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# SCIENTIFIC PROGRAM

## Symposium Schedule

	Monday, 30.08.21	Tuesday, 31.08.21	Wednesday, 01.09.21
7:00 - 9:00	Travel	Breakfast	Breakfast
9:00 - 9:15		Pres: Fischer Pres: Meng Pres: Schifferer	Pres: Giess Pres: Rotering Pres: Neufeld
9:15 - 9:30			
9:30 - 9:45			
9:45 - 10:00			
10:00 - 10:15		Break	Break
10:15 - 10:30			
10:30 - 10:45		Pres: Witteler Pres: Kraus P4 + P5 + P6 + P7	Pres: Schäfer Pres: Klabunde Pres: YazdanYar / Tischler
10:45 - 11:00			
11:00 - 11:15	Arrival and Welcome		
11:15 - 11:30			
11:30 - 11:45			
11:45 - 12:00			
12:00 – 13:00	Lunch	Lunch	Lunch
13:00 - 13:15	Introduction Pres: Ziegler Pres: Uttry	Guest speaker: Prof Sven Schneider	Pres: Nguyen Pres: Gugeler
13:15 - 13:30			
13:30 - 13:45			Break
13:45 - 14:00	Break		
14:00 - 14:15	Pres: Droste Pres: Kousik P1 + P2 + P3		Break
14:15 - 14:30			
14:30 - 14:45		P8 + P9 + P10 + P11 + P12	Break
14:45 - 15:00			
15:00 - 15:15		Break	Departure
15:15 - 15:30			
15:30 - 15:45	Break		
15:45 - 16:00	Poster session		
16:00 - 16:15	Poster session		
16:15 - 16:30			
16:30 - 16:45			
16:45 - 17:00			
17:00 - 17:15			
17:15 - 17:30		Social activity	
17:30 - 17:45			
17:45 - 18:00			
18:00 – 19:00	Dinner	Dinner	
19:00			

### Poster Pitches:

P1	Hande Acikalin	(CRC 1333)
P2	Sherri Lui	(CRC 1333)
P3	Sebastian Emmerling	(CRC 1333)
P4	Ann-Katrin Beurer	(CRC 1333)
P5	Felix Markus	(CRC 1333)
P6	Karina Abitaev	(CRC 1333)
P7	Marina Fuhrer	(CRC 1333)
P8	Manuel Kirchhof	(CRC 1333)
P9	Carolin Rieg	(CRC 1333)
P10	Mario Winkler	(CRC 1333)
P11	Charlotte Vogler	(CRC 1333)
P12	Philipp Lenz	(CRC 858)

## NOTES

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# TALK ABSTRACTS

## TALK PARTICIPANTS

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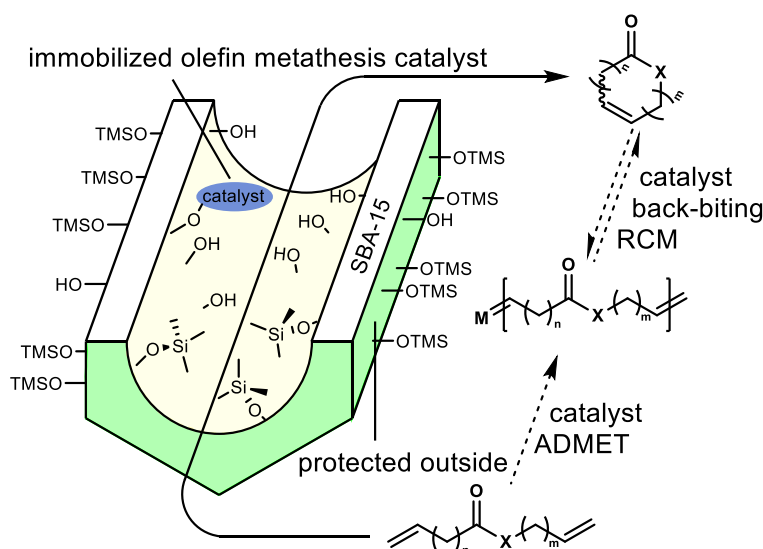
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## B2: Confinement Effects For Efficient Macrocyclization Reactions With Supported Cationic Molybdenum Imido Alkylidene N-Heterocyclic Carbene Complexes

F. Ziegler, M. R. Buchmeiser

University of Stuttgart, Institute of Polymer Chemistry, Stuttgart, Germany.

Ring closing metathesis of long chain dienes provides access to valuable macrocycles. However, state of the art methods require high dilution (1 mM), high catalyst loadings up to 25 mol-%, static vacuum and suffer from the formation of oligomerization products by competing acyclic diene metathesis (ADMET) polymerization.[1] Approaches to improve macrocyclization selectivity are the exploitation of the back biting reaction in combination with a tailored distillation apparatus[2] or the use of designed catalysts.[3] We showed that immobilization of a 2nd-generation Grubbs-Hoveyda catalyst or of tailored cationic Mo-imido-alkylidene-NHC-monoalkoxide complexes in confined spaces, i.e. inside the mesopores of a support material, suppress ADMET and allow for higher substrate concentrations.[4] Taking advantage of the special features of the Mo-based catalysts, macrocyclization selectivities up to 98% and high Z-selectivity can be achieved.



**Figure 1:** Concept for the synthesis of a variety of macrocycles with an olefin metathesis catalyst immobilized inside the mesopores of a support material.

- [1] M. E. Maier, *Angew. Chem. Int. Ed.* **2000**, 39, 2073-2077.
- [2] A. Sytniczuk, M. Dabrowski, L. Banach, M. Urban, S. Czarnocka-Śniadała, M. Milewski, A. Kajetanowicz, K. Grela, *J. Am. Chem. Soc.* **2018**, 140, 8895–8901.
- [3] C. S. Hgiman, D. L. Nascimento, B. J. Ireland, S. Audörsch, G. A. Bailey, R. McDonald, D. E. Fogg *J. Am. Chem. Soc.* **2018**, 140, 1604-1607.
- [4] F. Ziegler, J. Teske, I. Elser, M. Dyballa, W. Frey, H. Kraus, N. Hansen, J. Rybka, U. Tallarek, M. R. Buchmeiser *J. Am. Chem. Soc.* **2019**, 141, 19014-19022.
- [5] F. Ziegler, H. Kraus, M. J. Benedikter, D. Wang, J. R. Bruckner, M. Nowakowski, K. Weißer, H. Solodenko, G. Schmitz, M. Bauer, N. Hansen, M. R. Buchmeiser, **2021**, submitted

# Late-Stage $\beta$ -C(sp<sup>3</sup>)-H Deuteration of Carboxylic Acids<sup>1</sup>

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The use of C–H activation methodologies has emerged as a powerful tool to efficiently build up complex molecules, starting from simple, not pre-functionalized substrates. In this context carboxylic acids are highly interesting since this moiety is amongst the most common functional groups in drugs, natural products and general in organic chemistry. Carboxylates are comparably weakly coordinating to transition metal centers and multiple, competing coordination modes complicate the C–H activation.<sup>2,3</sup> Based on our finding that C–H activation is reversible under suitable reaction conditions, we envisioned a deuteration of carboxylic acids.

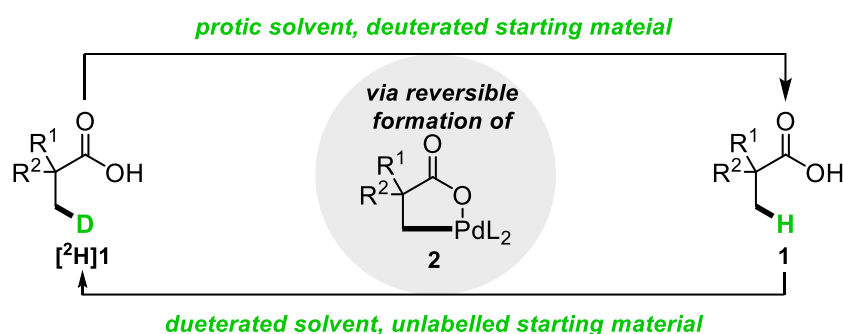


Figure 1: Concept: Develop/Optimize De-deuteration to Enable Late-Stage Deuteration

For practical and conceptual reasons, we chose to optimize the reversed transformation, namely the de-deuteration of deuterated carboxylic acids in protic solvents, while ultimately aiming for a deuteration reaction. We developed new ligands, which in contrary to previously reported ligands in C–H activation, bear a novel 2,4,6-substituted benzamides amide group which engages in the concerted-metalation-deprotonation step. The optimized reaction conditions were applied to the deuteration of a wide range of pharmacophores, natural products and related bioactive frameworks giving access to deuterated analogues with high deuteration degrees and a predictable regioselectivity for the hydrogen isotope exchange.

## References:

1. A. Uttry, S. Mal, M. van Gemmeren *J. Am. Chem. Soc.* **2021**, 143, 10895–10901.
2. A. Uttry, M. van Gemmeren *Synlett* **2018**, 29, 1937–1943.
3. A. Uttry, M. van Gemmeren *Synthesis* **2020**, 52, 479–488.



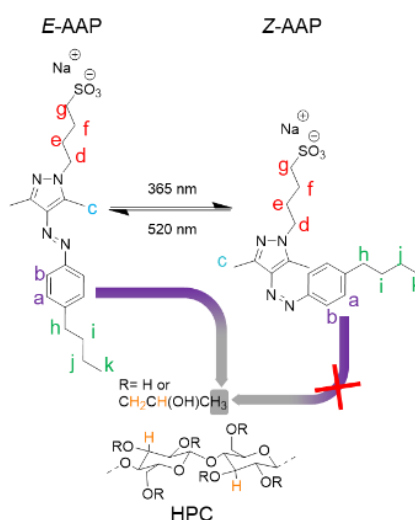
# High-Resolution Magic-Angle Spinning NMR – Assessing Molecular Structures In-Between Liquid and Solid-State

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Investigating the molecular structure of aggregated molecules is a challenging task. Whereas the aggregation process itself can be followed by liquid-state NMR, the resulting structures of e.g. supramolecular polymers and gel-like polymers are inaccessible in solution due to anisotropic NMR interactions, i.e., the NMR signals become severely broadened. Thus, to overcome this challenge, a combination of liquid-state NMR and solid-state NMR methods is advantageous.<sup>1,2</sup>



**Figure 1:** Schematic depiction of the interaction between *E*-AAP and *Z*-AAP with Hydroxypropylcellulose (HPC) which can be switched by light irradiation and temperature.<sup>3</sup>

In this talk high-resolution magic-angle spinning (HR-MAS) NMR methods are presented which gives access to molecules in-between liquid and solid state, e.g. gel-type samples. The application of this novel method is shown at the example of a thermoresponsive polymer combined with photoswitchable molecules (cf. Figure 1). Herein, the interaction between the surfactant and the polymer could be unraveled prior and after the coil-to-globule transition which can be controlled by light-switching and temperature for the *E*- and *Z*-isomer, respectively.<sup>3</sup>

## References:

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2. A. Langenstroer, K. K. Kartha, Y. Dorca, J. Droste, V. Stepanenko, R. Q. Albuquerque, M. R. Hansen, L. Sánchez, G. Fernández, *J. Am. Chem. Soc.* **2019**, *141*, 5192.
3. E. Weißenborn, J. Droste, M. Hardt, D. Schlattmann, C. Tennagen, C. Honnigfort, M. Schönhoff, M. R. Hansen, B. Braunschweig *Chem. Comm.* **2021**, *47*, 5826–5829.

## A5: Organic-inorganic hybrid materials with tunable pore size as catalyst supports

Shravan R. Kousik<sup>1</sup>, Diane Sipp<sup>1</sup>, Kaloian Koynov<sup>2</sup>, Joachim Bill<sup>1</sup> and Petia Atanasova<sup>1</sup>

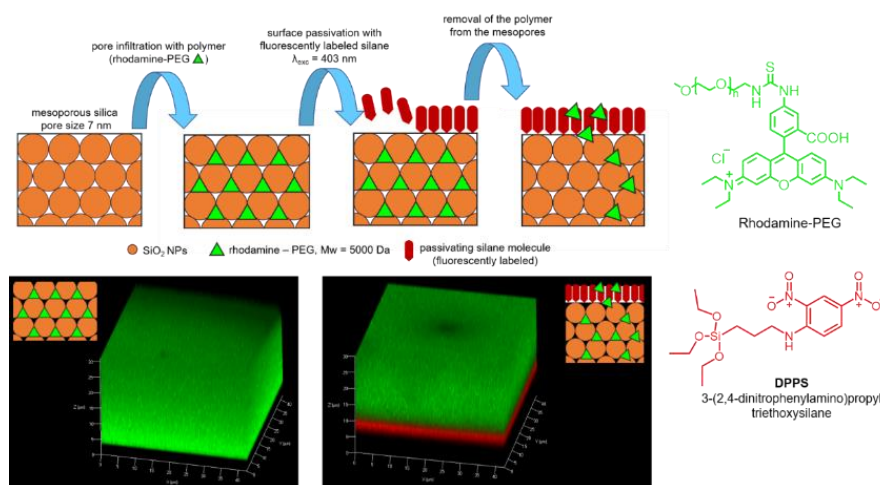
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A key requirement for observing the stereochemical effects associated with catalysis in confinement is the passivation of the porous support material. Pre-emptive determination of the passivation efficiency can greatly minimize the quantum of catalytic tests required during optimization experiments. In this regard, confocal laser scanning microscopy (CLSM) is used as an analytical tool to visualize the pore-filling and passivation processes in mesoporous SiO<sub>2</sub> with a pore size of 7 nm.<sup>[1]</sup> In addition, the permeability of different passivating films is assessed. The influence of the pore-filling process on the infiltration of a fluorescent perylene-based tracer is determined in conditions resembling the actual catalytic process. Passivated mesoporous SiO<sub>2</sub> with two different pore sizes (3.8 nm and 7 nm) are used as supports for olefin metathesis<sup>[2]</sup> using Molybdenum-NHC catalysts (B2) and the experimental results are corroborated with CLSM findings.

Furthermore, the fabrication and surface charge properties of monolithic quasi-mesoporous SiO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub> and ZnO inverse opals is described. The influence of the surface polarity of the oxides on the diffusion of tracer molecules will be studied using fluorescence correlation spectroscopy (FCS).

Additionally, the fabrication of single-oxide and hybrid organic-inorganic TiO<sub>2</sub> microtubes using inherently protective polycarbonate (PC) membranes as templates is discussed. Factors influencing the pore sizes of the microtubes are identified and studied. The immobilization of a fluorescent organosilane in the microtubes is analyzed using CLSM. The diffusion behavior of a fluorescent probe molecule in the channel-like pores of TiO<sub>2</sub> microtubes will then be compared with spherical TiO<sub>2</sub> inverse opal pores using FCS.



**Figure 1:** Visualization of pore-filling and surface passivation processes in mesoporous silica using CLSM

[1] N. Hartmann and D. Brühwiler, *Angew. Chem. Int. Ed*, **2009**, 48, 6354-6356.

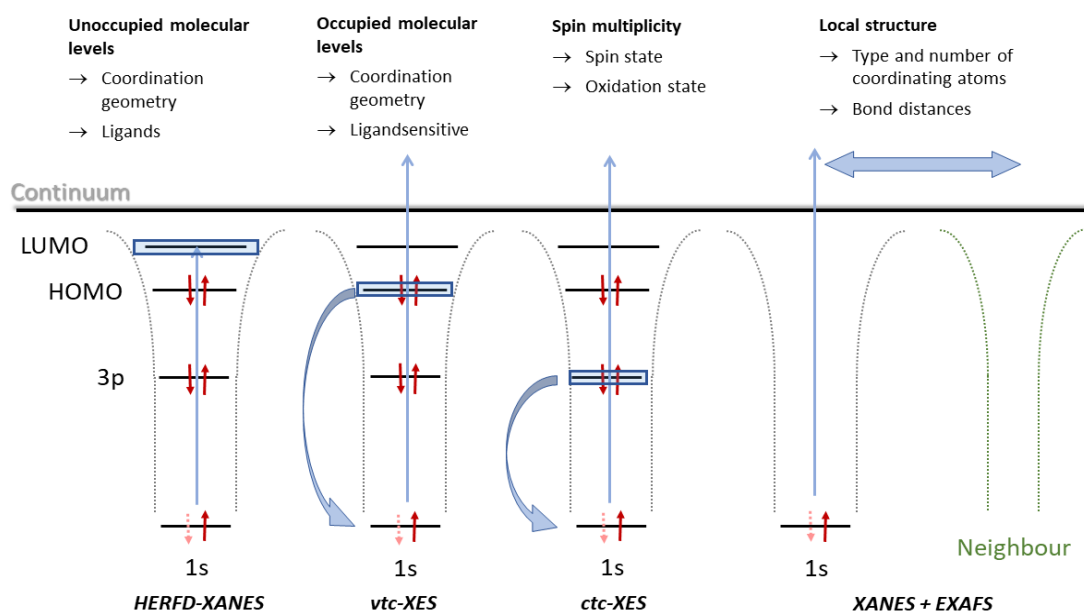
[2] F. Ziegler, J. Teske, et al., *J. Am. Chem. Soc.*, **2019**, 141, 48, 19014–19022.

## S1: Hard X-ray spectroscopy of molecular heterogeneous catalysts in mesoporous materials

Felix Richard Fischer<sup>1</sup>, Prof. Dr. M. Bauer<sup>2</sup>, Prof. Dr. B. Plietker<sup>1</sup>

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The goal of the CRC1333 is to perform heterogeneous catalysis in mesoporous materials by immobilizing molecular catalysts inside the pores and using confinement effects as key factor for selectivity. Both pore size and pore geometry are expected to have a significant impact on the reactivity as well as the coordination chemistry of the immobilized catalysts. In project S1, spectroscopy with hard X-rays is used to analyze these influences based on the excitation of electrons close to the atom nucleus, mainly the 1s-electrons. Hard X-rays enable the investigation of the molecular nature of catalytic complexes fully independent of the state of aggregation. The spectroscopic methods used in project S1 include XANES (X-ray absorption near structure) to get information about the oxidation state of the central atom and EXAFS (Extended X-ray absorption fine structure) to illustrate bond distances as well as type and number of the coordinating atoms. Moreover, HERFD-XANES (high energy resolution fluorescence- detected XANES) and vtc-XES (valence-to-core X-ray emission spectroscopy) provide the HOMO- and LUMO energies of the complexes and ctc-XES (core-to-core X-ray emission spectroscopy) enables the identification of their spin states (figure 1). The obtained data allow the comparison of the electronic and structural parameters of the molecular complexes in solution and inside the pores to get a deeper insight in the reaction mechanisms of the investigated catalytic reactions.<sup>[1]</sup>



**Figure 1:** Hard X-ray methods and provided information for the example of K-edge spectroscopy.<sup>[1]</sup>

[1] M. R. Buchmeiser, B. Plietker, CRC1333 Proposal *Molecular Heterogeneous Catalysis in Confined Geometries* **2018**, 361-374.

### **C3: Atom Probe Tomography of Mesoporous Silica**

Kuan Meng<sup>1</sup>, Patrick Stender<sup>1</sup>, Guido Schmitz<sup>1</sup>

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Atom Probe Tomography is a powerful 3D-chemical mapping technique with resolution up to 0.2 nm, which is suitable for visualizing the mesoporous materials.

In this talk, we present the APT study about the intermediate product of the Order Mesoporous Silica (OMS, from A4) before calcination, where the pores are filled with cetyltrimethylammonium bromide (CTAB). Firstly, pure silica, pure CTAB and their hybrid system were investigated respectively. The mass spectra of the hybrid system display a plausible peak distribution based on both pure components. Secondly, the evaporation behavior under different laser parameter was investigated. Moreover, methods like isosurface reconstruction and composition analysis were used for pore channel visualization and CTAB localization.

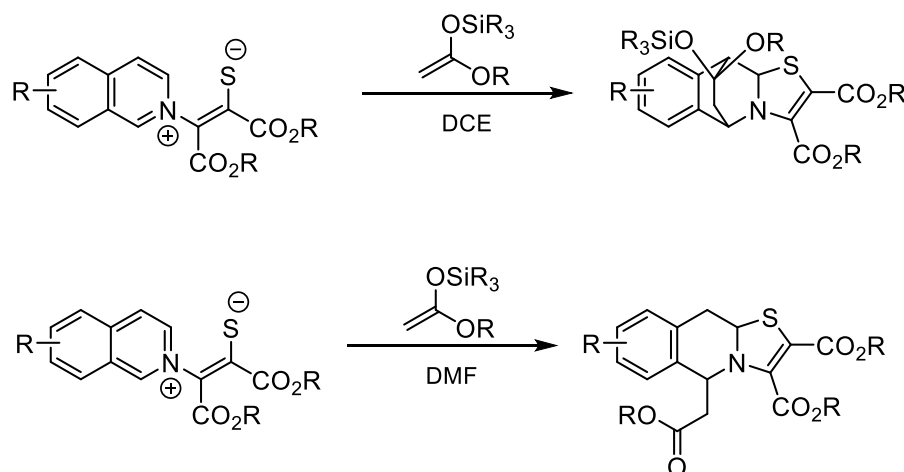
# Novel Cyclization Reactions of N–S Zwitterionic Species

L. Schifferer

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Organosulfur compounds are amongst one of the most important structural types in modern pharmaceutical and agrochemical chemistry.<sup>1</sup> In recent years, the 1,4-zwitterionic N–S synthon has received increased attention due to its stability towards air and moisture. Additionally, it does not suffer from the general drawback of strong odors.<sup>2</sup> Generally, these compounds have been exploited for either [3+m] or [5+m] type transformations. In [3+m] reaction types, the pyridinium moiety serves as a leaving group,<sup>3</sup> whereas in [5+m] reaction types the pyridinium is employed as a reactive moiety.<sup>4</sup> However, so far only pyridine- or quinoline based zwitterionic substrates have been reported and employed for chemical manipulations. Following up our work with *in situ* generated (iso)quinolinium 1,3-zwitterionic substrates,<sup>5</sup> we turned our attention towards isoquinolinium based 1,4-zwitterionic species. Due to the different reactivity of these substrates compared to their pyridine and quinoline analogs, we sought to employ them for intramolecular cyclization reactions. Herein, we report the synthesis of benchstable 1,4-zwitterionic isoquinolinium sulfides and the subsequent dearomatization to construct valuable N,S-heterocyclic compounds such as benzoisoquinuclidine derivatives.



**Figure 1:** Cyclization reactions of isoquinolinium based 1,4-zwitterionic substrates with silyl ketene acetals.

## References:

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2. S. Zhai, X. Zhang, B. Cheng, H. Li, Y. Li, Y. He, Y. Li, T. Wang, H. Zhai *Chem. Commun.* **2020**, 56, 3085.
3. B. Cheng, Y. Li, T. Wang, X. Zhang, H. Li, H. Zhai *Chem. Commun.* **2019**, 55, 14606.
4. B. Cheng, Y. Li, X. Zhang, S. Duan, H. Li, Y. He, Y. Li, T. Wang, H. Zhai *Org. Lett.* **2020**, 22, 5817.
5. L. Schifferer, O. García-Mancheño *Eur. J. Org. Chem.* **2020**, 7176.

## Towards Unraveling Reaction Mechanisms in On-Surface Chemistry

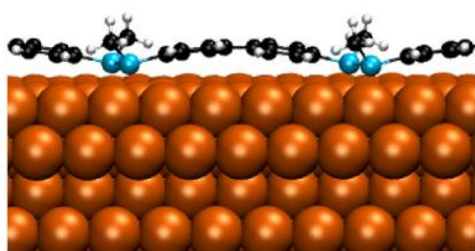
**M. C. Witteler, J. Neugebauer**

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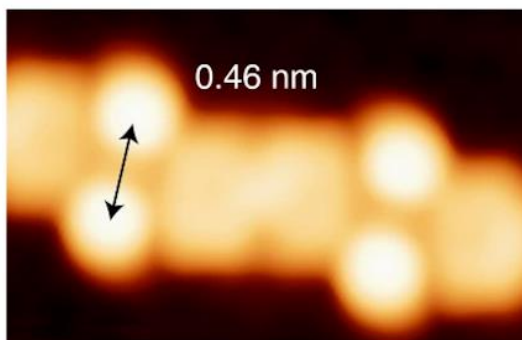
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On-surface chemistry has evolved into a very promising research area for the construction of novel materials such as functionalized surfaces and two-dimensional covalently bound organic networks, which may serve in nanotechnology and heterogeneous catalysis.<sup>1,2</sup> However, comparatively little is known about what happens at an atomistic level when organic molecules meet their substrate under ultra high vacuum conditions, and about how and why such polymerization reactions proceed.<sup>3,4</sup> Density functional theory (DFT) is a powerful tool to characterize and design new materials<sup>5,6</sup>, which has already provided important insights into the interactions between adsorbates and surfaces.<sup>1,2,7,8</sup> Here, we demonstrate how a close cooperation between theory and experiment can elucidate unexpected product structures and shed light onto novel on-surface reaction mechanisms.

DFT model



STM simulation



### References:

1. H. Klaasen, L. Liu, H.Y. Gao, L. Viergutz, P.A. Held, T. Knecht, X. Meng, M.C. Börner, D. Barton, S. Amirjalayer, J. Neugebauer, A. Studer and H. Fuchs, *Chem. Commun.* **2019**, 55, 11611.
2. L. Liu, H. Klaasen, M.C. Witteler, B. Schulze Lammers, A. Timmer, H. Kong, H. Mönig, H.Y. Gao, J. Neugebauer, A. Studer and H. Fuchs, *Nat. Chem.* **2021**, 13, 350.
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8. X. Meng, H. Klaasen, L. Viergutz, B. Schulze Lammers, M.C. Witteler, H. Mönig, S. Amirjalayer, L. Liu, J. Neugebauer, H.Y. Gao, A. Studer and H. Fuchs, *Angew. Chem. Int. Ed.* **2021**, 60, 1458.



## C5: An atomistic view on liquid phase adsorption

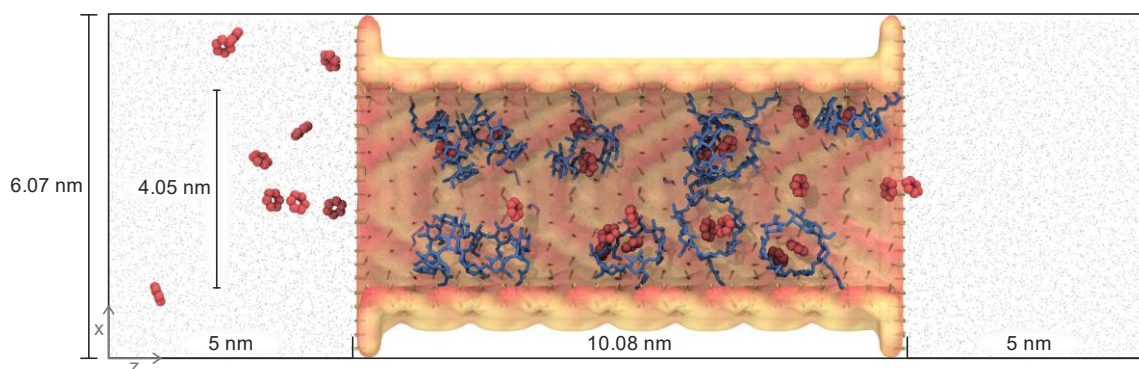
Hamzeh Kraus, Niels Hansen

*Institute of Thermodynamics and Thermal Process Engineering, University of Stuttgart, D-70569 Stuttgart, Germany*

The purpose of this project is to investigate the feasibility of calculating adsorption isotherms from the liquid phase using atomistic simulations. Here we study adsorption of aromatic molecules in a mesoporous silica support with and without  $\beta$ -cyclodextrin functionalization.

Huq et al. [1] reported that *p*-nitrophenol inside a non-functionalized silica pore does not adsorb onto the surface, whereas in a cyclodextrin functionalized pore, *p*-nitrophenol adsorbs onto cyclodextrin. On the other hand, Trofymchuk et al. [2] reported the presence of immobilized  $\beta$ -cyclodextrin groups on the inner pore surface increases the benzene adsorption ability of synthesized materials, thus concluding that cyclodextrin functional groups have a higher adsorption capacity compared to the bare surface.

These effects were observed in molecular dynamics simulations of pore systems (seen in Figure 1) generated by the python package PoreMS [3].



**Figure 1:** Pore system functionalized with eleven  $\beta$ -cyclodextrin groups using the surface linker proposed by Trofymchuk et al. [2] filled with water and benzene molecules, viewed from the side.

- [1] R. Huq, L. Mercier, P. J. Kooyman. *Chem. Mater.* 2021.
- [2] I. Trofymchuk, N. Roik, L. Belyakova. *Nanoscale Res. Lett.* 2017.
- [3] H. Kraus, J. Rybka, A. Hölzel, N. Trebel, U. Tallarek, N. Hansen, *Molecular Simulation*, 2021.

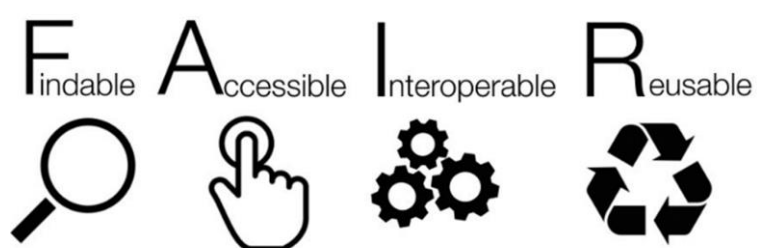
## INF: F.A.I.R. data management in heterogenous catalysis

Torsten Giess<sup>1</sup>, Jürgen Pleiss<sup>2</sup>

<sup>1,2</sup>*Institute of Biochemistry and Technical Biochemistry  
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With the ever-increasing volume and complexity of scientific data, processing, archiving, managing, and sharing of this data has become a daunting task. In chemistry, due to wide variety of disciplines with their diverse and often vendor-specific data formats, data management is particularly difficult.<sup>[1]</sup> However, to ensure sustainable scientific progress, there is an urgent need to address these issues. In 2016, WILKINSON et al. published the F.A.I.R. data principles (Figure 1) in *Scientific Data*, which now serve as the de-facto standard for scientific data handling.<sup>[2]</sup>

This talk will provide a brief overview of the F.A.I.R. data principles in contrast to the current state of data handling in chemistry, how the existing issues will be addressed by project *INF* in the course of the second funding period, as well as the preliminary work that has been done with different collaborators.



Note. From SangyaPundir,  
Wikimedia Commons  
([https://commons.wikimedia.org/wiki/File:FAIR\\_data\\_principles.jpg](https://commons.wikimedia.org/wiki/File:FAIR_data_principles.jpg)).  
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**Figure 1:** F.A.I.R. data principles.

- [1] Wang, B., Dobosh P. et al., *J. Phys. Chem. A* **2017**, 121, 298–307  
[2] Wilkinson, M., Dumontier, M. et al., *Sci Data* 3 **2016**, 160018



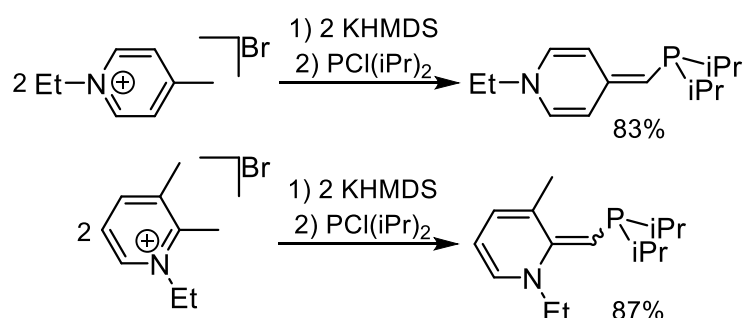
## Pyridinylidene-methylphosphines: Water-stable electron-rich organo phosphines

**Philipp Roting, Marius A. Wünsche, Fabian Dielmann**

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Ligands are indispensable in homogenous catalysis and the development of new ligands has enabled new catalytic pathways over the last decades. However, hydrolytic degradation of ligands is a major challenge in the search for the ideal catalyst that exhibit extreme stability, remarkable activity, and high selectivity. Since water is a common contaminant in regular chemical transformations, it is challenging to exclude traces of water which may affect the activity and selectivity of catalytic reactions. Furthermore, decomposition during the reaction or the workup is a critical factor concerning the recovery and reuse of the catalyst. The range of applications is thus limited by the stability of the free ligand in water.



**Figure 1:** Synthesis of Pyridinylidene-methylphosphines.

Herein, we report the scalable and modular synthesis of electron-rich pyridinylidene-methyl phosphines (PMPs) with one and up to three NHO-substituents. Their coordination behaviour against metals and their characteristics in protonation reactions were studied. Furthermore, the water-stability of PMPs has been explored systematically and comparative with a series of electron-rich phosphines.

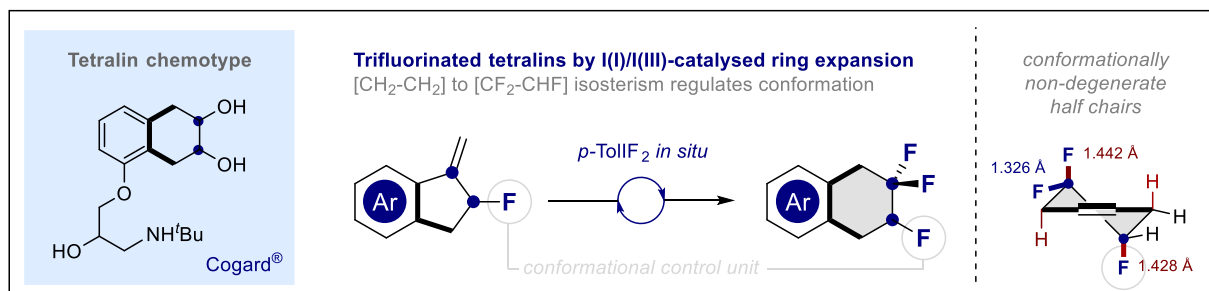
## Trifluorinated Tetralines via I(I)/I(III)-Catalysed Ring Expansion: Programming Conformation by [CH<sub>2</sub>CH<sub>2</sub>] → [CF<sub>2</sub>CHF] Isosterism

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Saturated, fluorinated carbocycles are emerging as important modules for contemporary drug discovery. To expand the current portfolio, the synthesis of novel trifluorinated tetralins has been achieved. Fluorinated methyleneindanes serve as convenient precursors and undergo efficient difluorinative ring expansion with *in situ* generated *p*-TolIF<sub>2</sub> (>20 examples, up to >95% yield). A range of diverse substituents are tolerated under standard catalysis conditions and this is interrogated by Hammett analysis. X-ray analysis indicates a preference for the CH-F bond to occupy a *pseudo*-axial orientation, consistent with stabilising hyperkonjugativen  $\sigma_{C-H} \rightarrow \sigma_{C-F}^*$  interactions. The isosteric replacement of the symmetric [CH<sub>2</sub>-CH<sub>2</sub>] motif by a non-symmetric [CF<sub>2</sub>-CHF] group removes the conformational degeneracy intrinsic to the parent tetralin scaffold leading to a predictable half-chair [ $\Delta V_{vdW}$  = ca. 13%]. The conformational behavior of this novel structural balance has been investigated by computational analysis and is consistent with stereoelectronic theory.



**Figure 1:** Trifluorinated tetralins by I(I)/I(III)-catalysed ring expansion.

### References:

J. Neufeld, T. Stünkel, C. Mück-Lichtenfeld, C. G. Daniliuc, R. Gilmour, *Angew. Chem. Int. Ed.* **2021**, 60, 13647-13651.

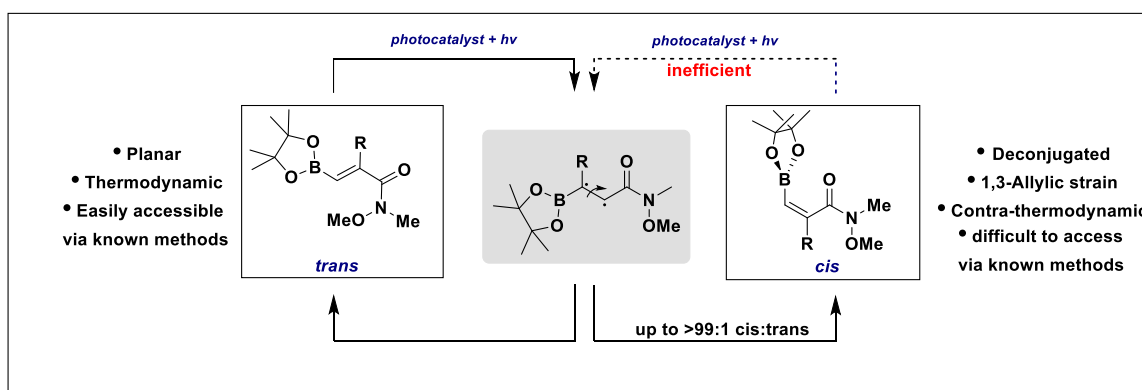
## "Boron-enabled geometric isomerization of alkenes via selective energy-transfer catalysis"

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Synthetic methods that enable the stereocontrolled assembly of complex polyenes remain undoubtedly a significantly underdeveloped challenge. Herein we report a general approach to control the stereochemistry of ambiphilic C<sub>3</sub>-linchpins via light induced energy transfer catalysis. This operationally simple protocol is applied to a wide variety of boron-substituted acrylates in up to >99:1 cis:trans selectivity and 99% yield with wide functional group tolerance.



**Figure 1:** Conceptual framework for the geometric isomerization of alkenes via selective energy-transfer catalysis.

Various mechanistic studies indicate that the proposed triplet energy transfer is the predominant mechanism. X-Ray analysis of the products as well as <sup>11</sup>B-NMR studies prove a boron-oxygen interaction is key for the origin of the observed selectivity. The synthetic utility of this strategy was demonstrated in various stereospecific reactions of the products, while both isomers were also applied as building blocks in the synthesis of two complex polyenes.

### References:

M. Schäfer<sup>†</sup>, J.J. Molloy<sup>\*†</sup>, M. Wienhold, T. Morack, C.G. Daniliuc, R. Gilmour<sup>\*</sup>, *Science* **2020**, 369, 302-306. <sup>†</sup>Contributed equally

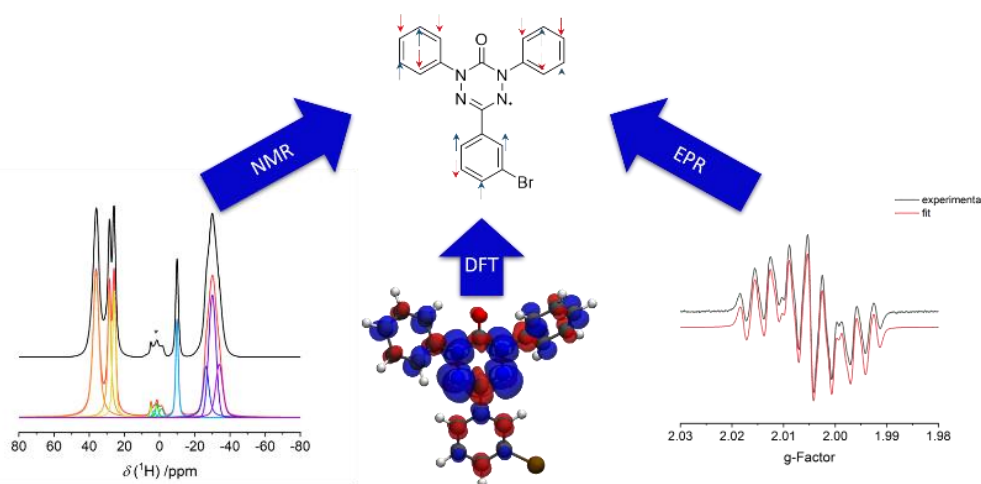
## EPR and solid-state NMR Spectroscopy and its Application on Mono and Diradicals

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Methods for the detection and structure characterization of radicals are important in organic chemistry, polymer chemistry, biology or medicine. But in the most cases it is not possible with standard methods like liquid-state NMR because of linebroadening effects of the unpaired electron. Electron paramagnetic resonance (EPR)-Spectroscopy is a very fast spectroscopic method to characterise the structure, symmetry and dynamic of organic radicals in solid and liquid-state. Furthermore, solid-state MAS NMR is a useful method to analyse the structure of organic radicals especially with high rotation frequencies. But a combination of EPR, solid-state NMR spectroscopy and DFT calculations of the spin density is the best opportunity to characterize the structure of radicals.



**Figure 1:** (left)  $^1\text{H}$  solid-state NMR spectrum at 62.5 kHz rotation frequency, (center) spin density calculation via DFT and (right) liquid-state EPR spectrum in toluene at room temperature of a 1,5-Diphenyl-6-oxo verdazyl radical.

This presentation will shortly introduce into EPR spectroscopy before discussing the application of EPR and solid-state NMR on different mono- and diradical like verdazyl or benzotriazinyl radicals in detail. 1,5-Diphenyl-6-oxo verdazyls are persistent radicals which have a broad range of application possibilities for example as building blocks for magnetic materials, spin labelling, spin trapping or redox flow batteries. In comparison benzo[1,2,4]triazinyl radicals be used as metal ligands or as mediators in stable free radical polymerization. <sup>[1,2]</sup>

### References:

- [1] J. Exner, I. Maisuls, A. Massolle, S. Klabunde, M. R. Hansen, C. A. Strassert, J. Neugebauer, H. Eckert, A. Studer, *Phys. Chem. Chem. Phys.* **2021**, 23, 2999–3007.
- [2] S. Eusterwiemann, C. Doerenkamp, T. Dresselhaus, O. Janka, M. De Oliveira, C. G. Daniliuc, H. Eckert, J. Neugebauer, R. Pöttgen, A. Studer, *Phys. Chem. Chem. Phys.* **2017**, 19, 15681–15685.

## C6: Self-assembled monolayers (SAMs) on zinc oxide surfaces: A DFT study

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In recent decades, a great deal of scientific research has been dedicated to the study of surfaces, and techniques to modify them with an increasing degree of control. One such approach is the synthesis of self-assembled monolayers (SAMs) on surfaces. Functionalized surfaces have a broad range of applications such as molecular electronics, bio-sensing and heterogeneous catalysis, only to name a few. In this work, we focus on zinc oxide surfaces. A high carrier mobility, wide band gap and certain other properties make zinc oxide a suitable candidate for use in photo- and optoelectronics [1]. Furthermore, high thermal and chemical stability aid zinc oxide to be an interesting choice in molecular heterogeneous catalysis [1]. In this work, we use density functional theory to investigate functionalized zinc oxide surfaces from several aspects, including the crystallographic plane, SAM head group, SAM coverage, and hydroxylation degree of the surface. Here, we consider SAMs of three methylene groups (CH<sub>2</sub>) in the chain with an azide functional group. We will rely on energetics of different systems to compare the interactions of SAMs with the zinc oxide surfaces, which we expect to be greatly impacted by the type of the head group of the SAMs. We will also provide details on the specific interaction sites of the head group with the surfaces. To approach a more realistic system, we will conduct studies on hydroxylated surfaces, taking the pH and the isoelectric point of ZnO into account.

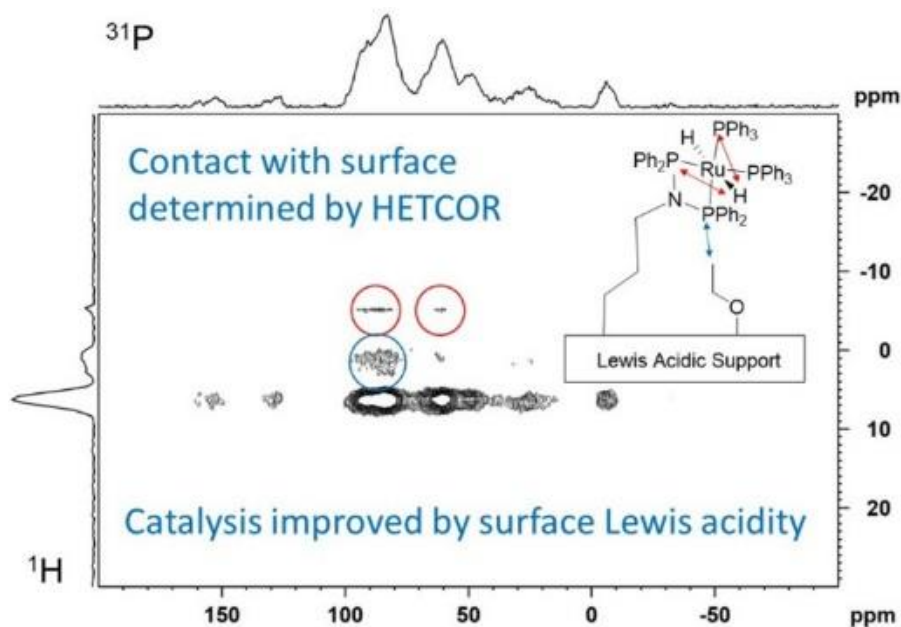
[1] P. Atanasova et al., *RSC Adv.* **2021**, 11, 5466-5478

## C7: Probing the Interactions of Immobilized Ruthenium Dihydride Complexes with Metal Oxide Surfaces by MAS NMR: Effects on CO<sub>2</sub> Hydrogenation

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Homogeneous catalysts immobilized on metal oxides often have different catalytic properties than in homogeneous solution. This can be either activating or deactivating and is often attributed to interactions of catalyst species with the metal oxide surface. However, few studies have ever demonstrated the effect that close associations of active sites with surfaces have on the catalytic activity. In this paper, we immobilize H<sub>2</sub>Ru(PPh<sub>3</sub>)<sub>2</sub>(PPh<sub>2</sub>)<sub>2</sub>N-C<sub>3</sub>H<sub>6</sub>-Si(OEt)<sub>3</sub> (**3**) on SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and ZnO and interrogate the relationship to the surface using IR, MAS NMR, <sup>1</sup>H-<sup>31</sup>P HETCOR, and XAS spectroscopies. We found that, while there are close contacts between the P atoms of the complex and all three metal oxide surfaces, the Ru-H bond only reacts with oxygen bridges on SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> forming new Ru-O bonds. In contrast, complex **3** stays intact on ZnO. Comparison of the catalytic activities of our immobilized species for CO<sub>2</sub> hydrogenation to ethyl formate showed that Lewis acidic metal oxides activate, rather than deactivate, complex **3** in the order Al<sub>2</sub>O<sub>3</sub> > ZnO > SiO<sub>2</sub>. The Lewis acidic sites on the metal oxide surfaces most likely increase the productivity by increasing the rate of esterification of formate intermediates.



**Figure 1:** <sup>1</sup>H-<sup>31</sup>P HETCOR spectrum of **3**-ZnO showing cross peaks at (86, -5.1), (61, -5.1), and (86, 1.1) ppm. The first two are attributable to correlations between trans-RuH<sub>2</sub> and PPh<sub>2</sub> and PPh<sub>3</sub>, respectively. The latter is likely due to correlations between the PPh<sub>2</sub> groups and the CH<sub>3</sub> groups of immobilized EtO groups.

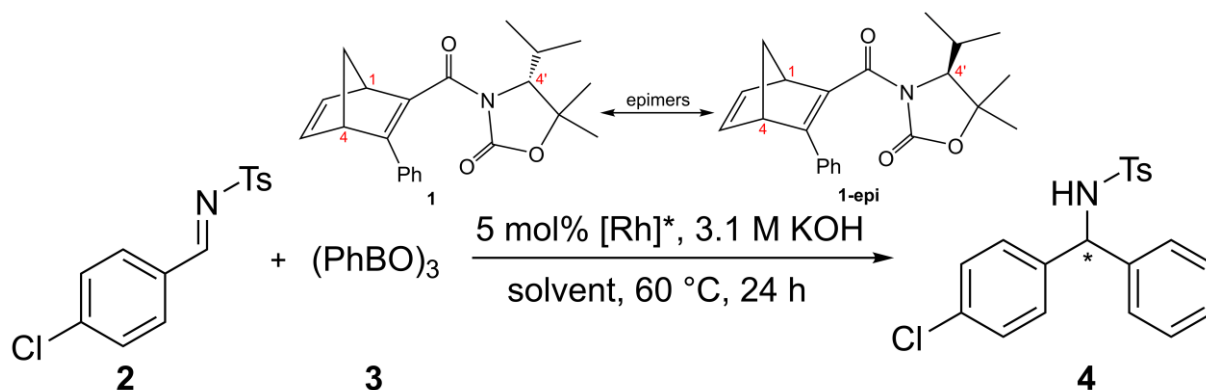
## C4: Simulation of the asymmetric Rh-catalyzed 1,2-addition reaction mechanisms and catalyst coordinations

Katrin Gugeler<sup>1</sup>, Johannes Kästner<sup>1</sup>

<sup>1</sup>Institute for Theoretical Chemistry, Universität Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany

Theoretical studies on the Rh-catalyzed asymmetric 1,2-addition of triphenylboroxine to *N*-tosylimine using newly synthesized ligands [1] were performed. Experimental studies using diastereomeric mixtures with different ratios of ligand **1** and its epimer **1-epi** revealed a non-linear like effect (NLLE). DFT calculations on the relevant transition states of both catalysts showed higher Gibbs energy barriers for the ligand **1-epi**, thus rationalizing the NLLE.

Furthermore, the coordination of various Rh-catalysts after immobilization on mesoporous SBA-15 was studied. It was found that for almost all different ligands the free coordination site at the Rh is blocked either via coordination by the triazol unit or by an oxygen atom of the ligand or via steric hindrance of a phenyl group. This results in monomeric catalysts that allow higher reactivity.



**Figure 1:** The 1,2-addition of triphenylboroxine to *N*-tosylimine.

[1] M. Kirchhof, K. Gugeler et al., *Organometallics* **2020**, 39, 17, 3131-3145

## TALK NOTES

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## TALK NOTES

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## TALK NOTES

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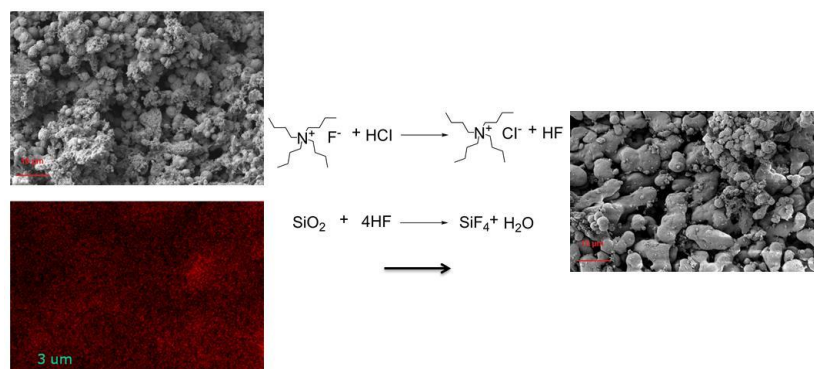
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## A1: Monolithic polymeric supports with uniform diameter pores for continuous catalytic reactions

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University of Stuttgart, Institute of Polymer Chemistry, Stuttgart, Germany



**Figure 1:** Synthesis of mesoporous ROMP-derived, poly(norborn-2-ene)-based monolithic supports with defined, unimodal mesoporosity in the range of 1-10 nm with flow-through pores in the micrometer range.

In the area of molecular heterogeneous catalysis, catalysts must be located at the surface of the structure-forming microglobules to be accessible for reactants. Given the dimensions of typical organometallic catalysts (ca. 1.5 nm), the choice of a mesoporous material (< 50 nm) raises the possibility that selective binding of a catalyst inside the mesopores of the support material provides sufficient levels of confinement to generate confined conditions during the continuous catalytic reactions. [1-2] The synthesis of a monolithic support is conveniently accomplished by solvent-induced phase separation (SIPS), which follows the Flory–Huggins theory. [3-4] Within the confines of choice in a one-step procedure, the use of appropriate amounts of monomer(s), crosslinker(s) and porogenic solvents offers access to design the polymeric monolithic support with defined, unimodal mesoporosity in the range of 1-10 nm with the flow-through porosity in the micrometer range that allows for fast mass transfer. The living nature of the ROMP-based polymerization allows for the synthesis of well-defined monoliths which are easily post-functionalized. [5] In course of our activities in the area of molecular heterogeneous catalysis in confined geometries, ROMP-derived, poly(norborn-2-ene)-based monolithic supports with tailored mesoporosity that fulfill the general requirements for polymeric monoliths such as dimensional stability, unitary structure, incompressibility, tailored mesoporosity, transport pores in the micrometer range, high linear flow (> 2 mm/s) at low back pressure (< 2 bar) have successfully been prepared under solvent-induced phase separation conditions. Currently, we pursue a systematic study of the influence of size and properties of tailored inorganic nanowires (SiO<sub>2</sub> (d x l : 10 nm x 200 nm)) used in a hard templating process on the size, size distribution, and morphology of the pores in the formed monoliths. Applications in catalysis under confined geometries will be outlined.

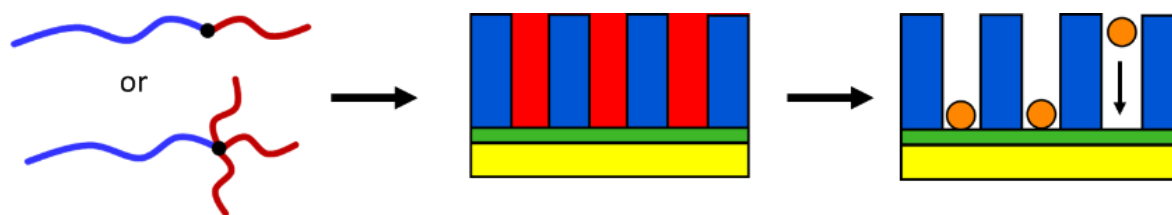
- [1] G. Y. Yang, N. Tsubaki, et al., *J. Am. Chem. Soc.* **2010**, 132, 8129-8136.
- [2] J. Yuan, A. M. Fracaroli, W. G. Klemperer, *Organometallics*. **2016**, 35, 2149–2155.
- [3] P. J. Flory, *J. Chem. Phys.* **1942**, 10, 51-61.
- [4] P. J. Flory, *J. Chem. Phys.* **1949**, 17, 223-240.
- [5] S. Lubbad, M. R. Buchmeiser, *Macromol. Rapid Commun.* **2003**, 24, 580-584.

## A2: Tunable Block Copolymer Templates for Spatially Controlled Immobilization of Redox Probes

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Polystyrene-*block*-polylactide PS-*b*-(PLA)<sub>3</sub> miktoarm block copolymers are synthesized using living anionic polymerization. Self-assembly controlled via solvent vapour annealing (SVA) followed by soft etching of the minority polylactide component leads to mesoporous templates. To achieve smaller features and lower domain spacing of the blockcopolymer morphology while still remaining in the strong-segregation regime, branched miktoarm architectures are explored. Additionally, pore bottom functionalization in porous PS-*b*-PLA templates through Click-chemistry of redox probes are investigated. The same SVA method is used for templating of the substrate. Characterization techniques such as PM-IRRAS, XPS, SEM, and CV are used to analyze efficiently of clicking of molecules at the pore bottom. [2]



**Figure 1:** Schematic of the two types of block copolymers for cylindrical porous templates for pore functionalization.

- [1] L. Stein, P. Dreier, T. Widder, K. Dirnberger, H. Frey, S. Ludwigs, *in preparation* (2021)
- [2] J. Kuhlmann, S.S.Y. Liu, A. Yazdan, M. Fyta, S. Ludwigs, *in preparation* (2021)



### A3: Interlayer Interactions as Design Tool for Large-Pore COFs

Sebastian T. Emmerling,<sup>a,b</sup> Robin Schuldt,<sup>c</sup> Sebastian Bette,<sup>a,d</sup> Liang Yao,<sup>a</sup> Robert Dinnebier,<sup>a</sup> Johannes Kästner,<sup>c</sup> and Bettina V. Lotsch<sup>a,b,e</sup>

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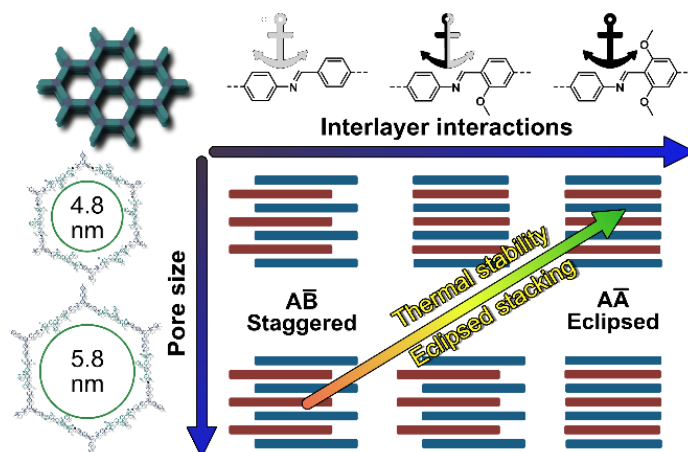
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Covalent organic frameworks (COFs) have emerged as a new class of molecularly precise, porous functional materials characterized by broad structural and chemical versatility, with a diverse range of applications.<sup>[1]</sup> However, COFs with a pore size beyond 5 nm are still rarely seen.<sup>[2]</sup> An elaborated synthesis of soluble large linkers as obvious complication and more subtle challenges, including pore occlusion and collapse, prevail as unique problems compared to COFs with smaller pores.<sup>[3]</sup> Here we present two, isoreticular series of large-pore imine COFs with pore sizes up to 5.8 nm and correlate the interlayer interactions, adjusted by methoxy groups acting as pore-directing “anchors”,<sup>[4]</sup> with the structure and thermal behavior of the COFs. A strong correlation between stacking energy towards highly ordered, nearly-eclipsed structures, higher structural integrity during thermal stress, and a novel, thermally induced phase transition of stacking modes in COFs was found. Our results shed light on viable design strategies for increased structural control and stability in large-pore COFs.



**Figure 1:** Correlations between interlayer interactions, pore sizes, stacking modes and thermal stability of large-pore COFs.

[1] M. S. Lohse, T. Bein, Adv. Funct. Mater. **2018**, 28, 1705553.

[2] C. Zhao, H. Lyu, et al., J. Am. Chem. Soc. **2020**, 142, 14450–14454.

[3] H. Deng, S. Grunder, K. E. Cordova, C. Valente, H. Furukawa, M. Hmadeh, F. Gándara, A. C. Whalley, Z. Liu, S. Asahina, H. Kazumori, M. O’Keeffe, O. Terasaki, J. F. Stoddart, O. M. Yaghi, Science **2012**, 336, 1018–1023.

[4] H. Xu, J. Gao, D. Jiang, Nat. Chem. **2015**, 7, 905–912.

### A3: Transformation of Imine- into Amide-linked Covalent Organic Frameworks *via* Post-Synthetic Oxidation in Flow

Lars Grunenberg,<sup>1,2</sup> Maxwell W. Terban,<sup>1</sup> Gökçen Savasci,<sup>1,2</sup> Robert E. Dinnebier,<sup>1</sup> Christian Ochsenfeld,<sup>1,2</sup> and Bettina V. Lotsch<sup>1,2,\*</sup>

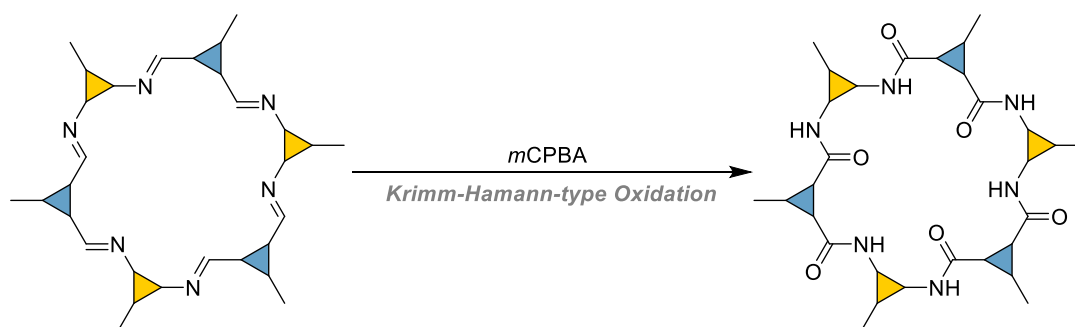
<sup>1</sup>Max Planck Institute for Solid State Research, 70569 Stuttgart

<sup>2</sup>Department of Chemistry, Ludwig-Maximilians-Universität München, 81377 München

In recent years, covalent organic frameworks have emerged as a modern and versatile class of materials for heterogeneous catalysis. Their ordered and tunable pore structures with high surface area and ability to absorb visible light offer great opportunities for gas storage, sensing, and heterogeneous photocatalysis.<sup>[1]</sup>

An important class of these materials are imine-linked covalent organic frameworks. Whereas during synthesis, the reversible formation of the imine bonds is crucial to obtain a well-defined crystalline material *via* dynamic covalent chemistry, the limited stability against hydrolysis also restrains their use for certain applications in catalysis.<sup>[2]</sup>

To address this disadvantage, we present a convenient post-synthetic locking strategy for imine-linked covalent organic frameworks based on a topochemical oxidation with *m*CPBA.<sup>[3]</sup> This protocol maintains both crystalline and porous features of the framework and allows to obtain new amide-linked frameworks in an atom-economic fashion applicable to batch and continuous flow processes.



**Figure 1:** Postsynthetic Oxidation of Imine-linked COFs with *m*CPBA.

[1] F. Haase, B. V. Lotsch, *Chem. Soc. Rev.* **2020**, 49, 8469-8500.

[2] L. Grunenberg, G. Savasci, et al., *J. Am. Chem. Soc.* **2021**, 143, 3430-3438.

[3] H. Krimm, K. Hamann, Patent DE952895C, **1956**.

## A4: Influence of the Template Removal Method on the Mechanical Stability of SBA-15

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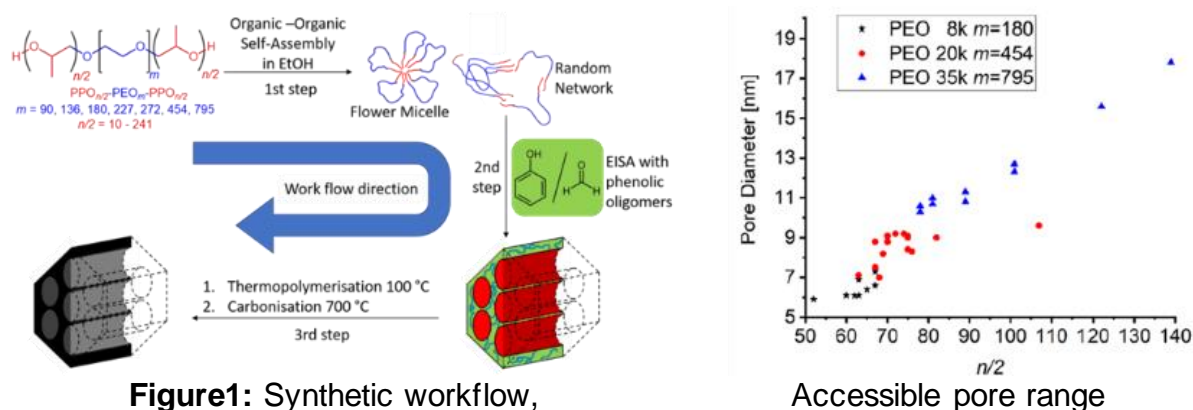
A necessary step in the synthesis of mesoporous silica materials is to remove the template from the pores after the polycondensation of the silica precursor. This guarantees the accessibility of the pores. We studied the influence of different template removal methods on the mechanical stability of SBA-15, especially the presence or absence of oxygen during the removal. Therefore, we compared the mechanical stability of SBA-15, which pores were opened either by calcination in air or by Soxhlet extraction with ethanol in combination with a thermal treatment in nitrogen. The template removal methods are described in the literature.<sup>[1]</sup> The investigations regarding the influence of the template removal method on the mechanical stability of the SBA-15 show that it is not necessary to calcine the material to obtain mesoporous silica materials, which are stable up to a pressure of 39 MPa.

## A6: Ordered Mesoporous Carbons with Continuously Tunable Pore Diameters

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“Reverse Pluronic”-type polyethers ( $\text{PPO}_{n/2}\text{-PEO}_m\text{-PPO}_{n/2}$ ) with tailored block lengths are prepared via dual-catalytic approach and deliver highly defined ( $\text{PDI} = 1.01 - 1.08$ ), high- $M_n$  (up > 50.000 g/mol) polymers. These polymers are then employed as structure-directing agents (SDAs) for generation of ordered mesoporous carbons (OMCs) via a soft-templating strategy. Hereby, a sequence of evaporation/thermally induced self-assembly, thermopolymerization (cross-linking at 100 °C) and carbonization (700 °C) delivers well-defined OMC with monomodal and narrowly distributed pore diameters in a 2D hexagonal arrangement ( $p6mm$ ). In a detailed study, > 100 different polymer SDAs were employed to prepare the corresponding OMCs. As evidenced by nitrogen sorption, SAXS-analysis, Raman-spectroscopy and EDX-mapping, perfectly uniform materials were received, only differing in mesopore diameters. The latter was successfully tuned by adaption of block lengths in the SDA, enabling access to large pore diameters in a range of 6-18 nm in a practically continuous manner (see figure).



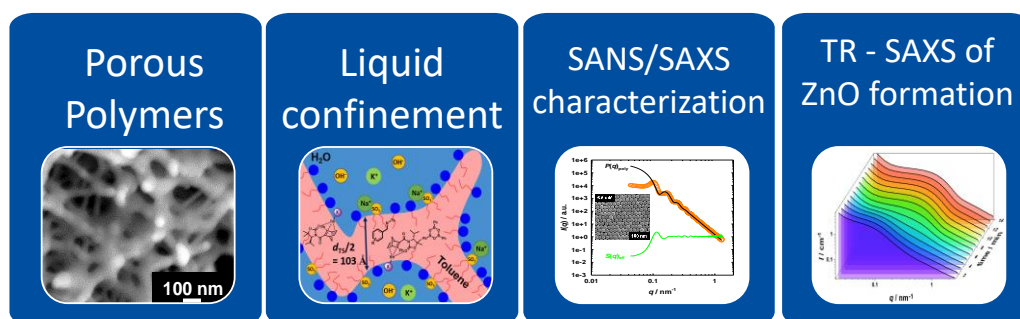
- [1] F. Markus, J. R. Bruckner, *Macromol. Chem. Phys* **2020** 1900437  
 [2] F. Markus, C. Vogler, *ACS Appl. Nano Mat.* **2021**, 4, 3486

## A7: Nanoporous Host Materials with adjustable Pore Size, Geometry and Distribution

Karina Abitaev<sup>1</sup>, Adbulwahab Abouhaileh<sup>1</sup>, Lennart Nebel<sup>1</sup>, Yassen Qawasmi<sup>1</sup>, Thomas Sottmann<sup>1</sup>

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The aim of this project is to provide mesoporous support materials for catalysis by using colloidal crystal templates of polymer nanoparticles with adjustable size and polydispersity. These templates are then transferred into either porous polymers or ZnO inverse opals (**A5**). The porous materials and the formation of ZnO during the mineralization process are studied by scattering techniques, like dynamic light scattering and small angle neutron (SANS) or X-Ray (SAXS) scattering – also time-resolved (TR). In an alternative approach mesoscopic liquid confinement for Rh-catalyzed 1,2 additions (**B3**) is provided by an amphiphilic film of non-ionic (/ionic) surfactants in a bicontinuous structured microemulsion.



**Figure 1:** Scope of project A7. Porous polymers or liquid confinement are provided and characterized by SANS or SAXS as well as the time-resolved formation of ZnO nanoparticles.

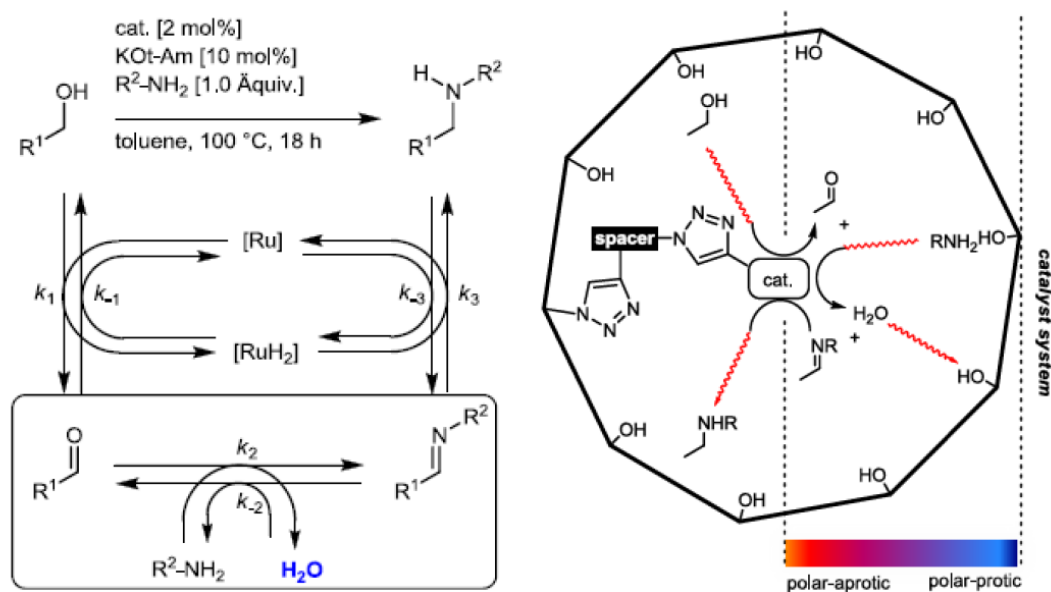
- [1] Abitaev, K., Qawasmi, Y., Atanasova, P., Dargel C., Bill J., Hellweg T., Sottmann T., *Colloid Polym Sci* **2021**, 299, 243
- [2] Kirchhof M., Abitaev K., Abouhaileh A., Gugeler K., Frey W., Zens A., Kästner J., Sottmann T., Laschat S., *submitted*

## B1: Immobilized Ru(NNNN)-Complex for the Directed H<sub>2</sub>-Autotransfer Catalysis

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<sup>1</sup>Institute of Organic Chemistry, Technical University of Dresden

The Plietker Group is focusing on the hydrogen-autotransfer catalysis with our Ru(NNNN)-complex<sup>[1]</sup>. The complex is immobilized via click-chemistry on mesoporous azide-SBA-15 material.<sup>[2]</sup> By de-functionalization of the outer surface of the material the exclusive immobilization of the complex to the inner pore surface can be ensured. Kinetic investigations of the isolated condensation process led to the assumption, this step might be the most problematic one. Therefore, the first tries to use the immobilized complex have been done for the reduction process and showed similar yields to the homogeneous reduction, whereby the polarity of the inner surface is playing a main role. After the reduction process the oxidation and finally the cascade reaction will be tested. In the next step, the insertion of the spacer molecule leads to a modification of the distance between complex and pore wall. This helps to understand the influence of the pore wall. Because of a possible stacking of the complex onto the pore wall the material head-group will be changed for implementing more rigidity into the whole material-spacer-complex-unit.



**Figure 1:** Reaction cascade of the H<sub>2</sub>-Autotransfer (left) and the scheme of the pore.

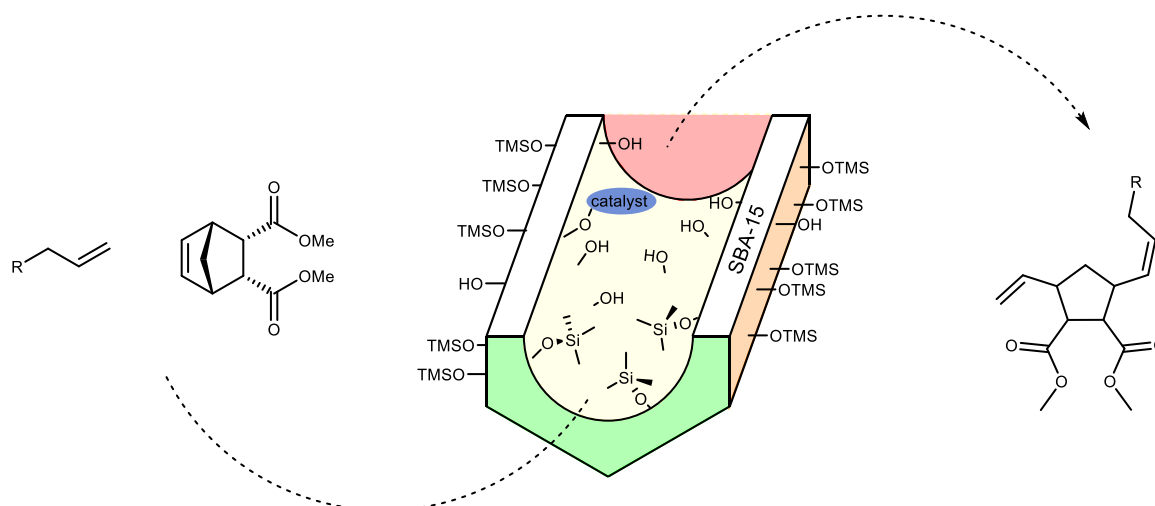
- [1] D. Weickmann, W. Frey, B. Plietker, *Chem. Eur. J.* **2013**, 19, 2741-2748;  
D. Weickmann, B. Plietker, *ChemCatChem* **2013**, 5, 2170-2173.  
[2] J. Nakazawa, B. J. Smith, T. Daniel P. Stack, *JACS* **2012**, 134, 5, 2750-2759

## B2: Metathesis in Confined Spaces: Investigation of E/Z selectivity

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We have recently demonstrated success in the selective macro(mono)cyclization of dienes via ring closing metathesis (RCM) by utilizing catalysts confined inside the pores of mesoporous silica.<sup>1</sup> Over the course of these studies, we noted a small but significant change in the E/Z selectivity of the RCM reaction under confinement. Based on these results, we decided to examine other metathesis reactions under confinement, particularly focusing on E/Z selectivity. Therefore, we proceeded to investigate the ring-opening cross metathesis (ROCM) of a norbornene derivative with a variety of olefin cross partners, a reaction we have previously reported under homogeneous conditions.<sup>2</sup> We were very pleased to observe a change in the E/Z selectivity of the ROCM reaction under confinement with most of the investigated cross partners, with smaller pore sizes showing larger effects.



**Figure 1:** Ring-opening cross metathesis under confinement.

[1] F. Ziegler et al. *J. Am. Chem. Soc.* **2019**, *141*, 19014–19022.

[2] M. Momin, G. M. Nagy, M. R. Buchmeiser, *Adv. Synth. Catal.* **2019**, *361*, 5596–5604.



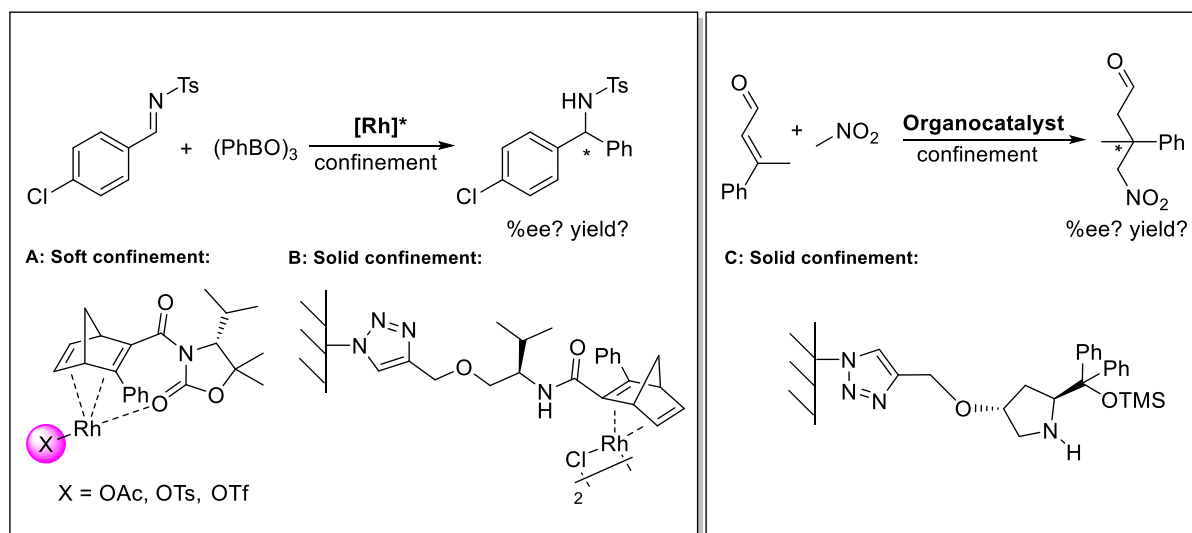
### B3: Immobilization of Diene-Rhodium-Catalysts and Organocatalysts on Mesoporous Supports

Zarfishan Dilruba, Manuel Kirchhof

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In the last two decades diene ligands have been used as chiral ligands for various Rh-catalyzed reactions such as 1,2-additions, isomerizations, cyclizations and others. Recently we developed unsymmetric norbornadienes for such purposes and applied them in the Rhodium-catalyzed 1,2- and 1,4-addition. With regards to the project of our CRC microemulsions were tested as nanostructured solvents to further understand soft confinement and its effect on enantioselectivity in the 1,2-addition (Figure 1, A).<sup>[1]</sup> Furthermore, alkyne-functionalized norbornadienes have been immobilized on SBA-15 with different pore sizes through the click reaction to investigate the 1,2-addition in solid confinement (Figure 1, B).<sup>[2]</sup>

Another important field where confinement might be beneficial is organocatalysis. In the recent past, the usefulness of proline-based Hayashi-Jørgensen organocatalysts for the asymmetric synthesis of pharmaceutical intermediates, biologically active compounds and natural products has been demonstrated. Usually, high catalyst loadings are required to achieve high yields, therefore immobilization of the catalyst onto SBA-15 would result in a useful pathway for the recycling of the precious catalyst. In order to understand confinement effects on organocatalysis and to tackle the formation of quaternary stereogenic centers, the asymmetric Michael addition of Michael donors such as nitroalkanes with enals will be probed (Figure 1, C). Our future aim is to combine Rhodium-catalysis and organocatalysis to enable tandem reactions in confinement and create multiple stereocentres in cascade reactions.



**Figure 1:** Rhodium- and organocatalysis in confined systems.

[1] M. Deimling, M. Kirchhof et al., *Chem Eur. J.* **2019**, 25, 9464–9476.

[2] A.-K. Beurer, M. Kirchhof et al., *ChemCatChem* **2021**, 13, 2407–2419.



## C1: Quantitative distinction between noble metals located in mesopores from those on the external surface

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<sup>1</sup>*Institute for Chemical Technology*

Phosphines ( $^{31}\text{P}\text{R}_3$ ) with different groups R (phenyl, 4-methoxyphenyl, 4-phenoxyphenyl), are demonstrated to be useful molecular probes for quantitatively characterizing the spatial distribution of noble metal (NM) atoms on mesoporous support materials, such as silica A200, mesoporous SBA-15 and MCM-41. We compare three methods for quantitatively distinguishing the location of noble metals (NM) in mesopores from those found on the external particle surface. MCM-41 and SBA-15 with NM either preferentially located in mesopores or on the external surface were prepared and characterized by TEM. We quantified arylphosphines forming complexes with NM by  $^{31}\text{P}$  MAS NMR spectroscopy. Phosphine/NM ratios drop from 2.0 to 0.2 when increasing the probe diameter from 1.08 to 1.54 nm. Confinement of NM within 3 nm wide MCM-41 mesopores slows down the complexation with  $\text{PPh}_3$  over weeks, whereas on the external surface the complexation is instantly accomplished in similar phosphine/NM ratio. A promising method was filling the pores using the pore volume impregnation technique with tetraethylorthosilicate (TEOS). TPP loading revealed that 66% of NM were located on the external surface of MCM-41. The pore filling method can be used in association with any probe molecule, also for the quantification of acid sites.

[1] Rieg, C., Dittmann, D., Li, Z., Lawitzki, R., Gugeler, K., Maier, S., Schmitz, G., Kästner, J., Estes, D..P. and Dyballa, M. (2021), Chem. Eur. J.. Accepted Author Manuscript.

## C1: Diffusion in different porous silica materials

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Molecular diffusion in pores is a crucial process for heterogeneous catalysis, which affect the final reactivity and selectivity of a catalyst. Herein the influence of confined geometry on molecular diffusion was observed by a non-invasive method, pulse-field gradient (PFG) NMR, with two non-polar molecules.<sup>[1]</sup> Silica surface slow down molecule diffusion and diffusion coefficients of surface diffusion is 85% of the free diffusion. Pressing can introduce visible mesopore/macropores but does not change the diffusion property in small crystal. Crystal size influences the diffusion inside the pores, D3 value, due to the mixing possibility between in-pore and out-of-pore diffusion: Slow molecule shows a slower D3 in small crystal compared with large crystal; Fast molecule shows faster D3 in small crystal comparing with large crystal. Diffusion of n-Hexadecane in mesoporous materials has no diffusion barrier.

[1] Kärger, J., Diffusion Measurements by NMR Techniques. In Adsorption and Diffusion, Karge, H. G.; Weitkamp, J., Eds. Springer Berlin Heidelberg: Berlin, Heidelberg, 2008; pp 85-133.

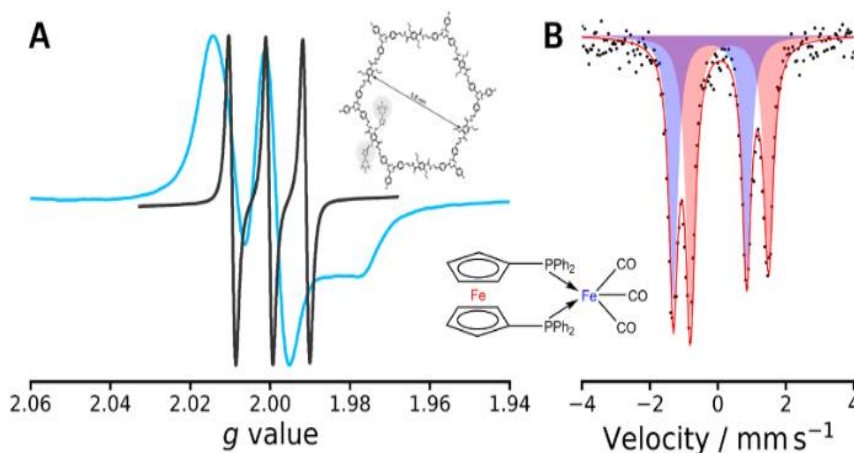
## C2: The electronic and geometric structure of catalysts in mesopores

M. Winkler<sup>1</sup>, M. Schnierle<sup>2</sup>, M. Ringenberg<sup>2</sup>, J. van Slageren<sup>1</sup>

<sup>1</sup>*Institute of Physical Chemistry, University of Stuttgart,*

<sup>2</sup>*Institute of Inorganic Chemistry, University of Stuttgart*

To understand the behavior of a catalyst in a pore, one must be able to probe the chemical properties of the compound inside and outside of the pore. This is why the (dppf)Fe(CO)<sub>3</sub> catalyst was chosen as the system of interest as it is highly functionalizable at the ferrocene moiety<sup>[1]</sup> and it allows several spectroscopic techniques in its oxidized, paramagnetic form, such as EPR spectroscopy, SQUID magnetometry, MCD spectroscopy, DFT calculations and Mößbauer spectroscopy, as we have shown in detail successfully<sup>[2]</sup>. As the chosen system shows an interesting, non-trivial behavior even without the incorporation into a pore, we chose to also investigate the behavior of a much simpler, well-known open-shell system, the organic radical TEMPO. Due to its recognizable EPR signal, it allows for more distinct approaches to the elucidation of the changes of the electronic and geometric structure of a catalyst/radical in a mesoporous system. We have successfully immobilised the species in COFs and SBA-15 and plan to determine the distance distribution of the spins/catalysts by double electron electron resonance (DEER) but the fast spin relaxation due to exchange interaction with remaining Cu-catalyst from the click reaction prevents us from doing so at the moment. We have since switched to a Ru-based catalyst.



**Figure 1:** (A) cw X-Band EPR of the immobilised and free TEMPO radical and (B) Mößbauer spectrum of the probe molecule (dppf)Fe(CO)<sub>3</sub>.

[1] M. Ringenberg et al., *Inorg. Chem.* **2017**, 56, 7501–7511

[2] M. Winkler et al., *Inorg. Chem.* **2021**, 60, 2856–2865

## C2: Three ways to bind metal complexes onto a surface/inside pores

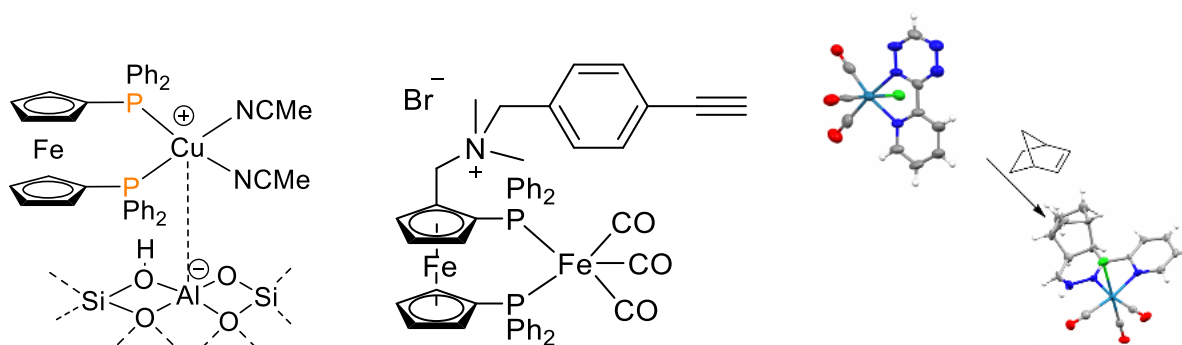
Marc Schnierle<sup>1</sup>, M. Winkler<sup>2</sup>, J. van Slageren<sup>2</sup>, M. Ringenberg<sup>1</sup>

<sup>1</sup>*Institut für Anorganische Chemie, Universität Stuttgart*

<sup>2</sup>*Institut für Physikalische Chemie, Universität Stuttgart*

Binding metal complexes onto a surface or inside of pores opens up new opportunities since both the reactivity as well as the stereoselectivity are influenced by the immobilisation, as was shown by Mr. Ziegler who is also part of the CRC1333.<sup>[1]</sup>

In this work, we focused on how to link the complexes to the material. To do so, we used the ionic interaction of Al-SBA-15 with a positively charged Cu(II) complex. We also functionalized a previously studied iron complex<sup>[2]</sup> with an alkyne group to make it ready for the well established Huisgen cycloaddition. In the last part, we focused on the novel [4+2] cycloaddition of tetrazines with dienes.<sup>[3,4]</sup>



**Figure 1:** Left: Interaction of a Cu(II) complex with Al-SBA-15. Middle: Alkyne-functionalized iron complex. Right: [4+2] cycloaddition of a tetrazine-based Re-complex.

- [1] F. Ziegler et al., *J. Am. Chem. Soc.* **2019**, *141*, 48, 19014-19022.
- [2] M. Winkler et al., *Inorg. Chem.* **2021**, *60*, 2856–2865.
- [3] M. Schnierle et al., *Chem. Commun.*, **2020**, 56, 12033–12036.
- [4] M. Schnierle, et al., *Inorg. Chem.* **2021**, *60*, 9, 6367–6374.

### C3: Atom Probe Study of 1-octadecanethiol self-assembled Monolayers on Platinum

Helena Solodenko<sup>1</sup>, Patrick Stender<sup>1</sup>, Guido Schmitz<sup>1</sup>

*<sup>1</sup>Institute for Materials Science, Chair for Materials Physics, University of Stuttgart, Heisenbergstr. 3, 70569 Stuttgart, Germany*

Atom probe tomography is a well-established characterization technique for metals, semiconductors, oxides, and minerals. However, measurement of organic matter and biological materials is still a challenging task. Field evaporation of organic species leads to detection of molecular fragments of C<sub>x</sub>H<sub>y</sub> groups instead of single atoms, as it is the case for metals [1,2]. The fragmentation of the molecules possibly depends on the applied electric field strength. By variation of the field strength, we expect to learn more about the field evaporation process and thus about the binding energies of self-assembled Monolayers (SAMs).

In this poster we present measurements of 1-octadecanethiol SAMs on platinum substrates by laser-assisted APT. The carbon backbone evaporates in the form of small hydrocarbon fragments consisting of one to four carbon atoms, while sulfur evaporates exclusively as single ions. With increasing laser power, a weak, but noticeable trend towards larger fragment sizes is observed. No hydrocarbon fragments containing S are detected, indicating that a strong S-Pt bond has formed. The observed surface coverage of S fits well with literature values and is higher for (111) oriented samples than for (200) [3].

- [1] Schwarz T.M. et al, Sci Rep **2020**, 10, 20271.
- [2] Meng K. et al, Microsc. Microanal **2021**. (accepted)
- [3] Solodenko H. et al, Microsc. Microanal **2021**. (submitted)

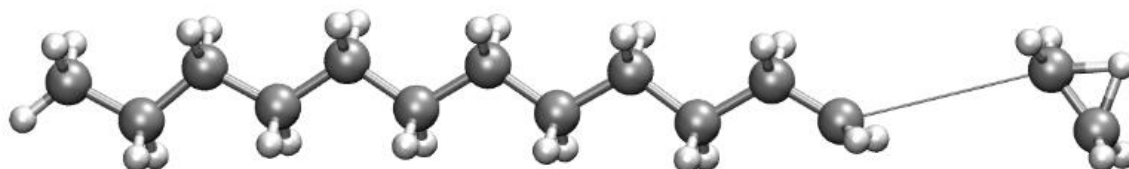
## C4: Field Evaporation of Organic Molecules

Carolin Ai'Lan Dietrich<sup>1</sup>, Johannes Kästner<sup>1</sup>

<sup>1</sup>*Institute for theoretical Chemistry, University of Stuttgart*

Atom Probe Tomography (APT) is a well-established measurement technique for investigating metallic probe samples with up to atomic resolution. The Schmitz Group (Project C3) is taking APT to the next level, by expanding its applicability to frozen liquids [1] and organic molecules [2].

The underlying mechanism of APT is field evaporation. While metals mostly evaporate as single atoms, molecular field evaporation is more complex. Therefore, the interpretation of the experimental data and the understanding of the evaporation processes are aided by simulations. In this case, the fragmentation of tetradecane ions is studied theoretically using DFT. Thanks to new developments, the fragmentation of ions can now be studied in the gas phase including external fields. The influence of the external electric field on the barriers for breaking bonds along the carbon backbone of the molecule and the charge distribution within the molecule were thoroughly investigated showing how the field can increase and decrease the barriers of different bonds.



**Figure 1:** Barrierless fragmentation of the Tetradecane ion ( $C_{14}H_{30}^+$ ) at field strengths between 9 and 10 V/nm.

[1] T. M. Schwarz, E. M. Weikum, et al., Sci Rep 10, 20271 (2020).

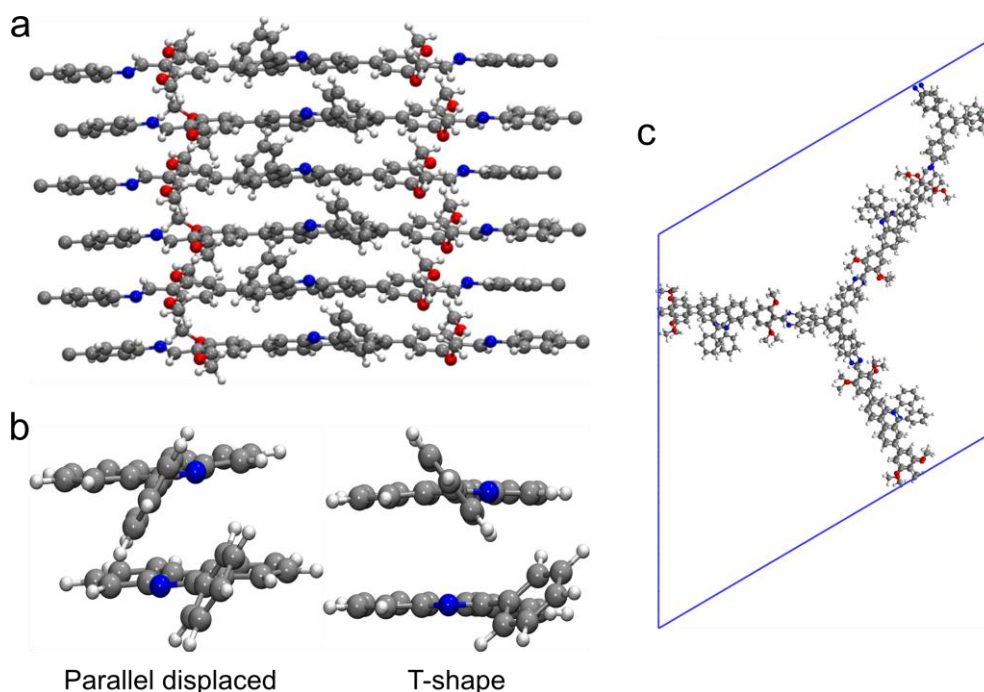
[2] C. Dietrich, R. Schuldt, et al., J. Phys. Chem. A 2020, 124, 41, 8633–8642

## C4: Theoretical Studies for Covalent Organic Frameworks

Robin Schuldt<sup>1</sup>, Johannes Kästner<sup>1</sup>

<sup>1</sup>*Institute for theoretical Chemistry, University of Stuttgart*

Covalent organic frameworks (COFs) are an emerging class of crystalline polymers which are used to construct porous structures, by stacking of several COF layers. We observed that inter-layer interaction and stacking behavior are mainly determined by non-covalent interactions. Stacked layers are shifted against each other to maximize favorable interactions. For a series of large pore COFs synthesized within project A3, structural parameters were calculated, an example unit-cell is shown in Figure 1c. Due to its non-planarity, an analysis of the COFs building blocks was conducted. It was found that favorable interactions are dependent on the spatial requirements of the phenyl linker groups. Combined with possible orientations of imines, interacting linkers with alternatingly stacked imines as shown in Figure 1a were identified as most stable. Adding methoxy groups to the imine sites lowers the overall energy difference between parallel and alternating arrangements [1]. For a smaller COF of the same series DFT calculations indicate, that the T-shape is strongly favored when using fluorinated linkers. Initial structure, cell parameters and partial charges were calculated for various planar COFs. Currently they are used to investigate gas adsorption, framework polarization as well as diffusion (cooperation with C5).



**Figure 1:** (a) Exemplary periodic combinations of blocks modeling a multilayer dPP-TAB COF pore wall. (b) Parallel-displaced and T-shape stacking arrangement of phenylphenanthridine units. (c) Final unit cell of dPP-TAB after geometry optimization.

[1] Emmerling, Sebastian; Schuldt, Robin; Bette, Sebastian; Yao, Liang; Kästner, Johannes; Lotsch, Bettina "Interlayer Interactions as Design Tool for Large-Pore COFs" submitted to *J. Am. Chem. Soc.* (2021)

## C5: Computer simulation of adsorption in covalent organic frameworks

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*Institute of Thermodynamics and Thermal Process Engineering (ITT)*

Molecular simulations on an atomistic level of resolution lead to a fundamental understanding of adsorption in porous media. As input a structure of the solid and a force field which models the fluid-fluid and the fluid-adsorbent interactions are needed.

Covalent organic frameworks (COFs) represent an emerging class of nanoporous crystalline materials, which are assembled from organic reactants via covalent bonds. Depending on the structures of building units, COFs can be formed into those with either two- (2D) or three-dimensional (3D) structures. Numerous applications such as gas storage, heterogeneous catalysis or separation are envisioned. Similar to other nanoporous materials such as zeolites or metal organic frameworks, thousands of hypothetical COF structures are possible. However, the structural order achieved in the synthesis of COFs is often not at all ideal. Therefore, molecular simulations conducted in idealized model structures provide only limited insight into real structure effects that matter in practical applications of these materials.

In the present work, Monte Carlo simulations are employed to study the effect of interlayer slipping on the adsorption behavior. Moreover, the effect of framework polarization upon adsorption is investigated to shed light on structure-property relations of these materials.



## **S2: Free energy considerations in confined heterocatalysis in a supported ionic liquid phase**

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<sup>1</sup>*Institute for Computational Physics, University of Stuttgart*

<sup>2</sup>*Institute of Thermodynamics and Thermal Process Engineering, University of Stuttgart*

<sup>3</sup>*Institute of Polymer Chemistry, University of Stuttgart*

The high potential of performing heterocatalysis in a confined mesoporous media within a supported ionic liquid phase (SILP) is studied using all-atom Molecular Dynamics (MD) simulations. Specifically, we investigate the possibility of immobilizing catalytic molecules in confined media in a biphasic solution consisting of an ionic liquid (IL) and heptane as second phase. The confined medium is made of a pore with a lateral size of about 5 nm. Divalent cationic Ru-alkylidene N-heterocyclic carbene catalysts are placed in the solution. We were able to monitor the immobilization of the catalysts within the IL opening up the route for achieving higher turnover rates in the respective catalytic reactions. We further analyze the accumulation and diffusion of all molecular species within the pore environment, the influence of steric and IL-specific effects, the structuring of a varying solvent environment, and their synergistic interactions with the catalytic molecules. The calculation of the free energies involved in the process reveals that the catalytic reaction between reactants and catalysts must occur at the interface between the diffusive heptane and the IL, while the IL is preferentially layered close to the pore wall controlling the biphasic interface. Our investigations are supported by experimental evidence and provide a deeper understanding on the inherent details that control a rational design of a linker-free catalyst immobilization in nanometer-sized templates for catalytic applications.

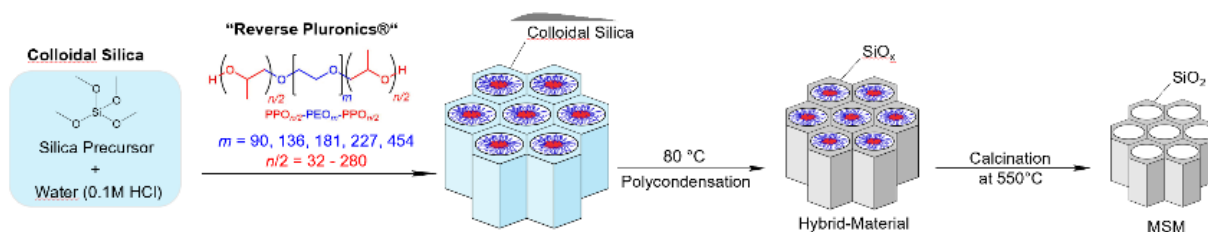
### S3: Highly Defined Mesoporous Silica Materials *via* True Liquid Crystal Templating

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The synthesis of *Reverse Pluronics* ( $\text{PPO}_{n/2}\text{-PEO}_m\text{-PPO}_{n/2}$ ) *via* novel, cooperative dual-catalysis approach delivers under controlled manners ( $\text{PDI} < 1.07$ ) high  $M_n$  polymers (up  $> 50.000$  g/mol) in a workup-free process. [1]

Their complex physical behavior in a binary polymer/water system makes them to an ideal template for synthesis of mesoporous materials. At a defined water concentration and a good hydrophilic/lipophilic balance (HLB), the formation of a hexagonal liquid crystal phase which is formed by a regular array of rod-shaped micelles whereby their long axes are aligned along a common direction could be observed. A hybrid structure could be generated by polycondensation of an added silica precursor (dissolved in the aqueous phase) around the block copolymer (surfactant) during a hydrothermal treatment ( $80^\circ\text{C}$ ). Subsequent calcination ( $550^\circ\text{C}$  with an air flow of  $150\text{L/h}$ ) removes the template and delivers a mesoporous silica material (MSM) with controlled porosity and pore diameter distribution. [2]



**Figure 1:** True Liquid Crystal Templating approach.

[1] C. Vogler, S. Naumann, RSC Adv. **2020**, 10, 43389-43393

[2] T. Feng, X Bu, Langmuir **2000**, 16, 5304-531

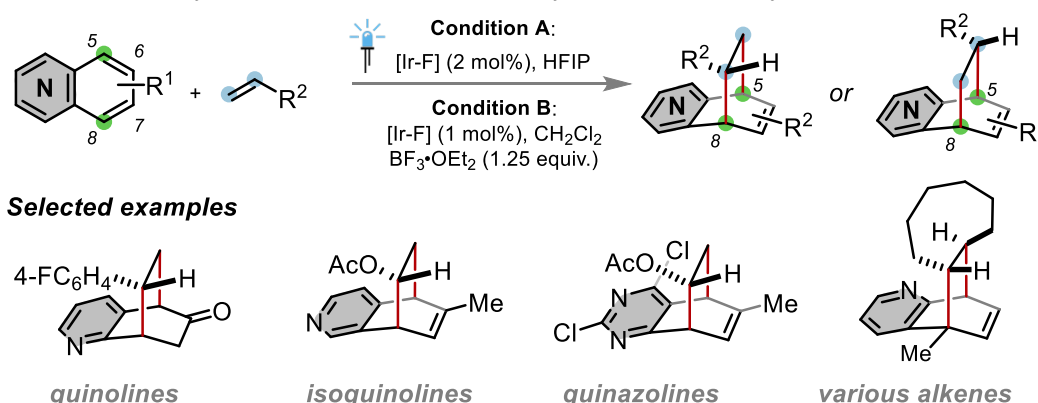
# Photochemical intermolecular dearomative cycloaddition of bicyclic azaarenes with alkenes

J. Ma<sup>†</sup>, S. Chen<sup>†</sup>, P. Bellotti<sup>†</sup>, R. Guo, F. Schäfer, A. Heusler, X. Zhang, C. Daniliuc, M. K. Brown\*, K. N. Houk\*, F. Glorius\*

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bellotti@uni-muenster.de

Dearomative cycloaddition reactions<sup>[1]</sup> offer an ideal mean of converting two-dimensional arenes into three dimensional scaffolds, which are of paramount interest in medicinal chemistry.<sup>[2]</sup> Despite containing latent diene and alkene fragments, quinolines, isoquinolines and quinazolines are rarely applied in cycloaddition reactions, due to their intrinsic low reactivity of aromatic systems and selectivity challenges.<sup>[3,4]</sup> We developed an energy-transfer catalyzed, regio- and diastereoselective intermolecular [4+2] dearomative cycloaddition reaction between bicyclic azaarenes with an array of electronically-diverse alkenes.<sup>[5]</sup>



**Figure 1:** Dearomative cycloaddition of azaarenes with alkenes via energy transfer, with selected examples.

By means of triplet energy transfer, a formally endoergonic and kinetically unfavourable process could be promoted under mild conditions, offering high levels of selectivity and general applicability.<sup>[6]</sup> Divergent regioselectivity – depending upon the azaarene substitution – and good to excellent *endo* diastereoselectivity were obtained upon either Brønsted or Lewis acid catalysis. The protocol proved amenable to substituted quinolines, isoquinolines and quinazolines, employing mono- and disubstituted alkenes and was applied towards the streamlined synthesis of a medically relevant compound. Furthermore, in-dept DFT calculations revealed the delicate balance between transition state polarity and dipole moment, as well as SOMO/C–H interactions, which decided the observed regio- and stereoselectivity.

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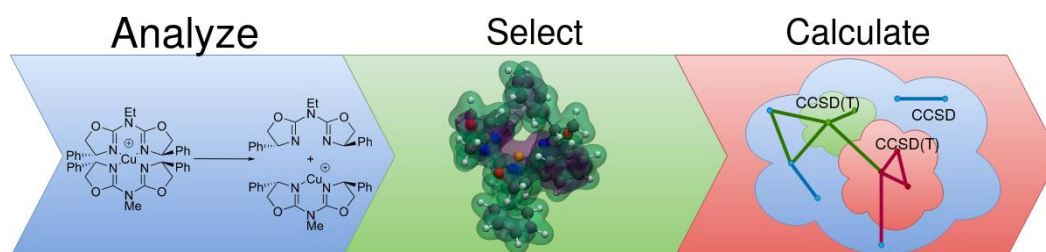
## Direct Orbital Selection within the Domain-based Local Pair Natural Orbital Coupled-Cluster Method

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Domain-based local pair natural orbital coupled cluster<sup>1,2</sup>(DLPNO-CC) has become increasingly popular for the calculation of reaction energies and barriers. It can be applied within in a multi-level DLPNO-CC-in-DLPNO-CC ansatz to reduce the computational cost and focus the available computational resources on a specific subset of the occupied orbitals.<sup>3</sup>



**Figure 1:** Illustration of the automatic DLPNO-CC multi-level approach. The occupied orbitals of reactants and products are analyzed automatically and partitioned into subsystems. The resulting orbital sets are then described at different accuracies to achieve a suitable accuracy—efficiency trade-off.

We demonstrate how this multi-level DLPNO-CC ansatz can be combined with the direct orbital selection<sup>4,5</sup> (DOS) approach to automatically select orbital sets for any multi-level calculation. We find that the parameters for the DOS procedures can be chosen conservatively such that they do not need adjustment between reactions. The resulting automatic multi-level DLPNO-CC method requires no user input and is extremely robust and accurate. The computational cost is reduced significantly without sacrificing accuracy.

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# Efficient Carrier Injection for Organic Field Effect Transistors using Fluorinated *N*-Heterocyclic Carbene Modified Electrodes

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<sup>§</sup> These authors contributed equally to this work.

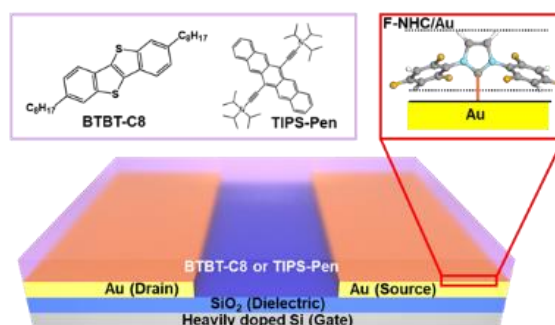
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Efficient carrier injection, defined as the transport of electrons and holes from the electrodes into active layers, is crucial for high performance organic electronics. Here we introduce a highly thermally stable, self-assembled monolayer of fluorinated *N*-heterocyclic-carbene (F-NHC) on gold electrodes. In comparison to devices without F-NHC modification, transistors with F-NHC modified gold electrodes show a significant improvement in carrier mobility owing to the low contact resistance achieved. Density Functional Theory calculations show that the introduction of fluorine atoms into the NHC leads to a reduction of charge transfer to the surface and therefore to an increase in the work function which lowers the injection barrier from electrode to semiconducting layer.<sup>1-3</sup>



**Figure 1:** Schematic diagram of the BC-OFET with F-NHC-modified Au electrodes.

The mobility of BTBT-C8 and TIPS-Pen transistors with F-NHC modified gold electrodes reached to the improvement of 33 and 9 times respectively in comparison to devices without F-NHC modifications, due to the decrease of the total device resistance by 92% and 79% for BTBT-C8 and TIPS-Pen OFETs. To our knowledge this report is the first example of a fluorine-substituted carbene molecule used as an electrode modifier in OFETs, which will lay the foundation for future applications of carbenes in organic electronics.

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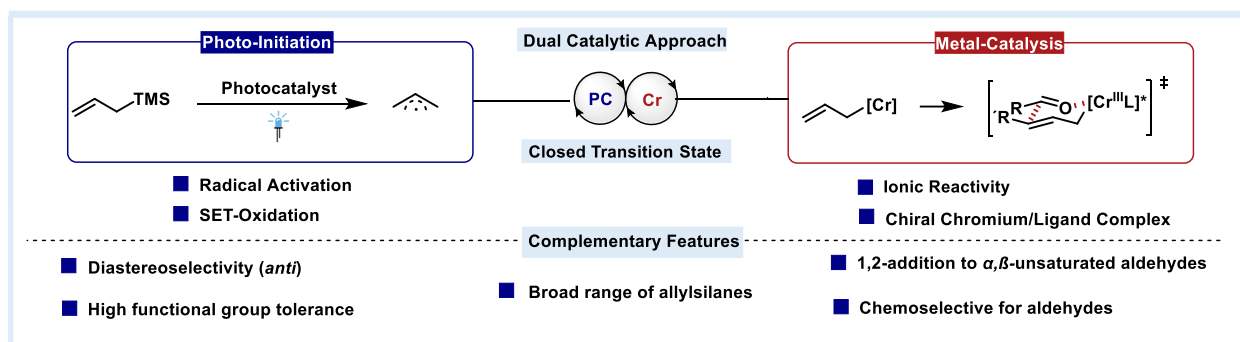
## Asymmetric Cr/photoredox dual catalytic coupling of aldehydes and allylsilanes – Complementing the Hosomi-Sakurai reaction in scope and selectivity

Subhabrata Dutta<sup>§</sup>, Felix Schäfers<sup>§</sup>, Roman Kleinmans and Frank Glorius<sup>\*</sup>

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The allylation of aldehydes is one of the most fundamental transformations in synthetic organic chemistry. Amongst the variety of available reagents, allylsilanes have been established as a preferred allyl source as reported by Hosomi and Sakurai, who found that these highly stable reagents readily add to carbonyls after Lewis acid activation.<sup>1</sup> The reported nucleophilic key step was found to proceed *via* an open transition state. Herein we show that by switching to a photocatalytic-radical mode of activation followed by a closed transition-state (chromium catalysis), we are able to obtain homoallylic alcohols from allylsilanes in complementary scope and opposite chemo- and diastereoselectivity to previously known methods. In addition, this dual catalytic approach<sup>2-4</sup> *via* Zimmerman-Traxler transition state induced an excellent level of enantioselectivity. The high functional group tolerance was highlighted by a broad scope, including enantioenriched, boron-substituted homoallyl alcohols as a highlight.



**Figure 1:** Asymmetric Synthesis of Homoallylic alcohols *via* Cr-photoredox dual catalysis

Moreover, we applied our method as the asymmetric key step in the synthesis of a bioactive compound and in addition showed different product diversifications as well as the late-stage functionalization of steroid derivatives. Detailed mechanistic experiments hinted a photo-initiated chain mechanism being responsible for the unusual high reactivity.

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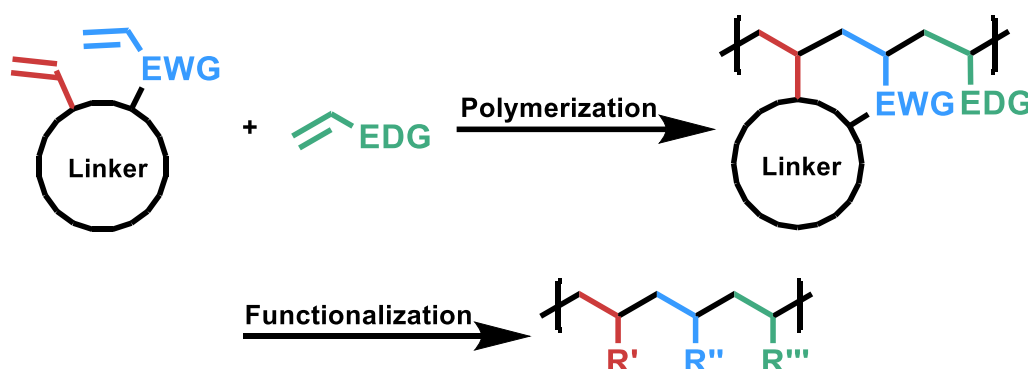
## Development of sequence-controlled Polymerization

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To this day, the control of monomer sequences remains one of the biggest difficulties of modern polymer chemistry. Although many viable methods for the multistep growth of polymer chains were introduced in the past years, they are often experimentally demanding, time consuming and yield mostly oligomers.<sup>1</sup> On the other hand polymers with simple sequences like an alternating structure can be easily prepared by radical polymerization, although it requires a special selection of monomers and only two monomers can be assembled in that way.<sup>2</sup>



**Figure 1:** Method for the synthesis and functionalization of alternating terpolymers.

With our novel divinyl monomer bearing a linker moiety we were able to prepare alternating terpolymers by utilizing this monomer in the reversible addition-fragmentation chain-transfer (RAFT) polymerization in combination with different vinyl ethers. Owing to the structure of the linker we are able to chemically modify these polymers by using different orthogonal polymer-analogous reactions. At first a thiol-ene click reaction followed by amidation of an active ester provided dual-functionalized polymers.<sup>3</sup> For the last modification either a transesterification or acylation was conducted.<sup>4</sup> With this method in hand the starting polymer was easily diversified and a small library of functionalized polymers was prepared, which were inaccessible with this sequence before.

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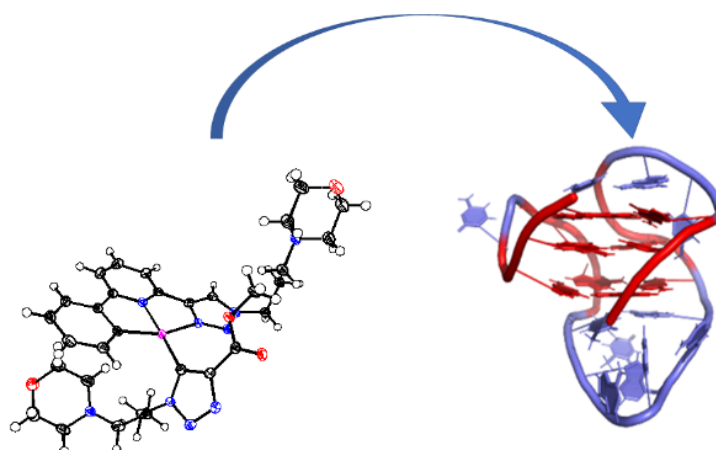
## Luminescent Pt(II) complexes for selective stabilisation of a tetra-stranded DNA structure

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Guanine quadruplexes (G4) represent tetra-stranded helical structures consisting of two or more stacked G-tetrads and exist in guanine-rich DNA sequences. These sequences are found near the promotor region of several oncogenes (*c-myc*, *c-kit*) and in telomeres. They are playing significant roles in the regulation of cell ageing and the transcription of genes. The interaction of small molecules with the G4-structures is important for the development of novel anti-cancer drugs.<sup>1</sup> The structural and electronic properties of planar metal complexes can be used to design new G4-binders. Different residues can bring further enhanced interactions through electrostatics or H-bonding with the phosphate backbone and nucleobases in the loops.<sup>2</sup>



**Figure 1:** Representation of platinum(II) complex designed to interact with quadruplex DNA (PDB ID: 148D).

Based on the work of Guha *et al.*, new luminescent platinum(II) complexes designed to interact with G4-DNA were synthesized and characterized.<sup>3</sup> The complexes are based on a functionalized tridentate N<sup>3</sup>C ligand. The variation of the ancillary ligand at the fourth coordination site of the platinum atom was used to introduce an additional hydrogen bond or electrostatic interactions.

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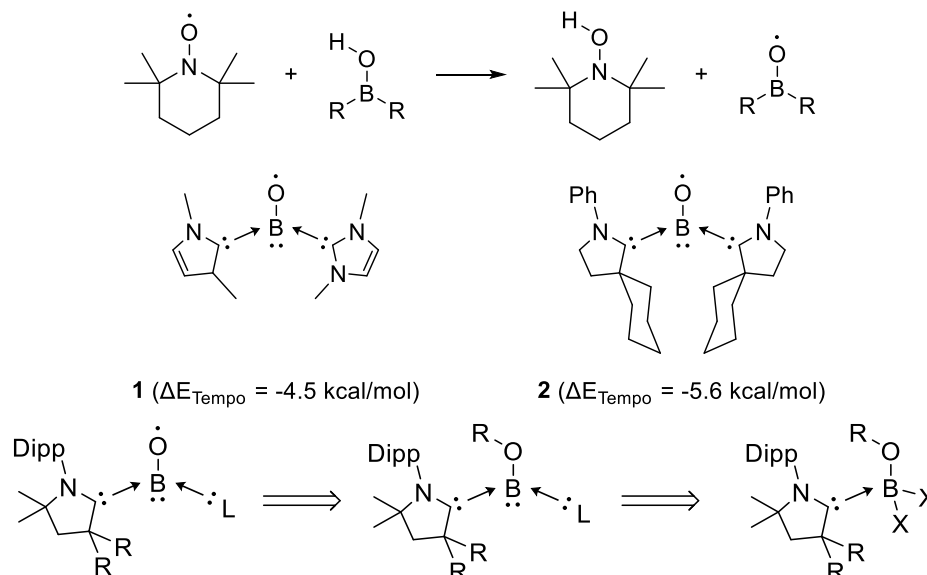


## Studies towards the Synthesis of a Bis(Lewis base)-Stabilized Boroxyl Radical

**Philipp Lenz, S. Klabunde, J. Tendyck, C. Mück-Lichtenfeld, C. G. Daniliuc, W. Uhl and A. Studer**

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**Figure 1:** Underlying Computational and Retrosynthetic Analysis of a Bis(Lewis base)-stabilized boroxyl radical.

Over the last century stable radicals have evolved from chemical curiosity to being of widespread utility in catalysis, spin labelling, materials and polymer synthesis.<sup>[1]</sup> While the variety of C-, S-, N-, O-, P-, and B-based stable radicals has been growing for decades,<sup>[1,2]</sup> the boroxyl radical, proposed over 50 years ago,<sup>[3]</sup> still remains undetected. Even though Chang et al. attributed a “stable” boroxyl radical a role as mediator in a living polymerization, literature still lacks evidence.<sup>[4]</sup>

To evaluate potential targets for a stable boroxyl radical their thermodynamic stability was assessed by DFT calculations<sup>[5]</sup> and the bis(Lewis base)-stabilized borylenes 1 and 2 showed promising thermodynamic properties (Figure 1).

Inspired by literature reports on chloroborylenes<sup>[6]</sup> the synthesis was envisioned from dihaloalkoxyboranes via coordination of CaaC and subsequent reduction to the corresponding oxygen-bearing borylene. Deprotection via oxidative as well as reductive pathways can be imagined (Figure 1).

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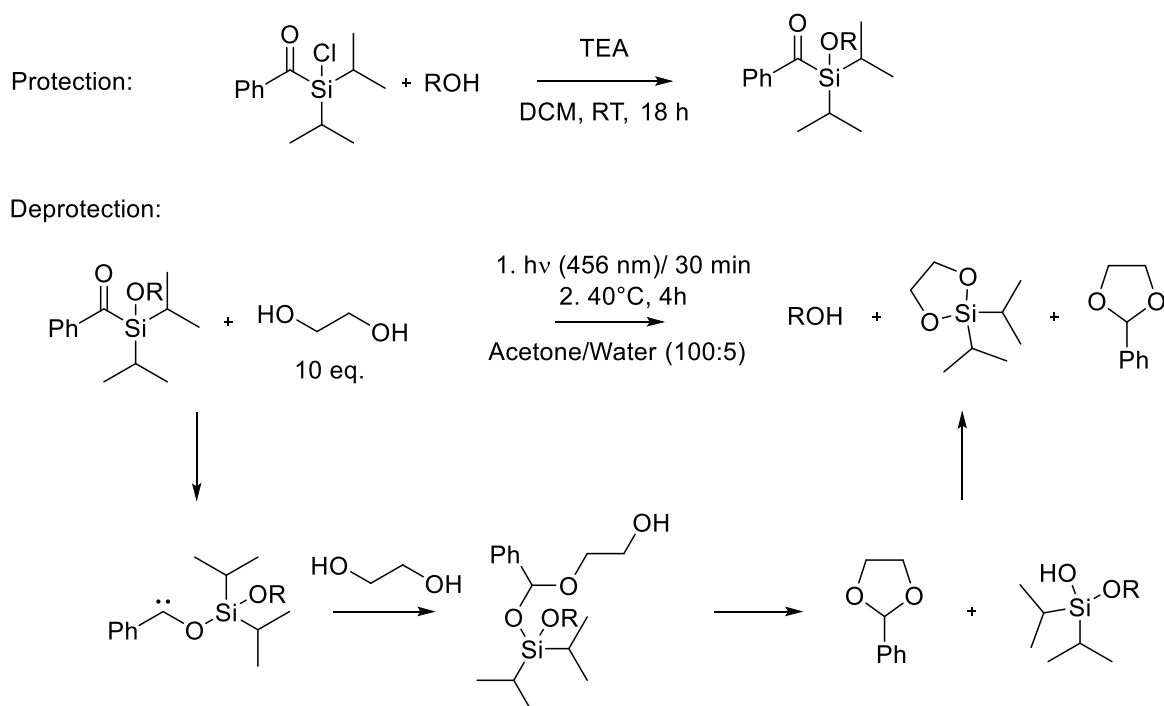
## A novel visible light photoactivatable protecting group based on acylsilanes

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The concept of a novel visible light photoactivatable protecting group for alcohols based on acylsilanes is presented. The protection occurs in a single step reaction by coupling of a primary or secondary alcohol with the acylsilylchloride protecting reagent. Deprotection occurs under mild conditions by irradiation with blue light (456 nm) and subsequent stirring at 40 °C using ethylene glycol as deprotecting reagent. Both, protection and deprotection proceed with very good to quantitative yield.



**Figure 1:** Protection and proposed deprotection mechanism

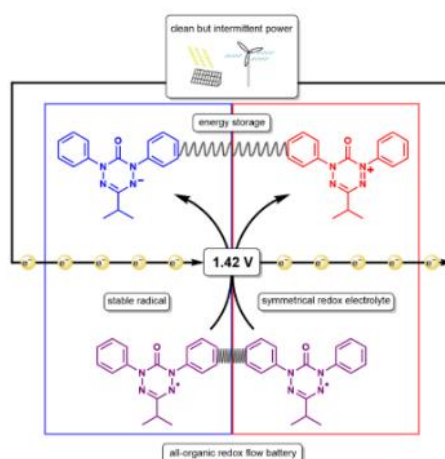
## Improving the properties of verdazyl radicals for organic redox flow batteries

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Redox flow batteries (RFBs) are an effective large-scale energy storage technology, offering an appealing solution to the problems of energy management in a grid fed increasingly by intermittent renewable sources. However, crossover of dissolved electrolytes between the two half-cells leads to self-discharge and irreversible capacity decay, which could be mitigated by the use of a single bipolar redox-active electrolyte.<sup>1</sup> Verdazyl radicals are highly stable organic radicals exhibiting reversible one-electron oxidation and reduction processes, and we recently demonstrated the promise of an all-organic oxoverdazyl-based symmetrical RFB.<sup>2</sup>



**Figure 1:** Schematic of the principle of the first-generation 1,5-diphenyl-3-isopropyl-6-oxoverdazyl RFB

The organic scaffold of verdazyl radicals presents the opportunity to vary the attached substituents and investigate structure-property relationships. We have adopted a joint synthetic-analytical-computational approach to rationally improve the electrochemical properties of new oxoverdazyls relative to our first-generation RFB, with particular focus on the cell potential ( $E_{\text{cell}} = E_{\text{ox}} - E_{\text{red}}$ ), key to overall energy density. By calculating the absolute redox potentials with DFT and comparing to experiment, clear trends are found in the effect of substituents on the redox potentials. Promising candidates, chosen based on either theoretical prediction or rational design principles, have been targeted for synthesis and characterized in order to evaluate the models. Assessment of the long-term stability and battery cycling performance of the verdazyls with the highest cell potentials is ongoing.

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## Fluorohydration of Alkynes via I(I)/I(III)-Catalysis

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Substrate specificity is highly present in biological catalysis, but less common in the domain of small molecule catalysis. Herein, we disclose an intriguing example of substrate specificity that was observed whilst exploring catalysis-based routes to generate  $\alpha$ -fluoroketones from terminal and internal alkynes under the auspices of I(I)/I(III) catalysis. Utilising *p*-Toll as an inexpensive organocatalyst with Selectfluor<sup>®</sup> as terminal oxidant and an amine:HF mixture as the fluoride source, the formation of protected  $\alpha$ -fluoroketones from simple alkynes was realised. Whilst the transient *p*-TollF<sub>2</sub> species generated *in situ* productively engaged with pentynyl benzoate scaffolds to generate the desired  $\alpha$ -fluoroketone motif, augmentation or contraction of the linker suppressed catalysis. The prerequisite for this sub-structure has been established by molecular editing and is complemented with a physical organic investigation of possible determinants.

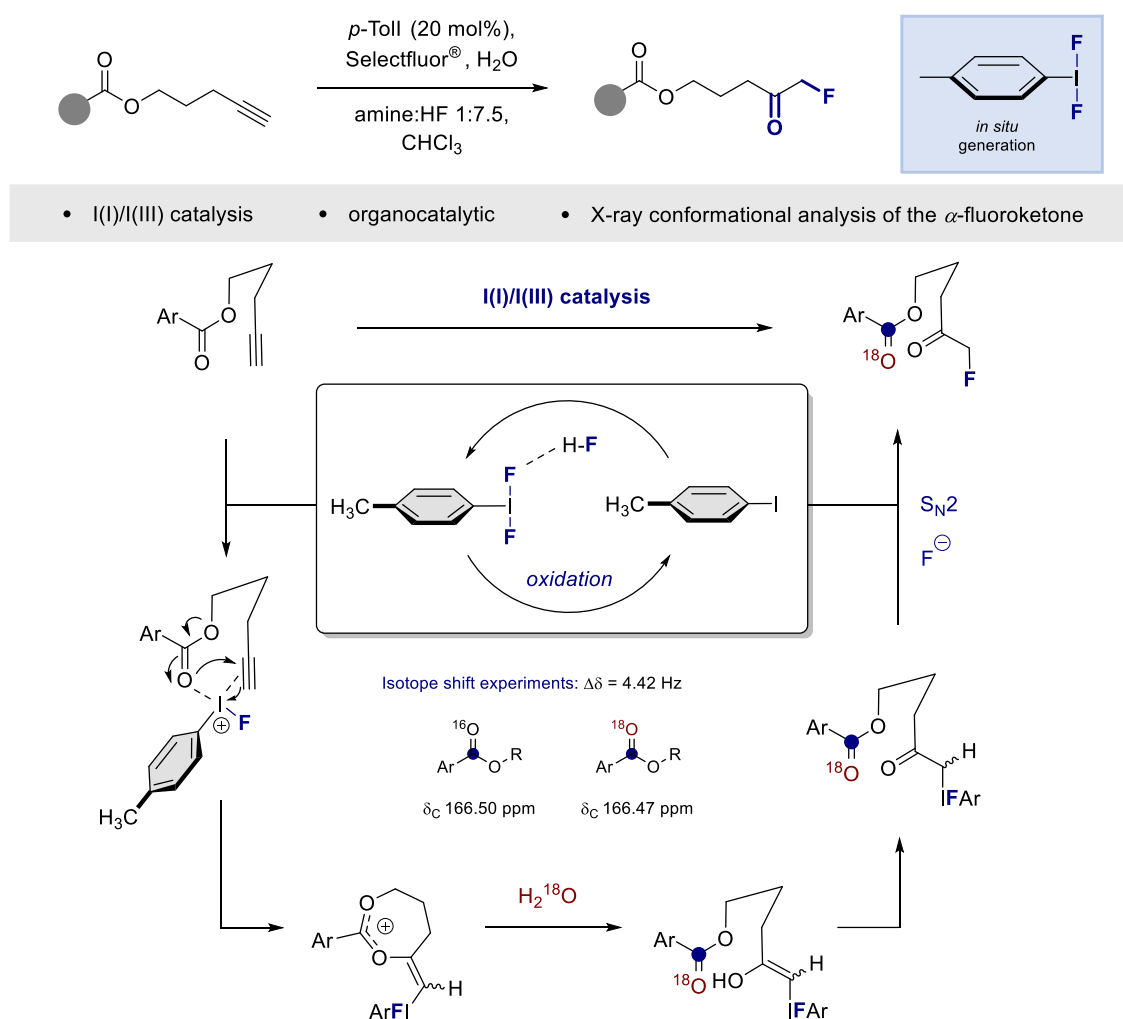


Figure 1: Fluorohydration of alkynes via I(I)/I(III) catalysis.

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J. Neufeld, C. G. Daniliuc, R. Gilmour, *Beilstein J. Org. Chem.* **2020**, *16*, 1627-1635.

## Azo bond formation on metal surfaces

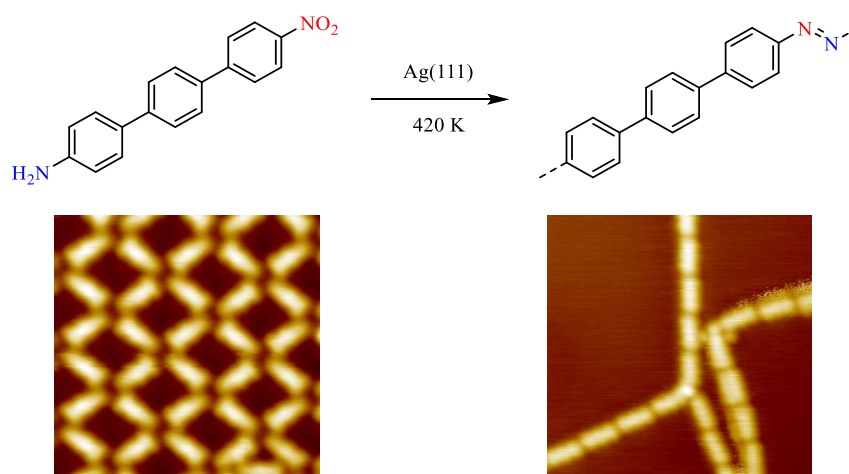
Dr. X. Meng, Dr. H. Klaasen, L. Viergutz, B. Schulze Lammers, M. C. Witteler, Dr. H. Mönig, Dr. S. Amirjalayer, L. Liu, Prof. J. Neugebauer, Dr. H.-Y. Gao, Prof. A. Studer, Prof. H. Fuchs

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On-Surface Chemistry has attracted extensive attention as a bottom-up strategy for the synthesis of two-dimensional materials with interesting properties and functions. Various organic reactions have been realized on metal surfaces.<sup>1-4</sup>

N-based functional groups such as azo groups show valuable properties in photo switching.<sup>5</sup> They are obtained through azo coupling using diazonium salts in solution phase chemistry, but the cross-coupling of nitro and amino compounds is still challenging. In on-surface chemistry, the redox cross-coupling of nitroarenes and arylamines was realized on a silver surface (Figure 1). In comparison with nitro-nitro and amino-amino homocoupling, this is the most efficient reaction on the surface.



**Figure 1:** Brutto reaction equation of the Redox Coupling of a bifunctional monomer to linear azo polymers and STM images of the nanostructures on Ag(111) before and after the reaction.

XPS measurements and theoretically and experimentally analyzed model compounds further support the correct structural assignment. It was found, that the metal type and the surface orientation have a significant influence on the reaction outcome. Based on DFT calculations a stepwise formation of partially oxidized/reduced precursors from the starting material along with N–N bond formation is suggested as the most likely reaction pathway.

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# Solid-state NMR on Frustrated Aluminum-Phosphorus Lewis Pairs

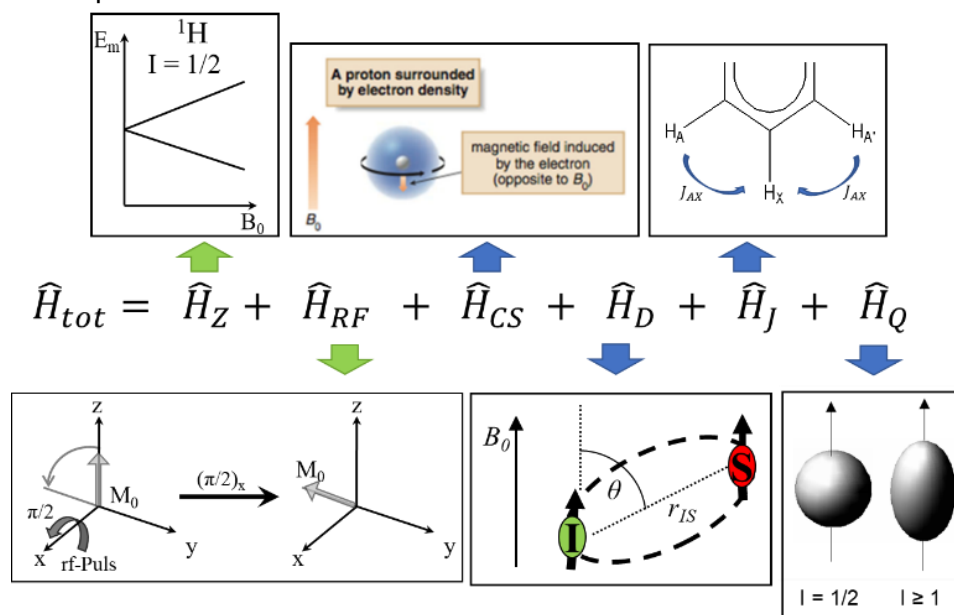
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Frustrated Lewis-pairs (FLPs) became in the last decades more important as metal-free reagents for adduct formation, catalytical or activation processes of small molecules. The structural investigation of such compounds is very interesting because of their high reactivity resulting from the frustration of the system.<sup>1,2</sup>

Solid-state NMR is a good tool for these analysis. With these technique it is possible to measure beside the external interaction many internal interaction which is quite challenging but we get many information about the electrical and nuclear environment of the investigated nucleus. Figure 1 shows the total Hamiltonian of an investigated nucleus which interacts with the external static field ( $\hat{H}_Z$ ), the electromagnetic radiofrequency pulse ( $\hat{H}_{RF}$ ), the surrounding electrodes ( $\hat{H}_{CS}$ ), the dipolar coupled nuclei through space ( $\hat{H}_D$ ) and via electrical bondings ( $\hat{H}_J$ ) and in case of quadrupolar nucleus also the interaction of the quadrupolar moment with the electric field gradient ( $\hat{H}_Q$ ). In liquid-state NMR many of the internal interactions average out because of the molecular motion. In solid-state NMR we use special technics to average the most interactions out and recouple only one of this interactions to see the influence of the individual interaction. On this poster I will show all these interaction that we can see on Aluminum-Phosphorus FLPs.<sup>3</sup>



**Figure 1:** Schematic illustration of all possible interactions in a solid-state NMR experiment. Green arrows marks the external and blue arrows the internal interactions.

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