reductions will be described, as well as reactivity towards proton and H-atom donors. Thermodynamics will be contextualized in terms of understanding competing mechanisms (protonation reduction versus reduction protonation) and selectivity (CO verses H₂ and formic acid). Overall, this work will help understand what parameters could be altered to favor a protonation-first mechanism.

P45. ELECTRIC FIELDS MODULATE PROTON-COUPLED ELECTRON TRANSFER REACTIONS IN CYTOCHROME C OXIDASE

Patricia SAURA,¹ Daniel RIEPL,¹ Daniel M. FREY,¹ Mårten WIKSTRÖM,² Ville R. I. KAILA¹

¹ Department of Biochemistry and Biophysics, Stockholm University, Stockholm, Sweden

² Institute of Biotechnology, University of Helsinki, Helsinki, Finland

E-mail: patricia.saura@dbb.su.se

Cytochrome c oxidase (CcO) functions as the terminal electron acceptor in aerobic respiratory chains, catalyzing the reduction of molecular oxygen to water that couples to proton pumping across the membrane. However, the molecular principles of how protons are sorted along these distinct *chemical* and *pumping* pathways remain poorly understood. Using a combination of large-scale quantum chemical density functional theory (DFT) calculations, hybrid quantum mechanics/molecular mechanics (QM/MM) simulations, and molecular dynamics (MD) explorations, we show that CcO employs oriented electric fields around its active site to direct the *pumped* and *chemical* protons along the distinct pathways. We find that reduction of the electron donor heme *a* couples to conformational changes that create a strong electric field along the *pumping* pathway. This proton transfer couples to reduction of the active site, which in turn creates an electric field along the *chemical* pathway for O₂ reduction. Our proposed mechanism shows similarities with other energy-converting enzymes, suggesting that oriented electric fields are generally employed to control enzyme catalysis.^[1]

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P46. Towards the Experimental Determination of the Thermodynamic Hydricities of Silanes

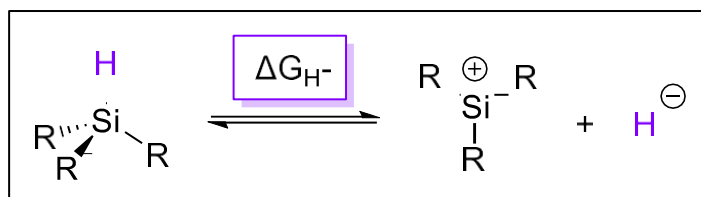
Laurent SEVERY,¹ Alexis MIFLEUR,¹ Thibault CANTAT¹

¹ Address: CEA Saclay, 91191 Gif-Sur-Yvette Cedex, France.

Email: laurent.severy@cea.fr

Silanes are versatile reagents for hydride transfer reactions. The ability of these reagents to reduce various functional groups under relatively mild conditions has made ubiquitous in organic synthesis ^[1,2]. Silanes also have been suggested as part of a class of metal-free reductants for the direct reduction and functionalization of CO₂ ^[3].

Despite their widespread use, the thermodynamic hydricity of silanes has so far only been calculated and experimental values are missing from literature. Here, we present our efforts to determine the hydricities experimentally. We report on our experiments investigating the hydricity values of trisubstituted silanes via the corresponding silylium species R₃Si⁺, using a hydricity bracketing approach as well as electrochemical methods.



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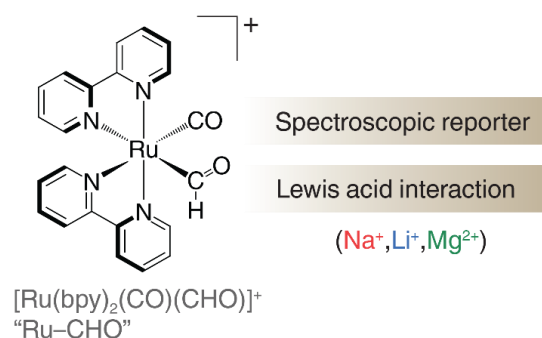
P47. LEWIS ACID-FORMYL ADDUCTS WITH ENHANCED DURABILITY AND REACTIVITY

Jake S. Sirlin,¹ Andressa V. Müller,² Alexander M. Deetz,¹ Nuwanthika D. Kumarage,¹ Mehmed. Z. Ertem,² Gerald. J. Meyer,¹ Javier Concepcion,² and Renato N. Sampaio¹

¹Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, NC, USA 27599-3290

²Chemistry Division, Brookhaven National Laboratory, Upton, NY, USA 11973-5000

The durability and reactivity of the formyl complex $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{CHO})](\text{PF}_6)$, abbreviated **Ru-CHO** where bpy is 2,2'-bipyridine, were characterized in neat acetonitrile and solutions containing Lewis acidic cations (Na^+ , Li^+ , and Mg^{2+}). Titration studies with both ^1H and ^{13}C NMR spectral assays revealed significant shifts to the resonances associated with the formyl group and proximal bpy hydrogens from which association equilibrium constants were extracted. The Mg^{2+} adduct was found to have a significant electrochemical and spectroscopic changes consistent with metal-carbene character. The self-catalyzed decarbonylation of **Ru-CHO** both in the absence and presence of Na^+ formed $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{H})]^+$, $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{CH}_3\text{CN})]^{2+}$, and an unidentified Ru species. In contrast, only 17% of **Ru-CHO** had reacted after ten days in the presence of Li^+ . In the presence of Mg^{2+} , **Ru-CHO** reacted to form $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ and $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{CH}_3\text{CN})]^{2+}$ in a 2:1 ratio, along with free methanol. The study shows that the reactivity and stabilization of a single formyl complex can be tuned by changing the Lewis acidic cation present in the electrolyte, suggesting a Lewis acid-activated room temperature pathway for the reduction of carbon monoxide to methanol. The impact of these findings on understanding multielectron/proton transfers involved in catalysis and fuel production will be discussed.



Scheme 2. Molecular structure of the $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{CHO})]^+$ formyl complex employed in this study.

• **Acknowledgements** This material is based upon work solely supported as part of the Center for Hybrid Approaches in Solar Energy to Liquid Fuels (CHASE), an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0021173. The University of North Carolina's Department of Chemistry NMR Core Laboratory is acknowledged for use of their NMR spectrometers that are supported by the National Science Foundation under Grant No. CHE-1828183.

P48. Reactivity of H-terminated Porous Silicon Surfaces

Eleanor STEWART-JONES,¹ James MAYER,¹

¹ 225 Prospect Street New Haven, CT 06511 eleanor.stewart-jones@yale.edu

Porous Silicon (p-Si) is a multifaceted, complex material with applications from microelectronics to drug delivery.^[1-3] After fabrication in HF, the surface is covered in Si-H bonds. The reactivity of these Si-H groups has been widely exploited, for instance using various hydrosilylation reactions for surface functionalization.^[4] However the fundamental chemical properties of the surface-bound Si-H bonds are relatively unexplored. For example, the surface Si-H bond strengths and radical reactivity have not been examined. A particular focus will be the ability of the surface to donate hydride (H⁻), as this could be relevant to light-driven solar-energy conversion of CO₂ and other substrates.^[5-8] The high surface area and IR activity of p-Si allow examination of this reactivity via molecular-type approaches.^[12] Additionally, temperature programmed desorption experiments coupled with IR absorbances of Si-H stretches will enable reactions involving surface hydrides to be made quantitative.

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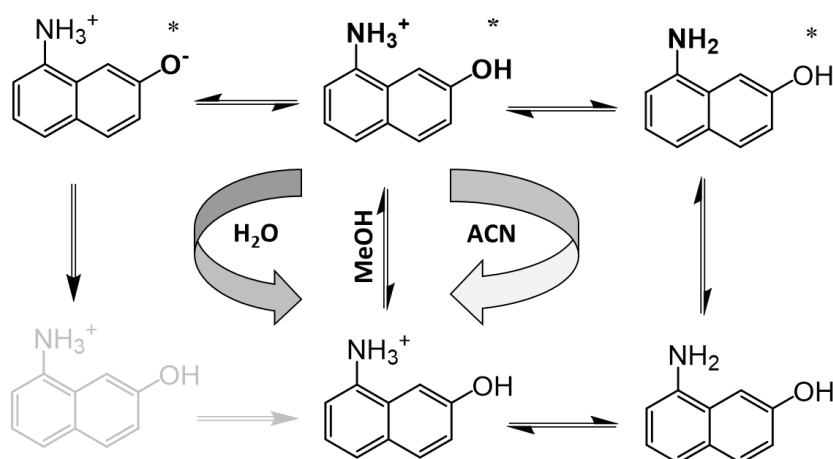
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P49. SOLVENT CONTROL OF EXCITED STATE PROTON TRANSFER PATHWAYS IN AMINONAPHTHOLS

Gabrielle VANDENDRIES, Alexander KREINES, Rachel NEALON, and Kana TAKEMATSU

¹ Address: Department of Chemistry, Bowdoin College, Brunswick, Maine 04011, United States;
ktakemat@bowdoin.edu

Photoinduced proton-coupled electron transfer (PCET) reactions play a key role in the harnessing of light energy. The solvent or reaction environment can greatly impact the PCET electronic landscape. In this study, we focused on how the solvent can drive different proton transfer (PT) pathways in the excited state. Photoacids are compounds that undergo excited state proton transfer (ESPT) upon excitation. Protonated aminonaphthols are a class of diprotic photoacids with competing PT pathways at the NH_3^+ and OH functional sites. We have used a combination of absorption and time-resolved emission spectroscopy to show that the ESPT pathway can be switched between the two PT sites in 8-amino-2-naphthol (8N2OH) using common solvents: water, acetonitrile, and methanol. The site-specific solvent-solute interactions were further probed using solvent mixtures. We will discuss how these results have informed our efforts to couple PT to photoinduced electron and energy transfer processes in both common and new solvent environments, including ionic liquids.



Scheme 1. Solvent control of the ESPT pathways for protonated 8N2OH.

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P50. HYDROGEN REDUCTION REACTION (HRR)

Hai-Xu WANG,¹ Wei Lun TOH,¹ Bryan Y. TANG,¹ Yogesh SURENDRANATH¹

¹ Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States. wanghx@mit.edu

The year 2023 marks the bicentennial of the discovery of heterogeneous H₂ catalysis. Nowadays, the hydrogen oxidation reaction (HOR), which converts H₂ to protons (H⁺), is one of the most important transformations in energy research. Meanwhile, hydrogenation reactions, which transfer net H-atoms (H[•]) to organic substrates from H₂, play pivotal roles in various chemical industries. In comparison, it is surprising to see that a heterogeneous catalytic reaction that directly converts H₂ to hydrides (H⁻) still remains elusive. Herein, we report the discovery of an electrocatalytic hydrogen reduction reaction (HRR) which in net reduces H₂ to H⁻ (Figure 1).^[1] The reaction proceeds by H₂ dissociation on a metal electrode to form surface M–H species, which are then negatively polarized to drive hydride transfer to molecular hydride acceptors with up to 95% Faradaic efficiency. We find that the hydride transfer reactivity of surface M–H species is highly reversible and tunable, and depending on the electrode potential, the thermodynamic hydricity of Pt–H on the same Pt electrode can continuously span a wide range of >40 kcal/mol. The discovery of HRR reveals the fundamental hydride transfer reactivity of surface M–H species and establishes a sustainable strategy for accessing reactive hydrides directly from H₂.

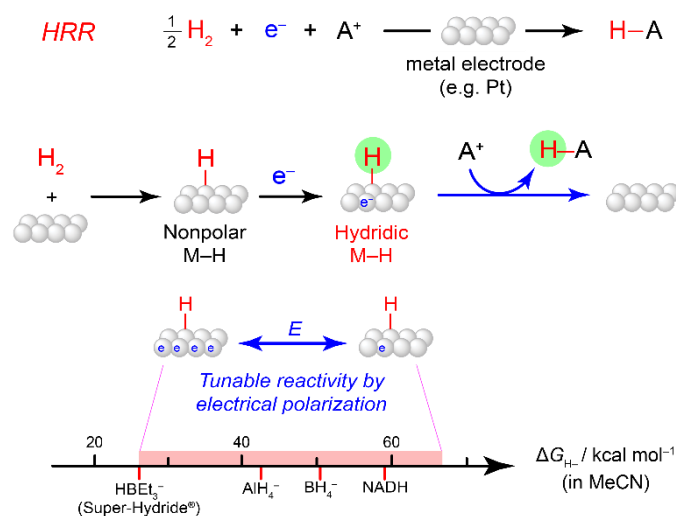


Figure 1. Heterogeneous hydride transfer via electrocatalytic hydrogen reduction reaction (HRR) which, in net, reduces H₂ to hydrides (top) and tunable hydricity of surface M–H by electrical polarization (bottom).

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P51. PHOTOPHYSICS OF ISOELECTRONIC Cr⁰, Mn^I AND Fe^{II} COMPLEXES CONTROLLED BY EFFECTIVE NUCLEAR CHARGE, LIGAND FIELD AND LIGAND π -CONJUGATION

Christina WEGEBERG,^{1,2} Daniel HÄUSSINGER,¹ Oliver S. WENGER¹

¹ Department of Chemistry, University of Basel, St. Johannis-Ring 19, 4056 Basel, Switzerland,

² Current address: Division of Chemical Physics, Department of Chemistry, University of Lund, P. O. Box 124, 221 00 Lund, Sweden. christina.wegeberg@chemphys.lu.se

The development of 3d⁶ metal complexes with emissive metal-to-ligand charge transfer (MLCT) excited states, analogously to those in Ru^{II}(4d⁶) and Ir^{III}(5d⁶) complexes, is of great interest, however, notoriously challenging to obtain due to the presence of low-lying and short-lived metal-centered (MC) states.^[1] Cr⁰, Mn^I and Fe^{II} are Earth-abundant elements with the 3d⁶ valence electron configuration, however, the effective nuclear charge increases significantly throughout the series, hence varying the sweet spot for desirable photoactivity (Figure 1a).

Previously, we discovered that chelating diisocyanide ligands (Figure 1b) provide access to Cr⁰ complexes (Figure 1c), which emit from ³MLCT excited states in solution at room temperature.^[2,3] In this study we explore how the photophysical properties alternate in a series of isostructural Cr⁰, Mn^I and Fe^{II} complexes. We attach extended π -systems in the ligand scaffold, allowing us to control the energy of the ligand centered (LC) states. The effective nuclear charge will largely control the energy of the MLCT state and the ligand field strength will have a key influence on the energy of the MC states. We determine the relative energies of the MLCT, MC and LC states and identify their individual contributions to the excited state dynamics of the isostructural 3d⁶ tris(diisocyanide) complexes.

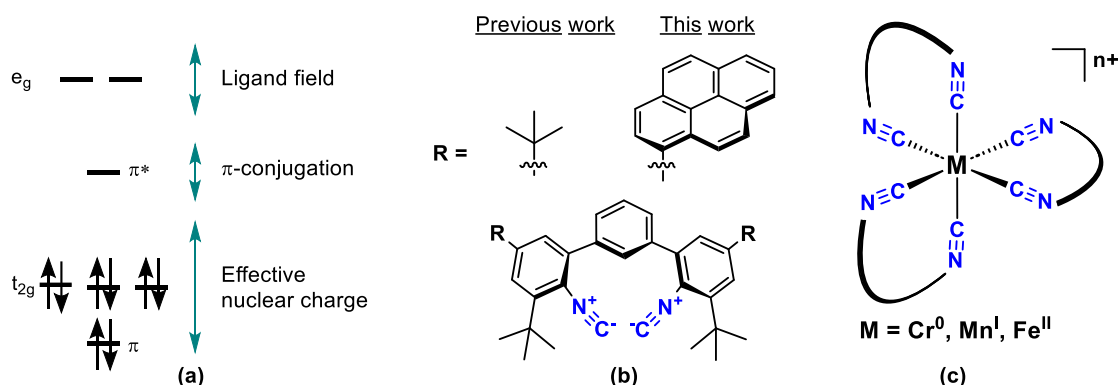


Figure 6. (a) Diagram depicting the frontier orbitals in a 3d⁶ complex and the key contributions (green arrows) connected to energy level of the t_{2g} , e_g and π^* orbitals (b) Molecular structures of diisocyanide ligands relevant for this study, (c) Generic structure of tris(diisocyanide) complexes; $M = Cr^0$, $n = 0$; $M = Mn^I$, $n = 1$; $M = Fe^{II}$, $n = 2$.

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P52. PHOTOCHEMICAL NITROGEN FUNCTIONALIZATION

Katharina WENDEROTH,¹ Maximilian FRITZ,¹ Sven SCHNEIDER¹

¹ Institute of Inorganic Chemistry, Georg-August-Universität, Tammannstr. 4, 37077 Göttingen, Germany; Katharina.Wenderoth@uni-goettingen.de

The splitting of multinuclear, N₂-bridged transition metal complexes is a potential entry into synthetic nitrogen fixation that has attracted considerable interest in recent years.^[1] Transition metal nitrides that result from thermal N₂ splitting often suffer from thermochemical overstabilization, hence low reactivity.^[1] Photochemically driven N–N bond cleavage provides an attractive strategy to obtain more reactive nitride products.^[2] However, compared with thermally driven pathways, a small number of well-defined systems have been reported that undergo light-driven N₂-splitting.

Our group reported light-driven N–N bond scission within the N₂ bridged dirhenium complex **II** (Figure 1).^[3,4] The resulting Re^V nitride **III** undergoes N-atom transfer in the presence of organic electrophiles (e.g. acid halides) upon chemical or electrochemical reduction at mild potentials.^[4] Here, photochemical reduction (Figure 1) is presented, which allows for the use of H₂ as reductant.

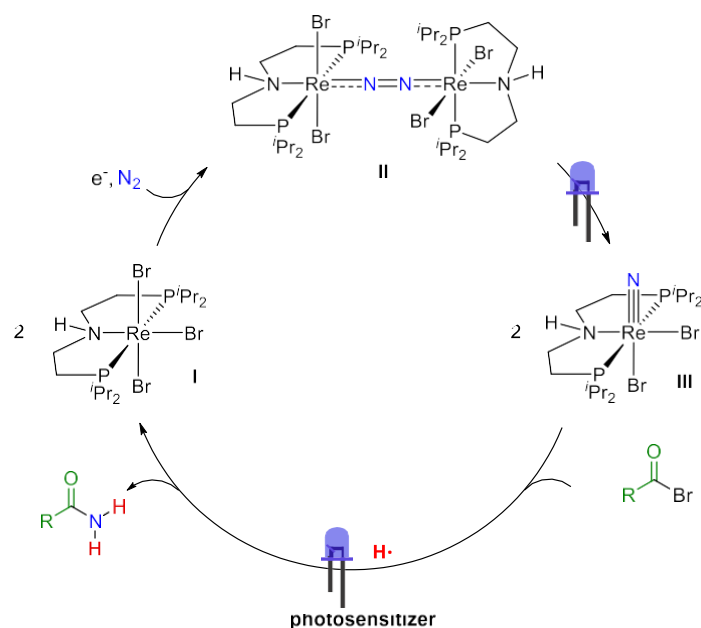


Figure 1. Photochemical N₂ functionalization to benzamide.

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P53. Pyrene Substituted Cyclam Complexes and Their Application as CO₂RR Catalysts

Wiebke WIESNER,¹ Ulf-Peter APFEL^{1,2}

¹ Ruhr University Bochum, Chair of Inorganic Chemistry I, Universitätsstraße 150, 44780 Bochum, wiebke.wiesner@rub.de

² Fraunhofer UMSICHT, Department of Electrosynthesis, Osterfelder Str. 3, 46047 Oberhausen

The ever-rising atmospheric CO₂ concentration brings the conversion of this greenhouse gas into reusable carbon-based products, such as CO or methanol, into focus. This conversion is often achieved by the use of transition metal complexes in the electro- or photocatalytic CO₂ reduction reaction (CO₂RR). Here, the well-known [Ni(cyclam)]²⁺ complex offers high selectivities towards defined CO₂ reduction products and a broad variety of spectroscopic possibilities for mechanistic investigations.^[1,2] Introducing a pyrene moiety in the ligand enables the immobilization of this catalyst class onto carbon nanotubes (CNTs), which was recently shown to be a highly efficient catalytic material.^[3] To direct fundamental research into a more application orientated way, herein this promising catalytic material will be applied in zero-gap electrolyzers. Further, complexes comprising pyrene containing ligand systems can be applied in photocatalysis without the necessity of using an external photosensitizer,^[4] which opens up another potential application field for pyrene substituted cyclam complexes.

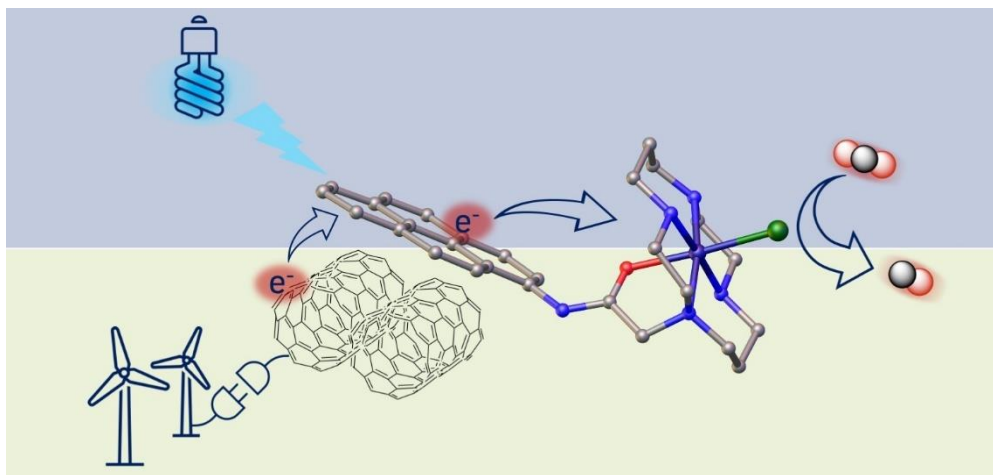


Figure 1. Schematic representation of CO₂ to CO Conversion of a pyrene substituted [Ni(cyclam)]²⁺ complex powered by either light or electricity.

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P54. Coarse Grained Model of Enzyme Complex for Coupling Hydrogen Splitting with CO₂ Reduction

Meritxell WU LU, Jovan DRAGELJ, Maria Andrea MROGINSKI, Armel F. TADJOUNG, Konstantin LAUN, Sagie KATZ, Stefan FRIELINGSDORF, Giorgio CASERTA, Ingo ZEBGER

Institut für Chemie, PC 14 Technische Universität Berlin, Straße des 17. Juni, 10623 Berlin, Germany

Enzymes are considered a powerful tool for bio-catalysis, as they offer several advantages such as high specificity, efficiency, and sustainability. They have shown tremendous potential in various industrial applications, including biotechnology, biomedicine, and green chemistry.^[1] With the increasing demand for sustainable and eco-friendly alternatives, the exploration of enzymes as catalysts has gained significant attention. Hence, it is essential to understand the catalytic mechanisms of these proteins, as well as their conformational stability and interactions with other molecules.^[2,3]

This work aims to assist the rational design and optimization of a hybrid Formate Dehydrogenase (FDH) (from *Rhodobacter capsulatus*) and Hydrogenase-linked enzyme (from *Capriavidus necator*) complex that catalyzes the H₂/formate interconversion, supplemented by computational techniques to refine the limited experimental data.^[4-6] Here, we investigated the thermal stability of these protein-complexes, which has been investigated using microsecond-long molecular dynamics simulations at Coarse Grain (CG) resolution. Thorough analysis of the complex will be centered on the distances between the metal centers of the two enzymes, which is essential for efficient direct electron transfer between the active sites of the two enzymes and hence catalytic coupling.

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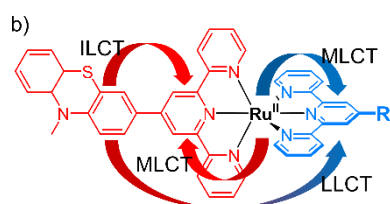
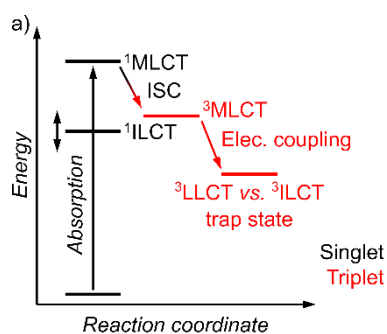
P55. The three kingdoms – Photoinduced electron transfer cascades controlled by electronic couplings

Guangjun YANG,¹ Georgina E. SHILLITO,¹ Clara ZENS¹, Benjamin DIETZEK-IVANSIC^{1,2},
Stephan KUPFER¹

¹ Institute of Physical Chemistry, Friedrich Schiller University Jena, Helmholtzweg 4, 07743,
Guangjun.yang@uni-jena.de

² Leibniz Institute of Photonic Technology, Albert-Einstein-Straße 9, 07745 Jena

Excited states are the key species in photocatalysis, while the critical parameters that govern the potential applications of such excited states are: i) excitation energy, ii) quantum yield, and iii) excited state lifetime. However, in molecular transition metal-based photosensitizers there is a design tension between the creation of long-lived excited (triplet). Long-lived triplet states have low spin-orbit coupling (SOC) and hence their population, either by direct photoexcitation or via subsequent excited state relaxation is low. If the SOC is increased, the triplet state population efficiency is improved – coming at the cost of decreasing the lifetime.



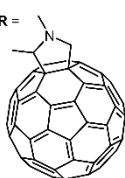
RuH: R = —H

RuPh: R = —C₆H₅

RuTol: R = —C₆H₄—CH₃

RuAn: R = —C₆H₄—OCH₃

RuC₆₀: R =



A promising strategy to isolate the triplet excited state away from the metal after intersystem crossing (ISC) is based on the combination of inorganic and organic chromophores. Here we elucidate the excited-state branching processes in a series of Ru(II)-terpyridyl push-pull triads^[1] by means of quantum chemical simulations. Scalar-relativistic time-dependent density theory^[2] simulations reveal that efficient ISC takes place along 1/3MLCT-gateway states. In the following, the kinetics of the underlying electron transfer processes were investigated within the semi-classical Marcus picture^[3].

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Figure 1. a) Jablonski scheme visualizing excited state processes b) Structure of investigated ruthenium(II) photosensitizers (**RuR**) incorporating a phenothiazine-tpy donor ligand (red) as well as a tpy-based acceptor ligand (blue).

8. Attendee List

Baptiste Andrin	CEISAM, CNRS	baptiste.andrin@gmail.com
Shane Ardo	University of California Irvine	ardo@uci.edu
Vincent Artero	Univ Grenoble Alpes, CNRS and CEA Grenoble	vincent.artero@cea.fr
Veronica Augustyn	NC State University	vaugust@ncsu.edu
Ally Aukauloo	ICMMO	ally.aukauloo@universite-paris-saclay.fr
Martin Axelsson	Uppsala University	martin.axelsson@kemi.uu.se
Benedikt Bagemihl	Ulm University	benedikt.bagemihl@uni-ulm.de
Véronique Balland	Université Paris Cité	veronique.balland@u-paris.fr
Julia Beerhues	ICIQ Tarragona	jbeerhues@iciq.es
Anna Beiler	ICIQ	ambeiler@iciq.es
Maria Besora	Universitat Rovira i Virgili	maria.besora@urv.cat
Sarah Bimmermann	Ruhr-Universität Bochum	Sarah.Bimmermann@ruhr-uni-bochum.de
Sébastien Blanchard	IPCM-Sorbonne Université	sebastien.blanchard@sorbonne-universite.fr
Alexandria Bredar	University of North Carolina at Chapel Hill	abredar@email.unc.edu
Matthew Chambers	Louisiana State University	chambers@lsu.edu
Rima Charaf	Uppsala University	rima.charaf@kemi.uu.se
Bronte Charette	University of Illinois	brontec@illinois.edu
Hye Won Chung	Massachusetts Institute of Technology	hyewonc@mit.edu
Javier Concepcion	Brookhaven National Laboratory	jconcepc@bnl.gov
Cyrille Costentin	Université Grenoble Alpes	cyrille.costentin@univ-grenoble-alpes.fr
Holger Dau	Freie Univ. Berlin	holger.dau@fu-berlin.de
Murielle Delley	University of Basel	murielle.delley@unibas.ch
Alisa Denisiuk	ICIQ	adenisiuk@iciq.es
Shubham Deolka	Okinawa Institute of Science and Technology Graduate University	Shubham.Deolka2@oist.jp
Dependu Dolui	Laboratoire d'électrochimie moléculaire	dolui.iitb@gmail.com
Pablo Durand	iciq	pdurand@iciq.es
Ouissam El Bakouri	University of Girona	ouissam.bakouri@udg.edu
Noémie Elgrishi	Louisiana State University	noemie@lsu.edu
Sergio Fernandez Martin	UNC-Chapel Hill	sergfm@unc.edu
Gabriela Garcia	Universidade de São Paulo (IQ-USP)	ggarcia@iq.usp.br
Carlos García Bellido	Fundació Institut Català d'Investigació Química (ICIQ)	cgbellido@iciq.es
Pablo Garrido Barros	Universidad de Granada	pgarridobarros@ugr.es
Ana M. Geer	Universidad de Zaragoza	anageer@unizar.es
Noah Gibson	Yale University	noah.gibson@yale.edu
Marcos Gil Sepulcre	Max Planck Institute for Chemical Energy Conversion	marcos.gil-sepulcre@cec.mpg.de
Carolina Gimbert Suriñach	Universitat Autònoma de Barcelona	carolina.gimbert@uab.cat
Sergio Gonell Gómez	Universitat Jaume I/Institute of Advanced Materials	sgonell@uji.es
Sergi Grau	ICIQ	sgrau@iciq.es
Saurav Kumar Guin	Maynooth University	sauravkumar.guin@mu.ie
Gregorio Guisado-Barrios	University of Zaragoza-CSIC	gguisado@unizar.es
Tatiana Guseva	Ruhr-Universität Bochum	tatiana.guseva@ruhr-uni-bochum.de
Josep Antoni Gutiérrez Orgaz	ICIQ	jagutierrez@iciq.es
Leif Hammarström	Uppsala University	leif.hammarstrom@kemi.uu.se
Sharon Hammes-Schiffer	Yale University	sharon.hammes-schiffer@yale.edu
Deiaa Harraz	Massachusetts Institute of Technology	dharraz@mit.edu
Phillips Hutchison	Yale University	phillips.hutchison@yale.edu
Hichem Ichou	CEISAM	hichem.ichou@univ-nantes.fr
Diane Isaacs	University of North Carolina	dpisaacs@live.unc.edu
Ivana Ivanovic-Burmazovic	Ludwig-Maximilians-Universität München	ivivch@cup.lmu.de
Megan Jackson	University of North Carolina at Chapel Hill	megan.jackson@unc.edu
Arpitha Kabbinala	University of Gothenburg	arpitha.kabbinala@gu.se
Matthew Kessinger	University of North Carolina at Chapel Hill	kessm05@email.unc.edu

Kai-Thorben Kuessner	Georg-August-Universität Göttingen	kai-thorben.kuessner@uni-goettingen.de
Stephan Kupfer	Friedrich-Schiller-University Jena	stephan.kupfer@uni-jena.de
Noah Lewis	Massachusetts Institute of Technology	noahblewis@gmail.com
Tianqi Liu	KTH Royal Institute of Technology	tianqil@kth.se
Chengyu Liu	Université Paris Cité	liucy1109@gmail.com
Antoni Llobet	ICIQ	allobet@iciq.cat
Julio Lloret Fillol	ICIQ	jlloret@iciq.es
Rosana Lopes	Texas A&M University	rosana.lopes@ag.tamu.edu
Zhimei Luo	ICIQ	zluo@iciq.es
Vennela Mannava	Massachusetts Institute of Technology	vmannava@mit.edu
Pedro Afonso Marquezini Leite	Texas A&M University	pedroafonso156@gmail.com
Mercè Martin Sabi	ICIQ	mmsabi@iciq.es
Roc Matheu	University of Barcelona	rocmatheu@gmail.com
Ellen Matson	University of Rochester	matson@chem.rochester.edu
Ann Marie May	University of North Carolina at Chapel Hill	ammay6@live.unc.edu
James Mayer	Yale University	james.mayer@yale.edu
Gerald Meyer	UNC Chapel Hill	gjmeyer@email.unc.edu
Alexander Miller	University of North Carolina at Chapel Hill	ajmm@email.unc.edu
Charlotte Montgomery	University of North Carolina at Chapel Hill	cmontgo@email.unc.edu
Ana Moore	Arizona State University	amoore@asu.edu
Victor Mougel	ETH Zurich	mougelv@ethz.ch
Manjitha Mukherjee	Department of Chemistry, University of Basel	manjitha.mukherjee@unibas.ch
Marluci Muller Rebelato	Texas A&M University	marluci.rebelato@gmail.com
Hannah Nedzbala	Yale University	hannah.nedzbala@yale.edu
Marco Nicaso	ICIQ	mnicaso@iciq.es
Vasilis Nikolaou	CEISAM, CNRS	vasileios.nikolaou@univ-nantes.fr
Manuel Oelschlegel	Georg-August University Göttingen	m.oelschlegel@uni-goettingen.de
Sascha Ott	Uppsala University	sascha.ott@kemi.uu.se
Andrea Pannwitz	University of Ulm	andrea.pannwitz@uni-ulm.de
John Peters	The University of Oklahoma	jw.peters@ou.edu
Jonas Peters	California Institute of Technology	jpeters@caltech.edu
Koushik Ranu	ICIQ – Institut Català d'Investigació Química	kranu@iciq.es
Marc Robert	Université Paris Cité - CNRS	robert@u-paris.fr
Helena Roithmeyer	University of Zurich	helena.roithmeyer@chem.uzh.ch
Carles Ros	ICFO	carles.ros@icfo.eu
Andrea Rosichini	Uppsala University	andrea.rosichini@kemi.uu.se
Guilin Ruan	Technion – Israel Institute of Technology	13glruan@gmail.com
Martina Salati	ICIQ	msalati@iciq.es
Fernando Federico Salomon	ICIQ	fsalomon@iciq.es
Daniel Sánchez Resa	ICIQ	dsanchez@iciq.es
Caroline Saouma	University of Utah	caroline.saouma@utah.edu
Aranya Sarkar	ICIQ	asarkar@iciq.es
Andrea Sartorel	University of Padova	andrea.sartorel@unipd.it
Patricia Saura	Stockholm University	patricia.saura@dbb.su.se
Sven Schneider	University of Göttingen	sven.schneider@chemie.uni-goettingen.de
Moritz Senger	Uppsala University	moritz.senger@kemi.uu.se
Laurent Severy	CEA Saclay	laurent.severy@cea.fr
Inke Siewert	Georg-August Universität Göttingen	inke.siewert@chemie.uni-goettingen.de
Jake Sirlin	University of North Carolina at Chapel Hill	jsirlin@unc.edu
Wenjing Song	Institute of Chemistry, Chinese Academy of Sciences	wsongunc@iccas.ac.cn
Martin Srnec	J. Heyrovský Institute of Physical Chemistry, Czech Academy of Sciences	martin.srnec@jh-inst.cas.cz
Eleanor Stewart-Jones	Yale University	eleanor.stewart-jones@yale.edu
Sven Stripp	Freie Universität Berlin	sven.stripp@gmail.com
Yogesh Surendranath	MIT	yogi@mit.edu

Kana Takematsu	Bowdoin College	ktakemat@bowdoin.edu
Cecilia Tommos	Texas A&M University	tommos@tamu.edu
Paula Tris-Marzo	ICIQ	ptris@iciq.es
Ludovic Troian-Gautier	UCLouvain	ludovic.troian@uclouvain.be
Hai-Xu Wang	Massachusetts Institute of Technology	wanghx@mit.edu
Jia-Wei Wang	INSTITUT CATALA D'INVESTIGACIO	jwang@iciq.es
Timothy Warren	Michigan State University	warre155@msu.edu
Christina Wegeberg	Lund University	christina.wegeberg@chemphys.lu.se
Oliver Wenger	University of Basel	oliver.wenger@unibas.ch
Katharina Wenderoth	Georg-August-University Goettingen	Katharina.Wenderoth@uni-goettingen.de
Wiebke Wiesner	Ruhr-Universität Bochum	Wiebke.Wiesner@ruhr-uni-bochum.de
Meritxell Wu Lu	Technische Universität Berlin	meritxell.wu.lu@tu-berlin.de
Guangjun Yang	University of Jena	guangjun.yang@uni-jena.de
Ming-Tian Zhang	Tsinghua University	mtzhang@mail.tsinghua.edu.cn