WWU
MÜNSTER

8th MÜNSTER SYMPOSIUM ON COOPERATIVE EFFECTS IN CHEMISTRY

2017
May 12th

Münster,
Germany

Book of Abstracts

SFB
858

Symposium Schedule

Friday, May 12th 2017, Aula, Schloss of the WWU Münster

9.55 am Opening — *Armido Studer, SFB 858 Spokesperson*

10.00 am **Peter R. Schreiner** — *Chair: Ulrich Hennecke*
Justus-Liebig-Universität Gießen, GER
London Dispersion Effects in Molecular Chemistry – Reconsidering Steric Effects

11.00 am **Susumu Kitagawa** — *Chair: Fabian Dielmann*
Kyoto University, JPN
Cooperative Functions in Porous Coordination Polymers / Metal-Organic Frameworks

12.00 Business Lunch
12.30 pm **Symposium Poster Session**

2.15 pm **MS_CEC Young Researcher Awards 2017** — *Chair: Frank Glorius*
Indrek Kalvet, MSc Chemistry,
RWTH Aachen, GER
Dr. Julius Kögel,
Universität Bremen, GER

3.00 pm **Frances H. Arnold** — *Chair: Andrea Rentmeister*
California Institute of Technology, Pasadena (CA), USA
Biocatalysts for Abiological Chemistry: Bringing New Chemistry to Life

4.00 pm **Benjamin List** — *Chair: Manuel van Gemmeren*
Max-Planck-Institut für Kohlenforschung Mülheim, GER
ACDC: A Powerful Approach to Asymmetric Lewis Acid Catalysis

5.00 pm **MS_CEC Poster Prize Announcements**
Closing Remarks

Poster Contributions

in alphabetical order (presenting author's surname)

Nr.	Authors	Institution	Title
01.	S. Arndt, M. M. Hansmann, P. Motloch, M. Rudolph, F. Rominger, A. S. K. Hashmi*	Ruprecht-Karls-Universität Heidelberg	Gold(I)-mediated Phosphane-Alkyne Addition - An FLP-Motivated Approach
02.	S. Auras, M.-L. Morkos, K. Zawatzky, O. Trapp*	Ludwig-Maximilians-Universität München	Interaction of *tropos* Ligands with Non-Covalent Chiral Additives and their Application in Asymmetric Reactions
03.	P. K. Biswas, S. Saha, M. S. Özer, M. Schmittel*	Universität Siegen	Design of four component supramolecular nanorotors and their dynamic properties
04.	M. Böhmer, F. Ekkehardt Hahn*	WWU Münster / SFB 858	Homo- and Heterobimetallic Bis(NHC) Complexes Featuring Different Coordination Modes
05.	T. Brandhofer, A. Gini, S. Stockerl, O. García Mancheño*	Universität Regensburg	Cooper-catalyzed oxidative Ugi-type multicomponent reaction using benzoyl peroxide as both mild oxidant and reagent
06.	J. S. Bruchhage, W. Uhl*	WWU Münster / SFB 858	Oligomerisaion Reactions with an Active LEWIS Pair
07.	A. Brzozowska, O. El-Sepelgy*, M. Rueping*	Rheinisch-Westfälische Technische Hochschule Aachen	Chemoenzymatic Asymmetric Reductive Acylation of Ketones
08.	B. Cacherat, X. Fang, B. Morandi*	Max-Planck-Institut für Kohlenforschung Mülheim	CO- and HCl-free synthesis of acid chlorides from unsaturated hydrocarbons via shuttle catalysis
09.	V. Caixeta, A. Guldbradsen, M. Vaudel, F. Berven, R. P. Zahedi, J. Nilsson, U. Westerlind*	Leibniz-Institut für Analytische Wissenschaften – ISAS Dortmund / University of Bergen (NOR), University of Gothenburg (SWE)	Development of Methodology for Glycopeptide Enrichment
10.	X. Chen, M. Albrecht*	Rheinisch-Westfälische Technische Hochschule Aachen	Stereo-Helicates as Molecular Spring

Poster Contributions

in alphabetical order (presenting author's surname)

Nr.	Authors	Institution	Title
11.	S. Das, A. Studer*	WWU Münster	[3+3]-Annulation and Ring Opening 1,3-Bifunctionalization of Donor-Acceptor Cyclopropanes
12.	C. Dobelmann, C. Renn, K. A. Jacobson, C. E. Müller, A. Junker*	WWU Münster	UDP-derived α,β-Methylene-diphosphonates as CD73 Inhibitors
13.	N. Drosos, E. Ozkal, B. Cacherat, B. Morandi*	Max-Planck-Institut für Kohlenforschung Mülheim	Selective Cleavage of C–O Bonds through Boron-Catalyzed Deoxygenation
14.	J. Carrillo-Castro, J. Flórez-Castillo, A. M. Escorcia*	Universidad de Santander UDES, Bucaramanga (COL) / Max-Planck-Institut für Kohlenforschung Mülheim	Molecular Docking Study of the Action Mechanism of the Antimicrobial Peptides Ib-M
15.	J. P. M. van Rijn, A. M. Escorcia*, W. Thiel	Max-Planck-Institut für Kohlenforschung Mülheim	QM/MM Study of the Taxadiene Synthase Mechanism
16.	A. Galstyan*, R. Schiller, U. Dobrindt	WWU Münster	Making and Breaking Barriers to Overcome Microbial Infections
17.	C. R. Göb, K. Iritani, Y. Tobe, I. M. Oppel*	Rheinisch-Westfälische Technische Hochschule Aachen / Osaka University	Triaminoguanidinium Based Ligands: Versatile Building Blocks in Supramolecular Chemistry
18.	A. Goswami, I. Paul, A. Ghosh, M. Schmittel*	Universität Siegen	Multicomponent Nanorotors based on different types of noncovalent interaction
19.	S. Hartmann, A. Gubaev, D. Klostermeier*	WWU Münster / SFB 858	Tools to enable complex fluorescence labelling schemes for single-molecule FRET experimentes
20.	V. Hirschbeck, P. H. Gehrtz, I. Fleischer*	Universität Regensburg / Universität Tübingen	Regioselective thiocarbonylation of vinyl arenes

Poster Contributions

in alphabetical order (presenting author's surname)

Nr.	Authors	Institution	Title
21.	P. Hofmann, P. Nikodemiak, U. Koert*	Philipps-Universität Marburg	Synthesis of substituted pentacene derivatives and functionalized cyclooctynes for the study of organic/semiconductor interfaces
22.	B. Jash, J. Müller*	WWU Münster / SFB 858	Specific detection of pyrimidine nucleobases by metal-mediated base pairing
23.	Z.-J. Jia, C. Merten, R. Gontla, C. G. Daniliuc, A. P. Antonchick, H. Waldmann*	Max-Planck-Institut für Molekulare Physiologie Dortmund / TU Dortmund / Ruhr-Universität Bochum	Comprehensive Strategy to Access Chiral Cyclopentadienyl Ligands for Asymmetric C–H Activation
24.	F. Kampert, F. E. Hahn*	WWU Münster / SFB 858	Selective C8-metalation of various purine nucleosides
25.	A. Kerbs, P. Mueller, C. Barner-Kowollik, L. Fruk*	University of Cambridge (UK) / Karlsruhe Institute of Technology	DNA Structuring using Laser Writing and Light Triggered Chemistry
26.	K. Klahr, J. Neugebauer*	WWU Münster / SFB 858	Benchmarking Structures and Vibrational Frequencies from Subsystem DFT
27.	F. Klepel, B. J. Ravoo*	WWU Münster / SFB 858	Supramolecular Gel Formation controlled by UV-Light induced Dynamic Covalent Chemistry
28.	R. Knitsch, M. R. Hansen*, H. Eckert*, D. Han, M. Joksch, T. Beweries	WWU Münster / SFB 858 / LIKat, Universität Rostock	Structural investigation of amorphous residues from catalytic dehydrogenation of hydrazine borane using solid state NMR
29.	J. F. Kögel, D. Margetić, B. Kovačević, X. Xie, L. H. Finger, J. Sundermeyer*	Universität Bremen / Philipps-Universität Marburg	Phosphorus Bisylides: A New Class of Superbases with Two Interacting Carbon Atoms as Basicity Centers
30.	D. Kolarskia, W. Szymanskia, B. L. Feringa*	University of Groningen (NED)	Metal-free synthesis of 6-azo-purines. Towards photoresponsive DNA and RNA

Poster Contributions

in alphabetical order (presenting author's surname)

Nr.	Authors	Institution	Title
31.	M. Körner, N. Krause*	TU Dortmund	Synthesis and Cycloisomerisation of Cryptochiral Allenes
32.	L. J. Kost, H. D. Mootz*	WWU Münster / SFB 858	Structural insight into multivalent SUMO-SIM interactions by a novel FRET sensor
33.	L. Legnani, G. Prina Cerai, B. Morandi*	Max-Planck-Institut für Kohlenforschung Mülheim	Direct synthesis of unprotected amino alcohols and anilines through iron(II) catalysis
34.	F. Lips,* J. Keuter, K. Schwedtmann, C. Mück-Lichtenfeld	WWU Münster	Synthesis and Characterization of a Stable Tetrasilatetraamide
35.	A. Mardyukov,* D. Niedek, P. R. Schreiner*	Justus-Liebig Universität Gießen	Generation and Characterization of Parent Phenylphosphinidene and its Oxidation to Phenyldioxophosphorane, the Elusive Phosphorous Analogue of Nitrobenzene
36.	J. J. Marek, U. Hennecke*	WWU Münster / SFB 858	Why DNA Is a More Effective Scaffold than RNA in Nucleic Acid-Based Asymmetric Catalysis ─ Supramolecular Control of Cooperative Effects
37.	K. Martinewski, W. Uhl*	WWU Münster / SFB 858	The Fascinating Reactivity of an Active Al-N Based Lewis Pair
38.	F. Mäsing, A. Studer*	WWU Münster / SFB 858	Light Mediated Preparation of Palladium Nanoparticles as Catalysts for Alkyne *cis*-Semihydrogenation
39.	A. Massolle, J. Neugebauer*	WWU Münster / SFB 858	New Strategies for Modeling Molecular Magnetic Properties
40.	P. Mehlmann, F. Dielmann*	WWU Münster / SFB 858	Imidazolin-2-ylidenaminophosphines: highly electron-rich phosphines with basic sites adjacent to phosphorus

Poster Contributions

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Nr.	Authors	Institution	Title
41.	J.-M. Menke, G. Storch, O. Trapp*	Ludwig-Maximilians-Universität München	Synthesis and analysis of stereodynamic BIPOL-phosphinites
42.	L. Mertens, K. J. Hock, R. Spitzner, F. K. Metze, C. Schmittmann, R. M. Koenigs*	Rheinisch-Westfälische Technische Hochschule Aachen	Enabling organic synthesis with uncommon diazo compounds
43.	J. B. Metternich, D. G. Artiukhin, M. C. Holland, M. von Bremen-Kühne, J. Neugebauer, R. Gilmour*	WWU Münster	Photocatalytic *E*→*Z* Isomerization Inspired by the Visual Cycle: Mechanistic Dichotomy and Origin of Selectivity
44.	N. Möller, P. Tegeder, F. Glorius*, B. J. Ravoo*	WWU Münster / SFB 858	N-Heterocyclic Carbenes Stabilized Nanoparticles – Synergistic Effects for Stability and Reactivity
45.	K. Müller, N. Krause*	TU Dortmund	Synthesis of α- and γ-Cyclodextrin-NHC-Gold Complexes
46.	F. Muttach, F. Mäsing, A. Studer, A. Rentmeister*	WWU Münster / SFB 858	Novel AdoMet analogues as tools for enzymatic transfer of photocrosslinkers and capturing RNA-protein interactions
47.	S. Neukirchen, C. Cabrele*	Paris-Lodron Universität Salzburg / Ruhr-Universität Bochum	Microwave supported SPPS of large Id2-protein fragments
48.	D. Niedek, S. M. M. Schuler, P. R. Schreiner*	Justus-Liebig Universität Gießen	Peptide-catalyzed Baeyer-Villiger Oxidation
49.	C. Nielinger, G. von Kiedrowski*	Ruhr-Universität Bochum	Overcome Product inhibition of Self-replication using a Photoswitch
50.	F. Octa-Smolin, J. Niemeyer*	Universität Duisburg-Essen	Rigidly tethered bis-phosphoric acids: Generation of tunable chiral fluorescent frameworks and unexpected selectivity for the detection of ferric ions

Poster Contributions

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Nr.	Authors	Institution	Title
51.	T. Olyschläger, A. Gansäuer*	Rheinische Friedrich-Wilhelms-Universität Bonn	Novel, Sustainable Catalyst Activation – Electrochemical Reduction of Titanocene Dichloride and Applications
52.	M. Patzke, G. von Kiedrowski*	Ruhr-Universität Bochum	A Peptide Nucleic Acid replicator for induction of chirality
53.	G. Prina Cerai, B. Morandi*	Max-Planck-Institut für Kohlenforschung Mülheim	Atom-economical cobalt-catalysed regioselective coupling of epoxides and aziridines with alkenes
54.	L. Rakers, C. Richter, A. Rühling, D. Wang, P. Drücker, D. Grill, A. Matos, H.-J. Galla*, V. Gerke*, F. Glorius*	WWU Münster / SFB 858	Application of lipid-inspired imidazolium salts for membrane interactions
55.	M. Rethmeier, G. von Kiedrowski*	Ruhr-Universität Bochum	Symmetry-breaking in PNA self-replication
56.	M. Richert, B. Braunschweig*	WWU Münster	Synergistic effects of protein aggregates in the stabilization of aqueous foam through structure-property relations
57.	S. Riebe, J. Balszuweit, J. Voskuhl*	Universität Duisburg-Essen	Facile Aromatic Ethers as Novel Class of Luminophores with Aggregation Induced Emission Properties
58.	F. Scheidt, P. Selter, N. Santschi, M. C. Holland, D. V. Dudenko, C. Daniliuc, C. Mück-Lichtenfeld, M. R. Hansen,* R. Gilmour*	WWU Münster / SFB 858	Emulating Natural Product Conformation by Cooperative, Non-Covalent Fluorine Interactions
59.	J. Schieven, N. Krause*	TU Dortmund	Synthesis of functionalized pyrazolidines by gold-catalysed three-component spirocyclization in micellar systems
60.	C. Schwermann, J. B. Ernst, F. Glorius*, N. L. Doltsinis*	WWU Münster / SFB 858	Molecular Adsorbates Switch on heterogeneous Catalysis: Induction of Reactivity by N-Heterocyclic Carbenes

Poster Contributions

in alphabetical order (presenting author's surname)

Nr.	Authors	Institution	Title
61.	A. Seper, G. Dyker*	Ruhr-Universität Bochum	Astonishing Temperature Dependence of the Williamson Ether Formation with *meso*-Tetrahydroxyphenylporphyrine
62.	M. Siedow, T. Wiegand, G. Kehr, G. Erker*, H. Eckert*	WWU Münster / SFB 858	Covalent Interactions and Cooperativity in Frustrated Lewis Pairs Studied by Solid State NMR
63.	J. Sklyaruk, J. Borghs, O. El-Sepelgy*, M. Rueping	Rheinisch-Westfälische Technische Hochschule Aachen	A simple Iron and lipase catalysed dynamic kinetic resolution of secondary alcohols
64.	A. Sowa, N. Riek, J. Voskuhl*	Universität Duisburg-Essen	Supramolecular Photosensitisers for Biomedical Applications
65.	K. F. Taupitz, W. Dörner, H. D. Mootz*	WWU Münster / SFB 858	Unraveling the mystery of SUMO interactions with light
66.	A. Thiel, D. F. Sauer, S. Mertens, A. Grimm, U. Schwaneberg, J. Okuda*	Rheinisch-Westfälische Technische Hochschule Aachen	Biohybrid Catalysts Based on Transmembrane Protein FhuA
67.	D. Van Craen, M. Albrecht*	Rheinisch-Westfälische Technische Hochschule Aachen	London Dispersive Forces In Hierarchically Assembled Helicates
68.	I. Versinskaite, N. Krause*	TU Dortmund	Synthesis of a γ-Cyclodextrin-based NHC-Gold Complex via Ruthenium-catalyzed Azide-Alkyne Cycloaddition
69.	D. von der Heiden, S. Bozkus, M. Klussmann, M. Breugst*	Universität zu Köln	Experimental Investigations of Iodine-Catalyzed Michael Additions
70.	M. Weisslocker-Schaetzel, P. Lulchev, D. Klostermeier*	WWU Münster / SFB 858	Is a minimal latch sufficient for reverse gyrase activity?
71.	C. Wiederhold, K. Föcker, C. Schulze, I. M. Oppel*	Rheinisch-Westfälische Technische Hochschule Aachen	Coordination compounds of C3-symmetric triaminoguanidinium based ligands with Ga(III)
72.	T. Winands, N. Doltsinis*	WWU Münster	Fitting coarse grained force fields using genetic algorithms

SFB 858

8th
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ON
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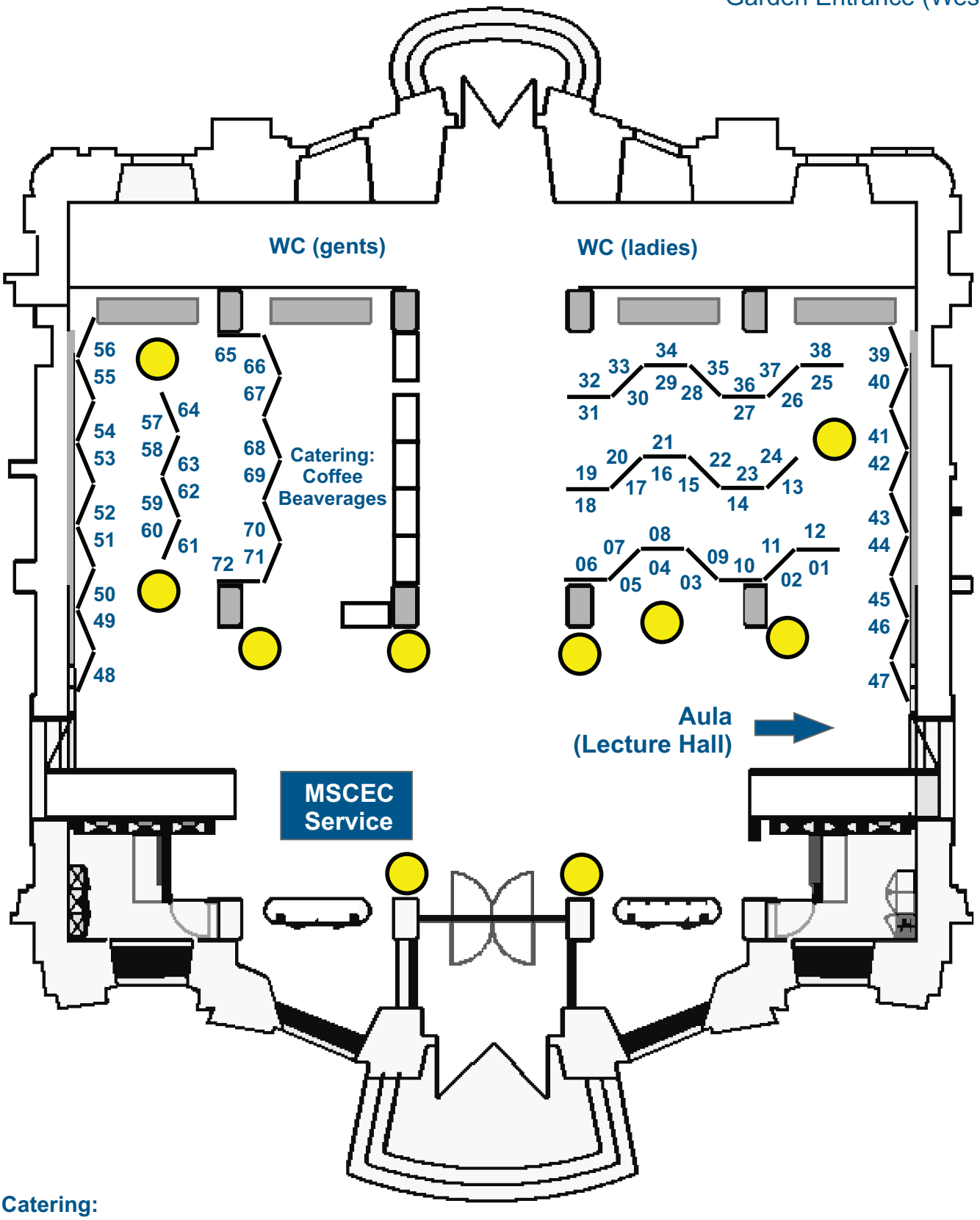
Poster Forum

Garden Entrance (West)



Catering:
Business Lunch
(external marquee)

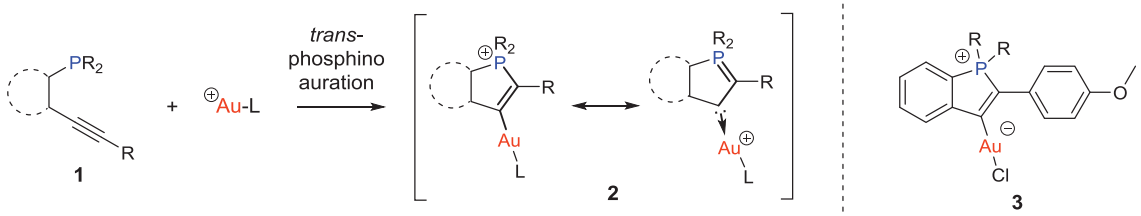
Main Entrance (East)

Gold(I)-mediated Phosphane-Alkyne Addition - An FLP-Motivated Approach

S. Arndt[1], M. M. Hansmann,*[1] P. Motloch,[1] M. Rudolph,[1] F. Rominger[1] and A. S. K. Hashmi*[1,2]

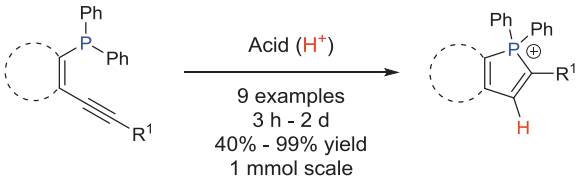
[1] Organisch-Chemisches Institut, Im Neuenheimer Feld 270, 69120 Heidelberg, Ruprecht-Karls-Universität Heidelberg, [2]Chemistry Department, Faculty of Science, King Abdulaziz University (KAU), Jeddah 21589, Saudi Arabia. Email: hashmi@hashmi.de

The gold-mediated intramolecular phosphane addition to alkynes is presented comprising the synthesis of stable, aurated phosphindolium complexes **2** from easy accessible (*o*-alkynylphenyl)phosphines **1**. In order to overcome the strong binding affinity of phosphine to gold, an FLP-motivated approach was attempted. Upon formation of a mixed phosphine NHC/phosphine phosphine gold species, elevated temperatures induced the cyclization to give **2**. This concept could furthermore be extended to overall neutral (phosphindolium)aurate complexes **3** featuring the yet unknown phosphindole ligand (Scheme 1).[1]

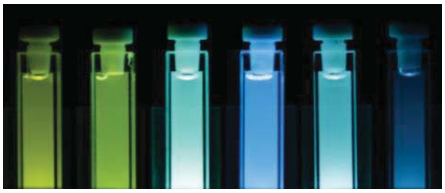


Scheme 1. Gold-mediated anti-phosphinoauration of unactivated alkynes.[1]

Furthermore, the synthesis of π-extended phosphindolium salts by simple proton-induced cyclization was developed. During the course of our study the acid-mediated cyclization was discovered (Scheme 2). The process allows for a general metal-free and extraordinary simple protocol towards the target structures. The rearrangement proceeds in complete atom economy without the need for further purification. Photophysical measurements recorded quantum yields up to 97% in solution (Scheme 3) and fluorescence was also observed in the solid state.[2]



Scheme 2. Protophosphonylation of (*o*-alkynylphenyl)phosphanes.[2]



Scheme 3. Fluorescence in solution.[2]

References

[1] S. Arndt, M. M. Hansmann, P. Motloch, M. Rudolph, F. Rominger, A. S. K. Hashmi, Chem. Eur. J. 2017, 23, 2542 – 2547.
[2] S. Arndt, M. M. Hansmann, M. Rudolph, F. Rominger, A. S. K. Hashmi, Chem. Eur. J. 2017, 23, 5429 – 5433.

Interaction of *tropos* Ligands with Non-Covalent Chiral Additives and their Application in Asymmetric Reactions

Stefanie Auras, Marie-Louise Morkos, Kerstin Zawatzky, Oliver Trapp*

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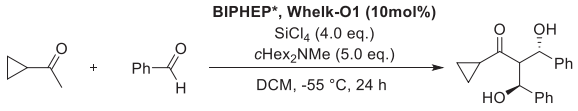
Tropos ligands like BIPHEPs and phosphoramidites with a flexible biphenol moiety as diol have become an important class of enantioselective catalysts and are applicable in several asymmetric reactions.[1]

By addition of external, non-covalent chiral additives a stereochemical bias can be generated onto the dynamic catalysts decorated with appropiate selectands. The adjusted equilibrium of the catalyst isomers is transfered to the enantiomeric ratio of the chiral product of catalysis.

The Whelk-O1 chiral stationary phase, first developed for the enantiomeric separation of nonsteroidal anti-inflammatory drug Naproxen by *Pirkle et al*.,[2] also shows significant separation ability for other α-propionic acids, e.g. Ibuprofen. We investigated the application of the Whelk-O1 selector as chiral additive in addition to a BIPHEP system in a double aldol reaction (Scheme 1), inducing a chiral change in the enantioselectivity.



Scheme 1: Double aldol reaction.

This work was supported by the European Research Council (ERC) through a Starting Grant (No. 258740, AMPCAT).

1 K. Mikami, M. Yamanaka, *Chem. Rev.* **2003**, *103*, 3369-3400; G. Storch, O. Trapp, *Angew. Chem. Int. Ed*. **2015**, *54*, 3580-3586; A. Alexakis, C.Benhaim, S. Rosset, M. Humam, *J. Am. Chem. Soc*. **2002**, *124*, 5262-5263.
2 W. H. Pirkle, C. J. Welch, B. Lamm, *Journal of Organic Chemistry* **1992**, *57*, 3854-3860; W. H. Pirkle, C. J. Welch, *Journal of Liquid Chromatography* **1992**, *15*, 1947-1955.

Design of four component supramolecular nanorotors and their dynamic properties

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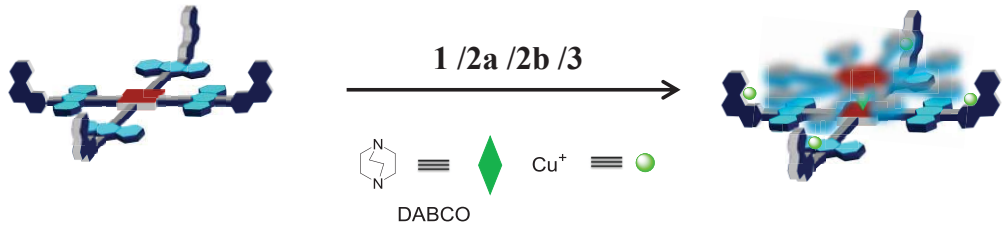
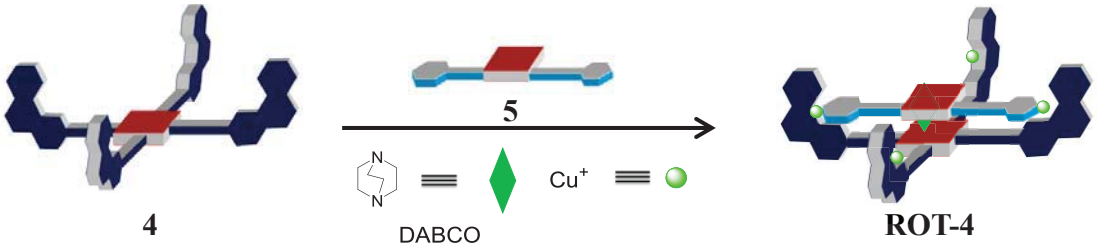
Center of Micro- and Nanochemistry and Engineering, Organische Chemie I, Adolf–Reichwein–Str. 2, D-57068 Siegen, Germany, E–mail: schmittel@chemie.uni–siegen.de

The rotational frequency of a four-component nanorotor changes drastically depending upon the structure of its rotator. As the rate-determining step in the rotary motion involves the dissociation of a copper(I) phenanthroline complexation site of the stator and of a pyridine terminal of the rotator, the activation barrier with the number of pyridine teminals in the rotator inreases in the nanorotors along the series E_a (monopyridine rotator) < E_a (di-pyridine rotator) < E_a (tri-pyridine rotator). However, there are even distinct differences in rate beween rotators exhibiting the same amount of pyridine terminals. The change of a *cis* to a *trans*-di-arm rotator enhances the rotational frequency by almost 1000 fold probably due to stronger binding of the *cis* rotator.



An off axis four components supramolecular rotor based on Salphen rotator was also constructed. Due to the high energy barrier of rotation the slow motion was monitored by ROESY spectra.



Homo- and Heterobimetallic Bis(NHC) Complexes Featuring Different Coordination Modes

Maximilian Böhmer and F. Ekkehardt Hahn

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The synthesis of polynuclear NHC complexes has attracted much attention due to their application in tandem or synergetic catalysis.[1] Polynuclear metal complexes present an efficient way for the construction of new catalytic systems for the transformation of organic molecules in a one-pot synthesis. Most of the synthetic strategies for preparation of polynuclear complexes start with the synthesis of polyazolium salts.[2] A stepwise metalation is in selected cases enabled by the topology of the ligand or by different reactivities at the metal centers.
Heterobimetallic dicarbene complexes were synthesized from an unsymmetrical bisazolium salt. NHC precursors [**1**] / [**2**] can be metalated in a stepwise manner, leading to homo- or heterobimetallic complexes containing one metal center in a chelating fashion. The second metal center is introduced by the transmetalation route and is only coordinated by one NHC donor.

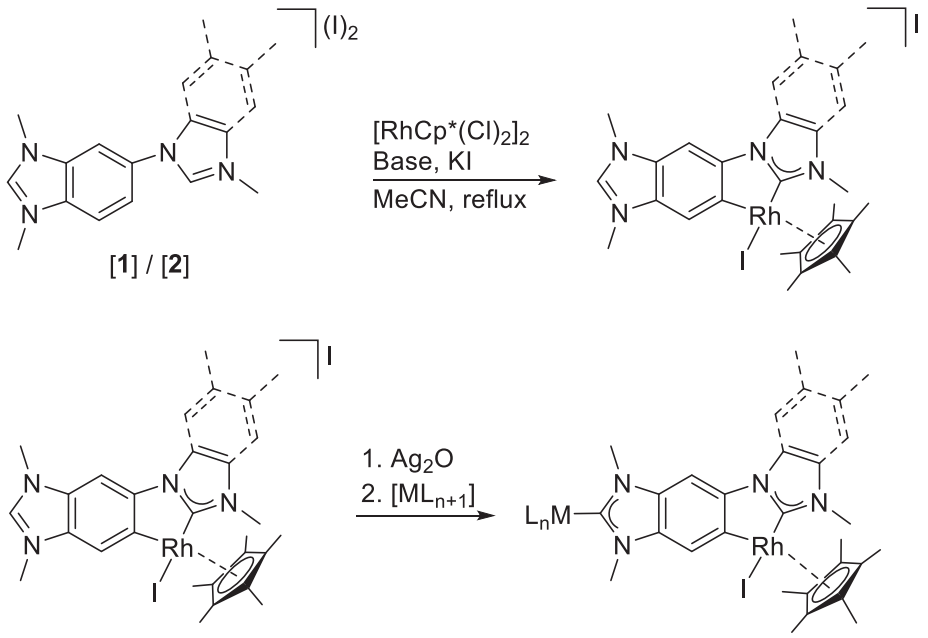

Figure 1: Stepwise metalation of the bisazolium salts [**1**] / [**2**] leading to homo- or heterodinuclear NHC complexes.

References

[1] (a) J. A. Mata, F. E. Hahn, E. Peris, *Chem. Sci.* **2014**, *5*, 1723−1732; (b) D. E. Fogg, E. N. dos Santos, *Coord. Chem. Rev*. **2004**, *248*, 2365–2379; (c) M. J. Bitzer, F. E. Kühn, W. Baratta, *J. Catal.* **2016**, *338*, 222–226.
[2] (a) R. Maity, H. Koppetz, A. Hepp, F. E. Hahn, *J. Am. Chem. Soc.* **2013**, *135*, 4966−4969; (b) R. Maity, C. Schulte to Brinke, F. E. Hahn, *Dalton Trans.* **2013**, *42*, 12857−12860; (c) S. Sabater, J. A. Mata, E. Peris, *Nat. Commun.* **2013**, *4*, 2553−2560.

Cooper-catalyzed oxidative Ugi-type multicomponent reaction using benzoyl peroxide as both mild oxidant and reagent

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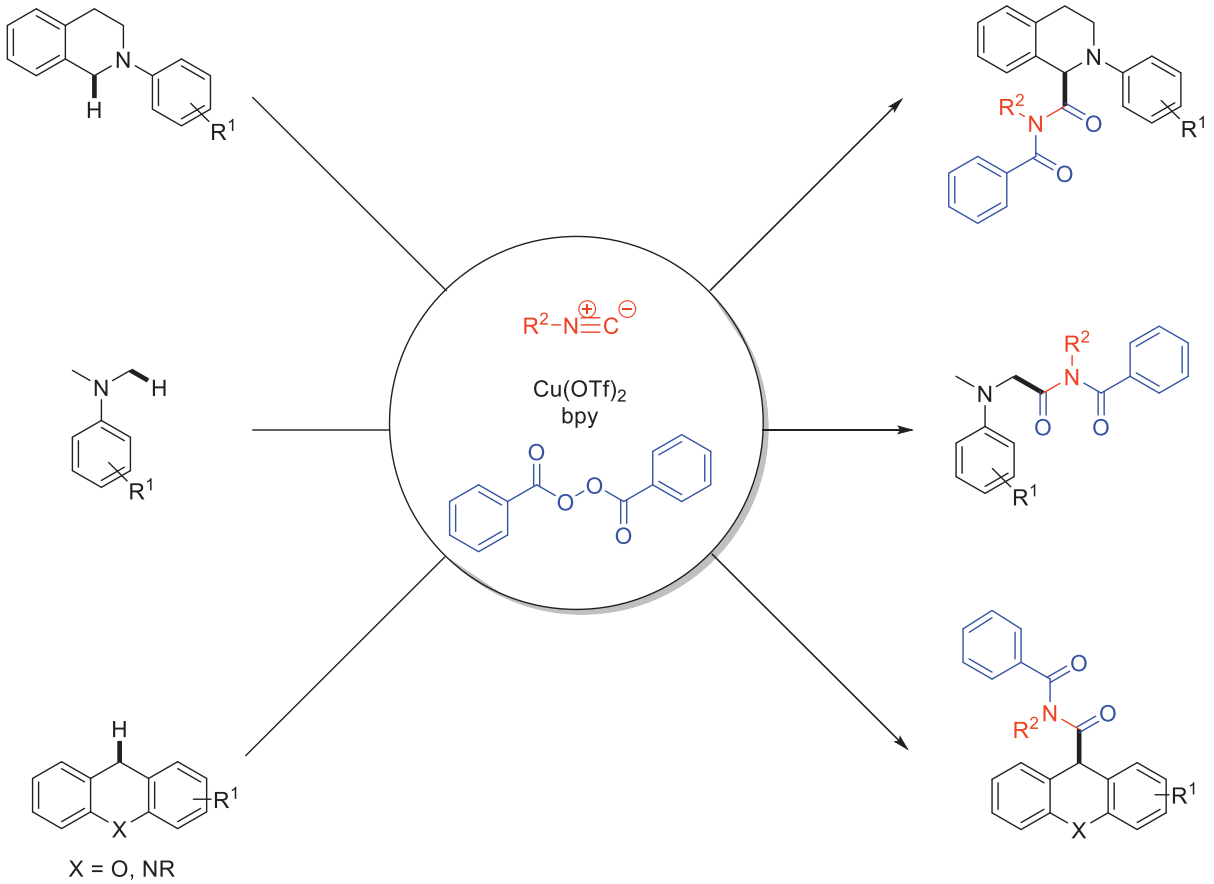
On the way of developing sustainable and more efficient transformations, multicomponent reactions provide an easy access of molecular scaffolds with a high diversity. [1] Recently, the utilization of oxidative C(sp^3)-H functionalization in multicomponent reactions attracted great attention. [2] However, it still represents a challenging task, being a continuous demand on novel and more efficient methodologies.

In this regard, a mild copper-catalyzed oxidative Ugi-type reaction in combination with benzoyl peroxide, which was used as both oxidant and reagent, was developed. Tertiary amines like *N*-aryl tetrahydroquinolines or *N,N*-dimethylanilines, as well as acridines and xanthenes, were employed as substrates, affording the corresponding imide-type products in moderate to very good yields.



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Oligomerisaion Reactions with an Active LEWIS Pair

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Monomeric aluminium/nitrogen-based active LEWIS pairs were obtained by hydro-alumination of hydrazones with different dialkylaluminium hydrides. The products feature strained AlN_2 heterocycles with a short polar covalent Al-N and a longer Al-N donor-acceptor bond. Cleavage of the coordinative Al-N bond leads to the formation of an Active LEWIS Pair, which is able to activate a variety of small molecules in a cooperative manner. [1, 2] The Active LEWIS Pair **1** showed a unique reactivity towards isocyanates and isothiocyanates. Depending on the stoichiometric ratio of the starting materials the insertion of one or two molecules of phenyl isocyanate into the Al-N bond was observed, the latter reaction yielded the unusual linear dimer of the isocyanate. [3] The nucleophilic reaction of **3** with carboxylic acid chlorides opens facile access to various unprecedented and highly functionalized organic after hydrolysis. Beyond that, the Al-N based LEWIS Pair **1** is a very effective catalyst for the oligomerisation of suitable monomers, such as methyl vinyl ketone or methyl methacrylate.

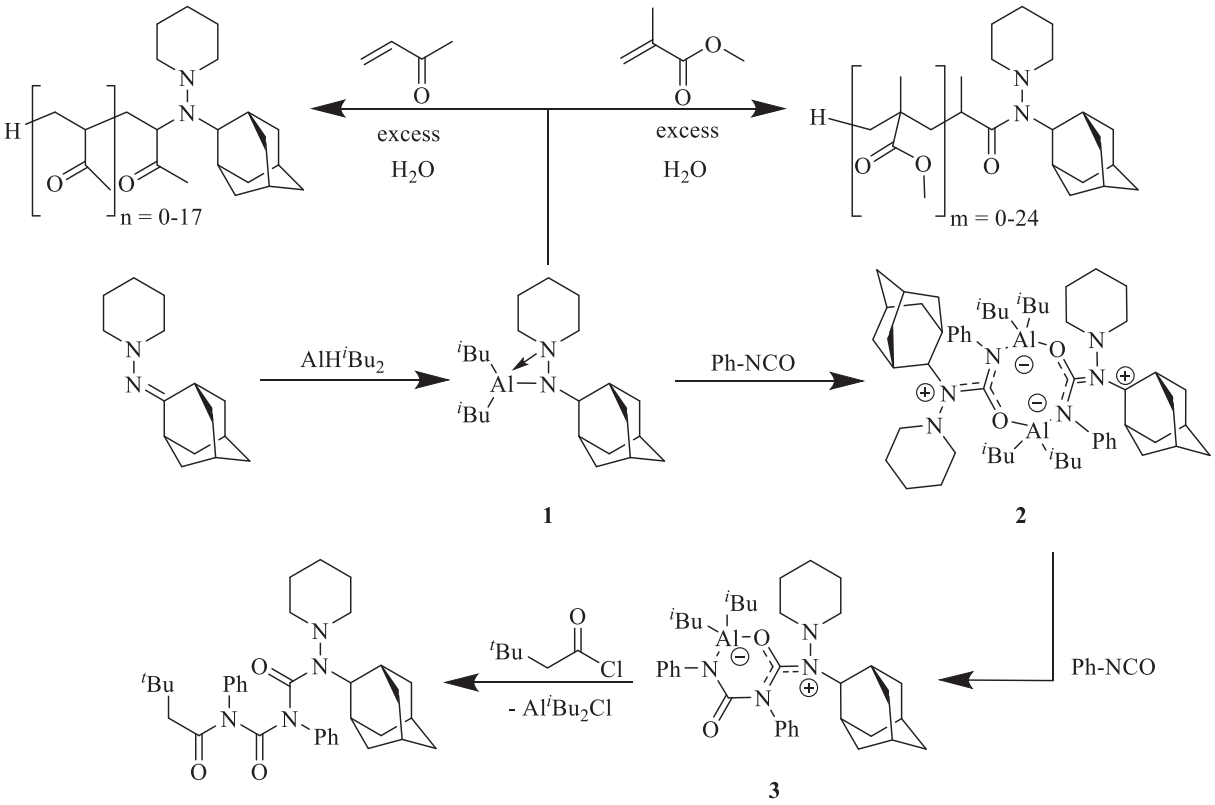

Figure 1: Synthesis of a monomeric Al/N LEWIS pair and insertion of one and two molecules of phenyl isocyanate. **3** reacts with electrophiles to afford oligo-functional secondary products. Oligomerisation reactions were observed for suitable monomers (e.g. methyl vinyl ketone and methyl methacrylate).

References:

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Chemoenzymatic Asymmetric Reductive Acylation of Ketones

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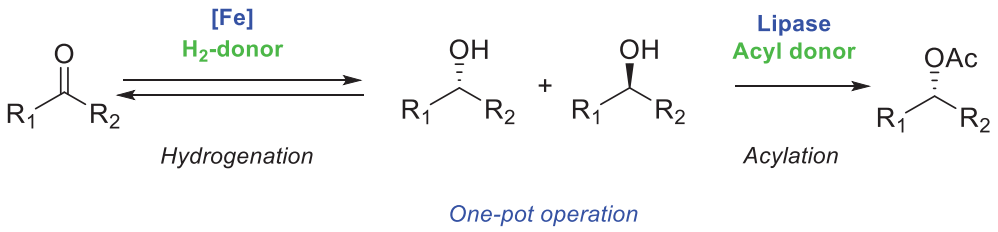
Enantiomerically pure alcohols are important building blocks in the manufacturing of a wide range of chemical products. The most commonly employed method in the industrial production of chiral alcohols and amines is the enzymatic kinetic resolution of their racemates. However, the limitation of this method is that the maximum theoretical yield is only 50%. To overcome this problem the enzymatic resolution can be combined with a metal-catalysed *in situ* racemization to perform the dynamic kinetic resolution. [1]

We will showcase the first example of a cooperative iron/lipase dual catalytic system for reductive acylation of various pro-chiral ketones. The advantage of this method is the application of an inexpensive iron and lipase multicatalytic system, avoiding the use of precious metal catalysts and expensive chiral ligands [2] [3].

The mild reaction conditions of this hydrogenation/dynamic kinetic resolution cascade process allow for broad substrate scope. The reductive acylation of benzylic, aliphatic and heteroaromatic ketones as well as diketones, afforded the corresponding chiral acetates with excellent yields and enantioselectivities.



Scheme 1. Synthesis of chiral acetates.

Literature:

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CO- and HCl-free synthesis of acid chlorides from unsaturated hydrocarbons via shuttle catalysis

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The synthesis of carboxylic acid derivatives from unsaturated hydrocarbons is of great interest in organic synthesis. The traditional Reppe-type carbonylation[1] has been underexploited in the laboratory, due to the safety hazards and the need for special equipment associated with the use of CO. Another drawback is the necessity to employ a different catalyst for each nucleophile, highlighting the need for a unifying approach. The preparation of acid chlorides as highly versatile synthetic intermediates without the use of toxic CO and corrosive HCl would potentially overcome these limitations (Figure 1).

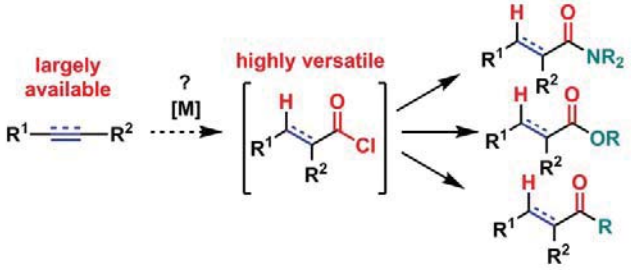

Figure 1: Elusive hydrochlorocarbonylation as a route to prepare carbonyl derivatives

Shuttle catalysis is an efficient approach to formally transfer a functional group from one molecule to another.[2–4] The use of this approach recently allowed us to unlock an elusive hydrochlorocarbonylation reaction, using the inexpensive reagent butyryl chloride as sacrificial donor to access acid chlorides.[5] The versatility of this process is demonstrated in a broad set of one-pot reactions (for some selected examples see Figure 2).

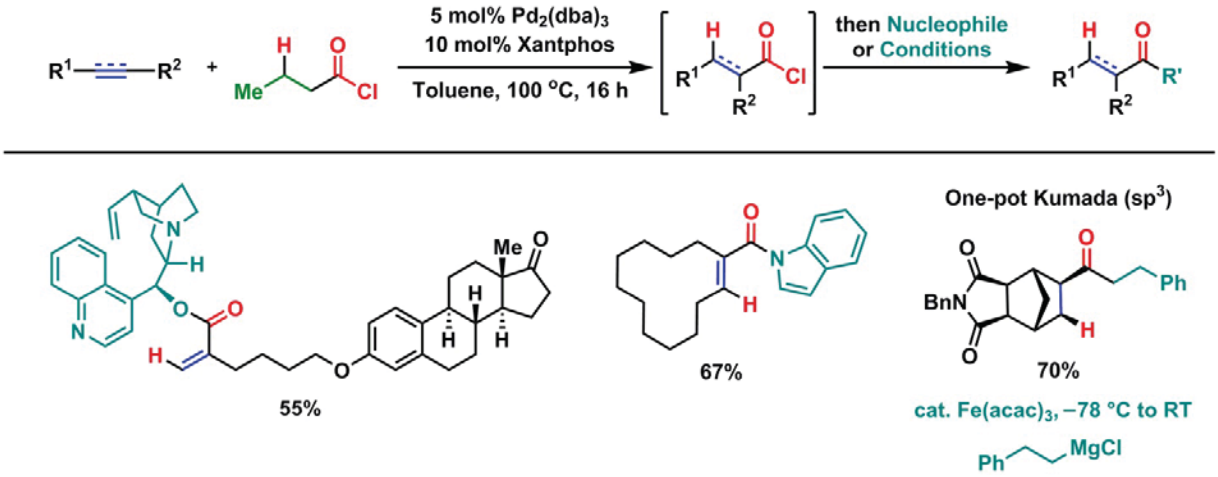

Figure 2: One-pot synthesis of carbonyl-containing products from unsaturated substrates

References:

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Development of Methodology for Glycopeptide Enrichment

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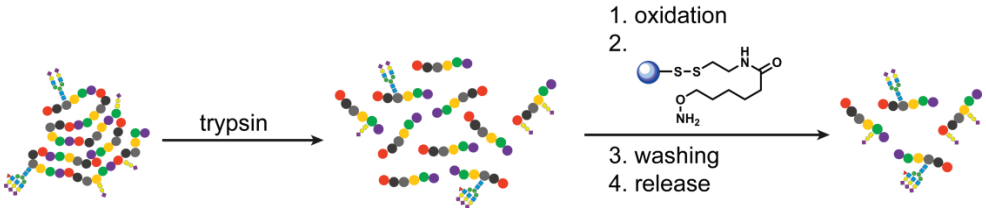
Glycoproteins are a potential source for biomarker discovery in order to detect diseases at early stage and to increase patient survival. It is known that disease progression is often related to pathway dysregulation including changes of the glycosylation extension as well as the carbohydrate structure.

Nowadays, a part of the strategies adopted for glycoproteins studies comprises chromatography separation methods or enrichment combined with standard proteomic analysis using mass spectrometry (MS). However, due to glycoprotein microheterogenity, it is hard to isolate glycopeptides obtained only in small quantites, compared to the total amount of peptides. For these reasons it is important to develop methodologies that specifically can enrich glycopeptides or glycoproteins from others.

A combined method for glycoprotein/glycopeptide enrichment and labeling is here described through introduction of bioorthogonal functional groups. Aldehydes react with hydroxylamine compounds to form an oxime linkage under physiological conditions. We have improved the methodology for oxime ligation enrichment of glycopeptides/glycoproteins by introducing a cleavable tag and labeling strategy. Our strategy enables the enrichment of negative charged and neutral glycopeptides.



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Stereo-Helicates as Molecular Spring

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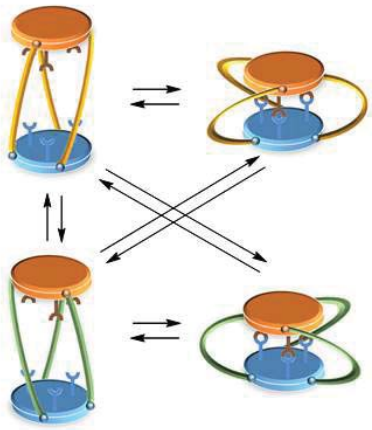
The helicate, in nature, is a specially attractive topology. As seen in biological systems, DNA uses stabilized supramolecular forces to form the shape of a double helix1, which performs crucial tasks, such as catalysis, gene expression, etc..

Our group is focusing on fabricating molecular springs by using self-assembled helicates. The molecular springs could expand and contract by releasing or binding of lithium. Further, by introducing the chiral group, the molecular springs show the opposite stereochemistry depending on the nature of the alkaline metal counteraction.



[3 + 3]-Annulation and Ring Opening 1,3-Bifunctionalization of Donor-Acceptor Cyclopropanes

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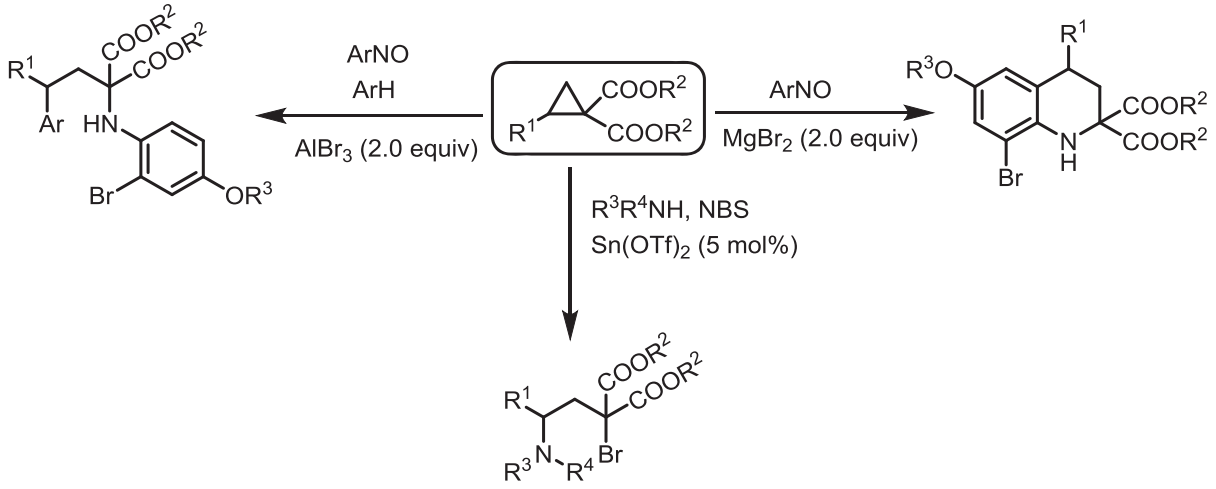
ABSTRACT: A chemodivergent process involving donor-acceptor (DA) cyclopropanes and nitrosoarenes under the influence of Lewis acids has been developed. In the presence of $MgBr_2$ as a stoichiometric Lewis acid and reagent, C-8 brominated tetrahydroquinolines are obtained via a stereospecific [3+3] annulation. On the other hand, with $AlBr_3$ as the stoichiometric Lewis acid a multicomponent ring opening reaction between DA-cyclopropanes, nitrosoarenes including the solvent as reaction partner is achieved. Along with that $Sn(OTf)_2$-catalyzed 1,3-aminobromination of donor-acceptor cyclopropanes with various sulfonyl amides or electron poor anilines and N-bromosuccinimide is also reported. Reactions which are easy to conduct proceed under mild conditions and the products can readily be further functionalized, rendering these processes highly valuable.



Scheme 1: 1,3-Bifunctionalization reactions of donor-acceptor cyclopropanes.

References:

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UDP-derived *α,β*-Methylenediphosphonates as CD73 Inhibitors

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Ecto-5'-nucleotidase (CD73) is part of the purinergic signalling and catalyses the hydrolysis of extracellular AMP to adenosine. The formed adenosine promotes the growth of several tumour cell lines by activation of P1 receptors, which suppress immune cells and promote angiogenesis.[1] Inhibition of CD73 has the potential of decreasing the extracellular adenosine level and is, therefore, offering a promising novel target for cancer therapy. Only a limited number of potent CD73 inhibitors was discovered so far.[1] Herein we present the development and pharmacological evaluation of a new class of potent UDP-derived CD73 inhibitors.

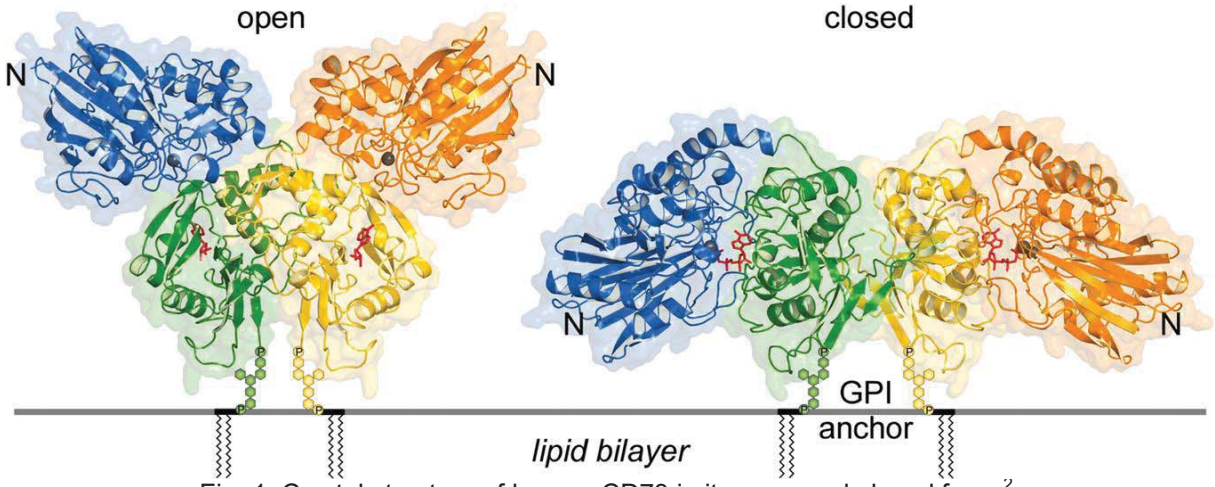

Fig. 1: Crystal structure of human CD73 in its open and closed form.[2]

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Selective Cleavage of C–O Bonds through Boron-Catalyzed Deoxygenation

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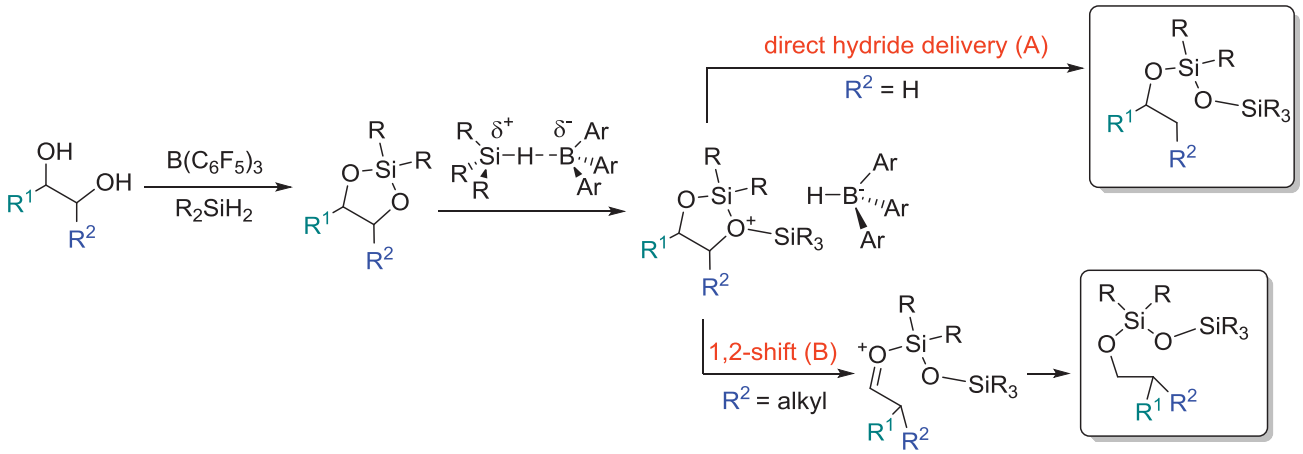
Abstract:

The alcohol group is one of the most widespread functional groups in organic synthesis. Moreover, the presence of alcohols in renewable feedstocks, such as carbohydrate derivatives, highlights the need for new methods that are able to transform hydroxyl groups selectively. A formidable challenge in this area is the predictable and selective deoxygenation of a single alcohol group within an array of hydroxyl groups.

In this context, we have developed a regioselective deoxygenation of 1,2-terminal diols at the primary position, facilitated by the strategic formation of a cyclic siloxane intermediate.[1-2] Furthermore, the same catalytic system, when applied to unactivated internal diols, can promote a unique, pinacol-type reductive rearrangement that proceeds via a concerted mechanism.[3]



References:

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Molecular Docking Study of the Action Mechanism of the Antimicrobial Peptides Ib-M

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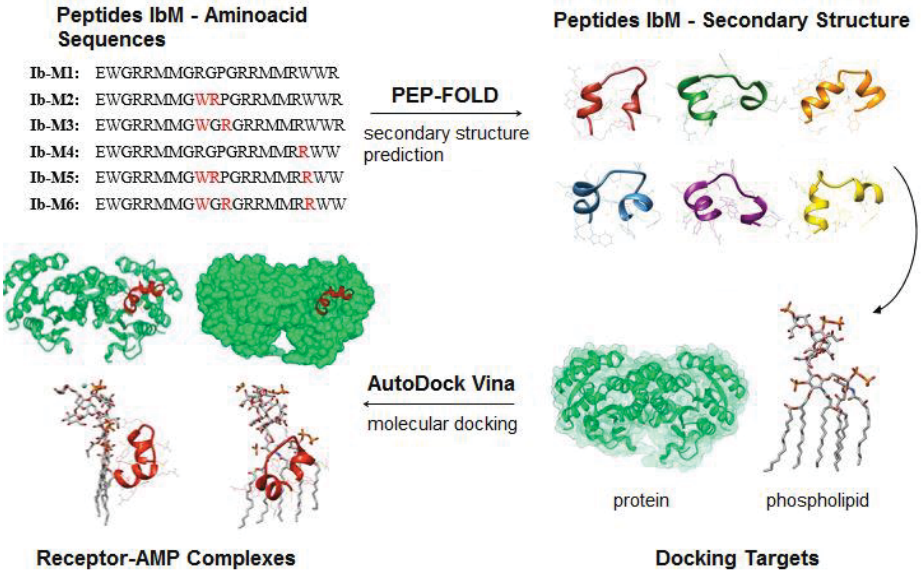
The extensive and indiscriminate use of conventional antibiotics for treatment of infectious diseases has led to an increased pathogenic resistance [1]. Therefore, the development of new antimicrobial compounds is of great importance. In this context, antimicrobial peptides (AMPs) have emerged as a promising alternative [2]. AMPs are a component of the immediate non-specific defense mechanism of all living organisms and exhibit a broad spectrum of antimicrobial activity, being active against bacteria, fungi, virus and parasites.

Recently, six AMPs analogues of Ib-AMP4 (a natural AMP isolated from seeds of *Impatiens balsamina*) were synthesized, which were denominated as peptides Ib-M and display potent antibacterial activity (IC_{50} = 1-50 μM) against *Escherichia coli* [3]. With the aim to gain a deeper understanding on the action mechanism of the peptides Ib-M, we have used a molecular docking approach to model the formation of non-covalent complexes between the latter and several potential targets of *E. coli*. PEP-FOLD [4] was used to predict the secondary structure of the peptides, while docking calculations were performed with AutoDock Vina [5] (Scheme 1). All receptor-IbM complexes were analyzed regarding peptide-binding site and binding affinity.



Scheme 1

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QM/MM Study of the Taxadiene Synthase Mechanism

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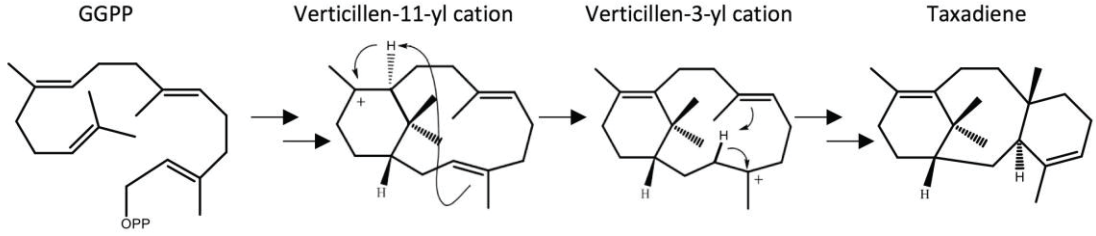
Taxol is a polycyclic diterpenoid natural product exhibiting a wide range of anticancer activity [1]. It is therefore widely used in chemotherapy. The current industrial production process of Taxol involves a very expensive semisynthetic route [2]. Therefore, the design of other synthesis strategies for its large-scale production is of great importance. Molecular insights into the pathway for the biosynthesis of Taxol may pave the way for the design of an improved synthetic route and is an active research area [3-5].

In this work, we present a detailed mechanistic view of the cyclization of (*E*,*E*,*E*)-geranylgeranyl diphosphate (GGPP) to taxa-4(5),11(12)-diene (taxadiene) catalyzed by taxadiene synthase (TXS), using a quantum mechanics/molecular mechanics (QM/MM) approach. See Scheme 1. This is the first committed step of Taxol biosynthesis in the Pacific yew (*Taxus brevifolia*). The reaction occurs via a carbocation cascade [3-5]. Explicit solvent molecular dynamics (MD) in water has been performed for the TXS verticillen-11-yl carbocation intermediate (Scheme 1) proposed to be a key reaction intermediate [3,4]. Several snapshots were selected from the MD trajectory and used in subsequent QM/MM calculations. In QM/MM geometry optimizations and reaction path calculations the MM region was treated using the CHARMM forcefield and density functional theory (M06-2X/TZVP) was used to treat the QM region.



Scheme 1. Geranylgeranyl diphosphate cyclization to taxadiene catalyzed by TXS.

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Making and Breaking Barriers to Overcome Microbial Infections

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Advanced methods for preventing and controlling hospital-acquired infections via eradication of free-floating bacteria and bacterial biofilms are of great interest. In this regard, attractiveness of unconventional treatment modalities such as antimicrobial photodynamic therapy (aPDT) continues to grow.[1] This study investigated a new and innovative strategy for targeting polysaccharides found on the bacterial cell envelope and the biofilm matrix using boronic acid functionalized and highly effective photosensitizer (PS) silicon(IV) phthalocyanine (Figure 1). This strategy has been found to be successful in treating planktonic cultures and biofilms of Gram-negative *E. coli*. An additional advantage of boronic acid functionality is a possibility to anchor the tailor made PS to poly(vinyl alcohol) and to fabricate a self-disinfecting coating.[2]

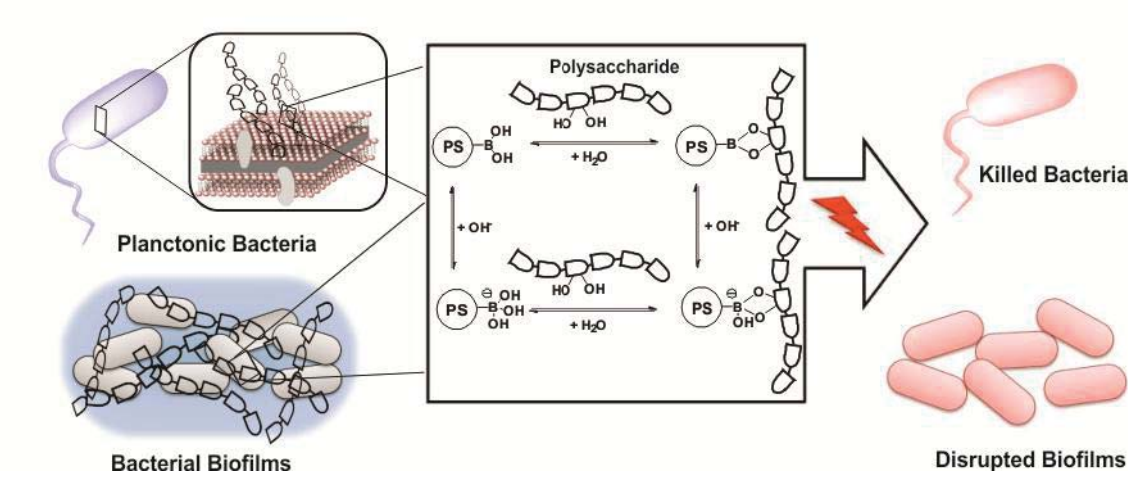

Figure 1. *Schematic illustration of interaction between photosensitizer and polysaccharides of the bacterial cell membrane and biofilm matrix*

Financial support from Deutsche Forschungsgemeinschaft (DFG), project GA 2362/1-1 and SFB 1009, TP B05, Fonds der Chemischen Industrie and GlaxoSmithKline is gratefully acknowledged.

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Triaminoguanidinium Based Ligands: Versatile Building Blocks in Supramolecular Chemistry

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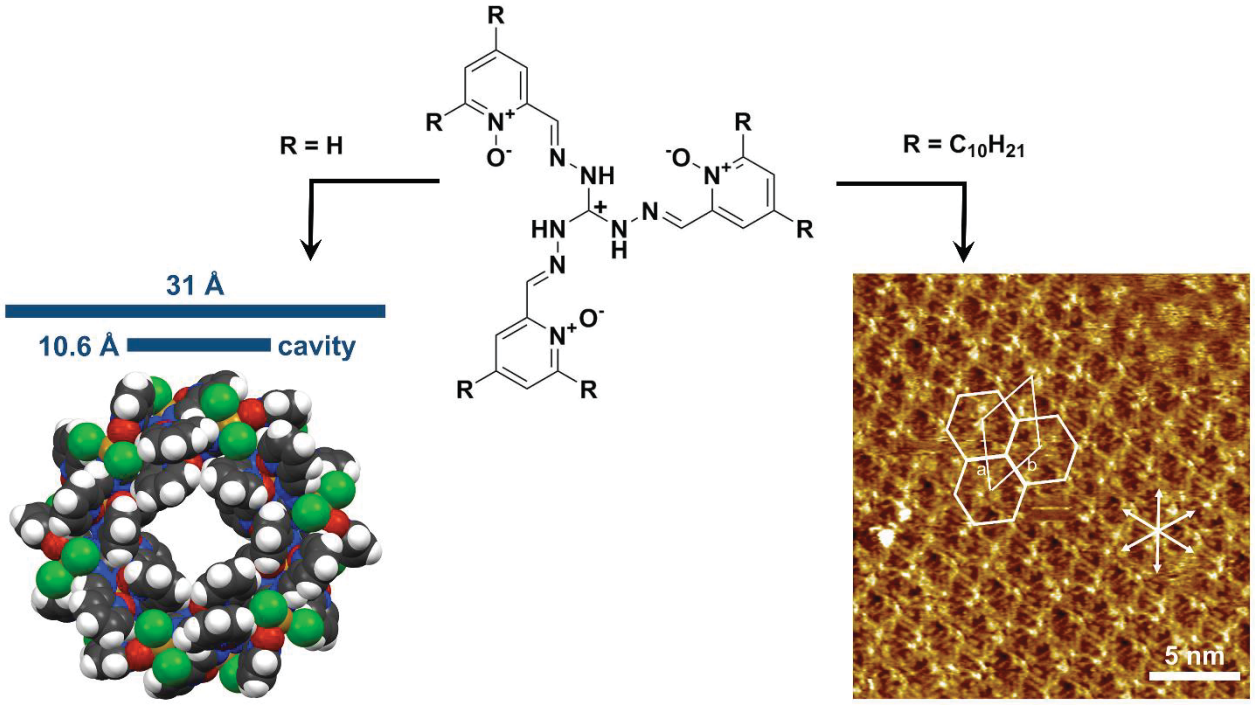
C_3-symmetric triaminoguanidinium based ligands are able to coordinate soft metal ions like Zn(II), Cd(II) or Eu(III) as well as hard metal ions like Ti(IV) or Zr(IV) in their tridentate chelating binding pockets. As the combination of ligands and metal ions provide flexible coordination environments, a variety of different discrete supramolecular coordination cages, such as tetrahedra, octahedra and trigonal bipyramids, are accessible.[1] Some of these compounds showed activity in ring opening lactide polymerization. A donut shaped coordination compound with a diameter of 31 Å will be presented which exhibits a spherical cavity of about 10.6 Å. This cavity can be utilized as selective reaction chamber. Attachment of long alkyl chains to the ligand leads to self-assembly in a honeycomb like structure at the liquid/HOPG interface.[2], [3]



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Multicomponent Nanorotors based on different types of noncovalent interaction

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Two different types of Nano rotors have been developed based on (i) $N_{pyridine}$→ZnPor coordination and (ii) dipolar electrostatic interaction between crown and triazolium moieties. The fusion of two homoleptic complexes was used to create a quantitative three-component Nanorotor **1** (Figure 1). The intra-supramolecular rotational dynamics in Nanorotor **1** leading to a rapid exchange of two $N_{pyridine}$→ ZnPor interactions was measured using VT-^{1}H NMR. The rate constant was determined to be k ~ 24000 s^{-1} at 298 K and the activation free energy $\Delta G^{\ddagger}_{298}$ = 48.3 kJ mol^{-1}. Nanorotor **2** was quantitatively self-assembled by addition of one equiv of Cu^+ to a 1:1 mixture of ligand **A** and **B** (Figure 2). The exchange of crown arm between two triazolium stations was not observed in VT-^{1}H NMR (up to 198 K), indicating a high rotational speed.

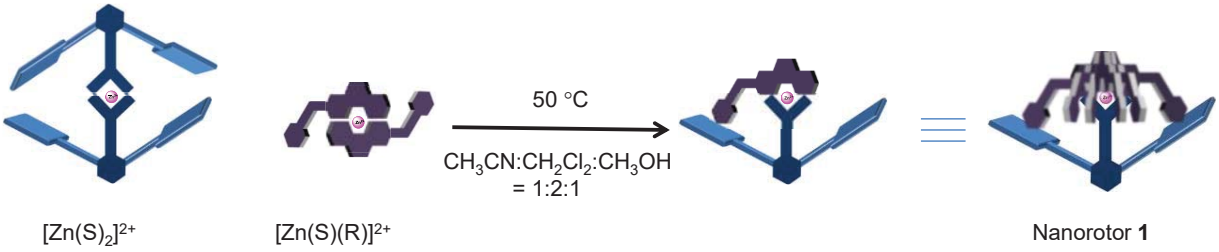

Figure 1. Cartoon representation of fusion process to produce Nanorotor **1**.

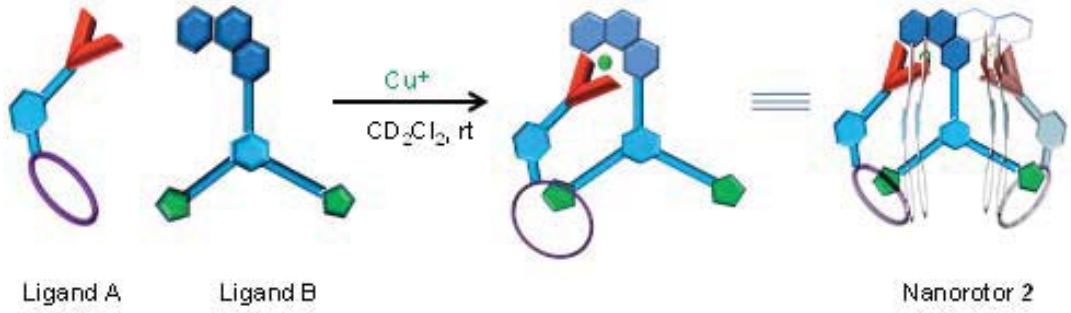

Figure 2. Cartoon representation of preparation of Nanorotor **2**.

Tools to enable complex fluorescence labelling schemes for single-molecule FRET experimentes

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DNA topoisomerases are molecular machines that convert chemical energy into conformational changes and couple these to the interconversion of different DNA topoisomers [1]. To observe such conformational changes and thereby gain insight into role of conformational dynamics for enzymatic activity single-molecule Foerster Resonance Energy Transfer (smFRET) has become a widely-used tool [2]. The fluorophore attachment is a sophisticated task which becomes even more demanding when a statistic labeling approach is inadequate. Though the introduction of non-canonical amino acids has given access to a wide variety of labeling chemistries, homodimeric proteins pose a particular challenge for protein chemists [3].

Here we present biochemical tools that can be used in combination to enable complex fluorescent labeling schemes, and illustrate how they can be exploited to dissect conformational changes by single molecule FRET – using the type II topoisomerase DNA gyrase as an example. DNA gyrase is a heterotetramer that consists of two GyrA subunits – forming a stable dimer – and two GyrB subunits ($GyrB_2 \cdot GyrA_2$). To ensure heterotetramer stability under single-molecule conditions we fused both subunits to form a GyrB-GyrA fusion protein [4]. To address the role of (a-)symmetry of DNA gyrase, we purified asymmetric fusion proteins using tandem affinity purification (TAP). Thereby, we were able to purify a protein containing one GyrB-GyrA subunit and one GyrA subunit, or other asymmetric combinations. Furthermore, we generated a GyrB-GyrA fusion protein using intein-mediated protein ligation (IPL). TAP allows one to separately purify subunits or even domains, which is especially usefull for homodimeric proteins, while retaining full enzymatic activity after the IPL. We also introduced non-canonical amino acids to be able to couple fluorophores site-specifically and are exploring on the use of donor/quencher pairs to monitor conformational changes. In conjunction, these approaches enable one to realize complex labeling schemes, and thereby follow simultaneous conformational changes in multi-domain proteins. Application of these approaches to other topoisomerases, such as reverse gyrase, will lead to a detailed mechanistic understanding of conformational changes and their role for enzymatic activity.

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Regioselective thiocarbonylation of vinyl arenes

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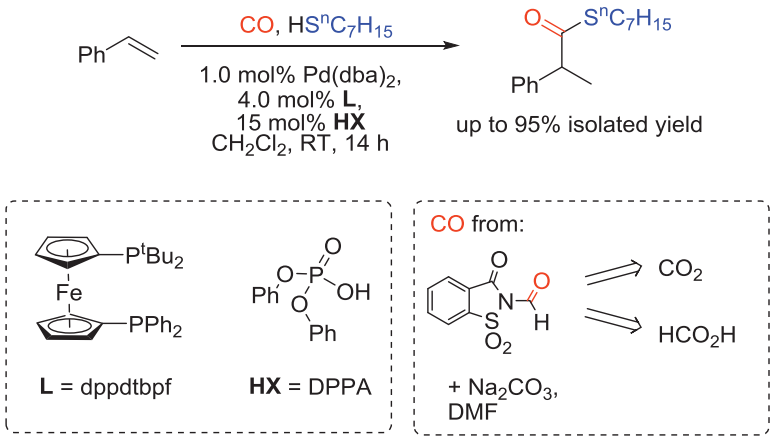
Synthesis of thioesters

Thioesters constitute a compound class with immense biological importance, since they are intermediates in many processes in which ATP is either used or regenerated.[1] Moreover, they are also of considerable interest for synthetic organic chemists.[2]

Among the known methods for the synthesis of thioesters, thiocarbonylation constitute the most atom-economic way to produce them from available feedstock. However hydrothioesterification of alkenes is only known from the transformation of allenes,[3] conjugated dienes[4] or vinylcyclopropanes[5], whereas those reactions require harsh reaction conditions such as high temperatures (100 °C), pressures (27 bar) and Pd-loadings from 3-5 mol%. We investigated the first regioselective thiocarbonylation of vinyl arenes, which moreover proceeds under mild conditions (2.5 bar CO pressure, RT, 1 mol%) and generates exclusively the branched product.[6] In order to avoid utilization of gaseous CO we were able to demonstrate the use of a recyclable CO surrogate (*N*-formylsaccharin) applying a two-chamber system.



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Synthesis of substituted pentacene derivatives and functionalized cyclooctynes for the study of organic/semiconductor interfaces

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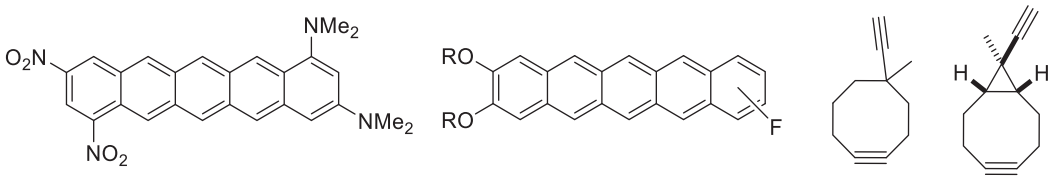
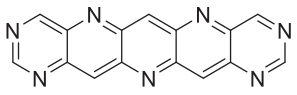
Internal interfaces between two solid phases like semiconducting- and organic-materials are an important issue for different applications in organic electronics.[1] To obtain a detailed understanding of the structure and dynamics at internal interfaces two different systems were investigated: Pentacenes as potential semiconducting materials (**A**) and cyclooctynes as precursors for thin film preparation of well-defined thickness (**B**).
The performance of pentacenes and *N*-heteroacenes in thin-film devices is determined by their solid-state packing motifs which can be influenced by introducing a permanent dipole moment.[2] Here we report on the synthetic progress towards compounds, comprising electron-rich and electron-poor moieties such as **1** and **2** as well as *N*-heteroacenes (like **3**) with an exceptionally high *N*-content which are potential n-type semiconducting materials.[3]



1 **A** **2** **4** **B** **5**



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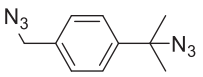

6

Necessary prerequisites for the construction of structurally defined layers with an “double-click” approach are cyclooctynes like **4** and **5**, bearing different functionalities and a bisazide **6** with inherently different reactivities. Preforming the layer-by-layer synthesis for a well-defined thickness an assembly on a three dimensional model system was applied. This model system with the bisalkynes (**4** and **5**) and bisazide **6** should give a prediction about the chemoselectivity on semiconducting surfaces.[4]

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Specific detection of pyrimidine nucleobases by metal-mediated base pairing

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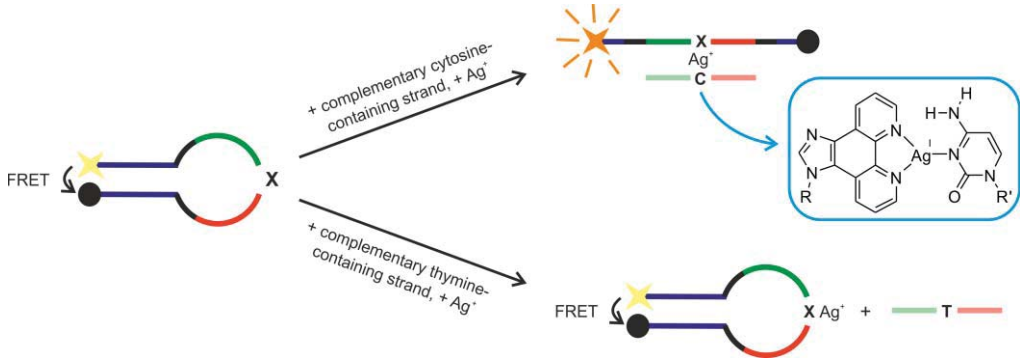
DNA is a biological macromolecule responsible for storage, transport and decoding of genetic information. A way to diversify nucleic acid is the introduction of artificial base pairs. These can either rely on hydrogen bonding or the hydrogen bonds can be replaced by coordinate bonds to metal ions. In these metal-mediated base pairs, the nucleobase can be formally substituted by a ligand which is predesigned to bind a certain metal ion. Here complementary bases are held together by coordinate bonds to the metal ion in the centre. The research of metal-mediated base pairs in nucleic acids is stimulated by the extraordinary success of its ability for site-specific functionalization. Possible application with artificial nucleobases include an expansion of the genetic four letter code, sensing of metal ions, charge transfer through DNA, synthesis of DNA-templated nanoparticles, metal dependent redox or photochemical catalysis etc. [1]

1,10-Phenanthroline (phen) is a very popular ligand because phen and its derivatives are widely used as receptors and DNA intercalating agents[2]. The planarity of its imidazole-appended derivative (imphen) makes it preferable as an artificial ligand-based nucleobase in DNA duplexes due to its stabilizing π-stacking interaction with neighbouring bases.

Here we report a GNA functionalized imphen for an introduction as artificial nucleobase. (GNA: glycol nucleic acid) We performed a systematic study of imphen-M-pyrimidine hetero base-pair formation, and thereafter developed a molecular beacon capable of discriminating the pyrimidine nucleobases.[3] The concept of molecular beacon was further used for the detection of SNP-related diseases like breast cancer and pancreatic cancer. The success of this approach significantly extends the application spectrum of metal-mediated base pairing. (SNP: single nucleotide polymorphism)



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Acknowledgements

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Comprehensive Strategy to Access Chiral Cyclopentadienyl Ligands for Asymmetric C–H Activation

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Cyclopentadienyl-based metal complexes are widely used as homogeneous transition-metal catalysts.[1] Despite their considerable potential, the corresponding enantioselective processes remain largely underexplored due to lack of chiral cyclopentadienyl (Cp) ligands with highly enantioselective catalytic efficiency. Currently only few chiral Cp ligands are available which are either widely applicable but limited in structural variability, or structurally variable but limited in applicability (Figure 1). Therefore, a conceptually general approach to chiral Cp ligand discovery would be invaluable that allows to discover widely applicable Cp ligands and to efficiently and rapidly vary and tune their structures.

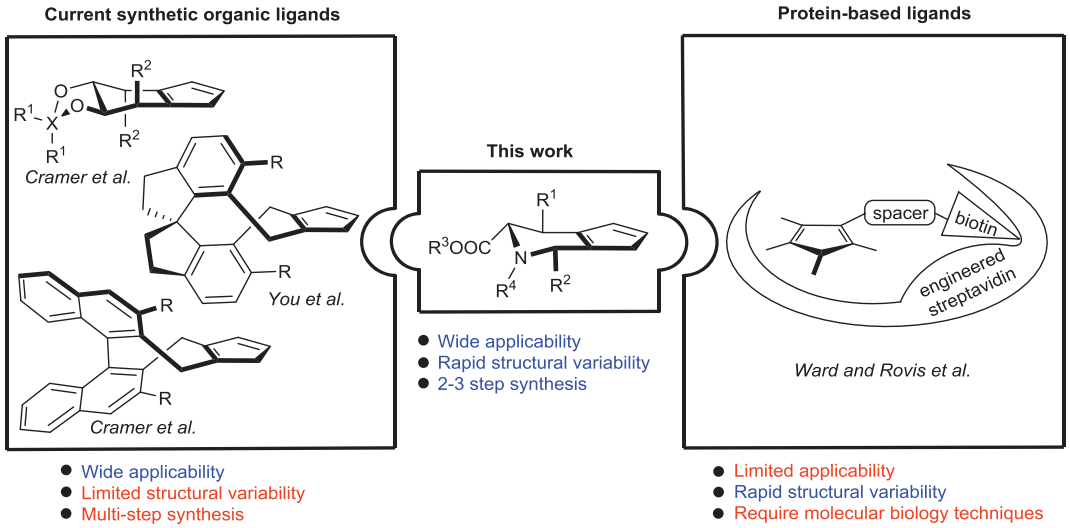

Figure 1. Present chiral Cp ligands and our strategy

Here we describe the 3-step gram-scale synthesis of a structurally diverse and widely applicable chiral Cp ligand collection through asymmetric [6+3] cycloaddition.[2] Their modular nature and their amenability to rapid structure variation enabled efficient discovery of ligands for three enantioselective Rh(III)-catalyzed C–H activation reactions, including one unprecedented transformation. This novel approach should enable the discovery of efficient chiral Cp ligands for various further enantioselective transformations.

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Selective C8-metalation of various purine nucleosides

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Purine nucleobases are essential building blocks of DNA and RNA, which provide important binding sites in nucleic acids. They are excellent ligands for metal ions and usually form Werner-type complexes using the N-donor atoms of the nucleobase skeleton. Most recently, the regioselective C-metalation of purines as caffeine and 9-methyladenine has been reported,[1] which are rare examples of a C8-metalated purine nucleobase synthesized by oxidative addition.

Here we show that not only free purine nucleobases can be C8-metalated but also nucleosides (nucleobase + pentose) such as adenosine and guanosine. For the oxidative addition the introduction of a carbon-halide bond (C8–Br) as well as the protection of the hydroxyl groups (here by acetylation) is essential (Figure 1).

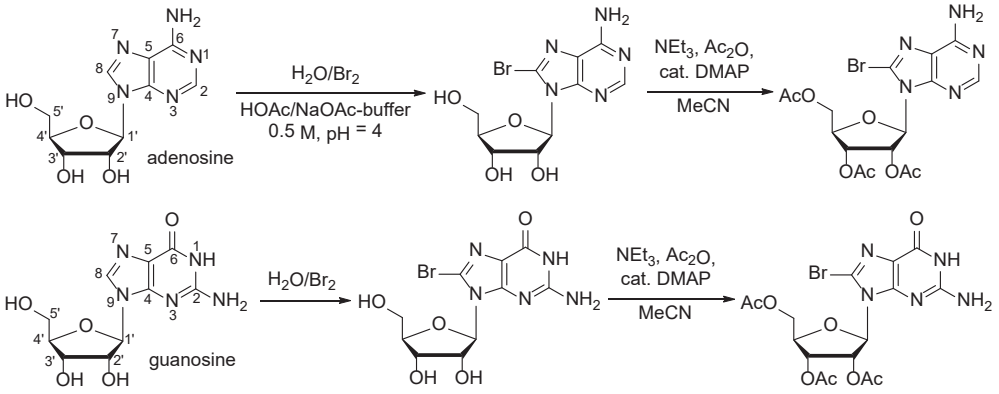
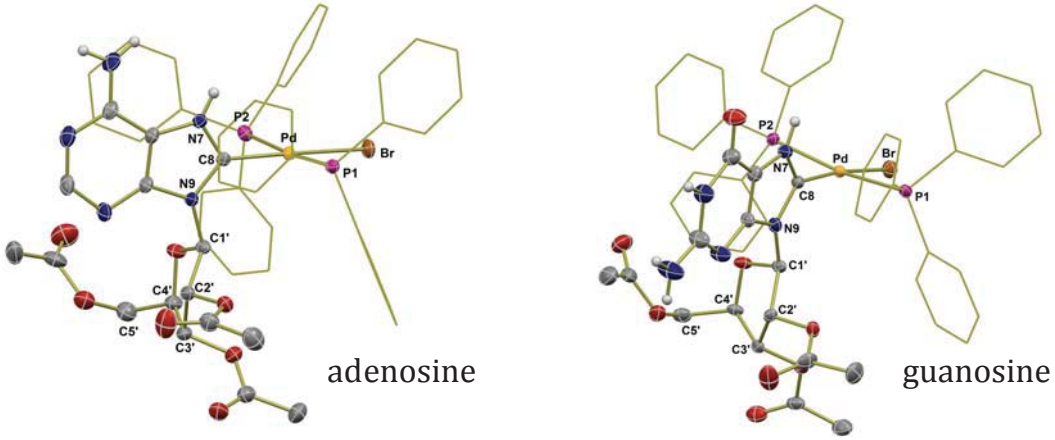


Figure 1: Synthesis of the brominated acetyl-protected nucleosides.

The purine nucleobase reacts selectively at the C8-position with metal precursors such as $[M^0(PPh_3)_4]$ (M =Pd, Pt), followed by N7-protonation, to form novel chiral C8-metalated nucleoside NHC metal complexes (see molecular structures below).



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DNA Structuring using Laser Writing and Light Triggered Chemistry

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Keywords: photo-active oligonucleotides, direct laser writing, DNA-directed immobilization

DNA patterned surfaces have found numerous applications in design of biological devices, biosensors and optoelectronic devices. Various attachment strategies, ranging from covalent to electrostatic, have been developed to obtain DNA functionalized surfaces.
Among the established structuring techniques, photolithography is widely used due to the relative ease of control over the structural features and positions of the molecules by use of the shadow masks. However, this requires mask preparation for each new pattern, the method is not capable of multiplexing and the resolution is restricted to several micrometers, which is not suitable for certain bioanalytical application such as studies of single cells or protein-protein interactions. To overcome these drawbacks and enable one-step fabrication of DNA patterns with sub-micrometer resolution, we have developed light triggered click chemistry and employed direct laser writing (DLW) to covalently anchor DNA to glass surfaces. Fully functional patterns containing multiple single stranded DNA sequences with sub-micrometer resolution were produced and used for further attachment of small molecules and proteins via DNA directed immobilization.
Such strategy will allow for development of advanced structured surfaces for use in bioengineering and cell immobilization.

References

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Benchmarking Structures and Vibrational Frequencies from Subsystem DFT

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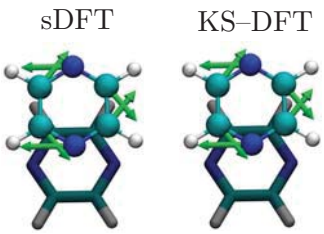
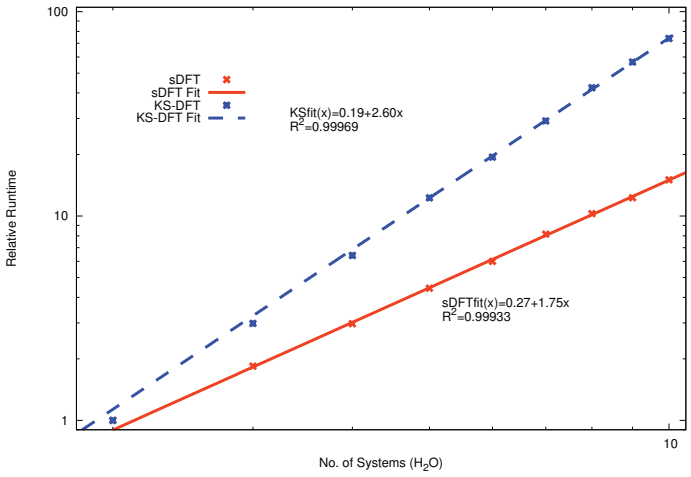
Describing reaction pathways with computational methods can be a demanding task even for Kohn-Sham density functional theory (KS–DFT), especially if explicit solvation needs to be considered. Subsystem DFT (sDFT), a fragment-based approach to density functional theory, is an efficient alternative to KS-DFT [1-4]. By partitioning the total electron density $\rho_{tot}(r)$ into a set of smaller subsystem densities, the ansatz introduces linear scaling with the number of subsystems.



Sample mode from S22 stacked pyrazine dimer structure at 1303.85 cm^1 (sDFT) / 1306.12 cm^1 (KS–DFT).



Comparison of supersystem gradient calculation relative run time with increasing system size for sDFT and KS-DFT on H_2O clusters.

Here, we discuss a benchmark study of our analytical sDFT gradient implementation into our groups quantum chemistry program Serenity [5]. In addition, an implementation of a semi-numerical Hessian as a prerequisite for thermochemistry and vibrational frequency calculations is presented. Numerical gradients and results of previous successful implementations of sDFT gradients based on subsystem approaches [6-7] serve as a reference for testing of the embedding gradients.

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Supramolecular Gel Formation controlled by UV-Light induced Dynamic Covalent Chemistry

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Dynamic covalent chemistry (DCC) covers equilibria of reversible reactions that involve breaking and bonding of covalent bonds.[1] The photo-induced radical disulfide metathesis is a dynamic covalent reaction, which requires presence of UV light to induce the homolytic cleavage of the covalent disulfide bonds, thus offering the opportunity to build systems that are inactive by default and can be made dynamic covalent on demand. [2]

We used the PRDM to generate two symmetrical disulfides from the corresponding mixed asymmetrical disulfide.[3] One of those homodimers is a well-known cystine based hydro-gelator. An aqueous solution of the heterodimer yields an opaque gel after about 3 h UV irradiation by a handheld 8 W UV lamp, as it can be commonly found in many labs.

In the Future we hope to utilize the photo-induced radical disulfide metathesis for other dynamic covalent systems, such as dynamic combinatorial libraries for molecular recognition.

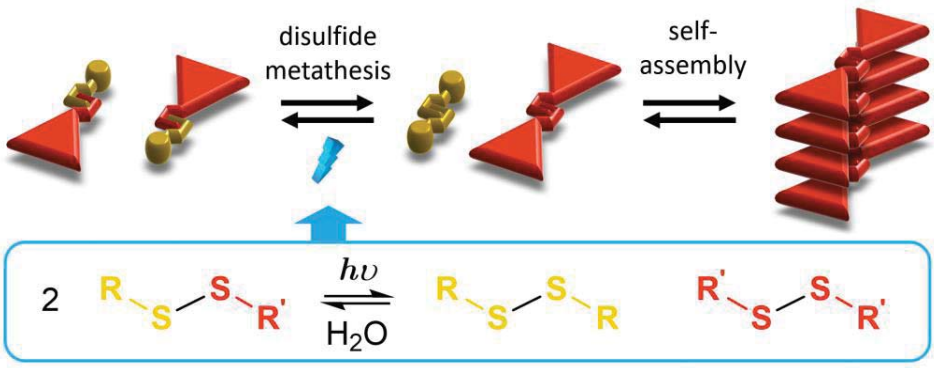

Figure 1: Generation of symmetrical disulfides from an asymmetrical disulfide by UV irradiation and subsequent gelation.

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Structural investigation of amorphous residues from catalytic dehydrogenation of hydrazine borane using solid state NMR

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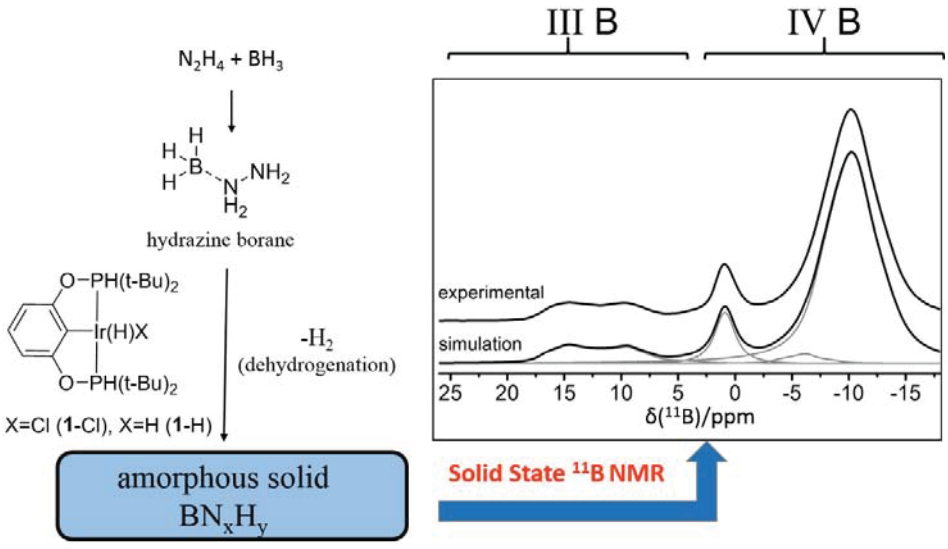
Research on chemical hydrides being feasible hydrogen storage materials has gained great attention over the last decades in the field of energy storage materials.[1] For a potential application of chemical hydrides as hydrogen storage materials the hydrogen abstraction reaction needs to be characterized. Our work focusses on the catalytic dehydrogenation of hydrazine borane (HB), one potential candidate for H_2-storage, leading towards abstraction of 1 eq. H_2 and precipitation of a solid residue.[2] To approach a potential cyclisation, characterization of this material is of high interest. As this compound is amorphous and insoluble in common NMR solvents, the use of widely applied methods such as x-ray diffractometry and liquid state NMR is unfeasible. Thus, our approach takes advantage of solid state NMR, a unique tool giving insight into the close surrounding of the observed nuclei. Especially by combination of various ^{11}B SS-NMR techniques we were able to gain knowledge on the various boron species contained in the material, their individual ratio and the number of hydrogen and nitrogen atoms bound to each boron species.



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Phosphorus Bisylides: A New Class of Superbases with Two Interacting Carbon Atoms as Basicity Centers

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Classical proton sponges (such as DMAN shown in Figure 1) are known for their extraordinary basicity based on the spacial proximity of two basic nitrogen centers.[1] The unexpectedly high pK_{BH^+} values can be referred to the unfavorable repulsion of the nitrogen atoms' lone pairs as well as the formation of a hydrogen bond between the basicity centers after protonation. The most basic representatives are bisphosphazenes which exhibit two interacting Schwesinger bases (see HMPN in Figure 1).[2]

Noticing the intrinsically higher basicity of ylides compared to phosphazenes, we designed MHPN bearing two ylidic entities attached in 1,8-position to a naphthalene backbone.[3] And indeed, with a pK_{BH^+} value of 33.3 in acetonitrile solution, MHPN is by more than a hundred times more basic than its bisphosphazene analog HMPN (pK_{BH^+} (MeCN) = 29.9). However, the basicity enhancement compared to the corresponding monoylide is based on principles completely different to those previously found for nitrogen based proton sponges. Instead of forming a hydrogen bond after protonation, a fast proton exchange between the two ylidic carbon centers is observed in MHPN's monoprotonated form. This phenomenon is studied by NMR spectroscopic methods, XRD analysis and theoretical calculations.

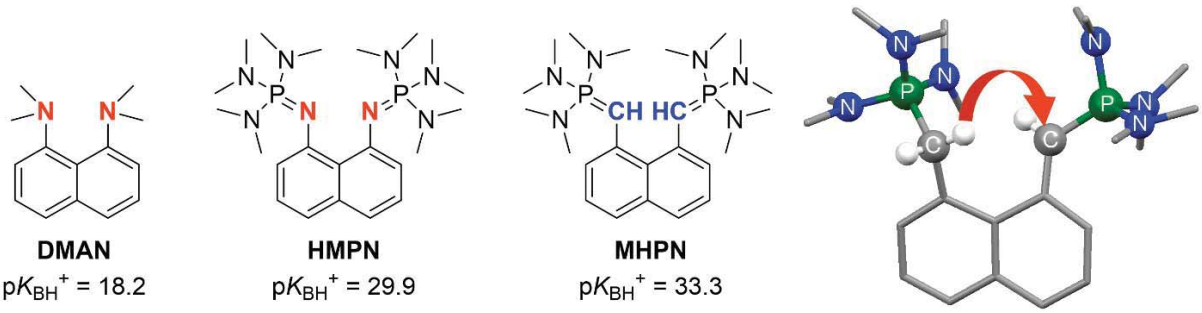

Figure 1. The first proton sponge DMAN was reported by Alder in 1968.[1] HMPN is an example of a bisphosphazene proton sponge.[2] The bisylide MHPN is the subject of our work published recently.[3] The picture on the right illustrates the proton hopping process between the basicity centers after monoprotonation.

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Metal-free synthesis of 6-azo-purines. Towards photoresponsive DNA and RNA

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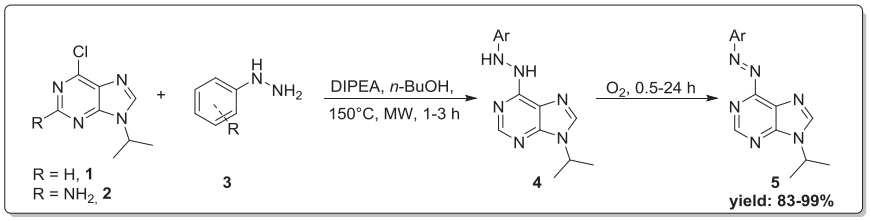
Abstract

Controlling biological processes with light is an emerging field of chemical biology.[1–5] Photopharmacology and photocontrol of nucleic acid function, as rising fields of chemical biology have constant needs towards discovery and synthesis of the new, simple and versatile biologically relevant photoswitches that are controlled by visible light. Herein, we report an efficient and diverse synthetic route to new heterocyclic azobenzenes based on the purine scaffold. This method involves metal-free microwave-assisted nucleophilic aromatic substitution of 9-isopropyl-6-chloro purines (**1** and **2**) with phenylhydrazines (**3**), followed by oxidation of *in situ* formed diarylhydrazine (**4**). The final 6-azopurines are obtained in high to excellent yields.



Scheme 1. Developed synthetic sequence, presenting diverse scope and broad tolerance of functional groups

Final compounds are shown to have red-shifted absorption maxima featuring high fatigue resistance. Their synthetic accessibility, high stability and visible-light-mediated isomerization make them ideal for biological applications.

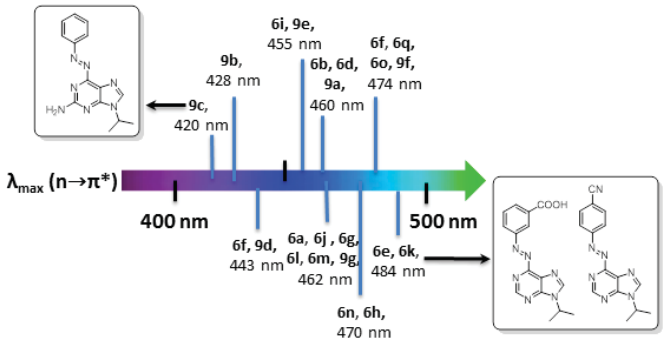


Figure 1. Spectral map that summarizes the absorption maxima (λ_{max}) that correspond to a low energy n-π* transition for a series of 6-diazopurines based on adenine (**6a-r**) and guanine (**9a-h**) scaffolds

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Synthesis and Cycloisomerisation of Cryptochiral Allenes

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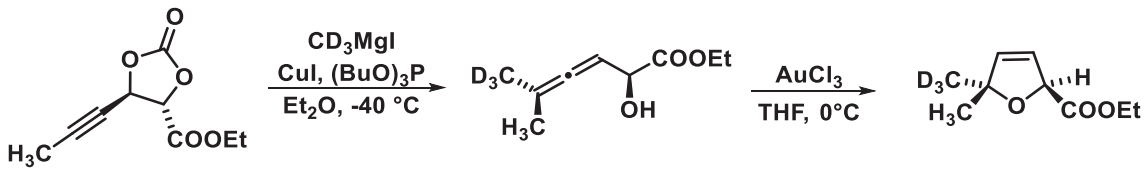
The use of organometallic reagents for the synthesis of allenes is highly developed, and several fundamentally different methods are now well established. Copper enjoys a rich history in organometallic chemistry and plays an important role in organic synthesis.[1]

The S_N2'-substitution of propargylic electrophiles with organometallic reagents is one of the most efficient method for the stereoselective synthesis of allenes. The transformation of propargyl oxiranes with organocopper compounds, which are the nucleophiles of choice, give allenes with high *anti*-stereoselectivity.[2] Likewise, an *anti*-selective S_N2'-reduction of propargyl oxiranes using an NHC-stabilized copper hydride catalyst has been developed.[3] A very promising alternative to propargylic oxiranes is the use of propargylic dioxolanones. They can easily be prepared from enynes via dihydroxylation, which can provide a route for the synthesis of enantiomerically enriched *α*-hydroxyallenes.[4]

Based on these results, we report the first synthesis of cryptochiral allenes. Cryptochiral compounds arising from the replacement of hydrogen atoms by deuterium are of interest in organic chemistry and biochemistry. These chiral compounds have a non-measurable optical rotation.[5] We used deuterated magnesium cuprates, which are formed *in situ* from a Grignard reagent and copper(I) salt in present of tributyl phosphite, for the *anti*-selective S_N2'-substitution of enantiomerically enriched propargyl dioxolanones. The cryptochiral allenes were cyclized to the corresponding 2,5-dihydrofurans with complete chirality transfer in the presence of gold(III)-chloride.[6]



Scheme 1: Synthesis of a Cryptochiral Allene by S_N2'-Substitution.

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Structural insight into multivalent SUMO-SIM interactions by a novel FRET sensor

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Posttranslational protein modifications by ubiquitin or Ubl (ubiquitin-like) proteins like SUMO (small ubiquitin-related modifier) can alter stability, location and activity of substrate proteins. [1] SUMO regulates many cellular processes, including transcription, DNA repair, signal transduction and cell-cycle control. [2] Misregulation of the SUMO pathway is related to many diseases like carcinogenesis, Alzheimer's, Parkinson's or Huntington's disease. SUMOylation of a target protein can provide a new binding site that enables non-covalent interactions between SUMO and an interaction partner containing a SIM (SUMO-Interacting motif). Most of the known target proteins are conjugated with SUMO monomers, but there is growing evidence that modification with SUMO chains also plays an important role in cellular regulation.[3] Proteins with multiple SIMs like RNF4 (RING finger protein 4) have a high affinity towards SUMO chains which is driven not by one single high affinity interaction but by the combination of multiple low affinity interactions.[4],[5]

Our aim is to investigate the structure and dynamics of SUMO chains. Therefore, we developed a linear SUMO dimer which is labeled with two organic dyes using bioorthogonal reactions. By employing FRET (Förster-resonance energy transfer), we are studying the influence of different interaction partners on the conformation of the SUMO dimer.

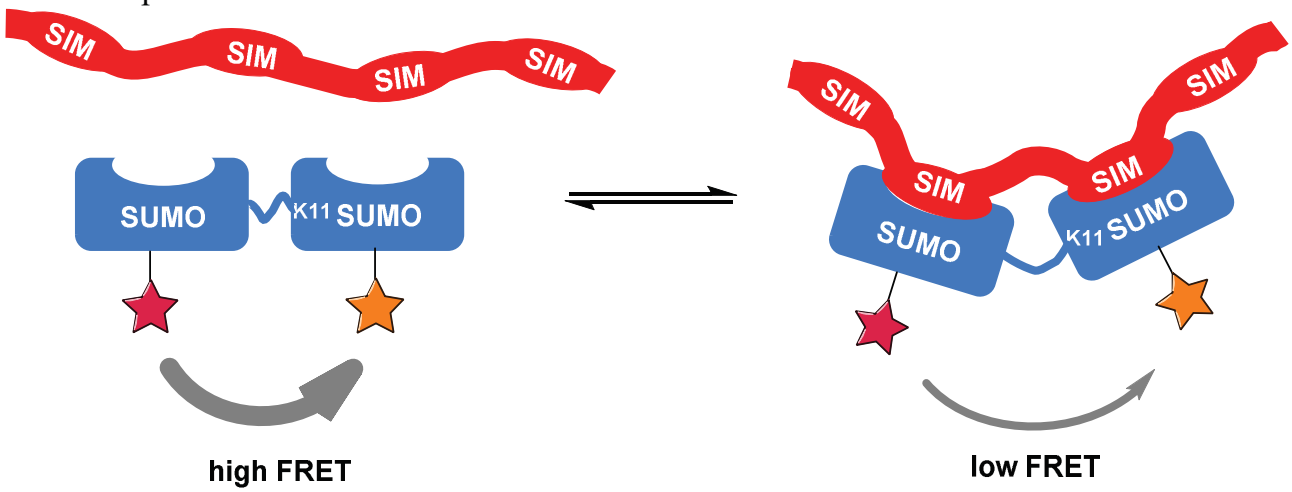

Figure 1: Conformational change of SUMO dimer due to multiple SUMO-SIM interactions

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Direct synthesis of unprotected amino alcohols and anilines through iron(II) catalysis

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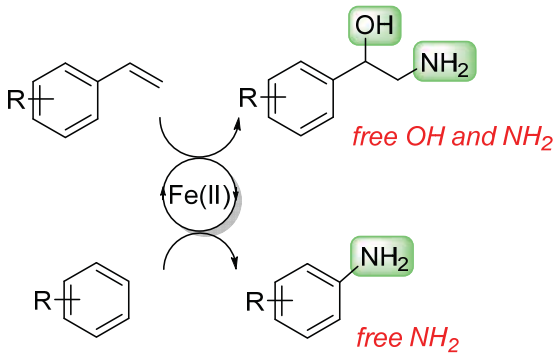
The direct introduction of unprotected functionalities represents a key challenge in organic synthesis.[1] The traditional methods that are able to introduce the amino group, a fundamental structural motif, are normally limited to the incorporation of a protected form of this functionality. The access to the unprotected primary amine is thus possible only after additional steps.[2] Herein, we describe an Fe(II) phthalocyanine-catalyzed method that is able to afford unprotected amino alcohols with perfect regioselectivity, starting from olefins.[3] The transformation was extended, with the use of an inexpensive Fe(II) salt, to the preparation of unprotected anilines from substituted arenes.[4] We demonstrated the power of this transformation to streamline the discovery of new medicines through the late-stage amination of functionalized drug molecules.



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Synthesis and Characterization of a Stable Tetrasilatetraamide

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The objective of this work is to study the formation mechanisms of strained geometry group 14 element clusters whose structures resemble the surface of the group 14 element [1]. In particular siliconoid clusters [2] are the focus of this work. The clusters will be investigated in reactions such as H_2 addition, ethylene absorption, addition of other small molecules, and redox processes.

For this purpose trihalogenosilanes [3] were synthesized and reduced with different reducing agents based on alkali and alkaline earth metals. With this approach a bicyclo[1.1.0]tetrasilatetraamide (see Figure) with two three- and two four-coordinate silicon atoms was obtained. The synthesis, characterization, and reactivity of this compound will be presented in this poster.

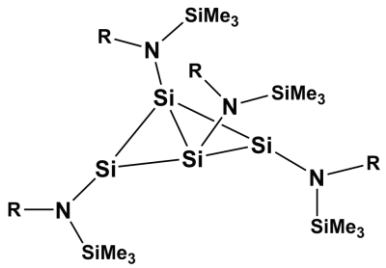

Figure 1. Structure of the Bicyclo[1.1.0]tetrasilatetraamide (R = 2,6-Diisopropylphenyl).

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Generation and Characterization of Parent Phenylphosphinidene and its Oxidation to Phenyldioxophosphorane, the Elusive Phosphorous Analogue of Nitrobenzene

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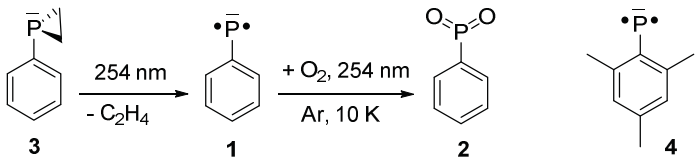
Phosphinidenes (R–P:) are the phosphorus analogues of carbenes and nitrenes. While the chemistry of carbenes and nitrenes has been well established,[1] that of the phosphinides has just begun blossoming.[2] Due to their high reactivity, the chemical properties of phosphinidenes have been deduced almost exclusively from trapping or complexation experiments.[3] Several methods for their generation have been reported in the literature.[4,5] One of the pioneering studies in this regard was the direct observation of triplet mesitylposphinidene (**4**) *via* EPR spectroscopy.[6] Phenylphosphinidene **1** is the parent of **4** and has never been observed experimentally.



Although **1** is highly reactive, its reactions with small molecules has only scarcely been studied; this would lead to several interesting novel species that have never been observed before. A prime example is the reaction of **1** with molecular oxygen (^3P-O_2) that may directly lead to phenyldioxophosphorane ($PhPO_2$, **2**), a novel compound that constitutes the phosphorous analogue of ordinary nitrobenzene.

Herein, we report the first synthesis, IR, and UV-Vis spectroscopic characterization of parent phenylphosphinide (**1**) and its oxidation product phenyldioxophosphorane (**2**). Triplet phenylposhinidene **1** was characterized by IR and UV-vis spectroscopy for the first time and matching of its spectra with density functional theory (DFT) computations. Matrix isolation studies of **1** reveal an unprecedented high reactivity towards molecular oxygen, in contrast to its nitrene analogue, even at temperatures as low as 10 K.[7]

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Why DNA Is a More Effective Scaffold than RNA in Nucleic Acid-Based Asymmetric Catalysis — Supramolecular Control of Cooperative Effects

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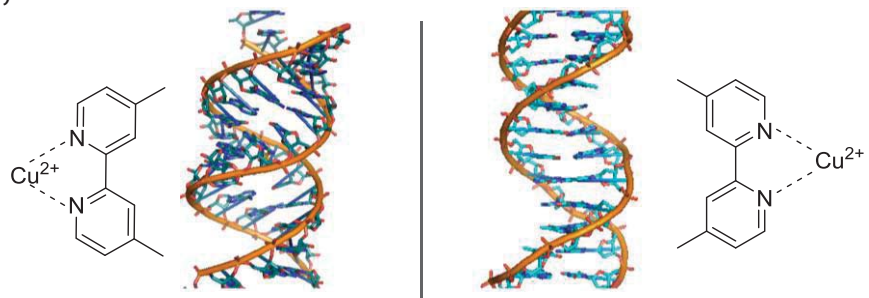
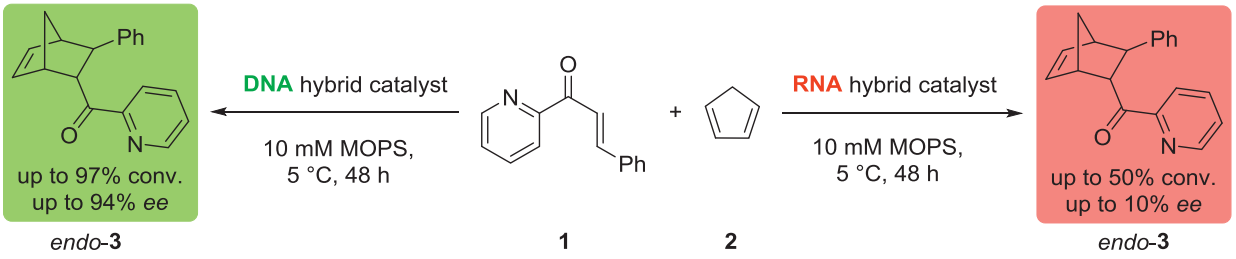
Nucleic acids have, in addition to their unique helical structure, many interesting features that make them an attractive scaffold for the development of new hybrid catalysts. Consisting of a transition metal complex and achiral ligands together with the chiral double-stranded nucleic acid, such a hybrid catalyst can be applied as a source of chirality in asymmetric synthesis.



The use of DNA-based hybrid catalysts in asymmetric synthesis was first demonstrated by *B. Feringa* and *G. Roelfes* in 2005.[1] In a copper(II)-catalyzed *Diels-Alder* reaction of azachalcone **1** and cyclopentadiene **2** the main product *endo*-**3** was generated with high enantioselectivity.[2] While DNA-based hybrid catalysts have been intensively studied, RNA-based hybrid catalysts have not been reported.

In our work we set out to investigate the suitability of RNA as a scaffold for nucleic acid-based asymmetric catalysis. More specifically, mechanistic investigations were carried out to understand the influence of nucleic acid secondary structure on catalysis in general and enantioinduction in detail.[3] To evaluate catalytic performance in a different structural context with reduced complexity, we also turned to nucleic acid hairpins, which have recently been shown to be a good model of *ds*DNA in DNA-based asymmetric catalysis.[4]



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The Fascinating Reactivity of an Active Al-N Based Lewis Pair

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Previously we reported on the synthesis of aluminium-nitrogen based active Lewis pairs. They were obtained by hydroalumination of ynamines with dialkylaluminium hydrides. These Al-N based Lewis pairs show a nice and unprecedented reactivity towards small molecules.[1, 2]

Reactions of the Al-N based active Lewis pair **1** are shown in **Figure 1**. An 8-membered heterocycle **2** was observed by treating the active Lewis pair with CO_2. This small molecule inserted in the Al-N bond and trimethylsilylacetylene was eliminated. Insertion was observed with phenyl isothiocyanate **3** by cleavage of the Al-C bond. Activation of *tert*-butyl isocyanate shows an unprecedented reaction pathway with pseudo-dimerization of the Lewis pair by condensation and formation of two new C-C bonds resulting in product **4**. In a strongly cooperative manner two C_2 and a C_1 building block are combined to afford a branched C_5 chain.

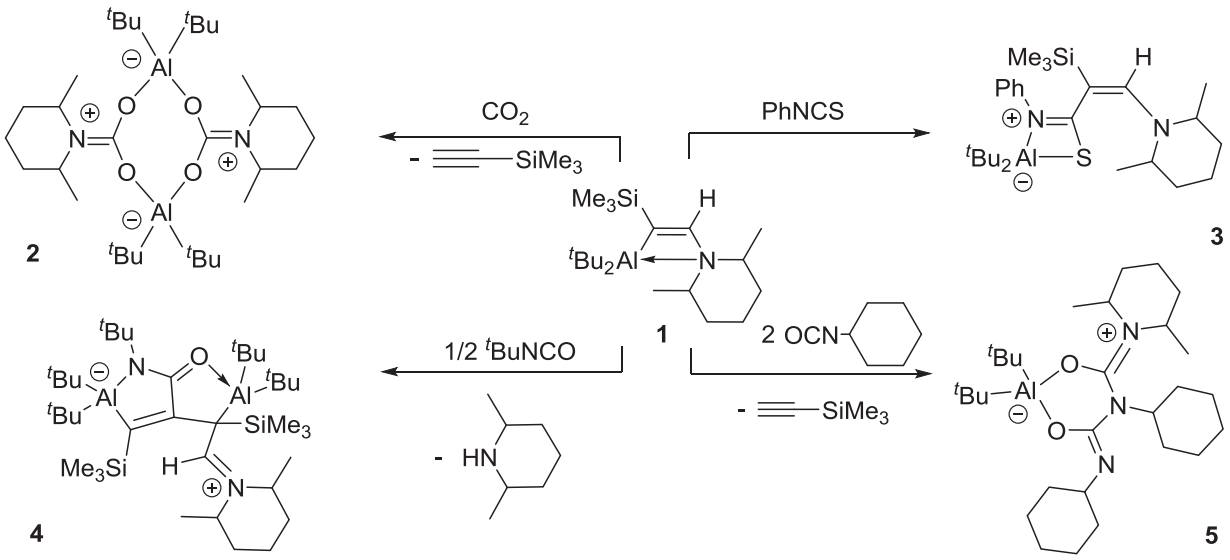

Figure 1 Overview about the differences of the reactivity of the active Lewis pair **1**.

The addition of cyclohexyl isocyanate to **1** affords **5** with a linear dimer of cyclohexyl isocyanate. Higher oligomers were observed after treating the active Lewis pair with cyanamides such as 4-morphiline carbonitrile. The resulting oligomers are linear, which is in contrast to the usually observed trimerization of nitriles to form cyclic trimers. The formation of the linear chains of the oligomers is caused by cooperativity.[3]

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Light Mediated Preparation of Palladium Nanoparticles as Catalysts for Alkyne *cis*-Semihydrogenation

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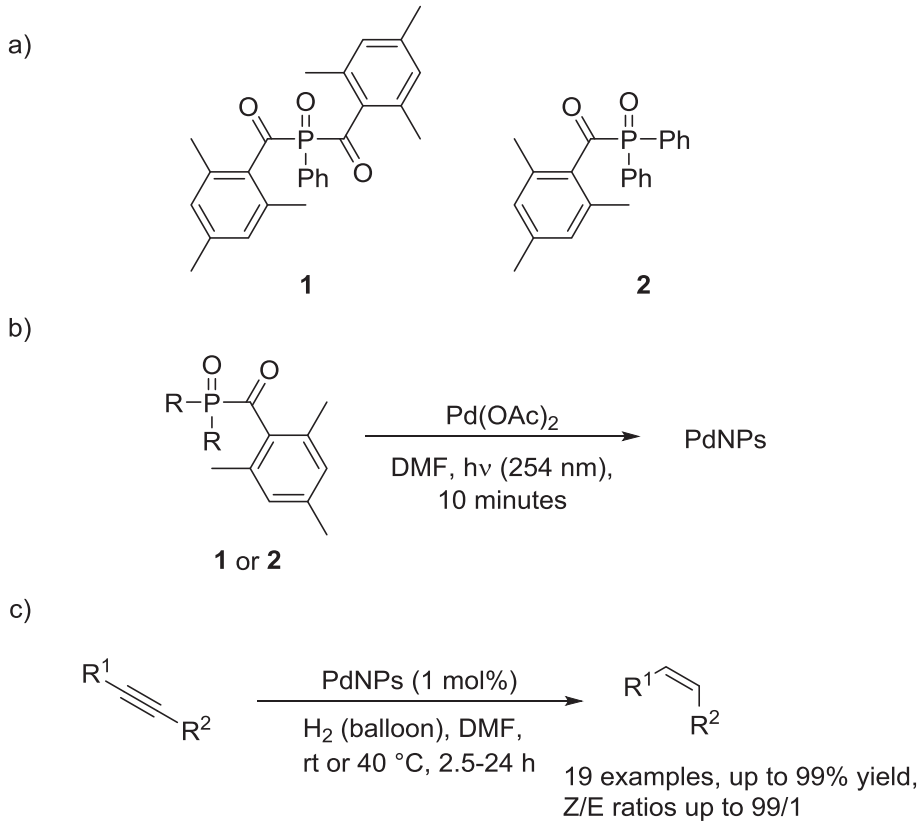
ABSTRACT: A new method for the photochemical preparation of Pd nanoparticles (PdNPs) using cheap and commercially available photoinitiators **1** and **2** was developed. Simple mixing of the photoinitiator and $Pd(OAc)_2$ in DMF and subsequent irradiation with UV-light leads to the formation of PdNPs. Importantly, PdNP preparation is very easy to conduct and reliably provides small PdNPs (2.8 nm) within a few minutes. The PdNP-hybrid material, characterized by TEM, XRD and mass spectrometry, was applied as efficient catalyst for the semihydrogenation of various internal alkynes to provide the corresponding alkenes in excellent yields (up to 99%) and Z-selectivities (Z/E-ratios up to 99/1) under mild conditions. The semihydrogenation shows broad substrate scope and tolerates various functional groups.



Scheme 1: a) Acylphosphine oxide photoinitiators **1** and **2** investigated; b) Light mediated preparation of PdNPs; c) Application of PdNPs as catalysts for the *cis*-semihydrogenation of internal alkynes.

New Strategies for Modeling Molecular Magnetic Properties

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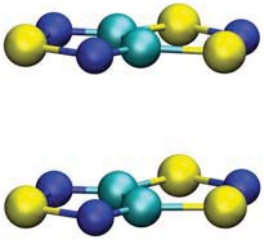
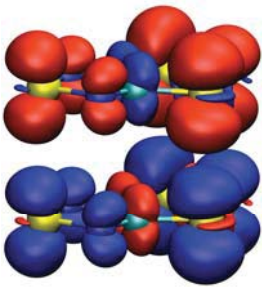
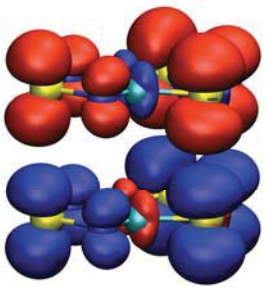
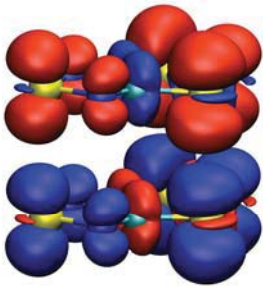
Modeling of macroscopic magnetism only from a solid-state structure is an error-prone task. Our group has recently developed a black-box approach [1] which is based on the so-called first-principles bottom-up approach [2] and qualitatively predicts and analyses the relation between a crystal structure and its magnetic properties. This method uses broken-symmetry (BS) Kohn–Sham density functional theory (KS–DFT) calculations for the prediction of magnetic coupling constants and was previously applied to various verdazyl radicals [1, 3].

KS–DFT		**sDFT**	
LDA	**B3LYP**	**LDA**	**B3LYP**
			

Nevertheless, KS–DFT has problems in describing polyradical systems due to the large system size. Subsystem DFT (sDFT) is computationally less demanding than KS–DFT and allows to predefine the spin state per subsystem. We demonstrate that sDFT is able to converge to BS-like states, even in cases where KS–DFT fails. We also illustrate that spin densities and exchange coupling constants calculated with sDFT are more robust than the ones obtained with BS KS–DFT, although the coupling constants appear to be systematically smaller.

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Imidazolin-2-ylidenaminophosphines: highly electron-rich phosphines with basic sites adjacent to phosphorus

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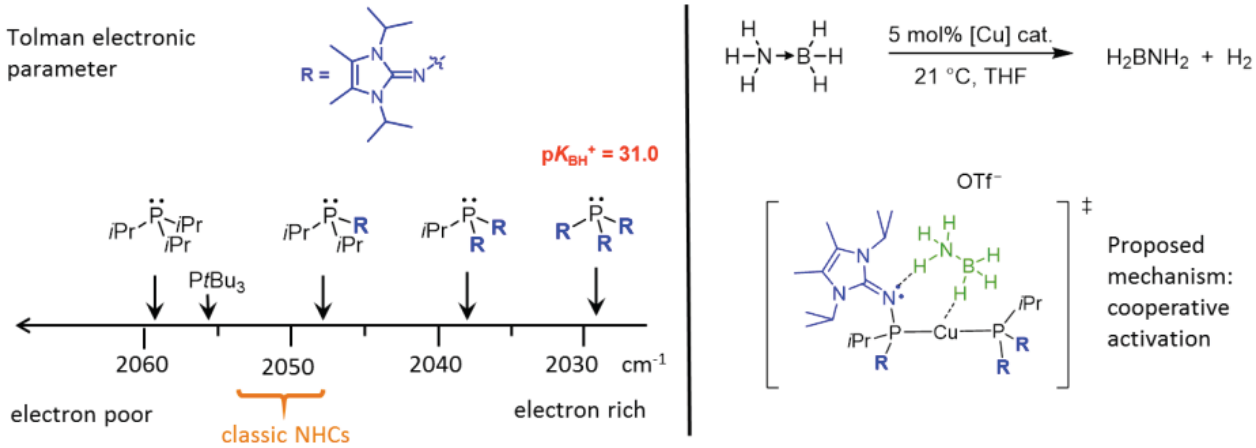
Phosphine ligands (PR_3) are widely used in transition metal-catalyzed reactions. One of their many attractive features is the fact that their steric and electronic properties can be easily adjusted in a predictable manner by variation of the R substituents. Their application as ancillary ligands in catalysis has led to major breakthroughs in many fields of academic and industrial research. Specifically, strong electron-donating alkylphosphines are the ligands of choice when electron-rich metal centers are required. As part of our program to enhance the donor strength of phosphines we reported a new approach to highly electron-rich phosphines based on the use of imidazolin-2-ylidenamino groups directly attached to the phosphorus atom.[1] These imidazolin-2-ylidenaminophosphines (IAPs) depict excellent donor abilities, which exceed that of N-heterocyclic carbenes.

Experimental determination of the basicity of the new phosphines reveals pK_{BH}^{+}(THF) values up to 31.0 that correlate with the phosphines donor strength.[2] The remarkable high basicity of IAPs and their coordination behavior will be discussed, and insights into their use as cooperative ligand for the Cu^{I}-catalyzed dehydrogenation of ammonia-borane will be provided.



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Synthesis and analysis of stereodynamic BIPOL-phosphinites

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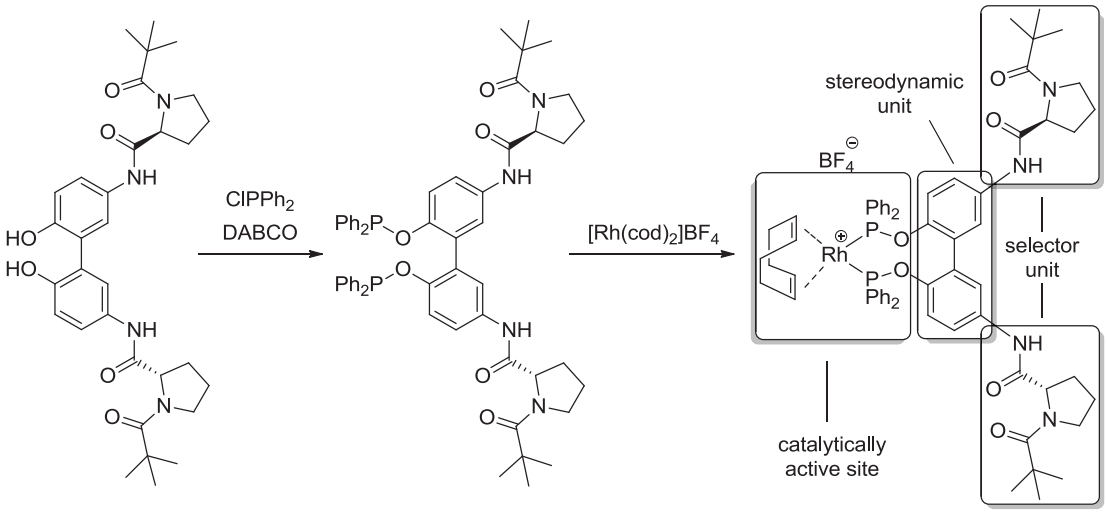
In the last decade stereodynamic ligands attract more and more attention. There are several examples of BIPHEP ligands in literature[1], whereas only few examples for phosphinites are known. One benefit of stereodynamic ligands is the possibility to use isomeric inpure catalysts for asymmetric reactions.

Amide based substituents at the phenyl group are very effective and allow interaction through space by H-bonding and v.d.W.-effects which lead to a preferred orientation of the catalytically active site.[2] The synthesis and application of chiral dynamic *tropos* ligands containing chiral amide selectors is quite challenging.[3] For deeper mechanistical understanding of *tropos* ligands for example determination of the stereodynamic behavior is crucial. In contrast to phosphines,[4] the rotation barrier of phosphinites has not been investigated yet.



Scheme 1: Synthesis of the phosphinite ligand and its rhodium-complex.

This work was supported by the European Research Council (ERC) through a Starting Grand (No. 258740, AMPCAT).

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Enabling organic synthesis with uncommon diazo compounds

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Ethyl diazoacetate is one of the best-studied acceptor-substituted diazo compounds since its first description in 1883 by Curtius and a commonly used reagent in organic synthesis.[1a] The closely related diazo acetonitrile was described by Curtius in 1898, but only found very little application.[1b] Similarly, trifluorodiazoethane is known since 1943[2a] and only in the past decade found application in organic synthesis. The corresponding difluoro diazoethane was first described in 2015 by Mykahiliuk.[2b]

These diazo compounds represent powerful reagents for chemical synthesis.[3] Herein, we report on enabling tools to access difluoro diazoethane and diazo acetonitrile.[4,5] We describe differences in chemical reactivity between these diazo compounds, which result in technology- and chemistry-driven approaches for scalable and safe applications of these diazo compounds. We probed these protocols on their robustness in cycloaddition reactions yielding heterocycles and carbocycles with unprecedent efficiency.

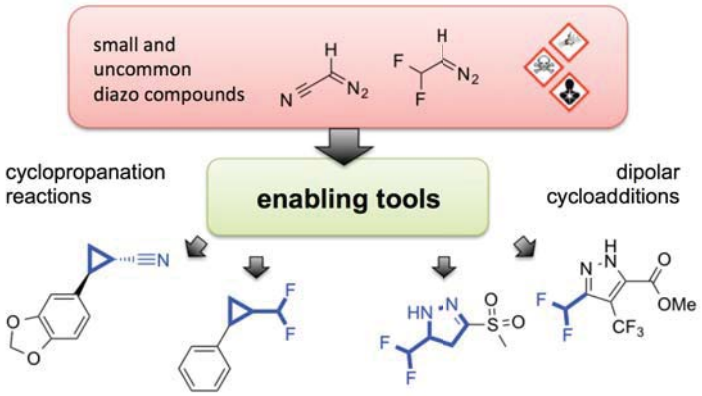

Figure 1: Applications of difluoro diazoethane and diazo acetonitrile.

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Photocatalytic *E*→*Z* Isomerization Inspired by the Visual Cycle: Mechanistic Dichotomy and Origin of Selectivity[1]

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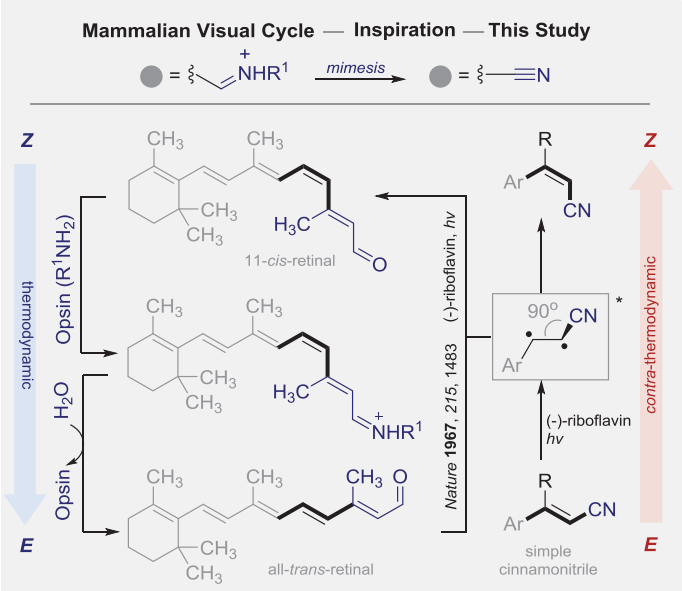
Recently, we disclosed the first highly *Z*-selective isomerization of polarized alkenes, employing the cinnamoyl chromophore as a retinal surrogate under UV-irradiation (402 nm) with (-)-riboflavin (vitamin B_2) as an inexpensive, organic photocatalyst.[2] This study was inspired by the propensity of crystalline (–)-riboflavin in the eyes of vertebrae to invert the intrinsic directionality of retinal isomerization.[3] Herein, we extend this methodology to include a bio-inspired, catalytic *E*→*Z* isomerization of α,β-unsaturated nitriles, thereby mimicking the intermediate Opsin-derived, protonated Schiff base in the visual cycle with simple polarized alkenes. Replacement of the iminium motif by a cyano group is well tolerated and gives an additional degree of versatility for post-isomerization functionalization. Broad substrate scope is demonstrated (up to 99:1 *Z*:*E*) together with evidence of mechanistic dichotomy *via* both singlet and triplet energy transfer mechanisms. Kinetic studies, temperature dependent photostationary state correlations and investigation of substituent-based electronic perturbation of the alkene identified polarization combined with increased *Z*-isomer activation barriers as the selectivity governing factors in catalysis. This investigation also demonstrated the importance of internal structural preorganization on photostationary composition and elucidated the augmented *Z*-selectivity upon hydrogen-alkyl exchange at the *β*-position of the alkene.



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N-Heterocyclic Carbenes Stabilized Nanoparticles – Synergistic Effects for Stability and Reactivity

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In the past few years the interest in nanoparticles has gained in importance due to their promising application in fields such as biochemistry, medicine, catalysis and materials science. A major challenge for these purposes is the stabilization of nanoparticles by suitable ligands. An emerging class of ligands in this research area are N-heterocyclic carbenes, which are tightly binding to metal nanoparticles and can be easily structurally adapted on demand.[1] Herein, we present the broad applicability of N-heterocyclic carbenes as mono- and bidentate ligands for precious metal-, alloy- and upconversion-nanoparticles.[2] In each case the carbene stabilized nanoparticles were synthesized by ligand-exchange reactions and characterized in detail. Additionally, catalytic hydrogenation reactions and photo-induced transformations were studied, which benefit in selectivity or reactivity from the adsorbed N-heterocyclic carbene ligands.

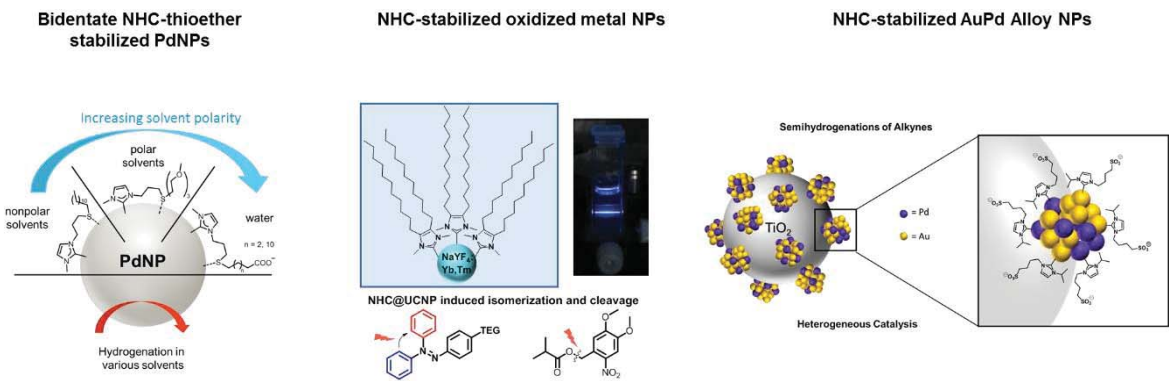

Figure 1: Schematic illustration of different metal nanoparticle systems stabilized by NHC ligands.

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Synthesis of *α*- and *γ*-Cyclodextrin-NHC-Gold Complexes

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Since the first isolation by Arduengo in 1991, *N*-heterocyclic carbenes (NHC's) are a topic of high current interest, in particular in transition metal catalysis.[1] They are an attractive alternative to phosphine ligands because of their strong *σ*-donating ability and low level of *π*-acidity.[2]

Nowadays Green Chemistry is getting more and more important. Catalysis contributes strongly to Green Chemistry.[3] Chemical reactions can be accelerated or selectively directed through catalysis. Other important issues of Green Chemistry are the recyclability of the catalyst, as well as the use of water as solvent due to its availability and environmental friendliness.[4]

Our current research is focused on gold-catalyzed reactions performed in water. To synthesize water-soluble gold catalysts, we combine NHC ligands with *α*- or *γ*-cyclodextrins. Cyclodextrins are cyclic oligosaccharides with a hydrophobic core and a hydrophilic shell, forming host-guest complexes with hydrophobic substrates.[5] The catalytic activity in different reactions, as well as the recyclibility in aqueous media, are currently being studied.[6]

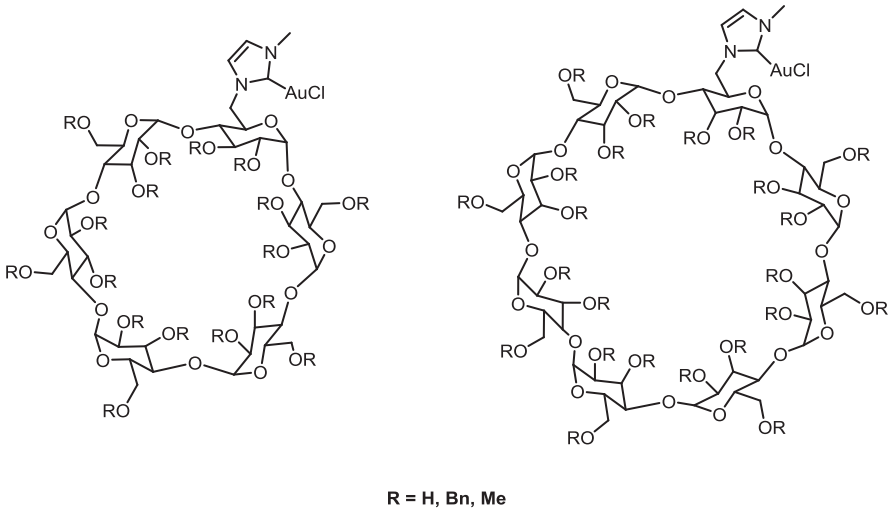

Figure 1: Structure of *α*- and *γ*-Cyclodextrin-NHC-Gold Complexes.

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Novel AdoMet analogues as tools for enzymatic transfer of photo-crosslinkers and capturing RNA-protein interactions

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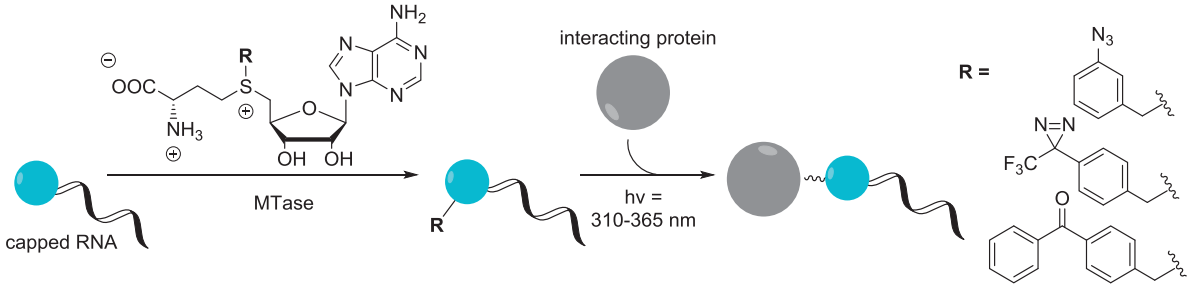
Elucidation of biomolecular interactions is of utmost importance in molecular and cellular biology. In the field of nucleic acids photo-crosslinking has become an indispensable technique for mapping protein-nucleic acid interactions, and for clarifying structures of larger complexes.[1] To date only few enzymatic approaches are described that allow the site-specific introduction of a photo-crosslinking moiety. Methyltransferases (MTases) are ideally suited for this purpose as they naturally transfer a methyl group from their cosubstrate *S*-adenosyl-L-methionine (AdoMet) to their target molecule with high specificity. In methyltransferase-based labelling strategies AdoMet analogues have been used to transfer functional moieties such as azides or alkynes.[2,3] However, AdoMet analogues with photo-crosslinking side-chains have not been described to date.

We here present three novel AdoMet analogues suitable for the transfer of the most widespread photo-crosslinkers (aryl azides, diazirines and benzophenones, Scheme 1).[4] Using the highly promiscuous *N7*-mRNA cap methyltransferase Ecm1[5] from *Encephalitozoon cuniculi* we transferred all photo-crosslinking moieties to cap analogues or capped RNA with high efficiency. We further performed crosslinking experiments to the cap-binding protein eIF4E, which proved successful for aryl azide- and diazirine-modified model RNAs, but not for the benzophenone modification. These photo-crosslinking results are corroborated by the binding affinities determined via microscale thermophoresis experiments.

Since multiple methyltransferases show promiscuity towards AdoMet analogues our enzymatic photo-crosslinking strategy should be directly applicable to other targets, setting the scene for identification and isolation of unknown interaction partners.



Scheme 1: Enzymatic transfer of photo-crosslinking moieties to the eukaryotic mRNA cap and subsequent photo-crosslinking to a cap-interacting protein.

References

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Microwave supported SPPS of large Id2-protein fragments

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The helix-loop-helix (HLH) proteins Id1-4 are key regulators during development as well as in cancer and vascular diseases (1). Through the formation of heterodimers with basic-HLH transcription factors, they negatively modulate the expression of genes involved in cell-cycle arrest and cell differentiation. As the Id proteins are overexpressed in several cancer cells and promote tumorigenesis and cancer stem cells renewal (2), they represent potential targets for cancer therapy. Thus, we are interested in the structural elucidation of the Id2 protein in the phosphorylated and non-phosphorylated state. In order to compare these to states, we decided to use the chemical protein synthesis approach that allows for the preparation of post-translationally modified proteins. Thus, to assess the feasibility of this approach, we investigated the accessibility of large fragments of Id2 by Fmoc-based solid-phase peptide synthesis (SPPS) (3) with and without the microwave support. The products have been characterized by HPLC and MALDI-TOF-MS analysis. Here we will present and discuss the results of the SPPS as well as the conformational properties of the Id2 fragments.

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Preferred type of presentation: Oral ☐ Poster ☒ Oral or Poster ☐
(please tick/highlight appropriate option)

Peptide-catalyzed Baeyer-Villiger Oxidation

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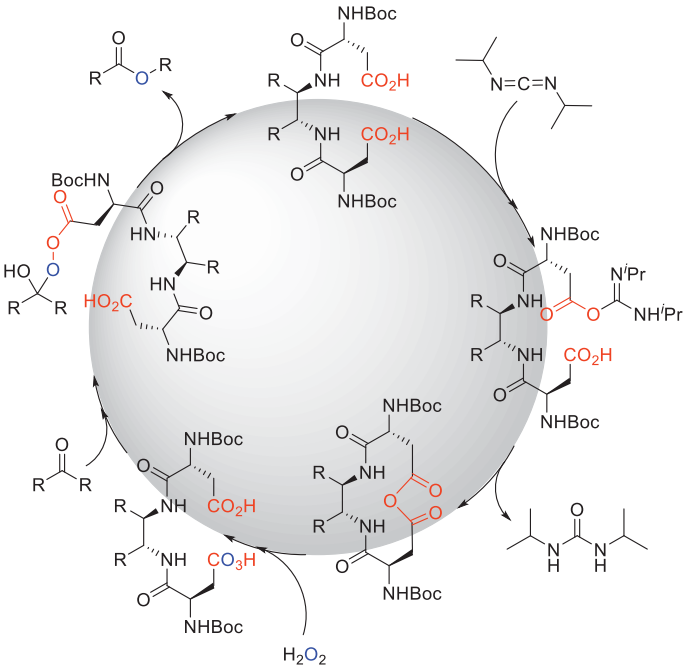
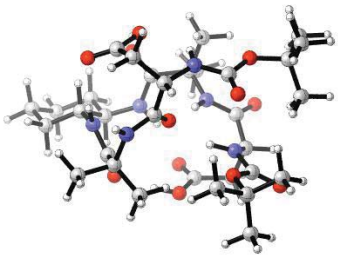
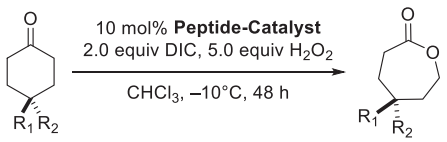
Since the discovery of the Baeyer-Villiger Oxidation (BVO) in 1899, reaction and its mechanism have been investigated intensively.[1] Up to now a variety of protocols using various oxidizing agents are described in the literature.[2] Based on this principle Miller *et al*. established the first organocatalytic and asymmetric BVO utilizing aspartic acid containing peptides.[3, 4]
Combining the concept of the peptide-catalyzed BVOs with our multicatalysis[5, 6] approach we try to entrench a more general and more catalytically active peptide also enabling the enantioselective oxidation of prochiral and aliphatic ketones. The preliminary results showed that C_2-symmetric peptides based on 1,2-(*R*,*R*)-(–)-diaminocyclohexane containing two aspartic acid moieties seem to be the most promising catalysts for BVO of several cyclohexanone derivatives. Our goal was to use particularly low-functionalized cyclohexanones. Therefore we focused on prochiral 4-substituted cyclohexanones which are also easily accessible.





B3LYP-D3(BJ)/6-31+G**



R_1 = H; **R_2** = Me, ^{t}Bu, Ph, NHBoc
R_1 = OH; **R_2** = H, Me, Et, Bu, Ph, Bn

Literature:
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Overcome Product inhibition of Self-replication using a Photoswitch

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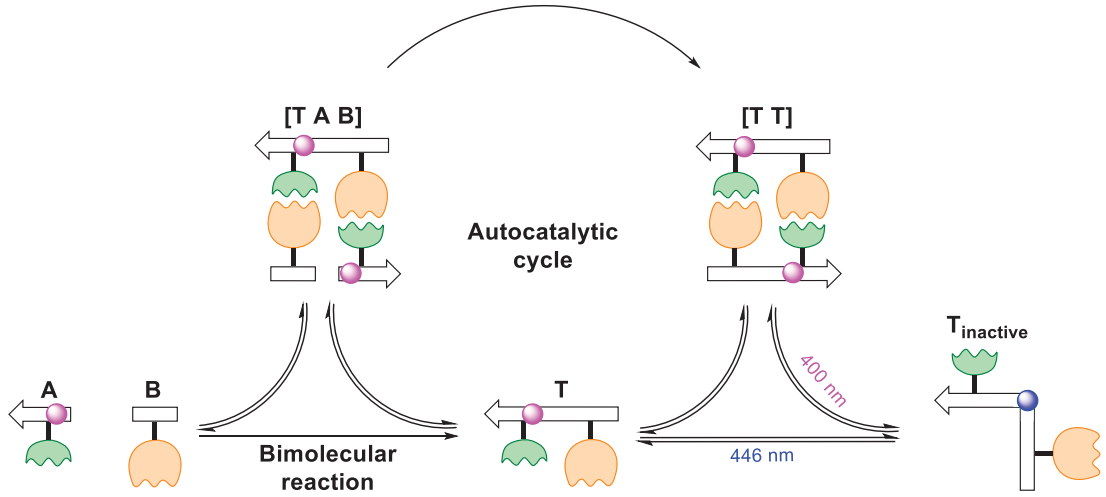
In every living system, self-replication occurs by huge biomolecules like DNA or RNA. These self-replicating molecules are responsible for biological information transfer, so that scientists desired to develop artificial self-replicating systems. In 1986 *von Kiedrowski* reported the first artificial oligonucleotide self-replicating system (SRS).[1] Several other artificial SRSs, also non nucleotidic SRSs, followed and were reported through the last three decades.[2] These SRSs can be classified into three main groups related to their product growth behavior: linear, parabolic and exponential growth.[3] Numerous experiments were performed to enhance the reaction rate of DNA SRSs[4] but until now no SRS exhibits perfect exponential growth due to slow template duplex dissociation (**TT** → 2 **T**). Nevertheless, an exponential growth is prerequisite to reach a molecular evolution in Darwinian sense.[5] Therefore, we are preparing an oligonucleotide SRS including a Photoswitch (PS) to install a template breaking unit which is externally controllable by light irradiation (**TT** → 2 $\mathbf{T}_{inactive}$ → 2 **T**). This PS has to meet following requirements: (i) highly efficient isomerization at (ii) wavelengths compatible to biological systems and (iii) substantial conformational change to break up the template duplex. The *N*-protonated benzylidene pyrroline, reported by *Sampedro,* meets these requirements and has also the advantage of easy control by rapid switching on/off the light (even isomerization). Moreover, the demanded wavelengths are available by laser with high spatial and temporal resolution.[6]



Scheme 1: Minimal model of a SRS including a reaction channel through light irradiation

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Rigidly tethered bis-phosphoric acids: Generation of tunable chiral fluorescent frameworks and unexpected selectivity for the detection of ferric ions[1]

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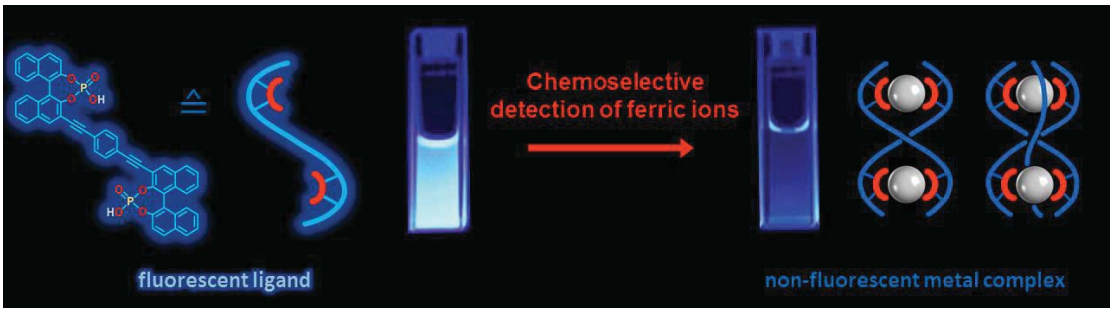
The 1,1´-binaphthyl-2,2´-diol (BINOL) framework has emerged as one of the privileged chiral backbones for a variety of applications.[2] Surprisingly the closely related bis-1,1´-binaphthyl-phosphoric acids have found little attention in this context so far. Diederich et al. have reported on the covalent linkage of 1,1´-binaphthyl phosphoric acids, resulting in tethered bis-phosphoric acids[3] and macrocyclic tetraphosphoric acids,[4-6] which were successfully used for the complexation of mono- and disaccharides. Recently, our group has reported on the synthesis of a bifunctional [2]catenane, featuring two 1,1´ binaphthylphosphoric acids which are noncovalently connected via a mechanical bond.[7]
In this account, we describe the straightforward synthesis of a series of bis-phosphoric acids, featuring two chiral 1,1´-binaphthyl-phosphoric acid units which are tethered by rigid, π-conjugated linkers. The nature of the linker has a profound influence on the properties of the bis-phosphoric acids, such as their self-association behavior and their interaction with metal ions. This led to the identification of one preferred bis-phosphoric acid, which shows selective fluorescence quenching through ferric ions, even in the presence of a variety of other metal ions. Due to the chiral nature of the bis-phosphoric acid, the interaction with ferric ions can also be followed by CD-spectroscopy, giving a complementary detection mode with the same probe.



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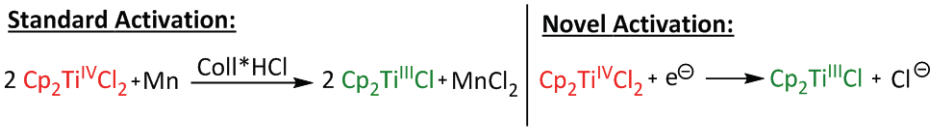
Novel, Sustainable Catalyst Activation – Electrochemical Reduction of Titanocene Dichloride and Applications

T. Olyschläger, Prof. Dr. A. Gansäuer

The titanocene catalyzed radical arylation of epoxides is an attractive synthetic tool to synthesize indolines and tetrahydroquinolines. For a properly working system, the catalyst needs to be activated by a metal reductant, which generates the catalytically active Ti^{III}-species (Scheme 1, standard activation). Additionally, collidinium chloride (Coll*HCl) is necessary to stabilize the active catalyst.[1]



Scheme 1: Generation of the catalytically active Ti^{III}-species.

These additives, however, lead to several waste products, which decrease the sustainability of this process. In order to minimize waste, the activation of the catalyst was envisioned by an electrochemical methodology (Scheme 1, novel activation). To achieve this goal, the active Ti^{III}-species should be generated through a constant potential electrolysis. Preliminary experiments have shown that the catalytically active Ti^{III}-species is observable via cyclic voltammetry, thus titanocene dichloride and different reaction conditions were analyzed by this technique (Figure 1).

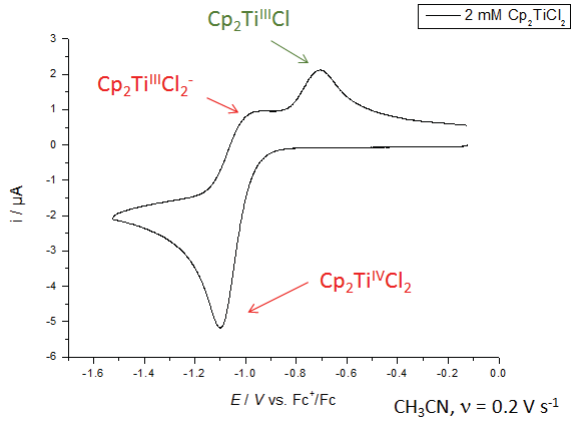


Figure 1: Cyclic voltammogram of Cp_2TiCl_2 (2 mM) in Bu_4NPF_6/CH_3CN (0.2 M) at v = 0.2 Vs^{-1}.

The most promising systems were applied to the constant potential electrolysis and the activated catalyst solution was then used for the arylation of epoxides.

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A Peptide Nucleic Acid replicator for induction of chirality

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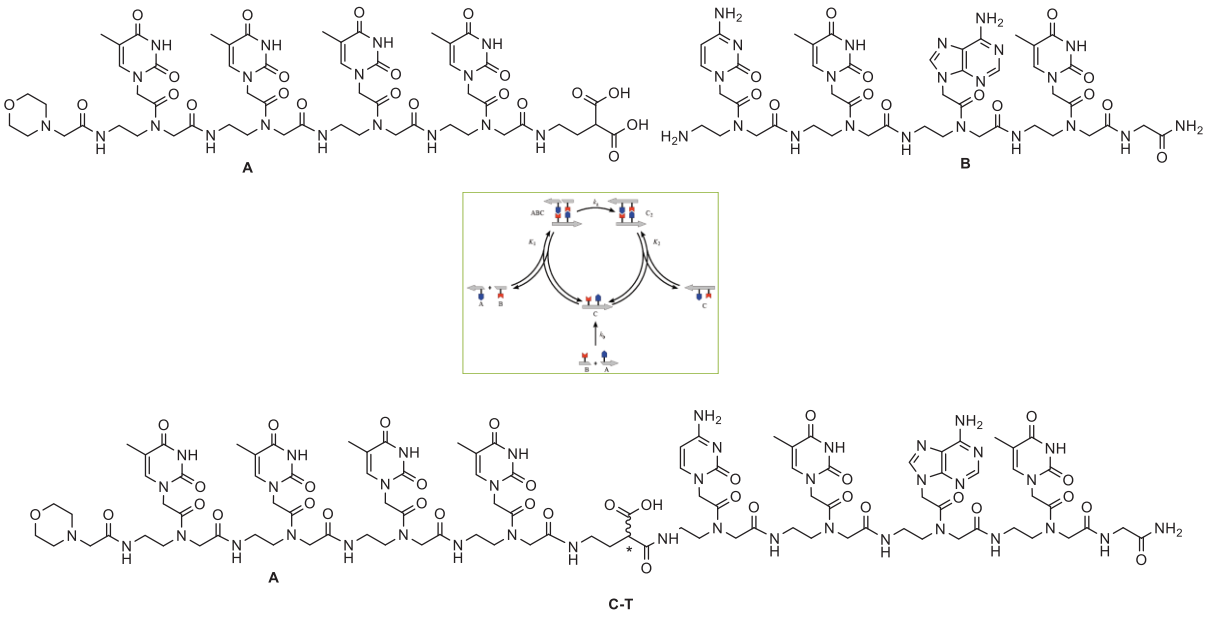
Peptide Nucleic Acids (PNA) are of great interest in diverse fields like chemistry, biology, and medicine (e.g. in drug discovery, genetic diagnostics and the origin of life).[1,2] Inspired by the origin of life theory, we recently developed a system capable of promoting self-replication.[3] Self-replicating systems are able to create identical copies of themselves and exist in form of small molecules as well as in form of macromolecules like natural oligonucleotides (DNA/RNA) and peptides. Knowing that PNAs can replicate, we intend to design a system capable of promoting self-replication and, furthermore, of creating a chiral centre during the replication process. The formation of a chiral center in combination with replication is an important aspect concerning the question of chiral symmetry breaking on the early earth.



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Atom-economical cobalt-catalysed regioselective coupling of epoxides and aziridines with alkenes[1]

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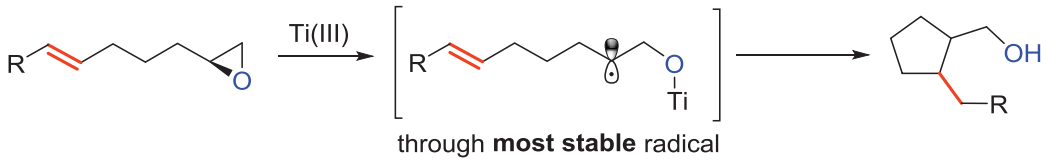
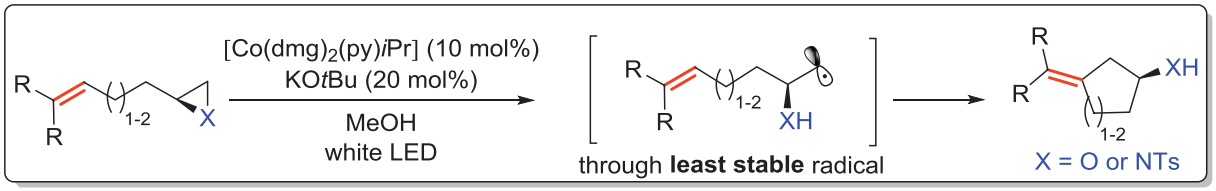
A classical approach to the coupling of epoxides and alkenes is the Ti-mediated radical cyclization of epoxyalkenes.[2] Despite the great utility and the widespread use in complex molecule synthesis, this methodology leads to complete reduction of the synthetically versatile double bond and in the case of terminal epoxides, to the loss of stereochemical information because the epoxide is selectively opened through the formation of the more stable secondary radical.

Classical approach[2]



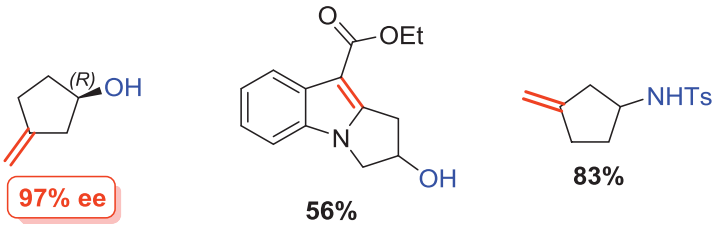
Herein we report an alternative catalytic protocol that retains the alkene moiety in the final product, as well as provide complementary regioselectivity to retain the epoxide´s stereochemistry.[1]

This work[1]



• *5- and 6-membered rings* • *epoxides and aziridines* • *conservation of ee* • *complete atom economy*

Selected examples:



A cobaloxime-type complex can catalyze the coupling of epoxides and aziridines with alkenes to generate homoallylic alcohols and amines. The reaction exhibits complete atom economy and complete retention of stereochemistry in the final product. Preliminary mechanistic studies suggest a radical mechanism.

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Application of lipid-inspired imidazolium salts for membrane interactions

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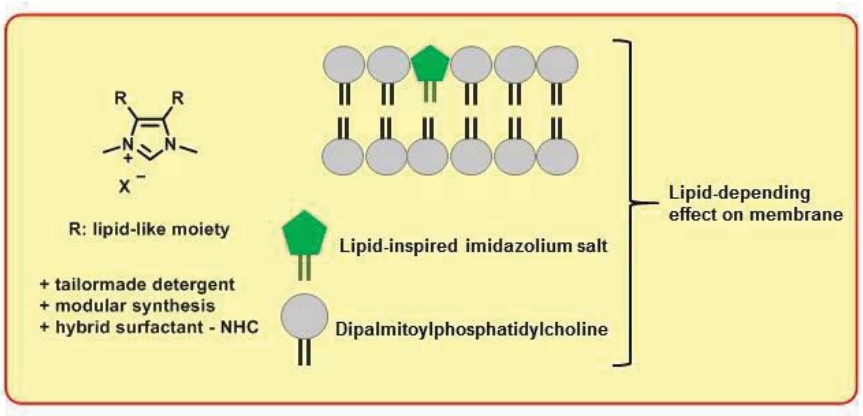
N-heterocyclic carbenes (NHCs) are well established ligands in organometallic chemistry, which results from their electron-rich character and directed steric demand towards the metal leading to strong transition metal to carbon bonds.[1] Despite the great success of NHCs, comparable little attention was paid to their salts. In 2014 we designed a NHC with long alkyl chains in the backbone to stabilize palladium nanoparticles.[2] Realizing the structural compliance with lipids we decided to investigate the biological activities of these salts.[3] Along with a second type of lipid-inspired imidazolium salt, biophysical measurements with Dipalmitoylphosphatidylcholine (DPPC) membranes were performed to identify the most suitable compounds for cellular applications.



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Symmetry-breaking in PNA self-replication

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Abstract

Peptide nucleic acids are a class of nucleic acid mimetics, which were introduced by Nielsen *et al.* in 1991[1]. With a high selectivity and sensitivity, they have found a wide application in gene- and biotechnology [2]. However, it is also believed that PNA might have played a role as prebiotic genetic material on primordial earth [3]. The informational transfer between nucleic acids and PNA has been demonstrated early [4,5] but due to its achiral and chemically robust structure, PNA is more likely to have survived under primitive earth conditions[6].

Based on a self-complementary PNA-replicator [7] recently published by our group, we wanted to expand this concept to the chiral level. Conjugation of achiral PNA to small chiral molecules like amino acids or oligonucleotides causes the strand to adopt a preferred helicity [8]. A replicator that simulates the *de novo* generation of a chiral ligation site might help to understand the transition from achiral PNA to chiral nucleic acid based genetic material.

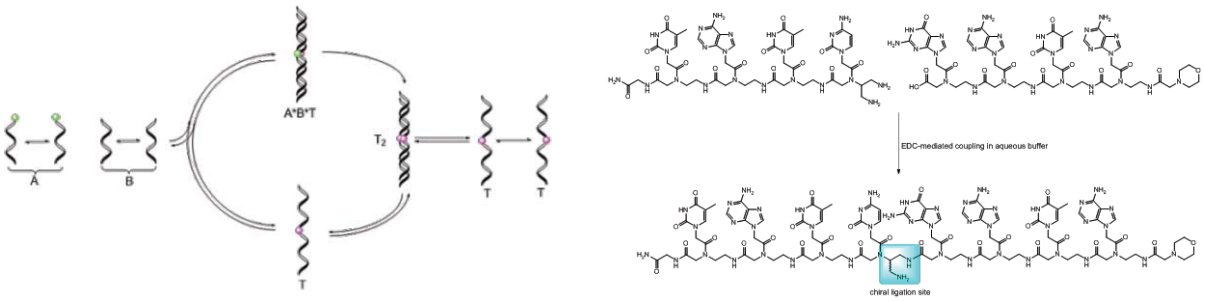

*Fig.1: Left side: Concept of a PNA replicator that contains a spontaneous symmetry breaking step. A pro-chiral PNA strand A is being ligated with a PNA strand B via a template-directed process (termolecular complex A*B*T) to form a chiral T_2-Duplex with a defined helix handednes. Dissociation of T_2 releases the templates for more autocatalytic cycles. Right side: self-complementary PNA-replicator with a symmetry-breaking step.*

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Synergistic effects of protein aggregates in the stabilization of aqueous foam through structure-property relations

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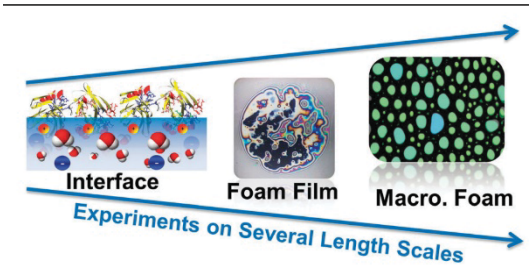

Fig. 1 Approach to study structure-property relations in aqueous foam. [3]

Native and fluorescein isothiocyanate (FITC) labelled bovine serum albumin (BSA) were used to investigate the role of protein aggregates in the stabilization of aqueous protein foams through structure-property relations that reach from the molecular to the macroscopic scale.

Protein modified air/water interfaces - which are ubiquitous in aqueous foam - were studied with tensiometry and vibrational sum-frequency generation (SFG). At the air/water interface, SFG and tensiometry provide information on surface coverage and the net charging state of the interface [1-4] and thus information on the interfacial isoelectric point (IEP) of labelled and native BSA. At the interfacial IEP a reversal of the phase of O-H stretching bands from interfacial H_2O molecules is observed in SFG spectra and is accompanied by a minimum in the surface tension. The latter can be attributed to the formation of protein aggregates at the interface which promote macroscopic foam stability. Using confocal fluorescence microscopy, aggregates of labelled proteins are found to be predominantly located inside foam lamella where they possibly form a gel-like network and thus cause non-DLVO like interactions.

In addition to the pH effects, the effects of solutions ionic strength was investigated as function of Ca^{2+} bulk concentrations in a 15 µM aqueous solution of β-lactoglobulin (BLG). Analogous to the changes at a pH near the IEP, there are similar changes in the molecular structure at the interface when the net charge is reversed by efficient binding of Ca^{2+} counterions to BLG proteins at concentrations of ~1 mM. At these concentrations foam film measurements show formation of common black films which is caused by a considerable decrease of the stabilizing electrostatic disjoining pressure. These observations also correlate with a minimum in macroscopic foam stability. For concentrations >30 mM Ca^{2+}, micrographs of foam films show clear signatures of aggregates which tend to increase the stability of foam films. Additionally, the kinetic data from surface pressure measurements show an acceleration of the adsorption process within the first few seconds which can explain the observed smaller bubble sizes due to the fact that the foam formation process is at similar time scales

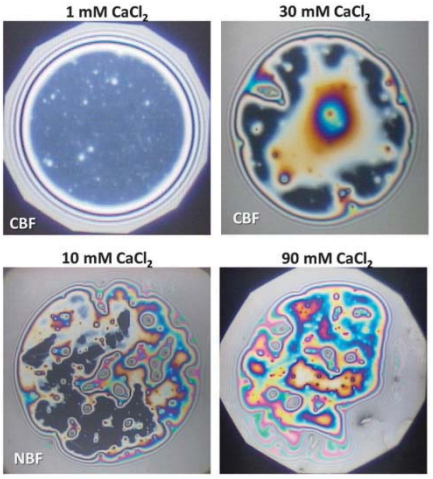

Fig. 2 Micrographs of foam films from β-lactoglobulin solutions in a thin-film pressure balance at different $CaCl_2$. [3]

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Facile Aromatic Ethers as Novel Class of Luminophores with Aggregation Induced Emission Properties

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The need of novel efficient fluorophors for the recognition and labeling of biomolecules such as proteins enzymes and cells is one of the most challenging disciplines in modern biosupramolecular chemistry. Our group uses a phenomenon called aggregation induced emission.[1] Molecules with this ability show fluorescence, contrary to normal fluorophores, when aggregated or in the solid state. Recently we found a novel class of facile ethers with this remarkable characteristic. Our system can be easily modified and was used for the detection of proteins and bacteria.[3] Furthermore we investigated the formation of fluorescent micelles using hydrogen bonding.[2] Currently different compounds were investigated concerning their fluorescence properties. Interestingly delayed fluorescence was observed for specific compounds leading to the assumption, that an intersystem crossing to a triplet state occurs, leading to a long lived fluorescence state, termed phosphorescence.

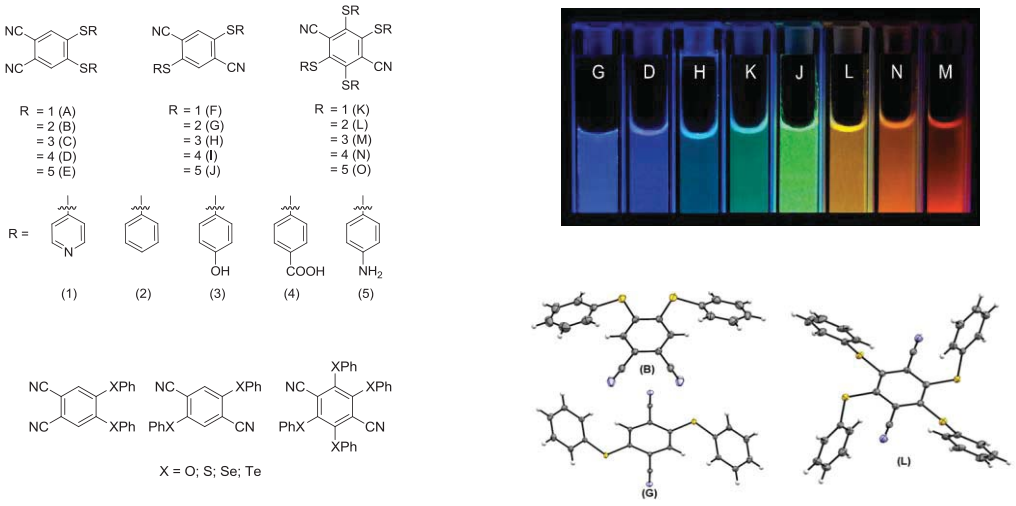

Fig.1: Molecular structures of the investigated molecules, photograph of selected compounds, when dispersed in water under UV-light irradiation and X-ray structures of compounds B, G and L.

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Emulating Natural Product Conformation by Cooperative, Non-Covalent Fluorine Interactions[1]

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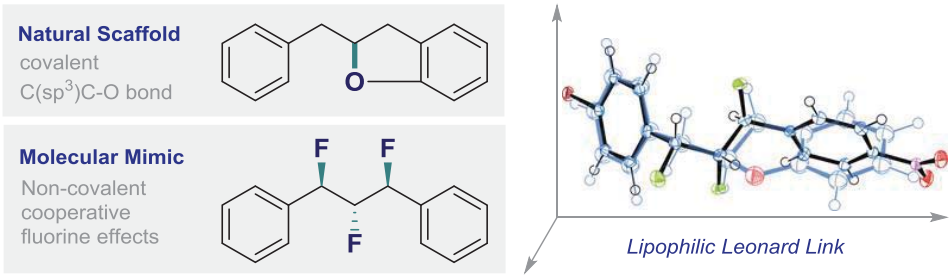
Pervasive in Nature, the propane unit is an essential component of numerous bioactive molecules. These range from acyclic systems, such as the neurotransmitter γ-aminobutyric acid, through to the bicyclic nuclei of various chromanes and dihydrobenzofurans. Conformational pre-organisation is a central tenet of structure-function correlations at the molecular level.[2]
In this study, the replacement of -[CH_2]- units by -[CHF]- centres is evaluated as a strategy to achieve acyclic conformational control by hindering the internal rotations of the propane unit. By exploiting cooperative neighbouring stereoelectronic effects in a *multi-vicinal* fluoroalkane it is possible to emulate the overall conformation of the dihydrobenzofuran scaffold found in a variety of natural products with an acyclic mimic.



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Synthesis of functionalized pyrazolidines by gold-catalysed three-component spirocyclization in micellar systems

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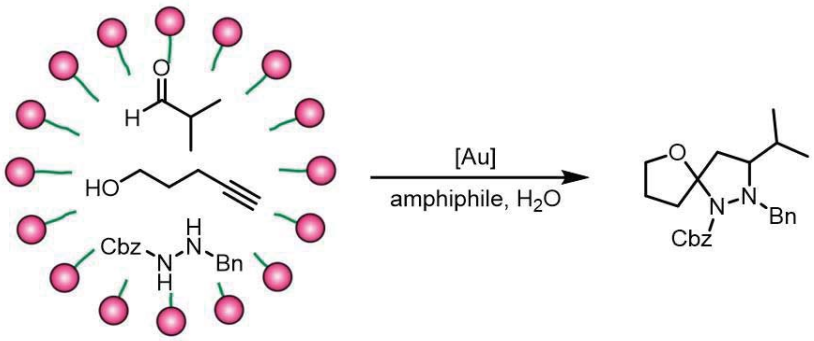
In medicinal chemistry natural products continue to be an inspiration for the design of new drugs. In this context spiroacetals have been found as a key structural unit in many biologically active and structurally diverse natural products.[1] Nevertheless, synthetic approaches to [N,O]-spiroacetals are not well explored. Recently, KRAUSE et al. have developed a gold-catalyzed one-pot approach to functionalized pyrazolidines. With this reaction different kinds of aldehydes, alkynols and hydrazines can be coupled to the corresponding [N,O]-spiroacetals with yields of up to 97%.[2]

Nowadays, preparative transformations are not only judged by efficiency and stereoselectivity, but also by safety and economic and environmental sustainability.[3] One way to improve the environmental sustainability of reactions is the use of micelles in bulk water instead of organic solvents. In these systems both polar and unpolar organic substrates and catalysts are soluble and can react in the nanometer-sized micelles.[4]

Herein, we report the synthesis of functionalized pyrazolidines via gold-catalyzed three-component spirocyclization in micellar systems (Scheme 1).



Scheme 1: Gold-catalyzed three-component spirocyclization in micellar system.

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Molecular Adsorbates Switch on heterogeneous Catalysis: Induction of Reactivity by N-Heterocyclic Carbenes

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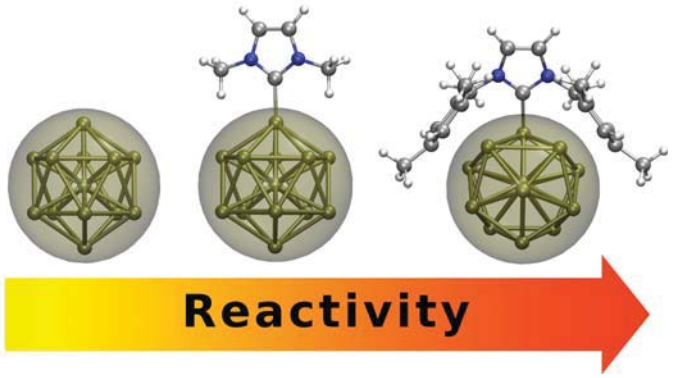
N-Heterocyclic carbenes (NHCs) have previously been applied to modify and stabilize surfaces and nanoparticles [1]. Employing *ab initio* calculations, their binding modes to nanoparticles can be unraveled and the resulting electronic effects on the catalyst can be analyzed. In here, the NHC-induced activation of a Pd nanoparticle catalyst is studied. Calculations give detailed insight into the interactions of the NHC with the surface and the processes which facilitate previously unknown reactivity.

Measured reaction rates for the hydrogenolysis of bromobenzene correlate with activation barriers calculated by potential hypersurface scans. The barriers on the other hand correlate with calculated ionization potentials. Adsorption of NHCs lowers the ionization potential of the nanoparticle significantly, with aromatic N-substituents binding covalently to the surface and donating density, thus amplifying this effect. These electronic effects are in turn confirmed by XPS measurements reporting decreased Pd 3d binding energies for NHC-stabilized nanoparticles [2].

This way, the cooperation of experiment and theory opens up the field of NHC-enabled heterogeneous catalysis and demonstrates the unique characterstics of NHCs as ligands for nanoparticles.



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Astonishing Temperature Dependence of the Williamson Ether Formation with *meso*-Tetrahydroxyphenylporphyrine

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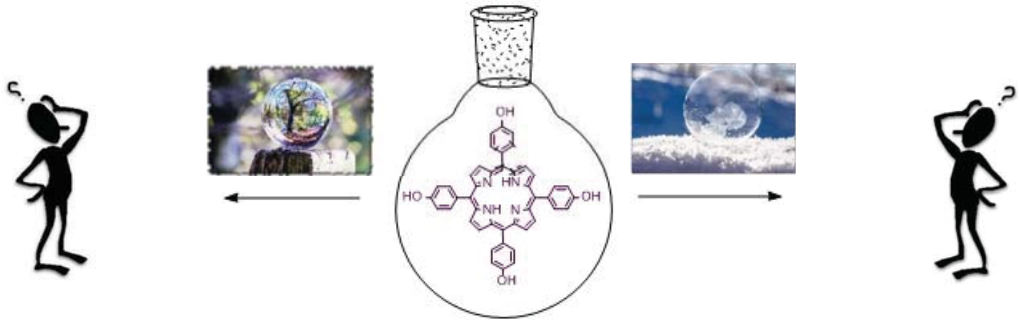

Calixarenes[1] in the cone-conformation, resorcinarenes[2] and *meso*-porphyrins[3] collectively exhibit a fourfold symmetry. Breaking this symmetry by a selective *mono*-, *bis*- or *tris*-functionalization is frequently a crucial step towards the application as building blocks for larger aggregates and arrays within supramolecular chemistry. Especially the *bis*- and *tris*-functionalization usually result in statistic mixtures, in the case of *bis*-substituted products further distributed on the distal and the proximal isomer. Sun *et al.*[4] reported yields up to 90 % for the synthesis of *tris*-functionalized porphyrins by the Williamson ether formation in DMF at reflux temperature using 2.9 equivalents of the alkylating agent.

We noticed a contradiction between the report of Sun *et al.* and the statistical distribution which predicts a maximum yield of 42 % for the *tris*-substituted porphyrin. Therefore we investigated the Williamson ether formation with *meso*-tetrahydroxyphenylporphyrine in detail, with various solvents and at various temperatures, searching for effects increasing the selectivity. As it turned out, the product distribution is strongly influenced by the reaction temperature, thus the outcome of ”room temperature reactions” might differ significantly when performed either in summer or in winter.

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Covalent Interactions and Cooperativity in Frustrated Lewis Pairs Studied by Solid State NMR

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Molecule design for special purposes can only be achieved based on profound knowledge of (local) structures and bonding modes. Most commonly used methods for structural elucidation are liquid state NMR and x-ray diffraction which can be linked by solid state NMR. The latter enables investigation of local environments and affords a distinction between static and dynamic disorder. Aside from the anisotropic chemical shift and quadrupolar interaction parameters, solid state NMR yields internuclear distance information. Quantum chemical calculations of NMR parameter using crystallographic input data validate the results.[1]
Investigations of intramolecular B/P frustrated Lewis pairs (FLPs) revealed that chemical shifts, electric field gradient tensors and direct/ indirect dipole-dipole interactions allow quantification of B-P covalent interaction strengths and hence serve to estimate the "degree of frustration".[2] This contribution focuses on the characterization of FLP reaction products with CO and of the reaction products of the latter with Piers Borane.[3] Characterization of these products was carried out using various multinuclear solid state NMR methods elucidating heteronuclear distances and *J* coupling constants between boron, phosphorus and carbon.

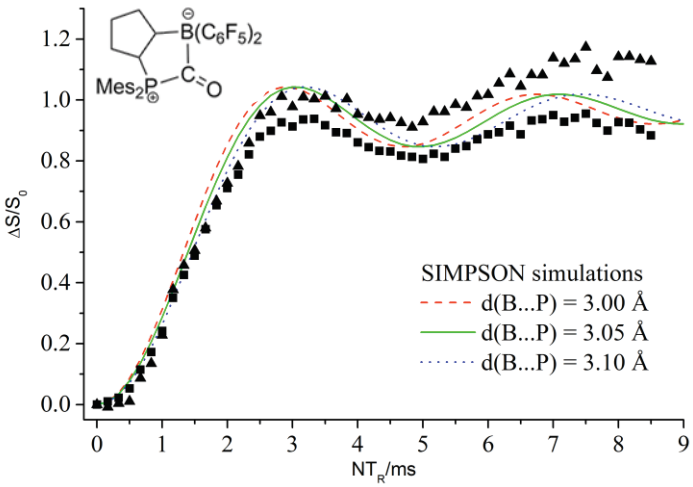

Figure 1: $^{11}B\{^{31}P\}$ REDOR curve (squares) and compensated REDOR curve (triangles) of a B/P FLP-CO adduct, acquired at B_0=7.05 T and 12.0 kHz spinning rate. The simulations suggest an internuclear B-P distance of 305±5 pm.[4]

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A simple Iron and lipase catalysed dynamic kinetic resolution of secondary alcohols

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Recently, we have reported the first iron and lipase catalysed dynamic kinetic resolution of secondary alcohols.[1,2] However, this method requires further improvements. In particular, the development of air-stable iron catalyst is of great importance. Furthermore, the substitution of the unfriendly aryl acetates by more atom economic acyl donors is highly desired.

In this presentation, we will showcase a practical method for the dynamic kinetic resolution of secondary alcohols by combining an air stable iron catalyst with a biocatalyst. Keeping the starting materials racemic during the transformation is promoted by the use of 5 mol% of an in situ generated iron catalyst that is derived from a simple, robust, and readily accessible iron tricarbonyl pre-catalyst. Another great advantage of our catalytic system is the use of simple ester as a highly atom efficient and compatible acyl donor with the metal-catalysed racemization via transfer hydrogenation. Hence, replaces the unfriendly aryl acetates. The utility of the approach was demonstrated by the efficient conversion of an array of racemic alcohols to highly enantiomerically enriched acetates in good yields.[3]

The advantages over the known methods
i) Air stable iron catalyst (5 mol %)
ii) atom efficient reversible acyl donor
iii) simple alcohol is the only byproduct

Scheme 1: Dinamic kinetic resolution of secondary alcohols using an air-stable iron precatalyst

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Supramolecular Photosensitisers for Biomedical Applications

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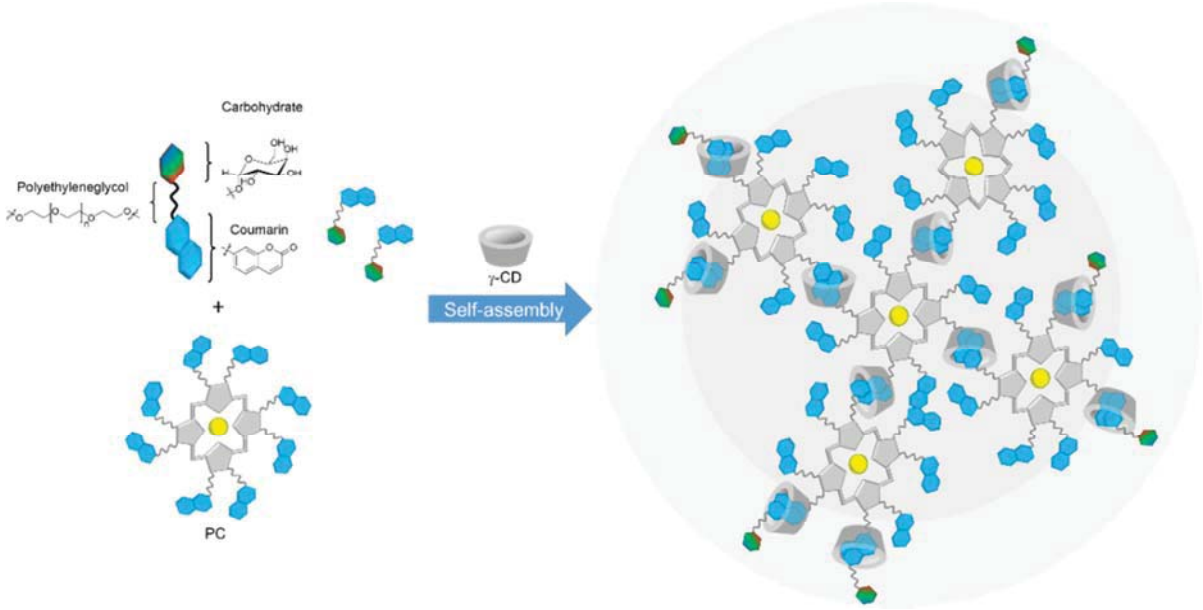
The photodynamic therapy is an important tool in therapies against cancer or to overcome the multi-resistance of pathogens.[1] Furthermore light-induced activation reduces unwanted side-effects of drugs.[2] Common photosensitisers are phthalocyanines (PCs) or porphyrins (PORs). They convert triplet oxygen ($^3O_2$) into cell toxic, singlet oxygen ($^1O_2$) when excited with long waved light.[3] The most challenging part is to prevent π-π stacking of the PCs in water leading to a significant decrease in the fluorescence and $^1O_2$ production.[4]

We have already shown that the generation of $^1O_2$ can be increased up to 300 % by immobilisation of unsymmetrical PCs on a supramolecular substrate.[5] In this project, we present a novel photoresponsive, biocompatible coumarin derivative (**Scheme 1**). Coumarin derivatives form 2:1-complexes with γ-cyclodextrins (γ-CD). They can undergo a reversible, UV-light-induced [2+2]-cycloaddition.[6] This allows the stabilisation of supramolecular networks. Furthermore multivalent coumarin decorated PCs can self-assemble in the presence of monovalent coumarin derivatives and γ-CDs as host molecules. They form size-tuneable, supramolecular nanoparticles (**Scheme 1**). The host-guest complex together with the polyethyleneglycol linker work as a spacer between the PCs. Therefore, a high local concentration of the PCs without aggregation is achieved which should increase the $^1O_2$ production.



Scheme 1: Structure of the novel coumarin derivative and self-assembly with PCs to supramolecular nanoparticles.

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Unraveling the mystery of SUMO interactions with light

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Posttranslational modifications represent one option for cells to react rapidly on external and internal stimuli. They have a direct influence on the activity, stability, conformation, intracellular localization and protein-protein interaction pattern of the modified protein. Besides the conjugation of small chemical moieties like phosphate groups, a protein can also be modified by small proteins such as ubiquitin or ubiquitin-like proteins (Ubls), e.g. SUMO (small ubiquitin-related modifier). Hundreds of proteins are SUMOylated in human cells. It has been shown that a misregulation of the SUMO conjugation / deconjugation cycle is related to the emergence of neurodegenerative diseases such as carcinogenesis, Alzheimer's, Parkinson's or Huntington's disease.

Aside from the covalent attachment SUMO can interact non-covalently with proteins that possess a SIM (SUMO-interacting motif) and thereby affect new protein-protein interactions. However, due to the relatively weak SIM-SUMO interaction, the precise role of SUMOylation is often difficult to study.

This work aims on a further investigation of the SIM-SUMO interaction by application of photoinducible chemical crosslinkers. These are introduced into the SIM interaction surface in SUMO and provide an experimental tool to stabilize a protein complex upon a SIM-SUMO interaction covalently by irradiation with UV light for further investigation.

This approach will contribute to a better understanding of the consequences of SUMOylation for new and altered protein-protein interactions.

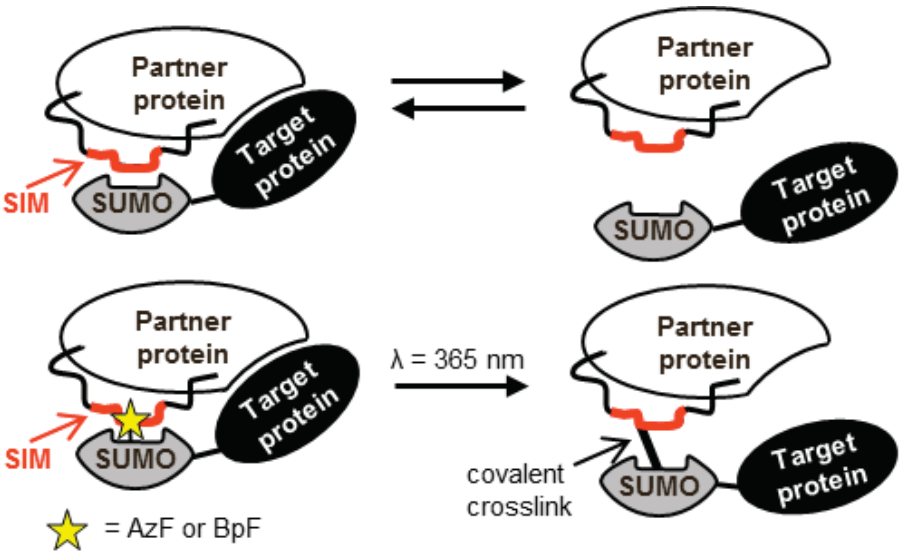

Figure 1: Concept of photoinducible crosslinking as a tool to study SIM-SUMO mediated interactions in multi protein complexes.

Biohybrid Catalysts Based on Transmembrane Protein FhuA

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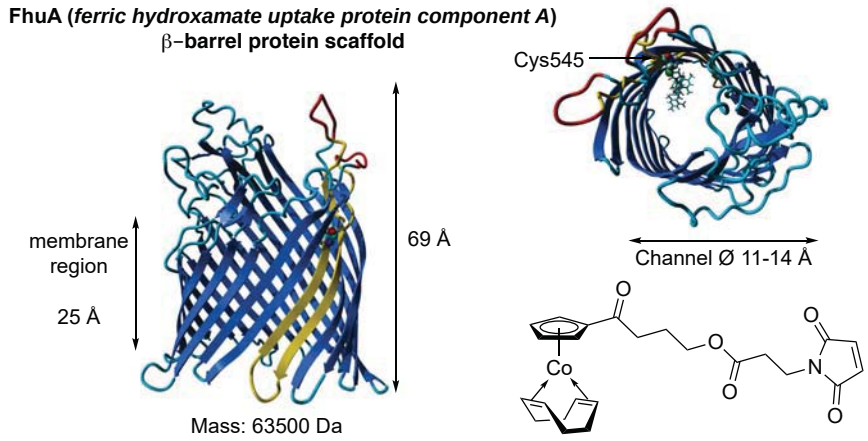

The incorporation of non-natural metal catalyst precursors into protein scaffolds results in so-called biohybrid catalysts in which the protein potentially affects the activity and selectivity.[1] Various metal catalysts were successfully anchored to the β-barrel transmembrane protein FhuA (*ferric hydroxamate uptake protein component A*), or to the soluble β-barrel protein nitrobindin. Ruthenium-based Grubbs-Hoveyda type catalysts in FhuA were used for olefin metathesis.[2] A copper *NHC* catalyst covalently anchored to FhuA catalyzed Diels-Alder reactions.[3] A cyclopentadienyl rhodium complex was anchored to both protein hosts and polymerized phenylacetylene.[6] Since biohybrid catalysts based on cyclopentadienyl rhodium[6] and iridium[7] complexes are established, we are developing cyclopentadienyl cobalt catalysts for biohybrid catalysts based on FhuA.

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London Dispersive Forces In Hierarchically Assembled Helicates

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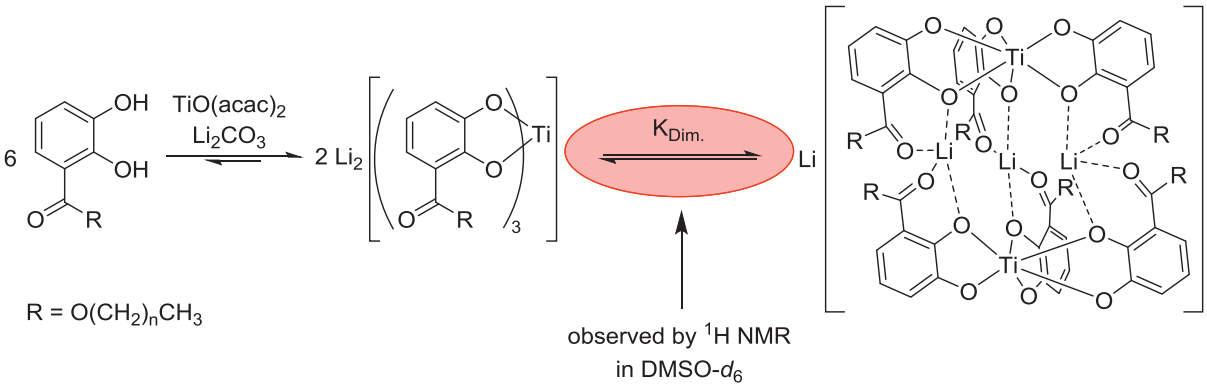
Since the beginning of life, helical structures such as DNA play a fundamental role in the chemistry of nature. On a macroscopic level this structural motif is found in springs, screws and even winding stairs to benefit from its unique properties. J.-M. Lehn defined the term “helicate” in 1987 and introduced this longstanding motif in chemistry.[1]

Hierarchically assembled lithium-bridged titanium helicates were developed by our group two decades later using catechols with keto or ester functionalities in the 3 position.[2] Since then a great variety of ligands were used to observe the equilibrium between a “Werner”-type triscatecholate complex and the corresponding dimer bridged by lithium cations.

This equilibrium, easily measurable via NMR spectroscopy, allows us to directly observe London dispersive forces in solution. Therefore long linear alkyl ester ligands are investigated and the synergy of enthalpic contribution and entropic energy loss is revealed.



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Synthesis of a γ-Cyclodextrin-based NHC-Gold Complex via Ruthenium-catalyzed Azide-Alkyne Cycloaddition

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The development of reactive, selective and recycable catalytic systems is of great importance for chemical research and industrial applications. In addition, modern chemistry is increasingly focused on the Twelve Principles of Green Chemistry.[1]

N-Heterocyclic carbenes (NHC) with their strong σ-donor and poor π-acceptor capacity are excellent ligands in transition metal catalysis and an attractive alternative to phosphine ligands.[2] Through simple and efficient methods, differently substituted NHC precursors can be transformed into NHC-gold complexes.[3] Homogeneous gold catalysts are soft carbophilic Lewis acids with the ability to activate π-systems for inter- or intramolecular nucleophilic attack.[4]

Since the development of the catalytic preparation of 1,2,3-triazoles with high regioselectivity,[5] a wide range of applications of click reactions in organic synthesis, medical chemistry, chemical biology and material science have been described in recent years.[6]

Herein, we report the synthesis of a γ- cyclodextrin-based NHC-gold complex. The key step is the coupling of an azido-substituted cyclodextrine derivate with an acetylenic imidazolium salt by ruthenium-catalyzed azide alkyne cycloaddition (RuAAC). The catalytic activity of cyclodextrin-modified NHC-gold complexes of this type in different reactions is currently studied.

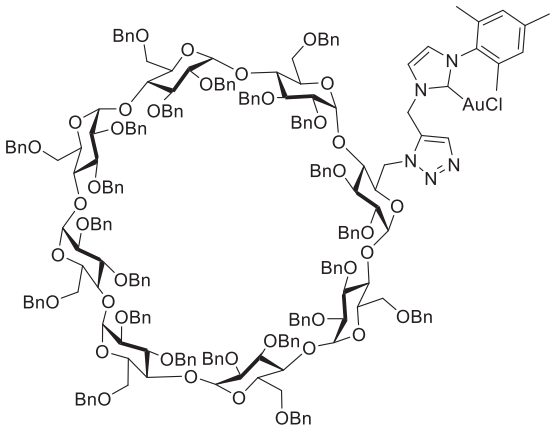

Fig. 1: γ-Cyclodextrin-based NHC-gold complex.

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Experimental Investigations of Iodine-Catalyzed Michael Additions

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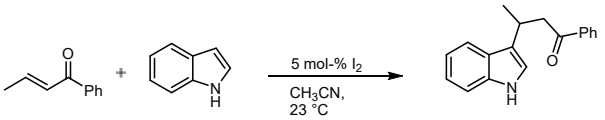
Since Hippert's first report on the catalytic potential of molecular iodine in the dehydration reaction of diacetone alcohol a century ago,[1] molecular iodine has been used as an excellent catalyst in many organic transformations.[2] Althrough plenty of papers, the mode of activation remains unknown.[2]

Inspired by the recent developments in the field of halogen-bonding,[3] we investigated the role of elemental iodine in various Michael reactions. Our kinetic studies of these reactions by reaction calorimetry and IR spectroscopy revealed a reaction order of one for the catalyst. Hidden Brønsted-acid catalysis, a frequently proposed alternative mode of activation, could be ruled out by a careful choice of additives (Figure 1).[4]



Catalytic System	Yield	Catalytic System	Yield
I_2	73 %	HI	40 %
I_2 + KI	0 %	HI + KI	40 %
I_2 + MS	78 %	HI + MS + KI	0 %

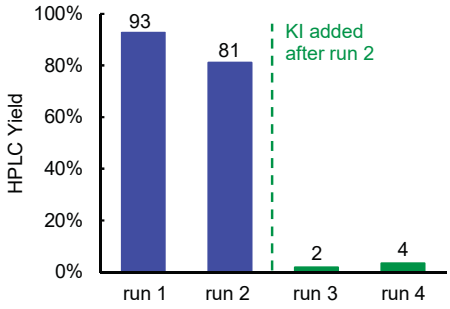


Figure 1. Isolated yields after 3 min in the presents of selected additive at 0.5 M substrate concentration (left). HPLC yield after successive substrate addition and addition of KI after run 2 (right).

Literature:

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Is a minimal latch sufficient for reverse gyrase activity?

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Reverse gyrase is a thermophilic enzyme consisting of a helicase-like and a topoisomerase domain. The cooperation of these domains allows for the ATP-dependent introduction of positive supercoils into DNA. The so-called latch is a key subdomain within the helicase-like domain [1]. The latch is involved in interdomain communication and is essential to couple ATP hydrolysis by the helicase-like domain to processing of the DNA-cleavage complex by the topoisomerase domain [2,3].

Alignment of latch sequences from 105 reverse gyrases shows a lack of conservation in sequence and length, with lengths ranging from 10 (*T. africanus*) to 120 (*P. kodakaraensis*) amino acids. According to homology models, however, the latch is always connected to the helicase domain by a short two-stranded beta sheet, composed of basic and hydrophobic amino acids. The latch in *T. africanus* reverse gyrase consists only of this beta-hairpin. We therefore hypothesized that this hitherto overlooked motif could be a "minimal latch". Indeed deletion of the entire latch, as studied previously with reverse gyrases from *T. maritima* [4] and *T. tengcongensis* [5], completely abolishes DNA supercoiling activity. In contrast, a *A. fulgidus* reverse gyrase mutant where this "minimal latch" motif was retained was still able to positively supercoil DNA, albeit less efficiently than the wild-type [6].

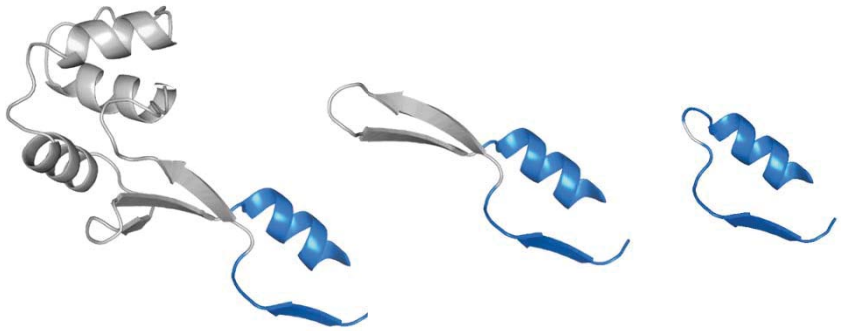

Figure 1 – Part of the structure of the helicase-like domain of wild-type *T. maritima* reverse gyrase (left) and homology model of the minilatch (middle) and Δlatch (right) variants. The latch is shown in grey, the helicase-like domain in blue.

To test our hypothesis, we produced two deletion variants of *T. maritima* reverse gyrase: one with a complete deletion of the latch (Δlatch) and one that retains the "minimal latch" motif (minilatch). Here we show that the minilatch variant of *T. maritima* reverse gyrase exhibits wild-type-like supercoiling activity in the presence of ATP whereas the Δlatch variant is only capable of relaxing DNA. We now aim at analyzing the effects of these two deletions on the ATPase and DNA unwinding activities of reverse gyrase as well as on its DNA- and nucleotide-binding properties. This will allow us to understand the role of the latch at individual steps during the supercoiling reaction and the specific contributions of the conserved attachment motif.

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Coordination compounds of C_3-symmetric triaminoguanidinium based ligands with Ga(III)

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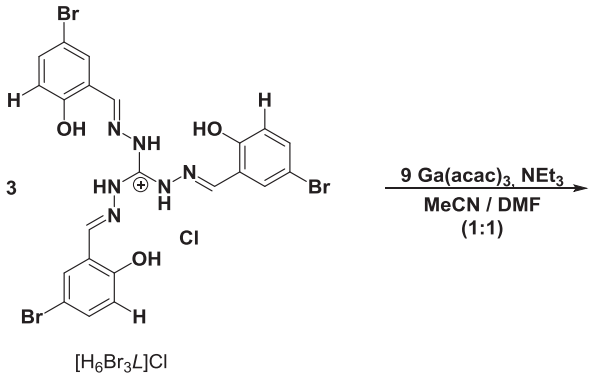
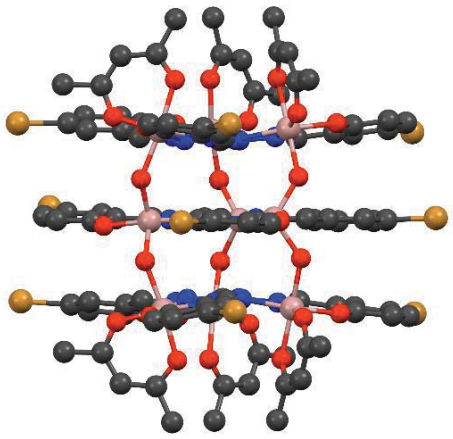
C_3-symmetric triaminoguanidinium based ligands are able to coordinate three metal ions in their tris-chelating binding pockets. They are synthesized by a condensation reaction between a triaminoguanidinium salt and a salicylaldehyde derivative. Discrete coordination cages such as tetrahedral, an octahedron or a trigonal bipyramid can be formed using different metal ions. Possible metal ions are soft ions as Pd^{2+}, Zn^{2+} and Cd^{2+} as well as hard ions like Ti^{4+} or Zr^{4+}.[1,2]

Coordination compounds with a triple-decker-like structure could be obtained using Ga^{3+} ions.[3,4] They are constituted of three ligands, where each ligand binds one Ga^{3+} ion in every coordination pocket. The Ga^{3+} ions are linked by hydroxy groups. The syntheses and structures are presented on this poster. We also report the synthesis and characterization of a coordination compound composed of only one ligand, binding three Ga^{3+} ions in its binding pockets. The influence of the counterion, solvents and concentration on building up coordination compounds consisting of either one or three ligands is described.



$[H_6Br_3L]Cl$



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Fitting coarse grained force fields using genetic algorithms

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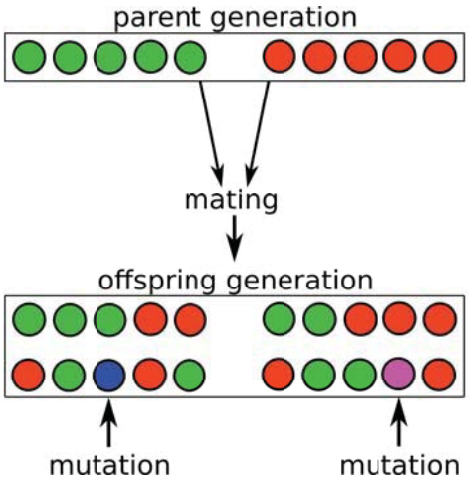
Coarse grained (CG) molecular dynamics simulations are an important tool for the study of large, complex systems in a variety of scientific fields such as biochemistry, polymer physics, and organic semiconductors and photovoltaics. The latter is rapidly evolving with many new donor and acceptor compounds being proposed [1, 2, 3, 4] for which CG force field representations need to be developed. Since existing methods such as the iterative Boltzmann or Boltzmann inversion techniques [5] all have their own weaknesses, this work follows an alternative approach.

Genetic algorithms are widely known in the area of computational sciences and constitute a global optimization technique based on the principles of natural selection. They are already established in the field of optimizing cluster geometries [6]. In this work, we apply genetic algorithms to fit the non-bonded CG interaction parameters – represented by several "genes" – so as to match a given structure obtained with an atomistic reference force field.



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