



UNIVERSITÄT
LEIPZIG

Summerschool Workshop

**September
9th 2021**

**From Molecules to Materials:
*Photocatalysis***



Summerschool Workshop "From Molecules to Materials: Photocatalysis" Examples from synthesis, material chemistry and biocatalysis"

Time	Lecturer	Title
Thursday, September 9th 2021, Location: ZOOM/<i>wherever</i>		
8:50	Hey-Hawkins/Zeitler	Welcome
9:00	Burkhard König	Visible Light Photocatalysis: Basic concepts, recent advances and future perspectives
9:45	Cristina Nevado	Photoredox Catalysis as a Versatile Tool for (Asymmetric) Synthesis
10:30 – 11:00 <i>Coffee break</i>		
Breakout Room with Burkhard König		Breakout Room with Cristina Nevado
11:00	Jan Weigand	Flowers as versatile photoredox catalysts
11:45	Bettina Lotsch	Beyond molecules: 2D frameworks as platforms for energy conversion and storage
12:30 – 13:30 <i>Lunch break</i>		
till 13:00 Breakout Room with Jan Weigand		till 13:00 Breakout Room with Bettina Lotsch
13:30	Jennifer Strunk	Supported molecular photocatalysts based on vanadium and titanium oxide: Mode of action characterization with <i>in situ</i> spectroscopy
14:15	Todd Hyster	Photoenzymatic catalysis – Using light to unlock new enzymatic functions
15:00 – 15:30 <i>Coffee break</i>		
Breakout Room with Jennifer Strunk		Breakout Room with Todd Hyster
15:30	Robert Wolf	Metal-Mediated Methods for the Functionalization of White Phosphorus
16:15	Hey-Hawkins/Zeitler	Closing Remarks
16:20 – 17:15 <i>Discussions, Socialising</i>		
Breakout Room with Robert Wolf		

register @ <https://uni-leipzig.zoom.us/meeting/register/u5wkc-urTMrEtHN6zNIMSPygr57invhgCHF>



Visible Light Photocatalysis: Basic concepts, recent advances and future perspectives

Burkhard König

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Visible light is an ideal reagent for chemical reactions: Easy to generate, safe to use and non-toxic, it is selectively applied to specific chromophores and will leave no trace even if used in large excess. The rediscovery of sensitized photochemistry of the last two decades has led to many applications in synthesis.[1] We will briefly review the basic concepts of sensitized photochemistry and photoredox catalysis and discuss some recent reactions that illustrate the power of the technology.[2,3,4] Finally, we will look at the current limitations in photochemistry and potential approaches to overcome these in the future.

[1] L. Marzo, S. K. Pagire, O. Reiser, B. König, *Angew. Chem. Int. Ed.* **2018**, *57*, 10034 - 10072.

[2] K. Donabauer, B. König, *Acc. Chem. Res.* **2021**, *54*, 242–252-

[3] M. Schmalzbauer, M. Marcon, B. König, *Angew. Chem. Int. Ed.* **2021**, *60*, 6270 – 6292.

[4] S. Wang, B.-Y. Cheng, M. Sršen, B. König, *J. Am. Chem. Soc.* **2020**, *142*, 7524–7531.

Photoredox Catalysis as a Versatile Tool for (Asymmetric) Synthesis

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The asymmetric construction of all-carbon quaternary centres within acyclic settings represents a long-standing challenge for synthetic chemists. One-electron processes, as available by photoredox catalysis, have recently gained traction in this context, as open-shell intermediates should be less sensitive to the steric constraints at play during the formation of congested C–C bonds.

This lecture will provide mechanistic insights and the latest developments of the group's photocatalytic work.^[1, 2]

References:

[1] C. Hervieu, M. S. Kirillova, T. Suárez, M. Müller, E. Merino, C. Nevado*, *Nat. Chem.* **2021**, *13*, 327–334. [2] A. García-Domínguez, R. Mondal, C. Nevado, *Angew. Chem. Int. Ed.* **2019**, *58*, 12286–12290.

Metal-Mediated Methods for the Functionalization of White Phosphorus

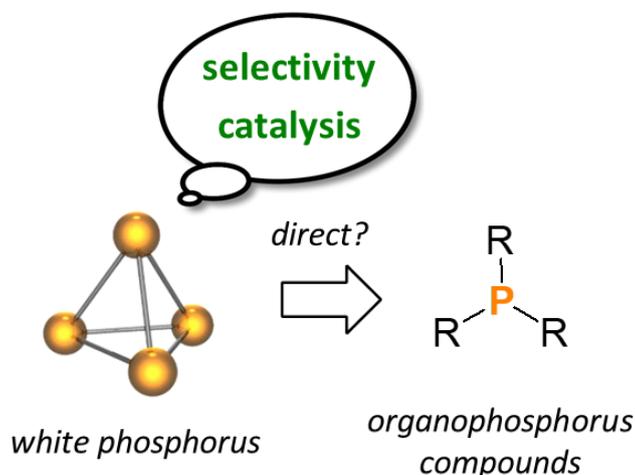
Robert Wolf

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Organophosphorus compounds are an important class of molecules with numerous industrial uses, e.g. as pharmaceuticals, flame retardants, chemical reagents and catalysts.^[1] State-of-the-art synthetic methods for all of these valuable and useful compounds rely on an atom inefficient and hazardous multi-step procedure involving the oxidation of white phosphorus (P_4) with toxic chlorine gas. Far superior would be direct and catalytic methods to form P–C bonds directly from P_4 . However, such methods have remained poorly developed despite extensive studies into P_4 activation and functionalization using main group element and transition metal reagents.^[2]

This lecture will describe new methods that directly transform P_4 into useful (organo-)phosphorus compounds in one pot. The first part of the lecture will present the development of a photocatalytic P_4 functionalization procedure, which affords triarylphosphines and tetraarylphosphonium salts.^[3] In the second part, we will show how the hydrostannylation of P_4 using tri-*n*-butyltin hydride can be used to effectively prepare a variety of industrially relevant monophosphorus species. Insights from mechanistic investigations and their possible implications on further method development will be discussed.



References:

[1] D. E. C. Corbridge, *Phosphorus 2000. Chemistry, Biochemistry and Technology*, Elsevier: Amsterdam, **2000**. [2] Recent reviews: a) C. M. Hoidn, D. J. Scott, R. Wolf, *Chem. Eur. J.* **2021**, *27*, 1886–1902; b) L. Giusti, V. R. Landaeta, M. Vanni, J. A. Kelly, R. Wolf, M. Caporali, *Coord. Chem. Rev.* **2021**, *441*, 213927. [3] a) U. Lennert, P. B. Arockiam, V. Streitferdt, D. J. Scott, C. Rödl, R. M. Gschwind, R. Wolf, *Nat. Catal.* **2019**, *2*, 1101–1106; b) P. B. Arockiam, U. Lennert, C. Graf, R. Rothfelder, D. J. Scott, T. G. Fischer, K. Zeitler, R. Wolf, *Chem. Eur. J.* **2020**, *26*, 16374–16382. [4] D. J. Scott, J. Cammarata, M. Schimpf, R. Wolf, *Nat. Chem.* **2021**, *13*, 458–464.

Beyond molecules: 2D frameworks as platforms for energy conversion and storage

B. V. Lotsch

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Transitioning towards a sustainable energy economy is contingent on new materials solutions. Due to their earth-abundance and low cost, carbon-based materials have become the backbone of a variety of sustainable energy technologies ranging from photovoltaics to supercapacitors. While many carbon materials lack structural definition, 2D frameworks such as carbon nitrides and covalent organic frameworks (COFs) are molecularly precise, crystalline and porous, and as such have the potential to put a new spin on the development of well-defined and robust metal-free semiconductors for photocatalysis [1].

In this talk, we will discuss recent developments and challenges lying ahead in the emerging field of “soft photocatalysis” using 2D frameworks as photoabsorbers, with a focus on the hydrogen evolution reaction [2]. We will then explore the rich interface between optoelectronic and optoionic properties in ionic poly(heptazine imide)-type carbon nitrides (PHI), which represent a new generation of “light storing” materials [3]. The intricate interplay between light harvesting and charge storage in PHI will be exemplified by the concepts of “dark photocatalysis” and direct solar batteries. Finally, we will showcase the design of light-driven microswimmers with photocapacitive properties, building a bridge between energy converting and autonomous systems [4].

[1] T. Banerjee, F. Podjaski, J. Kröger, B.P. Biswal, B.V. Lotsch, *Nat. Rev. Mater.* **2021**, 6,168–190.

[2] K. Gottschling, G. Savasci, H.A. Vignolo-González, S. Schmidt, P. Mauker, T. Banerjee, P. Rovó, C. Ochsenfeld, B.V. Lotsch, *J. Am. Chem. Soc.* **2020**, 142, 12146–12156.

[3] F. Podjaski, B.V. Lotsch, *Adv. Energy Mater.* **2020**, 202003049.

[4] V. Sridhar, F. Podjaski, J. Kröger, A. Jiménez-Solano, B.-W. Park, B.V. Lotsch, M. Sitti, *PNAS* **2020**, 117, 24748–24756.

Supported molecular photocatalysts based on vanadium and titanium oxide: Mode of action characterization with *in situ* spectroscopy

Jennifer Strunk

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Photocatalytic processes require well balanced absorption properties of the photocatalyst. If the band gap is too large, too little light from the solar spectrum can be absorbed. A smaller band gap allows absorption of a broader range of (ideally visible) light; however, the reduction and oxidation potentials of the photogenerated electron and hole, respectively, are very much reduced. A careful control of the size of photoabsorber moieties allows band gap engineering based on the quantum size effect, but the exact correlations between absorption properties, catalytic activity, and altogether photocatalytic performance are not yet known. Two examples are discussed here that provide new insight into the size-dependent mode of action.

For the case of supported vanadium oxide species, it was shown that only isolated VO_4 species or small oligomers on silica and alumina are capable to oxidize methanol selectively to formaldehyde. Larger agglomerates and crystalline vanadium oxide (V_2O_5) can catalyze the reaction thermally, but not light-induced, which is clear indication that the catalytic properties are appropriate, but the light absorption characteristics, likely the reduction and oxidation potential of electron and hole, are not sufficient to carry out the target reaction.[1,2] Using the same catalysts in the liquid phase, selective excitation studies with a Ti:sapphire laser revealed that monovanadates are also able to degrade dyes photocatalytically. Again, larger structures are inactive. Depending on the nature of the support, vanadium oxide species may be washed off into the liquid phase, where they function as homogeneous catalyst, with even higher activity than in the anchored state.[3]

In a second shorter part of the talk, very recent studies on the related system of supported titanium oxide species are reported. An *in situ* cell is currently under development to study the charge carrier characteristics with transient optical spectroscopy in more detail.

[1] B. Kortewille, I.E. Wachs, N. Cibura, O. Pflingsten, G. Bacher, M. Muhler, J. Strunk, *ChemCatChem* **2018**, *10*, 2360-2364.

[2] B. Kortewille, I.E. Wachs, N. Cibura, O. Pflingsten, G. Bacher, M. Muhler, J. Strunk, *Eur. J. Inorg. Chem.* **2018**, 3725-3735.

[3] B. Kortewille, O. Pflingsten, G. Bacher, J. Strunk, *ChemPhotoChem*, submitted.

Flowers as versatile photoredox catalysts

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Photoredox catalysis is a powerful and modern strategy for the synthesis of complex organic molecules which typically relies on the use of a limited range of metal-based chromophores or artificial organic dyes.

This lecture will open new avenues to photoredox catalysis by using dried plant materials as efficient catalysts as exemplarily shown by two typical photoredox reactions. This strategy provides a sustainable, efficient and an easy to handle alternative for a variety of visible light induced photocatalytic reactions.^[1]

References:

[1] J. Wang, K. Schwedtmann, K. Liu, S. Schulz, J. Haberstroh, G. Schaper, A. Wenke, J. Naumann, T. Wenke, S. Wanke, J. J. Weigand; *Green. Chem.* **2021**, 23, 881–888.

Photoenzymatic catalysis – Using light to unlock new enzymatic functions

Todd K. Hyster

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Enzymes are exquisite catalysts for chemical synthesis, capable of providing unparalleled levels of chemo-, regio-, diastereo- and enantioselectivity. Unfortunately, biocatalysts are often limited to the reactivity patterns found in nature. In this talk, I will share my group's efforts to use light to expand the reactivity profile of enzymes. In our studies, we have exploited the photoexcited state of common biological cofactors, such as NADH and FMN to facilitate electron transfer to substrates bound within enzyme active sites. In other studies, we found that enzymes will electronically activate bound substrates for electron transfer. In the presence of common photoredox catalysts, this activation can be used to direct radical formation to enzyme active sites. Using these approaches, we are able to develop biocatalysts to solve long-standing selectivity challenges in chemical synthesis.

