Young Chemists Summit

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Book of Abstracts

YC summit

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Mechanophotonics: Flexible Single-Crystal Organic Waveguides and Circuits

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We present the one-dimensional optical-waveguiding crystal dithieno[3,2-a:2',3'-c]phenazine with a high aspect ratio, high mechanical flexibility, and selective self-absorbance of the blue part of its fluorescence (FL). While macrocrystals exhibit elasticity, microcrystals deposited at a glass surface behave more like plastic crystals due to significant surface adherence, making them suitable for constructing photonic circuits via micromechanical operation with an atomic-forcemicroscopy cantilever tip. The flexible crystalline waveguides[1] display optical-path-dependent FL signals at the output termini in both straight and bent configurations, making them appropriate for wavelength-division multiplexing technologies. A reconfigurable 2x2-directional coupler fabricated via micromanipulation by combining two arc-shaped crystals splits the optical signal via evanescent coupling and delivers the signals at two output terminals with different splitting ratios. The presented mechanical micromanipulation technique could also be effectively extended to other flexible crystals[2].

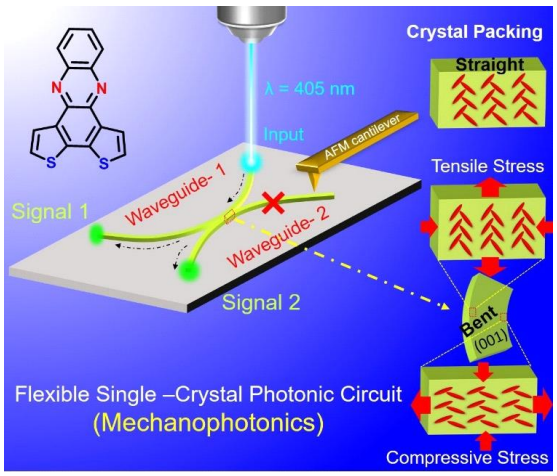

Figure: Cartoon representation of a 2x2-directional coupler constructed from two flexible organic crystals via mechanical micromanipulation with an AFM cantilever tip. The molecular movements in the (011) plane during bending are shown at the bottom right corner

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The MESI-STRAT consortium: exploring the crosstalk of metabolism and signaling for breast cancer patient stratification and targeted therapy design

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Breast cancer is a complex disease with high prevalence in Western countries. 80% of the patients suffer from estrogen receptor (ER)-positive tumours and are treated with endocrine therapies targeting the ER. As the ER is a signalling molecule, research and clinical trials on therapy resistance focus so far mainly on the crosstalk of the ER with other oncogenic signalling networks. As a result, compounds inhibiting signaling kinases are in clinical use and trials as second line therapies for ER-positive breast cancer. However, the success of these interventions remains limited as they are often not curative.

In contrast to kinase signalling, only little is known about the contribution of tumor metabolism to endocrine therapy resistance. Focusing on tryptophan and its metabolites, MESI-STRAT explores the interplay of amino acid metabolism with signaling networks to identify marker metabolites that predict relapse and guide targeted interventions at an early stage. Towards this goal, a pan-European team of oncologists, modelers, bioinformaticians and experimentalists develops new computational models in combination with network analyses and pharmacogenomics, to integrate multi-omics data and explore metabolic and signaling networks in breast cancer.

Deracemisation of Secondary Alcohols - a Phenomenon

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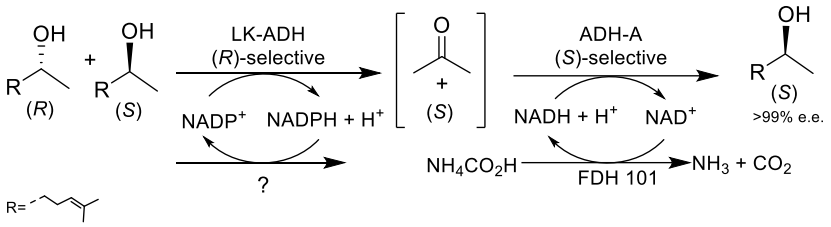
Enantiopurity is of high importance, especially when it comes to bioactive compounds or pharmaceuticals. To perform deracemisation and to obtain an enantiopure product three main different strategies can be applied nowadays. Kinetic resolution is limited to 50% theoretical yield, while dynamic kinetic resolution overcomes this issue and makes 100% theoretical yield feasible. Resolving a racemic mixture is based on the stereoinversion of one of the two enantiomers, while the other enantiomer stays untouched.[1,2] In this context, an oxidation-reduction sequence for the deracemisation of secondary alcohols was investigated.[3] More or less by serendipity it was found that deracemisation still occurred, even though NADPH oxidase responsible for the recycling of the cofactor was missing.



Scheme 1. Deracemisation system of secondary alcohols. The recycling of the NADPH cofactor is object to further research.

The deracemisation phenomenon was investigated using purified enzymes. After optimisation of the reaction conditions the corresponding (*S*)-alcohol product was obtained with an enantiomeric excess (e.e.) >99% starting from a racemic mixture. The FDH (formate dehydrogenase from *Pseudomonas* sp. 101) was suspected to recycle $NADP^+$ by reducing CO_2. Exploring the cofactor preferences of FDH in the oxidation as well as reduction mode showed that the enzyme indeed is capable to reduce CO_2 under certain conditions showing a preference for NADPH over NADH in der reduction mode. Following the enantiomeric excess over time revealed a lag-phase of around 40 h before the deracemisation is continued to further increase the optical purity of the corresponding product (*S*)-alcohol (e.e.s >99%). This peculiarity was explored in more details and presumably ascribed to the two components LK-ADH (alcohol dehydrogenase from *Lactobacillus kefir*) and NAD^+. In addition, oxygen as a third crucial part of the lag phase was identified. These components change within the lag phase, making the recycling of the NADPH cofactor possible. This phenomenon will be object to further research.

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Improvement of the biofuel production process through the reuse of wastewater and captured CO_2

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Without a doubt, renewable and sustainable energies are the challenge of the present and the bet of the future, especially for factories. But if we look at the energy resources studied currently, which cultivate microalgae for biofuels is still the leading, we meet many problems among them: a very high manufacturing cost which makes it difficult to market, the use of another source of energy with large quantity to run the system or compete food because it's generally installed on immense spaces... . This is why this presentation is come up with some solutions to those problems in a perspective of future factories.

This paper propose, an assimilation of a micro algae manufacturing process, where we will use a new design of the photo-bioreactor, based mainly on the principle of Parabolic Solar Day-lighting Systems coupled with Fiber Optic Wires and a Heat Filtering Device, which we will used for lighting; whereas for microalgae we will select a species adapted to the nature of industrial wastewater including micro-pollutants, and we will genetically modify them, in such a way as to push them to produce more lipids, and to accelerate their growth, in an other hand, we will consider water as a source of nutrients, as for the carbon will come from the CO_2 which will be released by the bacteria plus the one we will recover from the exhaust gases from the neighboring factory.

Afterwards, we will analyze the optimization model of this system whose target is to predict the cost of production in relation to the operating energy while taking into account the influence of biotic and abiotic parameters on the growth of microalgae in order to obtain the greatest quantity of biomass with good quality of crude oils extracted, which can be converted to different forms of fuels like gasoline, diesel fuel and jet or use it as raw material to produce biomaterials specially bio-composite which will be the material of the future.

Hybrid peptide-thiourea catalyst for asymmetric Michael additions of aldehydes to heterocyclic nitroalkenes

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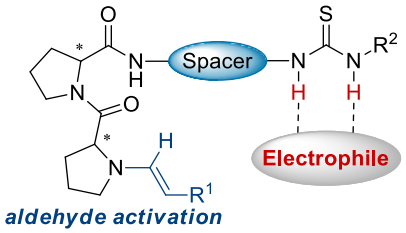
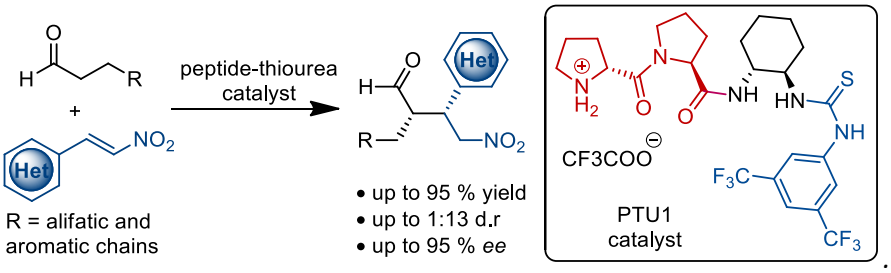
We have developed bifunctional hybrid peptide-thiourea catalyst (PTU), which combines advantages of short dipeptide catalysts and chiral thiourea derivatives. By using both covalent and non-covalent activation, these catalysts allow the enamine formation from the carbonyl functionality by the *N*-terminal proline moiety and the activation of the nitroalkenes by hydrogen bonding with thiourea. The effectiveness and applicability of this catalyst was outlined in solvent-free conditions (ball mill) and in solvents condition in Michael addition of various aldehydes to heterocycle-containing nitroalkenes. We performed NMR studies and DFT calculations to confirm mode of action as well as 3D structure of hybride peptide-thiourea catalyst.





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Overcoming inaccessibility of fluorinated imines

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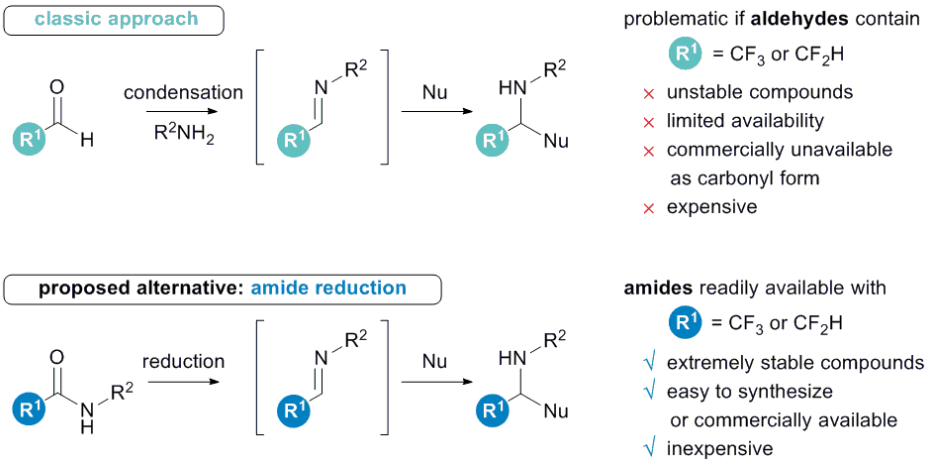
The imine moiety is one of the most versatile functional groups, used in the synthesis of a wide array of biologically and chemically relevant compounds. Due to their moderate stability, imines are usually prepared *in situ* by classic condensation reaction between aldehydes and amines. However, they are often isolable with either great effort or not at all.[1] As a consequence, the availability of imines is limited by the possibility of obtaining the corresponding aldehydes – a task that is often daunting as a number of aldehydes are either unstable or unknown at all. To this group belong, among others, fluorinated aldehydes.[2]

An alternative method to classic condensation between amine and aldehyde for fluorinated imines will be presented. The methodology based on the reduction of fluoroacetamides by zirconium-based hydride known as Schwartz's reagent and further one-pot addition to imines generated *in situ* was carried out.[3] The reaction covers a broad scope of substrates, show excellent functional group compatibility. Moreover, a wide range of applicable nucleophiles gives access to desirable in medicinal chemistry highly functionalized fluorinated amines. Our protocol makes it possible to avoid expensive and difficult to acquire aldehydes and as a source of fluorinated moieties proposes amides that are easily obtained from inexpensive fluoroacetic esters.[2] The developed methodology was illustrated by the synthesis of trifluoromethyl bioisosteres of valuable drugs – antiarrhythmic procainamide and prokinetic itopride.



Scheme 1. An alternative to classic condensation for the synthesis of virtually inaccessible fluorinated imines and their direct nucleophilic functionalization.

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Bond Dissociation Energies of [n]Helicene-Silver(I) Molecular Tweezer Adducts with n= 6-8

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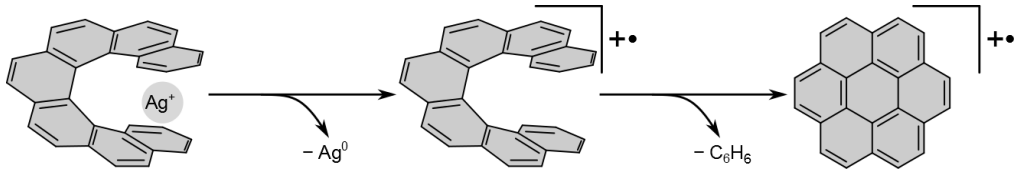
[n]Helicenes (n = 6 and 7) are known to form 1:1 complexes with silver cations, where the helicene acts as a molecular tweezer, attaching to Ag^+ in a bidentate fashion. The binding energies of these complexes have been recently examined in a combination of DFT calculation and ESI-MS/MS experiment.[1], [2] However, controversy arose since the mass spectra indicated the loss of a neutral silver atom rather than the silver cation from the complex. Therefore, a correct procedure would have to consider the charge transfer from Ag^+ to the helicene.[3] The present study intends to solve the dilemma by producing reliable values for the bond energies. Our MS/MS experiments confirm the charge transfer from the Ag^+ to the [n]helicene during CID (collision induced dissociation). This observation is consistent with the fact that [n]helicenes possess lower ionization energies than silver. Furthermore, the bond dissociation energy of [8]helicene could be measured in experiments by calibration of the energy scale with calculated energy values of Ag^+ complexes with [6] and [7]helicene.[1], [2], [3], [4]
The helicene radical cations are normally not accessible by ESI, but the observed charge transfer formation enables the investigation of the CID behavior of these ions. The [n]helicenes$^{+\bullet}$ (n = 6 - 8) do not only feature the dissociation behavior known from other PAHs (i.e. the loss of small C_nH_m units), but also the abundant formation of the coronene radical cation as a fragment. The fragmentation mechanism of the coronene formation has been elucidated by MS^n experiments.



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Isoxazolidin-5-ones as a Platform for Asymmetric Phase-Transfer Catalyzed Functionalizations: Access to Highly Enantioenriched $\beta^{2,2}$ Amino Acid Derivatives

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β-amino acids are present in a vast number of natural products and pharmaceuticals. It is therefore of great interest to access these structural motives in a stereochemically defined fashion. Isoxazolidin-5-ones, a class of β-amino acid precursors, show susceptibility towards different modes of asymmetric (organo)catalytic activation, as was impressively shown by the groups of Briere [1], Shibasaki [2] and Cossy [3].

Within this contribution we demonstrate efficient asymmetric phase transfer catalyzed α-substitution protocols for isoxazolidin-5-ones. Highly selective conjugated additions and heterofunctionalizations (SCF_3) are achieved by employing commercially available Maruoka-type catalysts in low loadings. Subsequent hydrogenation under mild conditions yields the desired enantioenriched $\beta^{2,2}$-amino acid derivatives [4-6].

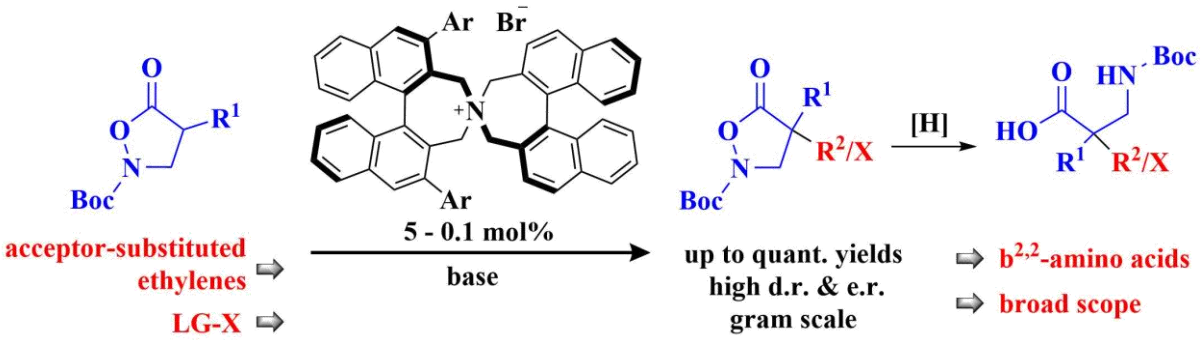

Figure 1: Synthesis of enantioenriched $b^{2,2}$-amino acids

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Exploring the potential of chanoclavine synthase in Ergot alkaloid pathway

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Ergot alkaloids constitute a group of indole-derived mycotoxins that are produced in various filamentous fungi. Due to their potential pharmacological activities for pharmaceutical applications, the chemical nature of this biomolecules and the biosynthetic routs have been studied for a long time. [1,2]

The biosynthesis of these generally quite diverse compounds follows a route via the intermediate chanoclavine-1, which is produced by a ring closure step through two enzymes, a FAD-dependent oxidoreductase (EasE) and a heme-binding catalase (EasC) after prenylation via a prenyltransferase (DmaW) (Figure 1). Previous studies on these key enzymes, relying on complementation in fungal strains, revealed EasE to be responsible for 1,3-diene formation and EasC the essential enzyme for oxidative ring closure. [3,4] Here we present characterization and optimization trials for implementation of an *in vitro* production platform by reconstitution of the early steps in the pathway.

First characterization of DmaW revealed L-tryptophan and L-abrine to be preferred substrates for prenylation by the prenyltransferase from *A. japonicus*. By optimization of conditions successful scale up of prenylation could be achieved and isolation was performed for further studies.

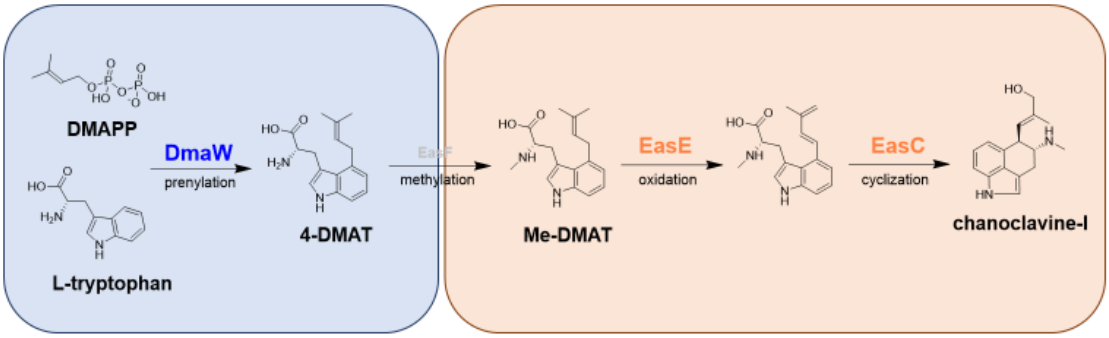

Figure 1: Conserved initial part of ergot alkaloid pathway, synthesizing chanoclavine-l

Moreover, with the aim of ergot alkaloids as pharmaceutical ingredient, another focus of the research will be based on production of semi-synthetic ergot-alkaloid derivatives. Implementation of the *in vitro* reconstituted chanoclavine synthase and further organic synthesis should lead to active ingredients like 1-propyl-agroclavine for pharmaceutical application.

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Synthesis, identification and evaluation of electrochemical performance of polymer gel separator for use in polymeric lithium batteries

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In this study, first an introduction to polymer batteries and we present the future of research. In addition, the characteristics and application of various materials used in the design, including PVDF, CMC, etc., have been discussed. Solvent and anti-solvent used in this project are selected according to previous studies. Various modified breeders are synthesized, and the pore structure and morphology of the improved surface of the separator was analyzed by scanning electron microscopy (SEM) images, and the result confirmed the formation of ideal and high performance separators. The porous layers are deposited on the separators at a relatively low temperature (65 °C) and the pore structure are controlled by varying the concentration of PVDF and CMC. Various parameters including the effect of evaporation temperature, electrolyte adsorption rate, ionic conductivity, shrinkage or degradation conditions of the separator, thermal stability of the separator, and finally its electrochemical performance are fully discussed.

Keywords: Synthesis, Separator, PVDF, CMC, Pores, Porous

Ammonium Salt-Catalyzed Ring-Opening of Aryl-Aziridines with β-Ketoesters

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Aziridines easily undergo ring-opening reactions with a variety of different nucleophiles and proved their applicability as building blocks in various different (asymmmetric) transformations [1]. Interesting γ-amino-carbonyl targets which are not easily accessible by other strategies can be accessed by reactions of aziridines with C-nucleophiles, i. e. enolate species.

Our group recently reported the asymmetric α-hydroxylation of β-ketoesters using racemic oxaziridines as O-transfer reagents and bifunctional ammonium salt (thio)-urea H-bonding catalysts [2]. Focussing on asymmetric ammonium salt catalysis we have been investigating the addition of enolates as pronucleophiles to aryl-aziridines [3].

This presentation gives an overview on the reaction of β-ketoesters with aryl-aziridines under (chiral) ammonium salt catalysis.

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Tailored solution-based *N*-heterotriangulene thin films: Unravelling the self-assembly

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Columnar (1D) triarylamine thin films from a dip-coating approach have been discussed in literature as potential candidates for functional n-type semiconducting layers and regarding both their solution processability and crystal structure [1]. Herein, we report on the facile realization of upstanding 2D-extended *N*-heterotriangulene ultrathin films via a solution-based processing method with thicknesses in the range of 5-20 nm.

Film preparation is inspected at different length scales (Fig. 1) by optical microscopy (OM) and atomic force microscopy (AFM). Long-range order, crystallinity and layer thickness decisively depend on the nature of the substituents attached to the core and peripheral positions of the polycyclic aromatic backbone. First steps to clarify the molecular orientation within prepared structures were taken via angle-resolved near edge x-ray absorption fine structure (NEXAFS) spectroscopy. Owing to their angulate core unit, compounds exhibiting a thioketone unit at the bridge position lack directional growth behavior and no preferential molecular orientation within fabricated thin films was observed via NEXAFS. On the contrary, compounds containing a carbonyl moiety were found to form long-range ordered, well-defined, layered systems with electron diffraction (SAED) confirming the crystalline structure of the thus obtained ultrathin layers. In addition, we found the nature of the peripheral substituents to influence the average orientation of the core unit within obtained films for carbonyl-bridged compounds (Fig. 1). Our work presents a fine tool ensemble for the unambiguous design and structure elucidation of high-quality, 2D *N*-heterotriangulene systems aiming at potential application fields such as layered organic electronics. This research is funded by the DFG within GRK1896.

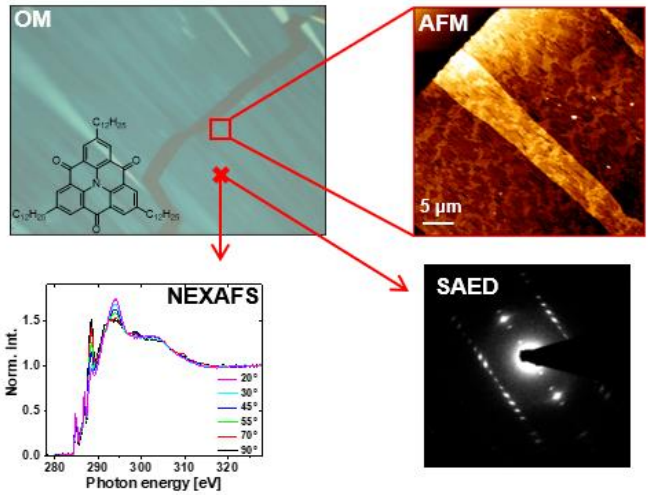

Figure 1: Microscopic (top) and spectroscopic characterization (bottom) of an ultrathin, well-defined *N*-heterotriangulene film revealing exceptional long-range crystallinity.

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Microextraction of cannabidiol from natural cosmetics using a new room temperature ionic liquid as extracting agent

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This study presents the synthesis of a novel asymmetric 1,3-di(alkyloxy)imidazolium based room temperature ionic liquid, and its innovative application as extracting solvent in quantitative liquid-phase microextraction of cannabidiol from natural cosmetics. Quantification was conducted, using a high performance liquid chromatography system coupled to ultraviolet detection. Molecular structure elucidation was performed by nuclear magnetic resonance spectroscopy. The extraction procedure was optimized by means of two different design of experiments for categorical and numerical parameters, using the software Design-Expert®. Additionally, a full validation was executed. A significantly higher selectivity could be achieved compared to a conventional extraction method with methanol. A good calibration model, ranging from 0.6 mg g^{-1} to 6.0 mg g^{-1} cannabidiol, was established. Accuracy and precision were demonstrated on four consecutive days. Recoveries, tested for low and high concentration within the calibration range, were 80%. Stability of extracted cannabidiol was proven for three days at room temperature and fourteen days at 4°C and -20°C. An autosampler stability for 24 hours was validated. Liquid-phase microextraction of cannabidiol from different formulated cream based cosmetics was performed, including four ointments and four creams.

2-Arylquinoline derivatives as selective estrogen receptor β agonists for the treatment of breast cancer

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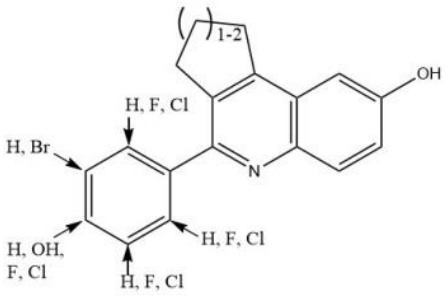
Estrogen receptors (ERs) comprise of the two subtypes ER α and ER β. ER α promotes the growth of tumor cells, while ER β inhibits tumor formation by leading to a G_2 cell cycle arrest [1]. Therefore, selective agonists binding to ER β are promising candidates for breast cancer treatment. Therefore, halogen substituents were introduced at 2-arylquinolines derivatives and their influence on ER subtype selectivity were studied.
Halogen bonding might be involved in the ER interaction. The anisotropic distribution of the electron density around the halogen atom allows electrophilic and nucleophilic interactions [2]. The final 2-arylquinolines are synthesized via the Povarov reaction with multiple substitution pattern and tested regarding their activity and ER selectivity.



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In-operando studies on thiophene based organic field-effect transistors

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Organic field effect transistors have attracted steadily increasing interest for novel electronic applications like backplanes for flexible displays or low-cost circuits for sensor applications. Main reason for this has been their growing performance due to the development of materials with improved charge carriers mobility and environmental stability [1]. Nevertheless, there are still remaining questions regarding charge carrier transport and its mechanism. To address this issue we performed Kelvin probe force microscopy (KPFM) studies to get insight into our devices during operation. We observe a permanent change in the surface potential after the first device stress (i.e., functional operation) and a reversible potential increase during device operation. Furthermore, we found that the permanent potential change is homogenous across the active channel while the reversible effect is strongly correlated to the local microstructure. We interpret these findings as different effects of charge trapping: the permanent charge trapping takes place inside the dielectric layer while the reversible charge trapping happens inside the organic semiconductor and at the organic-dielectric interface.
This research is funded by the DFG within GRK1896 and the BMBF (contract 05K19WE2)

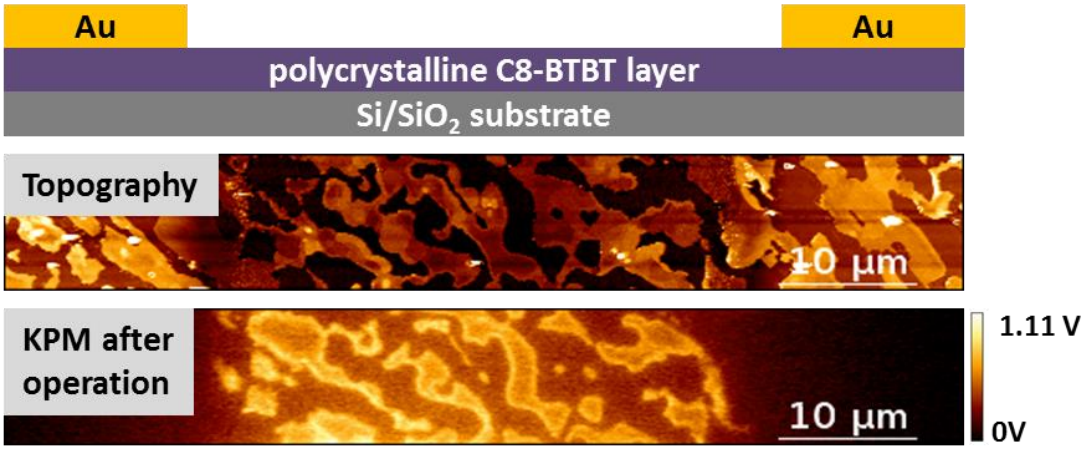

Figure 1: **(Top)** Schematic side-view of the probed region **(Middle)** Topography scan across active channel of a C8-BTBT based OFET **(Bottom)** Surface potential scan after device operation indicating strong charge trapping inside thinner areas of the active layer.

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Ruthenium(II) Polypyridine Complexes for Photodynamic Therapy

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During the last decades, cancer has emerged as one of the deadliest diseases worldwide. Photodynamic Therapy (PDT) has expanded the range of treatment opportunities for various types of cancer. In PDT, a preferably non-toxic photosensitiser (PS) is activated at a specific wavelength to generate reactive oxygen species. As these are highly reactive, they can rapidly interact with essential biomolecules present in cells to trigger their death. The first clinically approved PS was Photofrin®, which is used to treat various types of cancers (e.g. non-small lung, bladder, oesophageal or brain cancer). As the majority of clinically accepted and investigated PSs are based on the same structural scaffold, these compounds are usually associated with similar drawbacks including poor water solubility, tedious synthesis and purification, photodegradation and slow clearance from the body causing photosensitivity.[1] To overcome these limitations, there is a need for modification of existing PSs or the development of new classes of PSs. As an emerging class of compounds, Ru(II) polypyridyl complexes have gained much attention due to their attractive chemical and photophysical properties (e.g., high water solubility, high ROS production, chemical stability and photostability).[2-3] Despite recent research efforts, the majority of investigated Ru(II) polypyridyl complexes lack absorption in the biological spectral window (600-900 nm). This aim could be achieved by a red-shift of the 1-Photon (1P) absorption[4] or the use of a 2-Photon (2P) process, in which the compound absorbs two photons of low energy simultaneously.[5-6] Herein, we present the systematic investigation of novel Ru(II) polypyridyl complexes as PSs for long wavelength PDT.[6]

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Silver(I)-mediated oxidation of dihydrodiazapentacenes studied by ESI-MS(/MS)

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For mechanistic and kinetic studies, spectrophotometric methods are well established. In the last decades, Electrospray Ionisation Mass Spectrometry (ESI-MS) has become a promising method for these investigations as well.[1] We report here the oxidation of tetraphenyldihydrodiazapentacene (TPDAP-H_2) to tetraphenyldiazapentacene (TPDAP) using silver(I) in solution. This system is particularly interesting for ESI-MS analysis, because silver(I) cations are both involved in the oxidation reaction and additionally act as a charge tag for the molecules under study by complexation. The silver adducts of the TPDAP-H_2 reactant and the oxidized TPDAP product show distinctly different energy requirements for dissociation in energy-resolved collision-induced dissociation (CID) experiments. A breakdown graph with both species present, leads to a distinct plateau. The analysis of this plateau was used to monitor the reaction progress. Additionally, the fraction of TPDAP-H_2 and TPDAP was calculated from the isotope pattern of the MS^1.

MS^1 and MS/MS data were recorded as a function of the reaction time using q-ToF instrumentation, with the initial TPDAP-H_2 complexes gradually decreasing and turning into TPDAP complexes. We monitored the fragmentation of the dimeric- and monomeric complexes of the molecules (M) with silver(I) ions, i.e. MAg^+ and MAg^+M. The measurements were performed under the influence of light as well as in the dark. In day light, the oxidation reaction was completed within seven hours, while in the dark the complete conversion of TPDAP-H_2 into TPDAP took nine days.

The poster discusses mechanistic aspects of the silver(I)-induced oxidation of dihydrodiazapentacenes and provides insight into the kinetics of the reaction. The data obtained by MS/MS (energy-resolved CID breakdown graph) are carefully compared with those obtained in MS^1 mode by isotope pattern analysis.

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Hydrogen harvesting and phthalocyanine dye wastewater remediation by continuous electrocoagulation

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Hydrogen, compared to fossil fuels, is a clean with high caloric value and zero emission fuel. The need for hydrogen is increasing rapidly. In recent years, a major concern is to obtain hydrogen and energy from waste and industrial effluents by using them as an energy source. Electrocoagulation has proved to combine efficient removal of pollutants, such as recalcitrant dyes from wastewaters and simultaneously production of hydrogen gas at the cathode [1, 2].
In this work a continuously operated electrocoagulation process with sacrificial aluminum electrodes is presented for production of electrolytic hydrogen and decolorizing nickel phthalocyanine reactive dye containing wastewater. The electrocoagulator is equipped with a gas separation tank in a form of up-flow anaerobic sludge bed for harvesting the electrochemically generated hydrogen gas at the cathode.
The effects of all operating parameters on the pollutant removal efficiency and hydrogen production, such as solution pH, applied current density, conductivity and inlet flow rate were investigated.
Experimental results showed that the quality of the treated wastewater was very satisfactory. By working at a near neutral solution of pH 7.5 and a current density of 10 mA/cm^2, both, COD and color were quantitatively removed by >99 %. The energy yield via the harvested hydrogen amounted to 26 % of the electrical energy demand for the electrocoagulation process.
It can be concluded that the electrocoagulation treatment of dye containing wastewaters and dye-house effluents could be an effective approach for a double useful objective, namely environmental cleanup and energy harvesting.

Keywords: *electrocoagulation, nickel phthalocyanine dye, hydrogen production, pollutant removal.*

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The Effect of Base and Nucleophile on the Nucleophilic Substitution of Methoxytropone Derivatives: Steric Strategy to Synthesize 4-and 5-Substituted Multifunctional Azulenes

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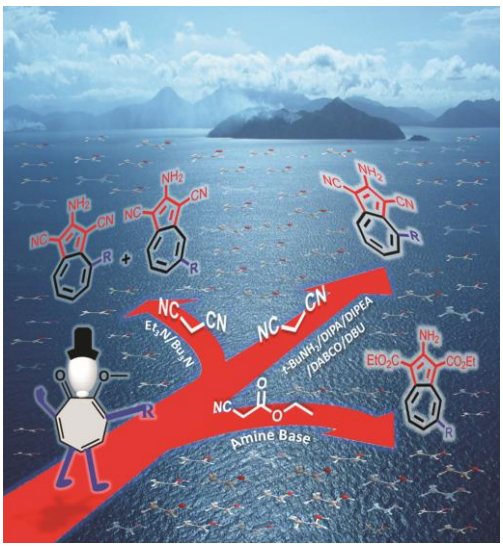
Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER) Kolkata, Mohanpur 741246, Nadia, West Bengal, India

Azulene-based conjugated systems have received increasing interest in recent years as optoelectronic materials.[1] Despite the routes available for the preparation of substituted azulene derivatives, there remain few methods that allow regioselective substitution on the seven-membered ring of azulenes due to the subtle reactivity difference among the various positions. This report explores the reactivity of substituted tropolones as the azulene precursors and also provides a new method to create 4- and 5-substituted azulenes. The nucleophilic substitution on 3-substituted 2-methoxytropones to form azulenes is dependent on the nucleophile and base employed. With bulkier nucleophiles (ethyl/methyl cyanoacetate), the reaction proceeds with the abnormal nucleophilic substitution (attack at C-7) irrespective of the base and with smaller nucleophiles the reaction follows base-dependent normal (attack at C-2) and abnormal nucleophilic substitution. Thus the methodologies are developed to selectively obtain 4-and 5-substituted azulene based on the nature of bases and nucleophiles employed. The experimental observations were also corroborated by DFT calculations.[2,3]



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Polarization assisted Exsolution of Metal Nanoparticles from Doped Perovskites for Enhanced Catalytic Performance

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Perovskite type oxides with the nominal composition ABO_3, if an easily reducible element is used as the B-site cation or as B-site doping, can be selectively reduced, thus exsolving this reducible element [1]. Under the proper conditions, the reduced metal forms finely dispersed nanoparticles on the surface of the perovskite material, which are well socketed in the oxide support. The result is a catalyst material that is easily prepared, highly catalytically active, thermally and chemically stable and shows a high resistance towards sintering and coking.

Several ferrites (Fe as main B-site element) that have been shown to be able to exsolve nanoparticles [2] were investigated with respect to their catalytic performance for methane dry reforming (MDR, CH4 + CO2 ⇌ 2 CO + 2 H_2). Besides the catalytic testing, in situ X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to characterize the materials' behavior during the reaction. The catalytic performance could be greatly increased by combining the addition of a small amount of Ni as a doping element on the B-site of the perovskite and a reductive pretreatment to cause exsolution of this doping element (Figure 1a).

Furthermore, when using the perovskites as the electrode materials of an electrochemical cell, it could be shown by in situ X-ray photoelectron spectroscopy (XPS) that the exsolution process can be controlled by applying an electrical polarization. Nanoparticles exsolved with the aid of polarization are visible in Figure 2b. The combined choice of the perovskite composition, reaction conditions and polarization allows for a tailored nanoparticle formation and thus precise control of catalytic reactions.

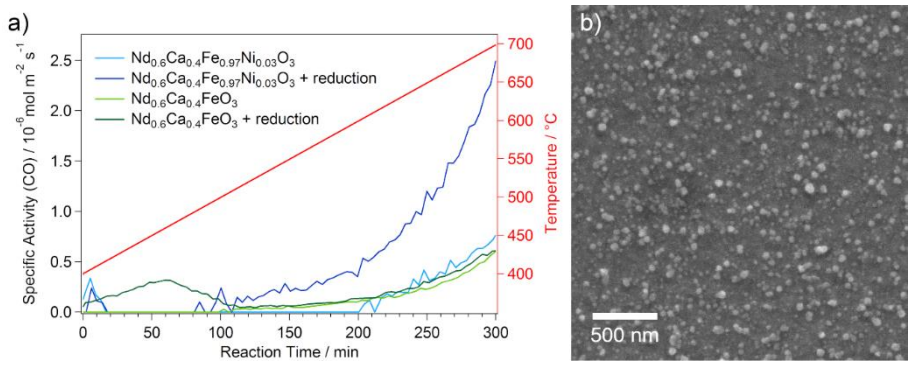

Figure 2: a) Results of the catalytic testing for MDR: CO production at increasing temperatures. b) SEM image of exsolved nanoparticles, after applying polarization in reducing atmosphere.

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Synergistic Ammonium (Hypo)Iodite/Imine Catalysis for the Asymmetric *α*-Hydroxylation of *β*-Ketoesters

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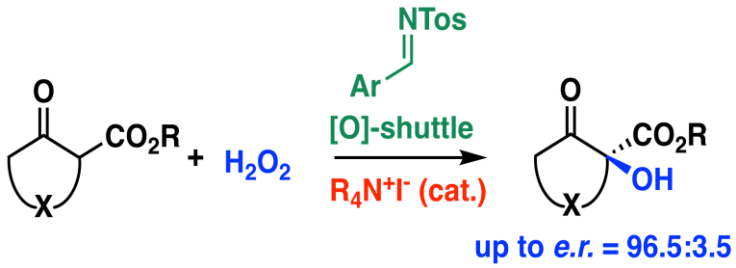
The *α*-hydroxy-*β*-oxo ester functionality is a common structural motif found in a variety of natural products, agrochemicals and pharmaceuticals, such as *kjellmanianone*, *vindoline*, *indoxacarb*, and *doxycycline*.[1] The enantioselective construction of *α*-hydroxy-*β*-dicarbonyl structures by means of direct *α*-oxidation of prochiral 1,3-dicarbonyls with electrophilic oxygen-transfer reagents has emerged as an important synthesis strategy.[2] However, organo-catalytic approaches using cheap and environmentally benign oxidants, i.e. hydrogen peroxide remain scarce.[3] Gratifyingly, we have recently reported the synergistic use of chiral bifunctional ammonium iodide catalysts in combination with simple catalytically relevant aldimines that allows for an unprecedented asymmetric *α*-hydroxylation reaction of *β*-ketoesters using H_2O_2. The reaction proceeds via *in situ* formation of a hypervalent iodine species which then reacts with the used aldimine to generate an activated electrophilic O-transfer agent, allowing for the highly enantioselective synthesis of a variety of chiral *α*-hydroxylated *β*-ketoesters under operationally simple oxidative conditions.[4]



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Efficient Reduction of Electron-Deficient Alkenes Enabled by a Photoinduced Hydrogen Atom Transfer

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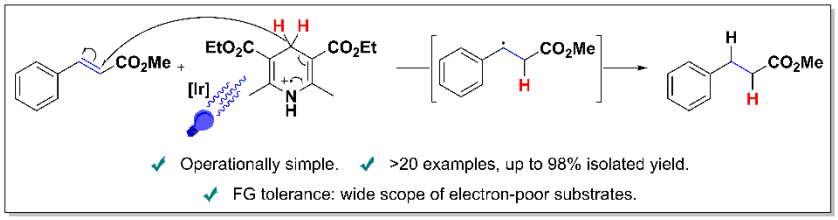
Reduction of carbon-carbon multiple bonds is one of the central transformations in chemical and pharmaceutical industries. Current methods, however, heavily rely on the use of high energy content reagents such as H_2 or hydride sources derived from fossil fuels, with a consequently very large carbon footprint. Furthermore, H_2 is a non-liquefiable and highly flammable gas, which makes it difficult to handle safely especially at an industrial scale [1]. For these reasons, it would be desirable to develop new transfer hydrogenation methodologies, avoiding the use of H_2 altogether.

In recent years, photocatalysis has been increasingly applied to the transformation of organic compounds as a unique way of generating radical intermediates that are otherwise not easily accessible [2]. While alkene activation by single electron transfer (SET) oxidation have been studied extensively for photocatalytic hydrofunctionalizations [3], examples involving SET reduction to the anionic radical species is scarce and the methods are limited by a narrow scope due to their low electron affinity. Pioneering work by Pac and co-workers demonstrated that extremely electron-deficient olefins such as dimethyl maleate and fumarate could be reduced using $Ru(bpy)_3Cl_2$ and N-benzyl 1,4-dihydroniconiamide (BNAH) as the reductant [4]. Unless highly reducing systems were employed, photoreduction of less-activated alkenes bearing one electron-withdrawing group has not been reported to date [5]. As an alternative to these methods that require either highly oxidizing or reducing conditions, we hypothesized that a different alkene activation strategy could be developed by exploiting hydrogen atom transfer (HAT) chemistry.

In this presentation, we will report an efficient and operationally simple photocatalytic reduction of cinnamate derivatives, enabled by HAT from the Hantzsch ester radical cation to olefins [6]. In addition to widening the scope of this type of transformation, this unprecedented mode of substrate activation offers new opportunities in the field of photoredox catalysis.



Scheme. Photoreduction of electron-deficient alkenes involving the activation of substrates through HAT from a Hantzsch ester derivative.

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Bond Dissociation Energies of [n]Helicene-Silver(I) Molecular Tweezer Adducts with n= 6-8

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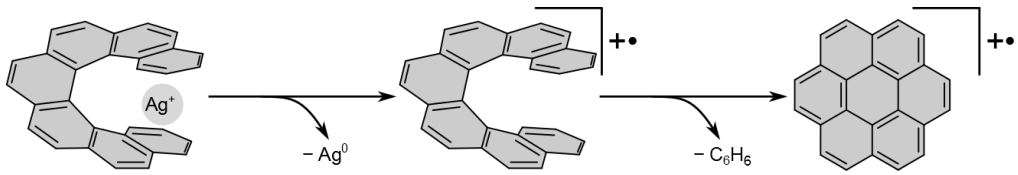
[n]Helicenes (n = 6 and 7) are known to form 1:1 complexes with silver cations, where the helicene acts as a molecular tweezer, attaching to Ag^+ in a bidentate fashion. The binding energies of these complexes have been recently examined in a combination of DFT calculation and ESI-MS/MS experiment.[1], [2] However, controversy arose since the mass spectra indicated the loss of a neutral silver atom rather than the silver cation from the complex. Therefore, a correct procedure would have to consider the charge transfer from Ag^+ to the helicene.[3] The present study intends to solve the dilemma by producing reliable values for the bond energies. Our MS/MS experiments confirm the charge transfer from the Ag^+ to the [n]helicene during CID (collision induced dissociation). This observation is consistent with the fact that [n]helicenes possess lower ionization energies than silver. Furthermore, the bond dissociation energy of [8]helicene could be measured in experiments by calibration of the energy scale with calculated energy values of Ag^+ complexes with [6] and [7]helicene.[1], [2], [3], [4]
The helicene radical cations are normally not accessible by ESI, but the observed charge transfer formation enables the investigation of the CID behavior of these ions. The [n]helicenes$^{+\bullet}$ (n = 6 - 8) do not only feature the dissociation behavior known from other PAHs (i.e. the loss of small C_nH_m units), but also the abundant formation of the coronene radical cation as a fragment. The fragmentation mechanism of the coronene formation has been elucidated by MS^n experiments.



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Complete Protonation and Methylation of Octacyanometalates

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Metal cyanide complexes are well known for their sensitivity against strongly acidic conditions. However, the octacyanometalates $K_4[W(CN)_8]$ and $K_4[Mo(CN)_8]$ were fully protonated in superacidic mixtures of HF/SbF_5 without decomposition. The resulting highly acidic homoleptic hydrogen isocyanide complexes $[W(CNH)_8]^{4+}$ and $[Mo(CNH)_8]^{4+}$ were characterized by fast proton exchange in solution (NMR), isotopic shifts of stretching vibrations (IR) and short contacts to the $[SbF_6]^-$ anions in the solid state (X-Ray).[1]

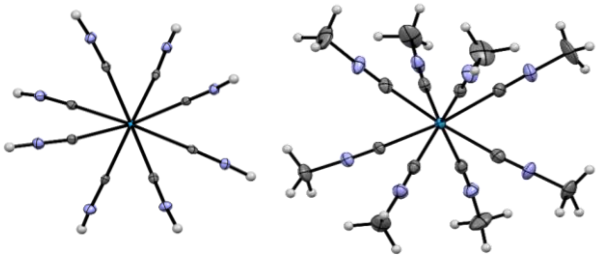

Fig. 1. X-Ray structures of the homoleptic hydrogen isocyanide complex $[W(CNH)_8]^{4+}$ (left) and the homoleptic methyl isocyanide complex $[W(CNMe)_8]^{5+}$ (right).

Homoleptic methyl isocyanide complexes normally have metal centers in low oxidation states due to moderate σ-donation and good π-backdonation. Herein we present the highest oxidized homoleptic methyl isocyanide complexes $[W(CNMe)_8]^{4+}$ and even $[W(CNMe)_8]^{5+}$. $[W(CNMe)_8]^{4+}$ can be easily prepared by the reaction of $[NBu_4]_4[W(CN)_8]$ with methyl triflate in dichloromethane. $[W(CNMe)_8]^{5+}$ is prepared by reacting $[NBu_4]_3[W(CN)_8]$ with the strongly methylating mixture MeF/AsF_5 in SO_2 at low temperatures (max. −30 °C) because of its thermal instability.[2]

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Antimicrobial activity of chlorido[(*N,N'*-bis(salicylidene)-1,2-phenylenediamine]iron(III) by ferroptosis

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The progressing increase of resistant bacteria such as *Staphylococcus aureus* and its methicillin-resistant phenotype (MRSA) is one of the leading challenges in medicine nowadays. Thus, research for innovative lead structures is essential to keep the infections under control caused by these pathogens. In the current structure-activity relationship study, a series of metal-based drugs was evaluated for their capability to treat microorganisms resistant to antibiotics. The chosen Ni(II), Cu(II), Zn(II), Mn(III), and Fe(II/III) complexes differ in their salen- and salophene-type Schiff base ligands. The *in vitro* activity was investigated using gram-positive (*S. aureus* and MRSA) and gram-negative strains (*Escherichia coli* and *Pseudomonas aeruginosa*). However, activity selectively against the gram-positive strains was observed. In particular, the iron(III) complexes exhibited auspicious antimicrobial effects , with MIC_{90} values ranging from 0.781 to 50 µg/mL. Among them the chlorido[(*N,N'*-bis(salicylidene)-1,2-phenylenediamine]iron(III) complex **6** had the most potent MIC_{90} value (0.781 µg/mL = 1.93 µmol/L) against *S. aureus* and MRSA. It was comparably active compared to established drugs ciprofloxacin against *S. aureus* (0.391 µg/mL = 1.18 µmol/L) and tetracycline against MRSA (0.391 µg/mL = 0.88 µmol/L). As mechanism of action of complex **6** the induction of ferroptosis was discovered. This represents a new strategy to treat harmful bacteria. Applying compound **6** (10 µg/mL), both gram-positive strains were killed within 20 min in PBS. This efficacy basically points out that iron(III) salophene complexes serve as promising lead structures for the further design of antibacterial metal complexes.

Decarboxylation of palmitic acid catalyzed by *Chlorella variabilis* fatty-acid photodecarboxylase (*Cv*FAP) in a custom-built photoreactor

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The need for lowering waste production and the increased demand for selectivity in organic synthesis, along with the rapid expansion of molecular biology, led to the development of biocatalysis as a viable option for industrial-scale synthesis of fine chemicals.[1] In parallel with biocatalysis, photocatalysis has demonstrated its synthetic utility, with an increasing number of activation modes in which photon energy is supplied to a photocatalyst which, upon excitation, is able to induce a unique reaction pathway not previously accessible by thermal control.[2] *Cv*FAP was first described in 2017 and represents a rare example of a natural photoenzyme, the photocatalytic activity of which is dependent on the FAD cofactor present in the active site.[3] Herein, the screening of reaction conditions for the *Cv*FAP-catalyzed photodecarboxylation of palmitic acid in a multi-purpose open-source photoreactor is described. The enzyme was heterologously expressed in *E. coli* and the corresponding lyophilized cell lysate was used as the catalyst. A reliable analytical procedure was developed for the screening of reaction conditions in 1 mL volumes. The wavelength, light intensity, and time dependence of the reaction was successfully established. The results obtained indicate that the constructed photoreactor provides reliable control of wavelength, light intensity, and temperature, establishing the basis for future studies of the substrate scope of *Cv*FAP, and with it the discovery of new sustainable methodologies for the synthesis of high-value small molecules.

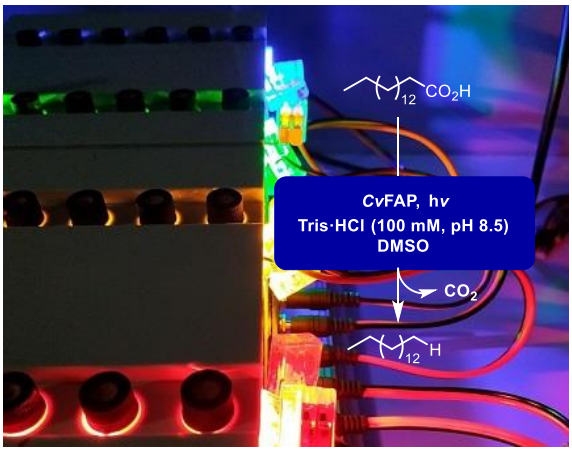

Figure 1. Photoreactor during a reaction screening of different wavelengths and the general reaction scheme.

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Theoretical Study of the Borono-Mannich Reaction with Pinacol Allenylboronate

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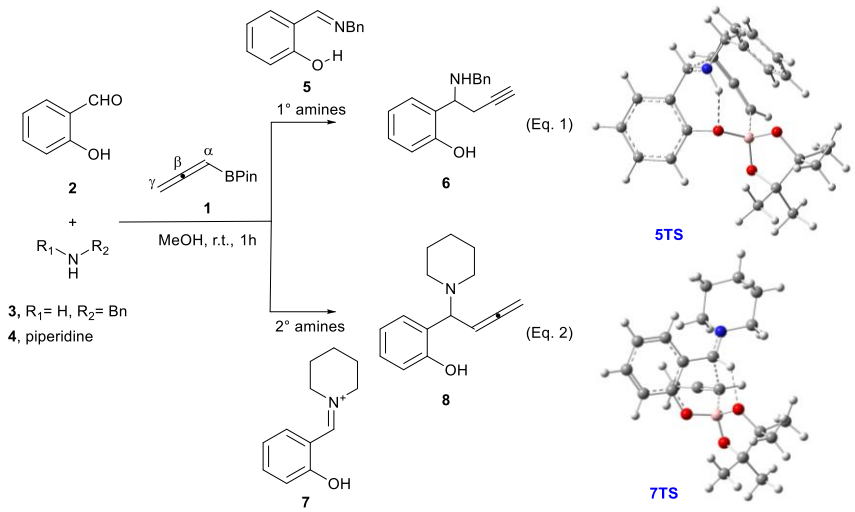
The Borono-Mannich reaction (BMR) is a multicomponent transformation that involves an aldehyde, an amine and a boronic acid to obtain diversified amines. The reaction can be applied to a wide range of boronate derivatives, such as, boronic acids, boronate esters and even trifluoborate salts. Recently, pinacol allenylboronate (**1**) has been used in the BMR for the obtention of allenylamines and propargylamines. Interestingly, when primary amines as benzylamine (**3**) are employed, propargylamine derivatives **6** are obtained, whereas the use of secondary amines as piperidine (**4**) affords the allenylamine derivative **8** (Scheme). In both cases, full regioselectivity was observed.[1]

To gain understanding about the observed regioselectivity of these reactions, we performed a Density Functional Theory (DFT) study of the BMR using the M062X/6-311+G** method in MeOH as solvent. For the first system, we analyzed the interaction of **1** with imine **5**, derived from benzylamine (**3**), and its corresponding iminium ion and salicylaldehyde **2** (Eq. 1). Also, we studied the system formed by reaction of **1**, with the iminium ion **7** generated from piperidine (**4**) (Eq. 2).



Scheme. Borono-Mannich Reaction of pinacol allenylboronate with primary amines (Eq. 1) and secondary amines (Eq. 2).

In the first case, it was observed B-O coordination *via* an eight-membered ring transition structure (**5TS**) stabilized by a hydrogen bond between the hydrogen attached to the nitrogen of the iminium ion and the phenolic oxygen to afford the propargylamine(γ-attack). On the other hand, **7TS** exhibits a non-classical hydrogen bond between the hydrogen attached to the imine carbon and one of the oxygens of the pinacol in the six-membered ring structure toward the allenylamine (α-attack).

Herein, we discuss the results of this study, as well as, the possible applications of this work to other systems in the Borono-Mannich Reaction.

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A stability data set of ene reductases towards organic solvents and the computational analysis

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After establishing a biotransformation on laboratory scale the addition of organic co-solvent during process intensification might be needed [1]. A poor substrate solubility or needs to simplify downstream processing might require the solvent as additive. Consequently the biocatalyst is exposed to organic solvents which might reduce its activity or even lead to a complete inactivation. Why one enzyme can tolerate a co-solvent while another one losses its activity entirely is not understood in detail, yet.

We aim to decipher the solvent resistance of different biocatalysts towards different solvents and shed light onto enzyme and solvent features that define the (in-)stability. To achieve this we combine experimental evaluation of stability with computational methods. In order to have a good data set for the computational analysis we have identified a representative set of ene reductases for which solvent stability was assessed [2]. We have measured the thermal stability in the presence of co-solvents and the influence of the co-solvents on the initial activity.

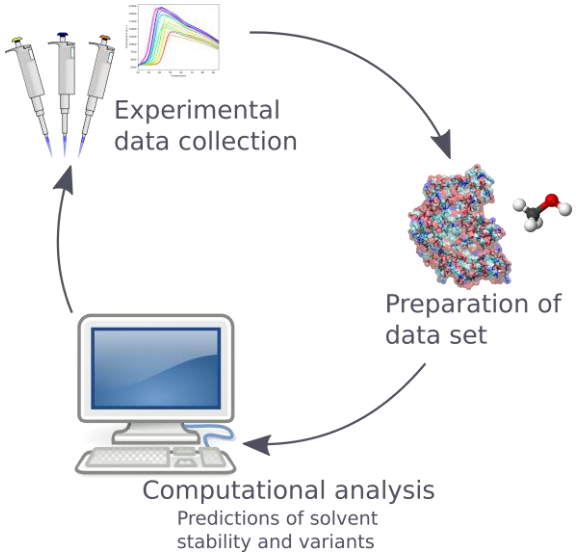

Figure 3: Strategy of stability analysis

The addition of the tested organic solvents led to a decrease of the melting temperature in all cases. The degree of destabilization seems to be dependent on the solvent type and concentration while the initial activity under the same conditions behaves different. In some cases the addition of the co-solvent led to an increase in the initial activity while it led to a decrease for other ene reductases or in combination with other co-solvents. Thus, a thermal destabilization does not necessarily go together with a reduction of the initial activity.

This variability within the experimental stability data is a good starting point for further computational analysis. The detailed analysis of this data set will give evidence on properties of solvent and enzyme that determine stability or instability. This opens possibilities to optimize the tolerance of enzymes towards solvents.

Acknowledgment: This work was funded by BASF SE.

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Surface fluorination and electrochemical investigations of Li metal

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The improvement of lithium-ion batteries is necessary to get a higher specific capacity which is especially needed for the electromobility to ensure higher ranges. State of the art batteries offer specific energy densities of about 200 Wh/kg, which can be raised up to 350 Wh/kg with lithium metal as anode material [1]. There are a few challenges upcoming with the usage of lithium metal due to its high reactivity. One approach to increase the chemical and electrochemical stability of lithium metal is a proper coating, where lithium fluoride is a promising candidate due to its chemical stability and high surface energy.
Different reported methods, resulting in very contrary outcomes, were used to obtain LiF layers with different morphologies and thicknesses e.g. immersion in a NH_4HF_2/DMSO solution or gas phase reaction with Freon 134a. To investigate the influence of LiF on lithium metal, different analytical methods were carried out, focusing on the chemical stability at ambient conditions and electrochemical performance during plating/stripping cycles. The aim of this project is to clarify the influence of LiF layers on the stability of lithium metal electrodes.

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CF_3-Containing *para*-Quinone Methides for Organic Synthesis

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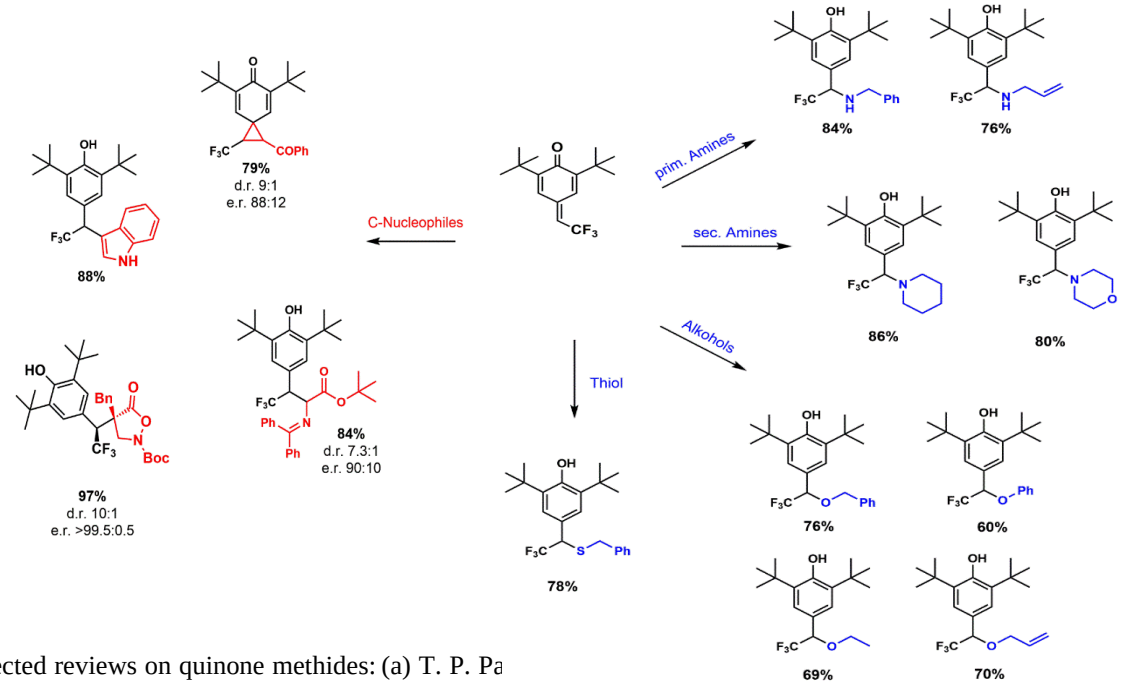
[b] Department Chemie, Ludwig-Maximilians-Universität München, Germany

The utilization of quinone methides as highly reactive electrophiles, which undergo a number of (asymmetric) 1,6-additions with carbon-, or heteroatom-nucleophiles under a variety of different (catalytic) conditions has been shown in the last years with remarkable success [1]. However, alternative ylidene groups are much less explored so far. In combination with the broad interest of CF_3-containing organic molecules for the medicinal or agrochemical industry [2] we envisioned a novel kind of *para*-quinone methides, which can act as prochiral starting material for a variety of compounds [3].

This work shows the synthesis of CF_3-containing *para*-quinone methides as well as their (asymmetric) reactions with carbon and heteroatom nucleophiles with a broad scope. For at least one compound the electorophilicity parameter E (according to Mayr's free energy relationship equation [4]) was determined, which enables the comparison to the well-established quinone methides.



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Fast Reaction Engineering of Photobiocatalytic Reactions through Parallelization

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The field of Photobiocatalysis merges two of the rising topics in organic synthesis: Biocatalysis and Photocatalysis [1]. However, due to the youth of the field, the equipment employed is often not fit for the degree of parallelization of small-scale reactions that is commonly used in biocatalytic research. In contrast, most of the available photoreactors were designed for single, iterative medium scale reactions that are mostly performed in synthetic research [2]. This may be one of the reasons, why the coupling of established chemical photocatalysis with biocatalysts has been extensively demonstrated, but that there is only a small number of true, natural photobiocatalysts reported up to date [1].

Herein we present the design and application of an open source photoreactor for the fast reaction engineering of three of the four known natural photobiocatalytic reactions *via* parallelization of up to 24 small scale reactions (Figure 1):

a) Photodecarboxylation using a fatty acid photodecarboxylase
b) C=C-reduction of protochlorophyllide using a light-dependent protochlorophyllide oxidoreductase
c) Photosynthesis in *Synechocystis sp*. cells

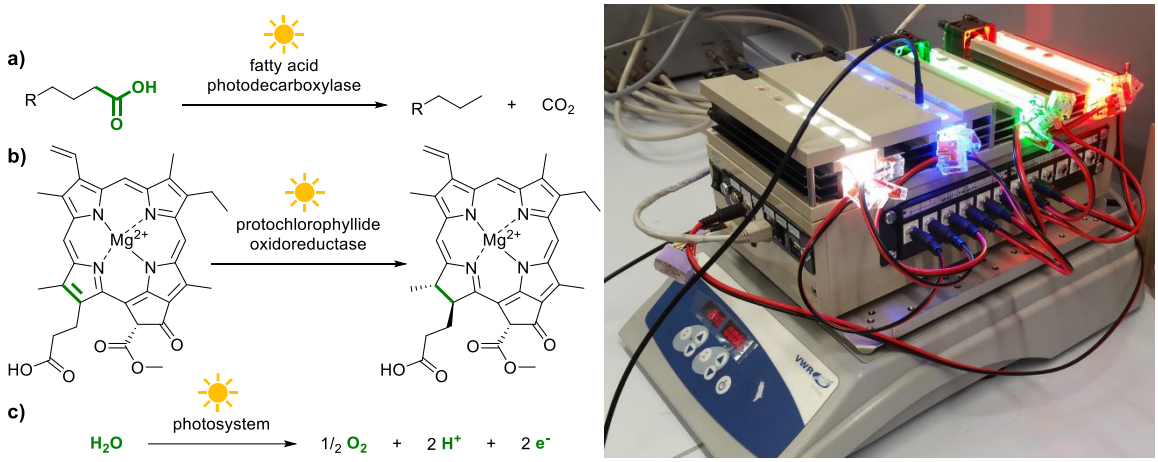

Figure 1: Investigated photobiocatalytic reactions and the applied photoreactor: a) photodecarboxylation; b) photobiocatalytic C=C-reduction; c) photosynthesis

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ASYMMETRIC BIOCATALYTIC PICTET-SPENGLER REACTION TO SHORTCUT ORGANIC SYNTHESIS

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[b]*UCLA, Molecular Biology Institute, Los Angeles, USA*
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The Pictet-Spengler reaction is a valuable route to produce chemically 1,2,3,4-tetrahydro-β-carbolines (THBCs) and isoquinolines from aldehydes and amines. β-Carbolines derivatives exhibit a wide range of psychopharmacological effects and isoquinoline scaffold are building blocks of important pharmaceutical drugs.[1,2] However, only few protocols were described using chiral catalysts to take directly the aldehyde and amine as substrate.[3] In nature, the very same reaction is catalyzed by Pictet-Spenglerases (PSases). One of the representatives is the strictosidine synthase (STR). The STR catalyzes the stereselective condensation of tryptamine and secologanin in order to form (*S*)-strictosidine. In the past, we could show that STR from *Ophiorrhiza pumila* (OpSTR) or STR from *Rauvolfia serpentina* (RsSTR,) accepted small non-natural aldehydes. But contrary to our expectations, the enzymes formed the (*R*)-product with an ee of > 98 %. [4]

Here, we investigate the switch of the stereopreference from (*S*) to (*R*) when using non-native aldehydes as substrates with tryptamine by the STR from *Ophiorrhiza pumila*. By combining forces with X-ray crystallography, mutational analysis, and MD simulations we suggest a rationale for this phenomenon. We propose that the short-chain aldehydes bind in an inverted fashion compared to secologanin leading to the preferred (*R*)-product.

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