WWU
MÜNSTER

10th MÜNSTER SYMPOSIUM ON COOPERATIVE EFFECTS IN CHEMISTRY

2019
May 17th

Münster,
Germany

Book of Abstracts

10 Years
MÜNSTER SYMPOSIUM ON COOPERATIVE EFFECTS IN CHEMISTRY

Synergistic Effects
in Chemistry - From
Additivity towards Cooperativity

SFB 858

Symposium Schedule

Friday, May 17th 2019 –
Schloss of the WWU Münster (Aula)

10 Years
MÜNSTER SYMPOSIUM ON COOPERATIVE EFFECTS IN CHEMISTRY

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

10.00 am **Lee Cronin** — *Chair: Gustavo Fernández*
University of Glasgow, UK
Exploring Chemistry with Autonomous Robots

11.00 am **Hendrik Dietz** — *Chair: Andrea Rentmeister*
Technische Universität München, GER
Designing Biomolecular Devices and Machines

12.00 Business Lunch

12.30 pm **Symposium Poster Session**

2.15 pm **MS_CEC Young Researcher Awards 2019** — *Chair: Frank Glorius*

Josep Cornellà
Max-Planck-Institut für Kohlenforschung, Mülheim a. d. Ruhr, GER

Marwin Segler
BenevolentAI London, UK & Organisch-Chemisches Institut, WWU Münster, GER

3.00 pm **Markus Reiher** — *Chair: Christian Mück-Lichtenfeld*
Eidgenössische Technische Hochschule Zürich, SUI
A Bright Future for Computations in Chemistry

4.00 pm **Greg C. Fu** — *Chair: Manuel van Gemmeren*
California Institute of Technology, Pasadena, USA
Nucleophilic Substitution Reactions:
A Radical Alternative to S_N1 and S_N2 Reactions

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

MSCEC 2019 Speakers

Lee Cronin

Lee Cronin (* 1973) is the Regius Chair of Chemistry at the University of Glasgow. He received his B.Sc. and Ph.D. degrees from the University of York. He was a Leverhulme fellow at Edinburgh (with Neil Robertson, 1997-1999), after that moving to Bielefeld (1999-2000) as an Alexander von Humboldt fellow. Cronin gave the opening lecture at TED-Global in 2011 outlining initial steps his team is taking to create inorganic biology, life composed of non-carbon-based material. He was awarded the Corday-Morgan medal (2012), the Tilden Prize (2015) and an ERC Advanced Grant. Cronin was the subject of the film Inorganica, which documents his research in inorganic biology and origins of life.

Hendrik Dietz

Hendrik Dietz (* 1977) studied physics in Paderborn, Saragossa (Spain) and at the LMU Munich. After completing his doctorate at TUM (2007), he worked at Harvard Medical School, Boston, USA. Dietz has been a professor of Experimental Biophysics at TUM since 2009. He ranks among the world's leading researchers in DNA nanotechnology, with particular interest in DNA origami. This includes uses in medicine – for diagnosis and therapy – and synthetic enzymes for biologically inspired chemistry. Amongst others, Dietz received two ERC grants (2010, 2016), and was awarded the Hoechst Dozentenstipendium (Aventis Foundation, 2012) and the Gottfried Wilhelm Leibniz-Prize of the DFG in 2015.

Greg C. Fu

Greg Fu (* 1963) is the Norman Chandler Professor of Chemistry at Caltech. He received a BS degree in 1985 from MIT (K. B. Sharpless) and after earning a PhD from Harvard (1991, D. A. Evans) he spent two years as postdoc (Caltech, R. H. Grubbs). After climbing the ranks at MIT (1993 to 2012), he returned to Caltech, where his laboratory is focused on the development of reagents and methods in organic synthesis, including catalysis, chiral catalysts & ligands, and photoinduced bond-forming processes. He became Alexander von Humboldt Fellow (2013), was awarded an Arthur C. Cope Scholar Award (1998), the Elias J. Corey Award (ACS, 2004) and, most recently a Herbert C. Brown Award (ACS, 2018).

MSCEC 2019 Speakers

Markus Reiher

Markus Reiher (* 1971) received his PhD in theoretical chemistry (J. Hinze, Bielefeld) in 1998. After habilitation (2002 with B. A. Hess, Erlangen-Nuremberg), he was professor at Bonn (2004/2005) and Jena (2005/2006). Since 2006 he is Professor for Theoretical Chemistry at ETH Zurich. Research in his group is devoted to general theoretical chemistry with a focus on the development of theory and algorithms for the calculation of electronic structures with the aim to selectively extract relevant information from strongly interacting systems without introducing arbitrary assumptions. Awards include the ADUC Prize, 2004), in 2010 the OYGA award of the Lise-Meitner-Minerva Center for Computational Chemistry.

MSCEC Young Researcher Awardees

Josep Cornellà

for his contribution

"Selective Functionalization of Aminoheterocycles by a Pyrylium Salt"

Daniel Moser, Yaya Duan, Feng Wang, Yuan-hong Ma, Matthew J. O'Neill, Josep Cornella,

Angew. Chem. Int. Ed. **2018**, *57*, 11035-11039.

Marwin Segler

for his contribution

"Planning chemical syntheses with deep neural networks and symbolic AI"

Marwin H. S. Segler, Mike Preuss, Mark P. Waller,

Nature **2018**, *555*, 604-610.

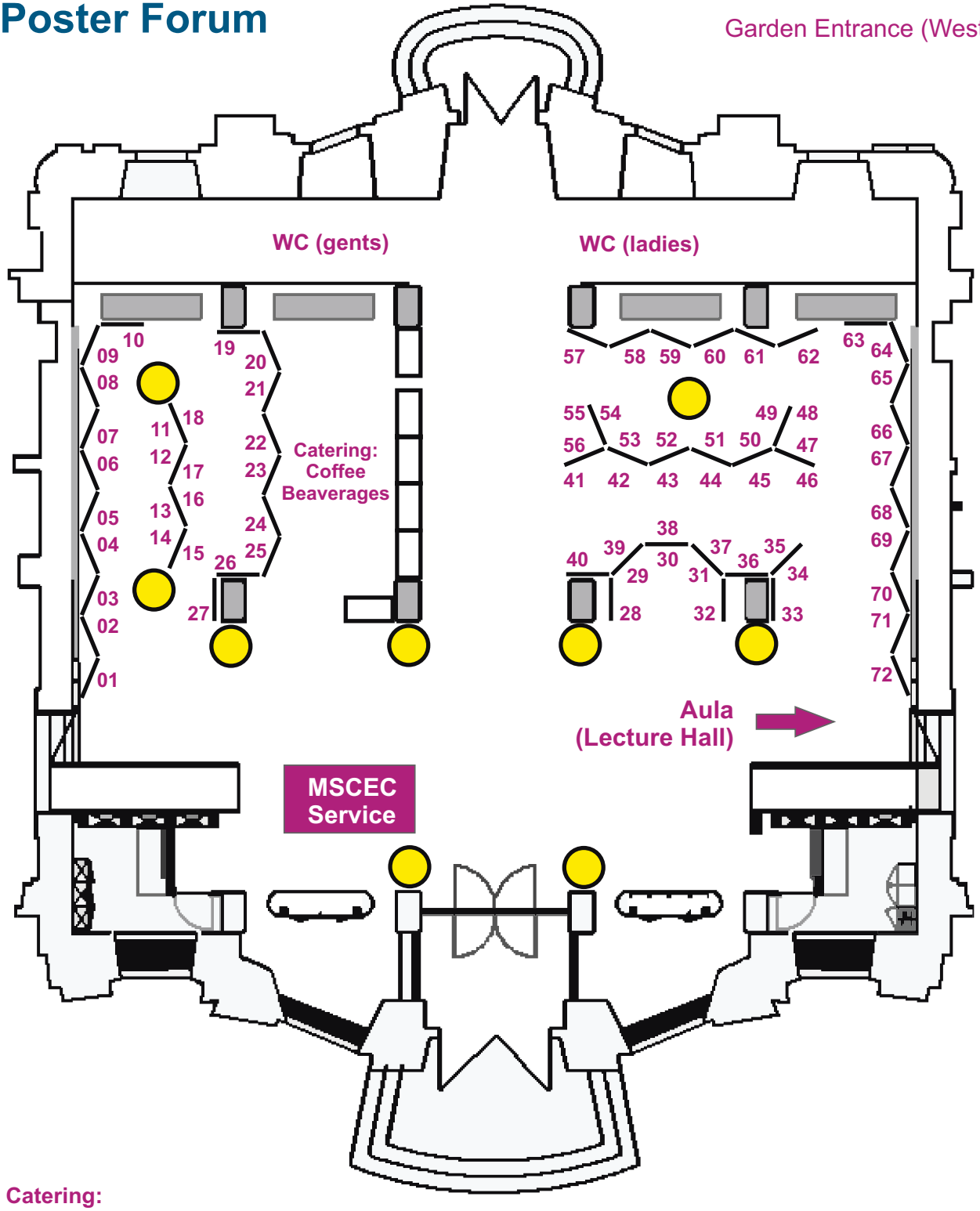
SFB 858

10th MÜNSTER SYMPOSIUM ON COOPERATIVE EFFECTS IN CHEMISTRY

10 Years MÜNSTER SYMPOSIUM ON COOPERATIVE EFFECTS IN CHEMISTRY

Poster Forum

Garden Entrance (West)



Catering:
Business Lunch
(external marquee)

Main Entrance (East)

Poster Contributions (in alphabetical order (presenting author's surname))

01. **Adaptive switching of interaction potentials in the time domain**
Jim Bachmann, Nikos Doltsinis*
Westfälische Wilhelms-Universität Münster / Sonderforschungsbereich 858

02. **Development of a Surfactant-Bound Catalyst for Micellar Catalysis**
Monika Ballmann, Paul Charles Ruer, Norbert Krause*
Technische Universität Dortmund

03. **Photochemical Dearomatization of Polyaromatic Hydrocarbons**
Johannes Bayer, Lukas Holz, Thomas Huhn, Tanja Gaich*
Universität Kostanz

04. **Reaction Energies from Automated "Exact" DFT Embedding**
Moritz Bensberg, Johannes Neugebauer*
Westfälische Wilhelms-Universität Münster / Sonderforschungsbereich 858

05. **Bidentate NHC-Ligands on Metal Surfaces: A Computational Study**
Melanie Börner, Johannes Neugebauer*
Westfälische Wilhelms-Universität Münster / Sonderforschungsbereich 858

06. **Identification of multi-SIM proteins in the SUMO pathway by photoinducible crosslinking**
Kira Brüninghoff, Wolfgang Dörner, Kim F. Taupitz, Henning D. Mootz*
Westfälische Wilhelms-Universität Münster / Sonderforschungsbereich 858

07. **Role of the Latch Domain in Reverse Gyrase DNA Supercoiling**
Frederic Collin, Pavel Lulchev, Marine Weisslocker, Dagmar Klostermeier*
Westfälische Wilhelms-Universität Münster / Sonderforschungsbereich 858

08. **Metal-Free Desilylative C-C bond Formation by Visible Light Photoredox Catalysis**
Tobias Danelzik, Mustafa Uygur, Olga García-Mancheño*
Westfälische Wilhelms-Universität Münster / Sonderforschungsbereich 858

09. **Chemoselective Cross-Coupling of Aryl Iodides Enabled by a Cationic Palladium Trimer**
Claudia J. Diehl, Thomas Scattolin, Franziska Schoenebeck*
Rheinisch Westfälische Technische Hochschule Aachen

10. **Development and Synthesis of Selective and Highly Potent Nucleotide-derived CD73-Inhibitors**
Clemens Dobelmann, Christian Renn, Vigneshwaran Namasivayam, Shanu Jain, Ramachandran Balasubramanian, Christa E. Müller, Kenneth A. Jacobson*, Anna Junker*
Westfälische Wilhelms-Universität Münster

Poster Contributions (in alphabetical order (presenting author's surname))

11. **Direct Synthesis of Alkynylated Cyclopropenes By Au/ Ag-Cooperative Catalysis**
Kirsten Emler, Yangyang Yang, Prof. Dr. A. Stephen K. Hashmi*
Ruprecht-Karls-Universität Heidelberg

12. **Economic Synthesis of α-Chlorosulfones *via* Visible-Light-Mediated Cu(I) and Cu(II) Photocatalysis**
Sebastian Engl, Asik Hossain, Eugen Lutsker, Oliver Reiser*
Universität Regensburg

13. **Verdazyl-Blatter-Diradicals: seeking magnetic properties through inter- and intramolecular interactions with a new class of diradicals**
Jessica Exner, Sina Klabunde, Oliver Janka, Constantin G. Daniliuc, Michael R. Hansen, Armido Studer*
Westfälische Wilhelms-Universität Münster / Sonderforschungsbereich 858

14. **Photoredox catalysis in the dark: Near IR-light driven photoredox catalysis by upconversion nanoparticle/photoredox catalyst systems**
Matthias Freitag, Nadja Möller, Andreas Rühling, Cristian A. Strassert, Bart Jan Ravoo*, Frank Glorius*
Westfälische Wilhelms-Universität Münster / Sonderforschungsbereich 858

15. **Deoxygenative Borylation of Secondary and Primary Alcohols**
Florian W. Friese, Armido Studer*
Westfälische Wilhelms-Universität Münster

16. **Development of Automated Methods for catalytic C-H activation**
Robert Gathy, Holger Butenschön*
Leibniz Universität Hannover

17. **Synthesis and evaluation of new heterocyclic compounds as potential antitrypanosomal agents**
Daniel Gedder Silva*, J. Robert Gillespie, Ranae M. Ranade, Zackary M. Herbst, Uyen Nguyen, Frederick S. Buckner, Flavio da Silva Emery, Michael H. Gelb, Anna Junker*
Westfälische Wilhelms-Universität Münster

18. **Hydrogen Bond Dynamics of N-Heterocyclic Carbenes**
Sascha Gehrke, Roberto Macchieraldo, Oldamur Hollóczki, Barbara Kirchner*
Rheinische Friedrich-Wilhelms-Universität Bonn

19. **Photocatalytic activation of alkyl chlorides by assembly-promoted single electron-transfer in microheterogenous solutions**
Maciej Giedyk, Rok Narobe, Burkhard König*
Universität Regensburg

Poster Contributions (in alphabetical order (presenting author's surname))

20. Reversible reconfiguration of catalytic networked machinery
Abir Goswami, Michael Schmittel*
Universität Siegen

21. Metal-Free *gem* Selective Dimerization of Terminal Alkynes Enabled by Boron-Ligand-Cooperation
Max Hasenbeck, Tizian Müller, Urs Gellrich*
Justus-Liebig-Universität Gießen

22. Aggregation-Induced Emission as a versatile read-out Tool for Biomolecule Recognition
Matthias Hayduk, Jens Voskuhl
Universität Duisburg-Essen

23. Total Synthesis of Putative Chagosensine
Marc Heinrich, John H. Murphy, Marina K. Ilg, Aurélien Letort, Jakub Flasz, Petra Philipps, Alois Fürstner*
Max-Planck-Institut für Kohlenforschung Mülheim a. d. Ruhr

24. Photomediated Iodo Perfluoroalkylation of Alkenes with Visible Light Using Phosphine Catalysts
Lucas Helmecke, Michael Spittler, Kai Baumgarten, Constantin Czekelius*
Heinrich-Heine-Universität Düsseldorf

25. Tailoring The Generalized Spectral Overlap Integral For Advanced Plasmon-Coupled sm-FRET Pair Investigations
Janning F. Herrmann, Christiane Höppener*
Westfälische Wilhelms-Universität Münster / Leibniz-Institut für Photonische Technologien Jena

26. Enantioselective Conjugate Azidation of α,β-unsaturated Ketones
Jorge Humbrías-Martín, María del Carmen Pérez-Aguilar, Rubén Más-Ballesté, José A. Fernández-Salas*, José Alemán*
Universidad Autónoma de Madrid, Spain

27. Extension of Dynamic Polymer Networks *via* Nitroxide Mediated Polymerization
Yixuan Jia, Yannick Matt, Qi An, Stefan Bräse, Audrey Levot, Manuel Tsotsalas*
Karlsruher Institut für Technologie

28. Triazole-based XB donors and their application in catalysis
Mikk Kaasik, Sandra Kaabel, Andrus Metsala, Anna Peterson, Kadri Kriis, Ivar Järving, Riina Aav, Kari Rissanen, Jasper Adamson, Tõnis Kanger*
Tallinn University of Technology, Estonia

Poster Contributions (in alphabetical order (presenting author's surname))

29. **Late-Stage Diversification through Manganese-Catalyzed C–H Activation: Access to Acyclic, Hybrid, and Stapled Peptides**
Nikolaos Kaplaneris, Torben Rogge, Rongxin Yin, Hui Wang, Giedre Sirvinskaite, Lutz Ackermann*
Georg-August-Universität Göttingen

30. **Mechanistic Insights on CO_2 Reduction Reactions at Pt/[BMIM][BF_4] Interfaces from In Operando Spectroscopy**
Andre Kemna, Björn Ratschmeier, Natalia García Rey, Björn Braunschweig*
Westfälische Wilhelms-Universität Münster

31. **Micellar Brønsted Acid-Mediated Synthesis of DNA-Tagged Heterocycles**
Mateja Klika Škopić, Katharina Götte, Christian Gramse, Sabrina Pospich, Stefan Raunser, Ralf Weberskirch, Andreas Brunschweiger
Technische Universität Dortmund

32. **Host-Guest-Interactions Between a Novel Metallacycle and Goldclusters**
John M. A. Kollath, Christian R. Göb, Rebecca Liffmann, Ulrich Simon, Iris M. Oppel*
Rheinisch Westfälische Technische Hochschule Aachen

33. **Iodine-Catalyzed Nazarov Cyclization**
Jonas J. König, N. Gildemeister, T. Arndt, J.-M. Neudörfl, Martin Breugst*
Universität zu Köln

34. **Palladium-Catalyzed Decarboxylative Heck-Type Coupling of Aliphatic Carboxylic Acids Enabled by Visible Light**
Maximilian Koy, Frederik Sandfort, Adrian Tlahuext-Aca, Andreas Lerchen, Tobias Knecht, Johannes B. Ernst, Linda Quach, Constantin G. Daniliuc, Klaus Bergander, Frank Glorius*
Westfälische Wilhelms-Universität Münster

35. **Reductively Degradable Polymer-Nanocontainers for Intracellular Delivery of labeled Phospholipids**
Sergej Kudruk, Wilke C. de Vries, David Grill, Maximilian Niehues, Anna Matos, Maren Wissing, Armido Studer, Bart Jan Ravoo*, Volker Gerke*
Westfälische Wilhelms-Universität Münster / Sonderforschungsbereich 858

36. **Rotating Catalysts Are Superior: Suppressing Product Inhibition by Anchimeric Assistance in Four-Component Catalytic Machinery**
Pronay Kumar Biswas, Suchismita Saha, Thomas Paululat, Michael Schmittel*
Universität Siegen

Poster Contributions (in alphabetical order (presenting author's surname))

37. **Short and Efficient Preparation of Mono- & Tri-functionalized Resorcin[4]arenes**
Dirk Loose, Alexandra Aniol, Martin Feigel, Gerald Dyker*
Ruhr-Universität Bochum

38. **DNA-Supported Bimetallic Photoredox Catalysis**
Fabian Lutz, Jochen Niemeyer*
Universität Duisburg-Essen

39. **Ni-catalyzed Reductive Liebeskind-Srogl Alkylation of Heterocycles**
Yuanhong Ma, Jose Cammarata, Josep Cornella*
Max-Planck-Institut für Kohlenforschung Mülheim a. d. Ruhr

40. **Insights into the Immobilization of Enzymes onto Hybrid Hairy Isotropic and Janus Particles**
Claudia Marschelke, Dorina Köpke, Anke Matura, Martin Müller, Alla Synytska*
Leibniz-Institut für Polymerforschung Dresden / Technische Universität Dresden

41. **Competing Pathways in a BODIPY-based Metallosupramolecular Polymer**
Beatriz Matarranz, Jörn Droste, Michael R. Hansen, Gustavo Fernández*
Westfälische Wilhelms-Universität Münster / Sonderforschungsbereich 858

42. **Genetically Encoded Homocysteine Derivatives Carrying Enzymatically Removable Protecting Groups**
Pascal Meyer-Ahrens, Annika Aust, Marie Reille-Seroussi, Henning D. Mootz*
Westfälische Wilhelms-Universität Münster / Sonderforschungsbereich 858

43. **Photocatalytic Oxidative Iodination of Electron-Rich Arenes**
Rok Narobe, Simon Josef Siegfried Düsel, Jernej Iskra,*, Burkhard König*
Universität Regensburg

44. **A Highly Reduced Ni–Li–Olefin Complex for Catalytic Kumada–Corriu Cross-Couplings**
Lukas Nattmann, Sigrid Lutz, Pascal Ortsack, Richard Goddard, Josep Cornella*
Max-Planck-Institut für Kohlenforschung Mülheim a. d. Ruhr

45. **Halogen-bonded boxes employing azobenzenes**
Esther Nieland, Tom Kunde, Thomas Topornicki, Bernd M. Schmidt*
Heinrich-Heine-Universität Düsseldorf

Poster Contributions (in alphabetical order (presenting author's surname))

46. Heterobifunctional rotaxane catalysis: Cooperative effect of alkali metal phosphate and amine
Noël Pairault, Jochen Niemeyer*
Universität Duisburg-Essen

47. Bi(I)-Catalyzed Transfer Hydrogenation with Ammonia-Borane
Oriol Planas, Feng Wang, Josep Cornella*
Max-Planck-Institut für Kohlenforschung Mülheim a. d. Ruhr

48. Visible Light-Mediated Synthesis of γ-Cyclobutane Amino Acids and their Application as Foldamers
Eva Plut, Sabine Kerres, Oliver Reiser*
Universität Regensburg

49. Solid-phase bound DNA – Less instable than expected
Marco Potowski, Verena Kunig, Florian Losch, Janina Dahmen, Andreas Brunschweiger*
Technische Universität Dortmund

50. Catalysis in Confined Space – From Metal-Organic Frameworks to Supramolecular Coordination Cages
Sonja Pullen, Sascha Ott, Guido H. Clever*
Technische Universität Dortmund / Uppsala University, Sweden

51. Synthesis of Trifluormethylated Pyridines via Rearrangement of Propargyl Vinylamines
Johannes Rath, Norbert Krause*
Technische Universität Dortmund

52. Design of a photo-controlled mRNA-cap guanine-*N*7 methyltransferase
Dennis Reichert, Julian Simke, Bart Jan Ravoo, Andrea Rentmeister*
Westfälische Wilhelms-Universität Münster / Sonderforschungsbereich 858

53. Titanium-Catalyzed Hydroaminoalkylation of Ethylene with Secondary Amines
Michael Rosien, Sven Doye*
Carl von Ossietzky Universität Oldenburg

54. Switching the Electron-Donating Ability of Phosphines through Proton-Responsive N-heterocyclic Imine Substituents
Philipp Rotering, Paul Mehlmann, Fabian Dielmann*
Westfälische Wilhelms-Universität Münster / Sonderforschungsbereich 858

Poster Contributions (in alphabetical order (presenting author's surname))

55. **Self-Assembled Functionalized Coordination Cages**
Robin Rudolf, Witold M. Bloch, Guido H. Clever*
Technische Universität Dortmund

56. **Pd-catalyzed Decarboxylative γ-Arylation for the Synthesis of Tetrasubstituted Chiral Allenes**
Ina Scheipers, Christian Mück-Lichtenfeld, Armido Studer*
Westfälische Wilhelms-Universität Münster

57. **Enantioselective Nucleophilic Dearomatization of Quinolines *via* Triazole-based Anion-Binding Catalysis**
Lukas Schifferer, Qui-Nhi Duong, Olga García-Mancheño*
Westfälische Wilhelms-Universität Münster / Sonderforschungsbereich 858

58. **Photochemically Driven Reverse Water-Gas Shift Reactivity**
Felix Schneck, Jennifer Ahrens, Markus Finger, A. Claudia Stueckl, Christian Wuertele, Dirk Schwarzer, Sven Schneider*
Georg-August-Universität Göttingen

59. **1,3-Diaza-2-oxophenoxazine as a luminescent cytosine analog in silver(I)-mediated base pairing**
Isabell Schönrath, Vladimir B. Tsvetkov, Timofei S. Zatsepin, Andrey V. Aralov, Jens Müller*
Westfälische Wilhelms-Universität Münster / Sonderforschungsbereich 858

60. **Supercooled Water Droplet Impact on Chemically Heterogeneous Surfaces**
Madeleine Schwarzer*, Thomas Otto, Ilia V. Roisman, Alla Synytska*
Leibniz-Institut für Polymerforschung Dresden / Technische Universität Dresden

61. **NHC-based Molecular Motors on Gold Surfaces**
Christian Schwermann, Nikos L. Doltsinis*
Westfälische Wilhelms-Universität Münster / Sonderforschungsbereich 858

62. **Glycomimetic polymers with brush-like structures**
Fadi Shamout, Markus Giesler, Laura Hartmann*
Heinrich-Heine-Universität Düsseldorf

63. **Soft matter interfaces with controllable underwater adherence: Influence of polymer molecular architecture and charge density**
Ugo Sidoli, Ivan Raguzin, Alla Synytska*
Leibniz-Institut für Polymerforschung Dresden / Technische Universität Dresden

Poster Contributions (in alphabetical order (presenting author's surname))

64. Supramolecular host-guest complexes – biocompatible-, stabilizing and spacing unit in green nanoparticles for biomedical applications
Andrea Sowa, Jens Voskuhl*
Universität Duisburg-Essen

65. Carboxylate Linked Dimeric and Polymeric Coordination Compounds
Lisa Sturm, Christian R. Göb, Iris M. Oppel*
Rheinisch Westfälische Technische Hochschule Aachen

66. Chiral Receptors for Lysine Based on Covalently Linked Bis- and Trisbinaphthylphosphoric Acids
Maike Thiele, Jochen Niemeyer*
Universität Duisburg-Essen

67. Cobaltaelectro-Catalyzed C–H/N–H Activation by Water-Tolerant Cobalt Complexes at Room Temperature
Cong Tian, Leonardo Massignan, Tjark H. Meyer, Lutz Ackermann*
Georg-August-Universität Göttingen

68. Synthesis of Cyclodextrin-based NHC-Gold Complexes
Indre Versinskaite, Norbert Krause*
Technische Universität Dortmund

69. Regioselective Hydroaminoalkylation of Alkyl-Substituted Alkenes with Secondary Amines
Michael Warsitz, Sven Doye*
Carl von Ossietzky Universität Oldenburg

70. To Investigate the Magic Behind the Design of Layered Structures
Constanze B. Wiederhold, John M. A. Kollath, Iris M. Oppel*
Rheinisch Westfälische Technische Hochschule Aachen

71. A Second Gold Atom Stabilises Intermediate in Gold Catalysed Ring Openings of Cyclopropenes
Jonas Wunsch, Florian F. Mulks, A. Stephen K. Hashmi*
Ruprecht-Karls-Universität Heidelberg

72. Experimental Insights into Dispersion Interactions in Self-Assembled Supramolecular Host-Guest Systems
Bo Zhang, Axel Wuttke, Susanne Löffler, Mark Johnstone, Ricardo A. Mata, Guido H. Clever*
Technische Universität Dortmund

Adaptive switching of interaction potentials in the time domain

Jim Bachmann[1], Nikos Doltsinis[1]

[1] Westfälische Wilhelms-Universität Münster

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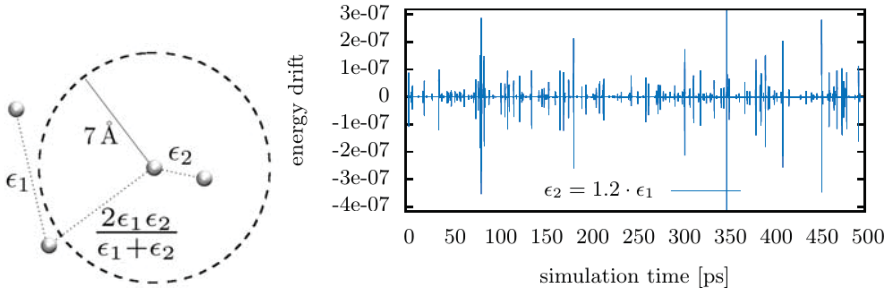
48149 Münster
jim.b@wwu.de

Within computational chemistry there is a wide selection of methods to describe phenomena at different levels of accuracy, time scales and length scales, e.g. classical Molecular Mechanics (MM) or quantum mechanical (QM) methods incorporating the electronic structure [1]. Each method is characterized by its own interaction potential and switching between them generally results in discontinuities. M. Böckmann, N. Doltsinis, and D. Marx proposed a scheme for switching smoothly between different interaction potentials in the time-domain, while an extended Hamiltonian yields a conserved quantity to determine the quality of the switching process[2]. In this work, we extend the method to allow for consecutive switching processes in an adaptive partitioning scheme.

Because the method is applicable to any time- and velocity-independent interaction potential, we employ a simplified test system, allowing for rapid simulation and generation of thousands of test cases. The two interaction potentials are generated by different parametrizations of an ideal gas interacting by Lennard-Jones (LJ) potentials, where within a radius around a certain prespecified atom different LJ parameters are applied. When a particle diffuses into or out of the switching radius, reparametrization and thus switching is necessary.



Along the trajectory, the conservation of energy, temperature and the extended Hamiltonian are monitored. We also evaluate the distances atoms diffuse from the switching radius until they are fully switched to their new representation.

[1] A.W. Duster, C.H. Wang, C.M. Garza, D.E. Miller, H. Lin, WIREs Comput. Mol. Sci., **2017**, 5, 1310

[2] M. Böckmann, N. Doltsinis, D. Marx, J. Chem. Theory Comput., **2015**, 11, 2429-2439

Poster No.2

Development of a Surfactant-Bound Catalyst for Micellar Catalysis

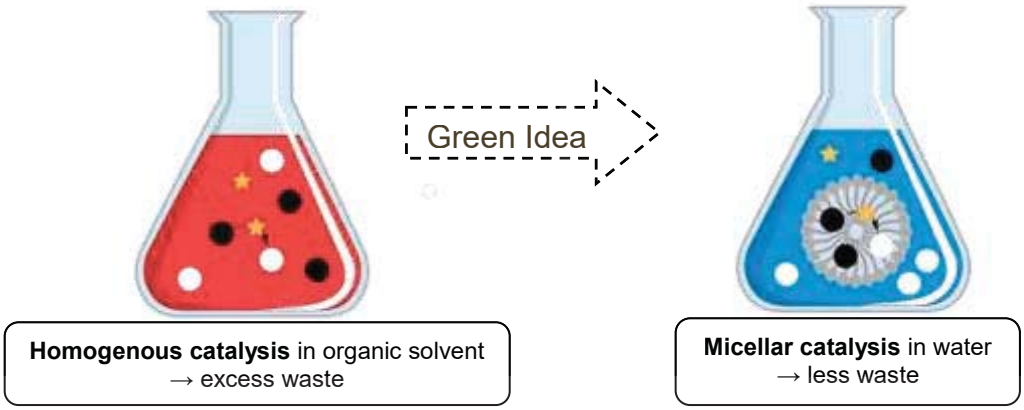
Monika Ballmann, Paul Charles Ruer, Norbert Krause (monika.ballmann@tu-dortmund.de)

TU Dortmund, Fakultät für Chemie und Chemische Biologie

Otto-Hahn-Straße 6, 44227 Dortmund

From the Green Chemistry point of view, catalysis is an efficient alternative to the use of stoichiometric reagents. For most homogeneous catalytic reactions, an organic solvent is necessary for dissolving all organic compounds. Unfortunately, this goes along with an increased waste production.[1]

Our goal is to find environmentally friendly alternatives to conventional homogenous catalysis. An advantageous approach is micellar catalysis with water as bulk solvent, which has no effect on environmental pollution. Micelles are able to incorporate unpolar reactants within their hydrophobic core where the reaction occurs.



To improve the E-factor of the micellar catalysis, the catalyst should be able to catalyze more than one reaction cycle. But one challenging problem is the leaching of the catalyst from the reaction medium during product extraction. Therefore, the current research goal is the covalent attachment of the appropriate catalyst to the surfactant so that catalyst leaching during product isolation is prevented. For the development of a suitable amphiphile-bound catalyst in the frame of this research project, the surfactant PQS[3] was chosen, which was linked to an NHC ligand for binding a gold catalyst.

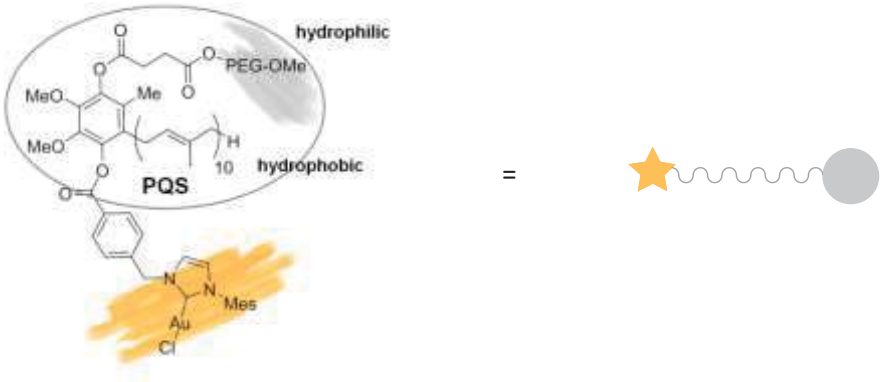


Figure 1: Development of a surfactant-bound gold catalyst.

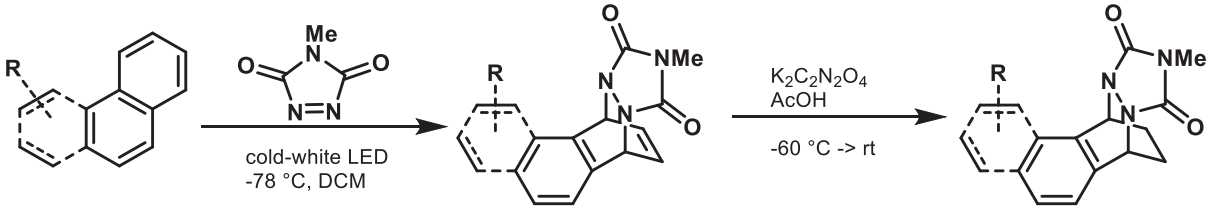
[1] R. A. Sheldon, I. Arends, U. Hanefeld, Green Chemistry and Catalysis, Wiley VCH, Weinheim, **2007**.
[2] S. R. K. Minkler, B. H. Lipshutz, N. Krause, *Angew. Chem. Int. Ed.* **2011**, *50*, 7820-7823.
[3] B. H. Lipshutz et al., *Adv. Synth. Catal.* **2012**, *354*, 3175-3179.

Photochemical Dearomatization of Polyaromatic Hydrocarbons

Johannes Bayer, Lukas Holz, Thomas Huhn, Tanja Gaich

Thomas Huhn (thomas.huhn@uni-konstanz.de), Department of Chemistry, University of Konstanz, Universitätsstrasse 10, 78464 Konstanz (Germany)

Photochemical reactions constitute powerful tools for diverse organic chemistry.[1] They enable a straightforward access to complex molecular structures that are difficult to obtain using other methodologies. The arene-based dearomatization of aromatic compounds *via* photocycloadditions represents an interesting methodology to provide functionalization of polyaromatic hydrocarbons.[2] Sheridan was the first to report the unique transformation between naphthalene and N-methyl-1,2,4-triazoline-3,5-dione (MTAD) upon irradiation with visible light yielding the para-cycloadduct, which was reported to be labile with rapid cycloreversion above – 10 °C.[3] Recent studies in the group of Sarlah towards the *in situ* derivatization of this cycloadduct have shown, that this method allows rapid dearomative difunctionalization of simple aromatic compounds into functional small molecules suitable for further diversification.[4-5]



We adopted this methodology to obtain new cycloadducts of MTAD with higher annulated arenes by irradiation with cold-white LEDs. Subsequent diimide reduction of the olefin moiety provided stable compounds.

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Reaction Energies from Automated "Exact" DFT Embedding

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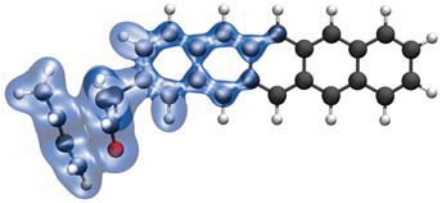
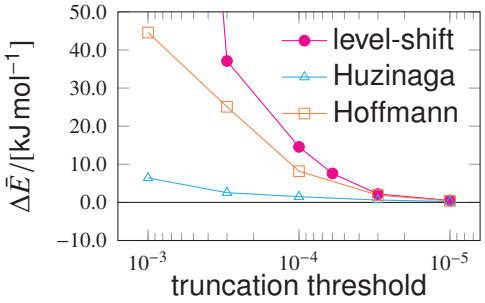
Describing the reaction energetics of large molecules can be a demanding task for correlated wavefunction (WF) methods or (double) hybrid functionals. Embedding approaches like WF-in-density functional theory (WF-in-DFT) [1, 2, 3] can help reducing this cost. Exact embedding (within a DFT context) of the desired method can be achieved using projection-based embedding (PbE) [4]. However, the computational cost of the embedded calculation is only reduced significantly if PbE is used in combination with a basis set truncation scheme [5, 6]. Furthermore, the results of the embedding ansatz depend highly on the choice of the embedded region [7].





In this work the effect of basis set truncation in DFT-in-DFT embedding in combination with different approaches [4, 8, 9] to PbE is investigated and an automatization scheme for the selection of the active region for chemical reactions is presented. Example reactions are investigated based on this novel approach.

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Bidentate NHC-Ligands on Metal Surfaces: A Computational Study

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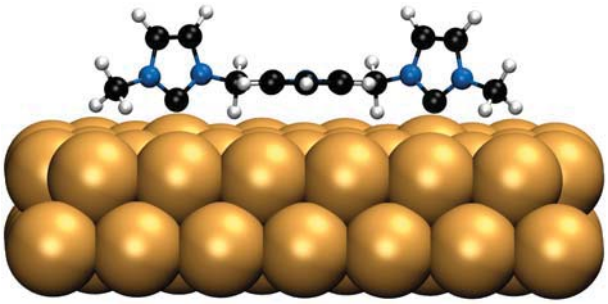
N-heterocyclic carbenes (NHCs) have emerged as valuable ligands for the functionalization of metal surfaces [1–3]. Such modified surfaces show enhanced stability compared to their thiol-modified equivalents [4,5] and were successfully utilized in biosensing [6] and catalysis [7,8]. Lately, it has been shown that multidentate NHCs can be employed to achieve improved material stability as well as enhanced catalytic activity for selected reactions, taking advantage of the chelate effect [7,9]. However, the influence of the nature of the linker connecting the NHC-units remains to be investigated in order to access the full potential of applications. Density functional theory (DFT) is a powerful tool to characterize and design new materials [10,11], which has already provided important insights into the interactions between NHCs and surfaces [4,12–14]. Here, we compare the adsorption geometries of bidentate NHC-ligands connected by various linkers and examine how the structure of the linker affects the adsorption properties on different metal surfaces.



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Poster No.6

Identification of multi-SIM proteins in the SUMO pathway by photoinducible crosslinking

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Posttranslational modifications are an important mechanism to regulate cellular events including signal transduction and protein interactions by influencing protein activity, stability and conformation. Apart from the modification with small chemical moieties like phosphate or acetyl groups, target proteins can be covalently linked with small proteins like ubiquitin or SUMO (*small ubiquitin-related modifier*). The SUMOylation of target proteins provide a new binding site mediating a non-covalent interaction with proteins that contain a SUMO interaction motif (SIM). Thousands of proteins are SUMOylated in the cell and misregulation of the SUMO pathway is related to neurodegenerative diseases.

This study aims to investigate the SUMO interaction network in more detail by identifying SIM-mediated SUMO interaction partners. Due to the transient nature of the SUMO-SIM interaction, the purification and identification of the resulting protein complex is challenging. To stabilize the SUMO-SIM recognition, a novel covalent capture strategy is used. A genetically encoded photoinducible crosslinker is incorporated in the SIM binding interface of SUMO such that after UV irradiation SUMO-SIM interaction partners are linked covalently.[1]

This photocrosslinking approach will be applied to enrich SUMO binding partners from mammalian cell extracts and identify the bound proteins by tandem mass spectrometry. We currently focus on the identification of multi-SIM containing proteins by using SUMO chain mimic probes.

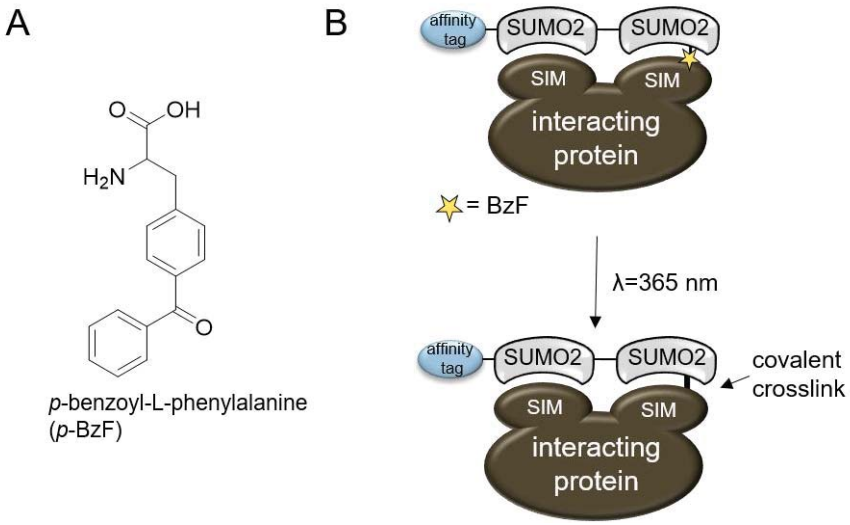

Figure 1: A Unnatural amino acid (BzF) incorporated for photocrosslinking. **B** Concept of photoinducible crosslinking as a tool to study SUMO-SIM mediated interactions.

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Role of the Latch Domain in Reverse Gyrase DNA Supercoiling

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Biological processes involving DNA such as transcription and replication generate DNA torsional stress and produce deleterious DNA structures such as DNA knots and catenanes. Topoisomerases are enzymes dedicated to the maintenance of DNA topology in the cell and thus regulate torsional stress and resolve unwanted DNA structures. Reverse Gyrase is the only topoisomerase known to introduce positive supercoils in DNA, found only in hyperthermophilic organisms its unique activity has been linked to tolerance to high temperature. Reverse Gyrase comprises two domains: a type 1A topoisomerase domain and a DEAD-box helicase domain. Type 1A topoisomerases are generally involved in the relaxation of negatively supercoiled DNA and decatenation of DNA, so understanding how the helicase and topoisomerase domain cooperate to produce a novel activity would prove valuable both to understand mechanisms of topoisomerases and molecular machines. Apart from the conserved helicase and topoisomerase domain, Reverse Gyrase possesses additional features: a zinc finger in each domain, a globular insert in the N-terminal RecA helicase domain, and another insert named the Latch in the second RecA helicase domain. The Latch domain is proposed to have a major role in the Reverse Gyrase catalytic cycle by coordinating the communication between the helicase and the topoisomerase domains. There is a wide variation of the Latch size between organisms from 10 to 120 residues. The smallest known Latch domain belong to *Thermosipho africanus* but only genomic data are available for this enzyme. Two Reverse Gyrase crystallographic structures have been published: *Archeoglobus fulgidus* and *Thermotoga Maritima*, the latter having higher resolution. Latches of *A. fulgidus* and *T. maritima* Reverse Gyrase are respectively 71 and 70 residues long and are organized as a globular domain on top of a beta-hairpin. Interestingly the beta-hairpin domain is homologous to the 10 residues long Latch of *T. africanus*, suggesting that this feature might be a minimal Latch able to support Reverse Gyrase supercoiling activity. To address this question we produced a mutant of *T. maritima* Reverse Gyrase where the globular region of the Latch has been deleted. We compared the activity of this mutant to the wild type Reverse Gyrase and a deletion variant lacking the entire Latch domain. We show that indeed the beta-hairpin domain of the Latch is sufficient to support Reverse Gyrase supercoiling, however the globular domain of the Latch promotes supercoiling and appears to be involved in the communication with the topoisomerase domain in particular by influencing the catalytic step of DNA-religation.

Metal-Free Desilylative C-C bond Formation by Visible Light Photoredox Catalysis

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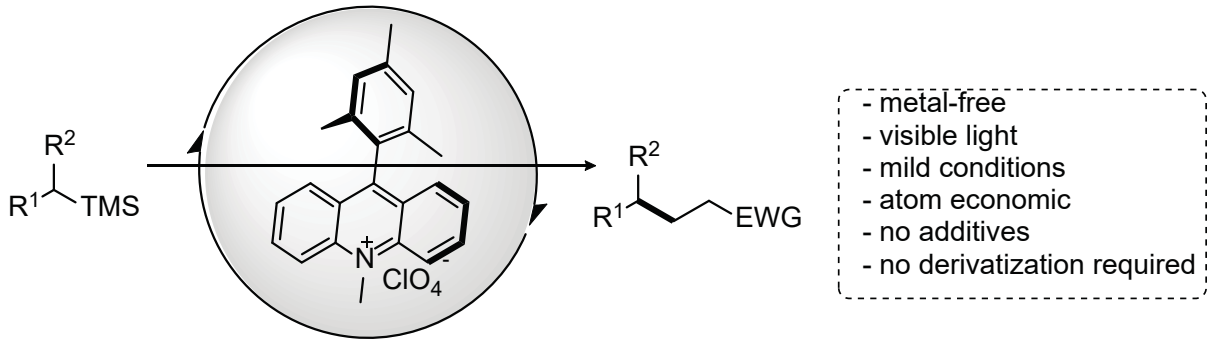
The application of visible light photoredox catalysis in the activation of organosilanes is a rarely described research area due to the high stability of these compounds. So far, the C-Si cleavage requires UV-irradiation or pre-derivatization of the substrates to the corresponding activated silicates.[1],[2],[3] In this work, a newly developed methodology for the use of organosilicon compounds as radical precursors under visible light and metal-free conditions is presented. The catalyst 9-mesityl-10-methylacridinium perchlorate is able to form an extremely strong oxidant in its exited state. This species enables the formation of the organosilicon compounds to the carbon centered radicals, which were trapped by various alkenes. Quenching experiments, quantum yield determination and deuterium labeling studies were performed to give a deep mechanistic insight into this organophotocatalyst mediated desilylative C-C bond formation, which proceeds under remarkably mild conditions without any external additive.



visible light photoredox catalysis

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Chemoselective Cross-Coupling of Aryl Iodides Enabled by a Cationic Palladium Trimer

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Both Csp^2-Csp^2 and Csp^2-Csp^3 cross-coupling reactions are key transformations generating valuable building blocks for synthesis, materials as well as pharmaceutical and agrochemical applications.[1] Through site-selective couplings and orthogonal reactivities of diversely poly(pseudo)halogenated arenes, highly functionalized molecules can be generated from relatively simple substrates using sequential coupling reactions.

Chemoselectivities in cross-coupling reactions strongly depend on the interplay of electronic and steric effects of the substrate, pre-catalyst, the ligand choice, solvent and additives. Thus, ideal conditions for site selective couplings of a given substrate mostly need to be identified for each and every substrate through wasteful optimization. While the relative selectivity of C-Br vs. C-OTf vs. C-Cl can now be controlled,[2] the selective C-C coupling of C-I bonds in the presence of C-Br sites is a hitherto unsolved challenge. As part of our ongoing program to explore alternative catalysis modes with dinuclear Pd^I catalysts, we recently discovered the formation of an air- and moisture stable cationic palladium trimer selectively activating aryl iodides while bromides and chlorides remain untouched. Applying this Pd trimer to cross-coupling conditions, chemoselective arylations and alkylations at C-I sites were achieved in the presence of C-Br and C-Cl bonds. Experimental and initial computational data suggest that direct trimer reactivity is feasible.[3]

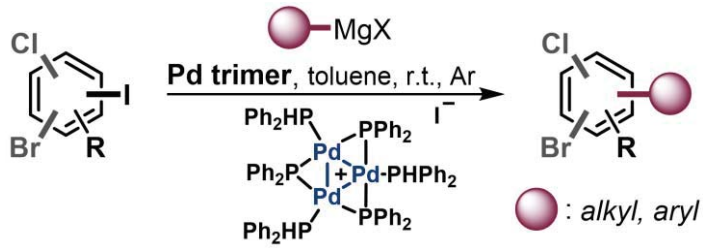

Figure 1: Chemoselective cross-coupling of aryl iodides over bromides and chlorides catalyzed by a cationic palladium trimer.

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DEVELOPMENT AND SYNTHESIS OF SELECTIVE AND HIGHLY POTENT NUCLEOTIDE-DERIVED CD73-INHIBITORS

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In 2018 *J. P. Allison* and *T. Honjo* won the Nobel Prize in Medicine "for their discovery of cancer therapy by inhibition of negative immune regulation."[1] *Ecto*-5'-nucleotidase (CD73), an enzyme which catalyzes the hydrolysis of extracellular AMP to adenosine, is a possible target for immunotherapy. Unfortunately, inhibition of CD73 often suffered either from low inhibitory activity[2] of the compounds or from their low selectivity towards other purinergic targets (e.g. P1 receptors).[3] To overcome these issues, we developed and synthesized a novel uridine- and cytidine-based class of CD73 inhibitors.[4] Our inhibitors display inhibitory activities in the low nanomolar range and the most active compound **9h** additionally shows selectivity over the P1, $P2Y_6$ and $P2Y_{14}$ receptors.[4]

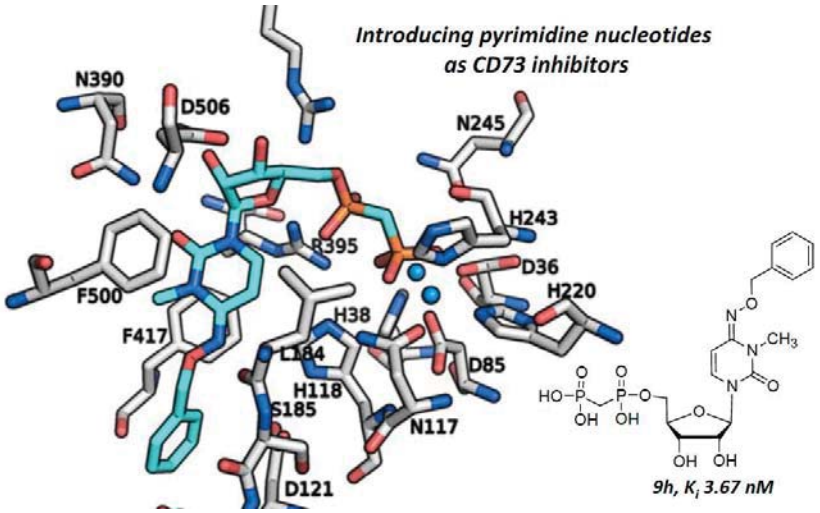

Fig. 1: Interactions of the CD73 inhibitor **9h** with the active site of CD73.[4]

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Direct Synthesis of Alkynylated Cyclopropenes By Au/ Ag-Cooperative Catalysis

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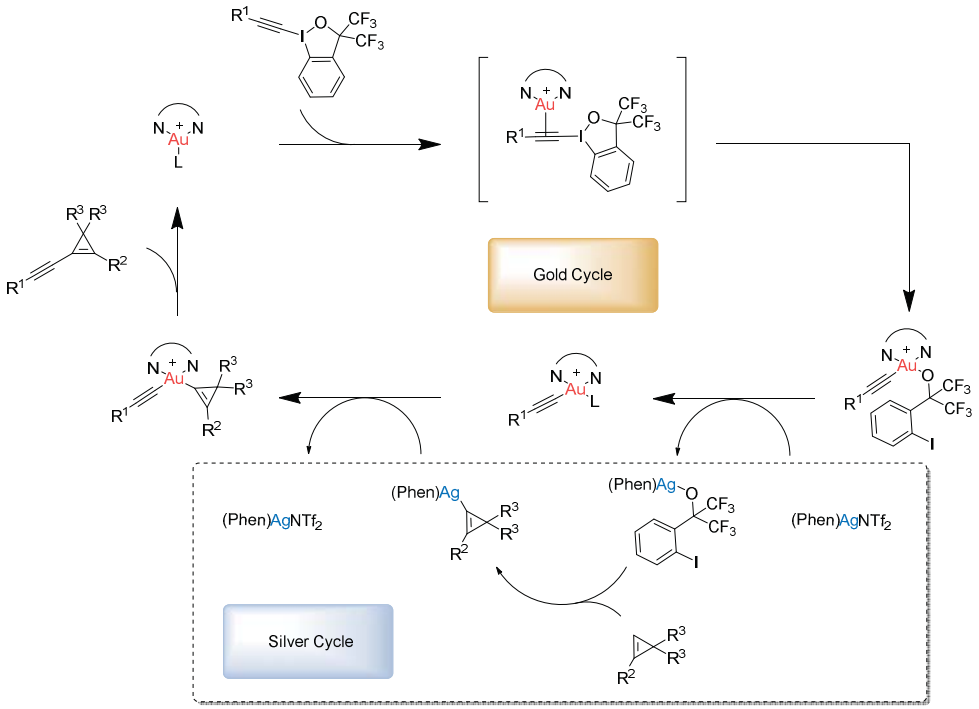
Abstract: The alkynylation of cyclopropenes by using a gold(I)-catalyst has been investigated. In this reaction a Au(I)/Au(III) redox cycle was proposed and $AgNTf_2$ was used as a co-catalyst for transmetalation and C-H activation. Based on a variety of analyses like X-ray, NMR and dynamic experiments the proposed mechanism has been proofed.



Scheme 1: Proposed mechanism.

Literature:

Alonso, J. M., M. P. Muñoz, **2018,** *57*(17), 4742; Hopkinson, M. N., A. Tlahuext-Aca, F. Glorius, *Acc. Chem. Res.* **2016,** *49*(10), 2261.

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Economic Synthesis of α-Chlorosulfones *via* Visible-Light-Mediated Cu(I) and Cu(II) Photocatalysis

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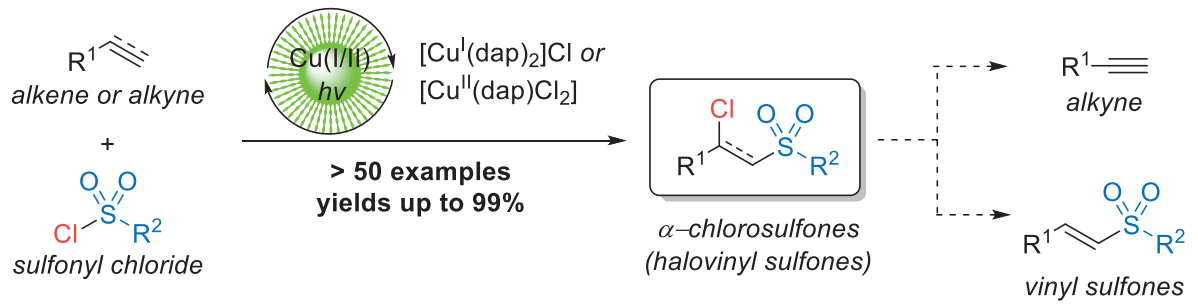
In recent years the important role of copper on photoredox catalysis was reflected by an increasing number of reports.[1] Herein, a visible-light-mediated copper catalyzed protocol is presented to convert a large variety of olefins into their chlorosulfonylated products. Besides the Cu(I)-complex $[Cu^{I}(dap)_2]Cl$, now well-established in photo-ATRA processes[1], the corresponding Cu(II)-complex $[Cu^{II}(dap)Cl_2]$ proved to be often even more efficient in the title reaction, being advantageous from an economic point of view, but also opening up new avenues for photoredox catalysis. Moreover, those outperformed commonly used ruthenium, iridium or organic dye based photocatalysts, owing to their ability to stabilize or interact with transient radicals by inner-sphere mechanism. In contrast to activated olefins, the use of stochiometric Na_2CO_3 in combination with copper catalyst was found to be essential to convert unactivated olefins to the desired products.[2] Additionally, the obtained products can be smoothly converted in one step giving rise to the corresponding vinyl sulfones in almost quantitative yields, which are of great importance for several fields in synthetic organic as well as medicinal chemistry.[3]



Scheme 1. Visible-light-mediated copper catalyzed chlorosulfonylation of alkenes and alkynes.

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Verdazyl-Blatter-Diradicals: seeking magnetic properties through inter- and intramolecular interactions with a new class of diradicals

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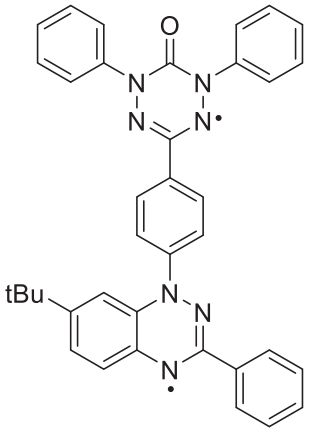
Diradicals possess two unpaired electrons, each formally located at different atomic centers. These molecules and their unpaired electron can interact inter- and intramolecularly and enhance therefore desired physical properties. For this reason, diradicals have gained much attention in recent years – both in the field of organic magnetic materials and molecular electronics. However, only a few organic radical classes have reasonable stability to be suitable for the design of organic magnetic materials, such as nitroxide, nitronyl nitroxide, verdazyl, thiazyl and benzotriazinyl (known as Blatter-radicals).[1]



Verdazyl and benzotriazinyl radicals are synthetically accessible, stable under ambient conditions and have been studied regarding their magnetic properties.[2,3] Herein we present the combination of those two radicals to introduce a new class of diradicals, which can be synthesized in only five steps. The physical properties were investigated by magnetic susceptibility and EPR measurements and the crystal structure could be solved. More examples with different substitution patterns are currently under investigation.

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Poster No.14

Photoredox catalysis in the dark: Near IR-light driven photoredox catalysis by upconversion nanoparticle/photoredox catalyst systems

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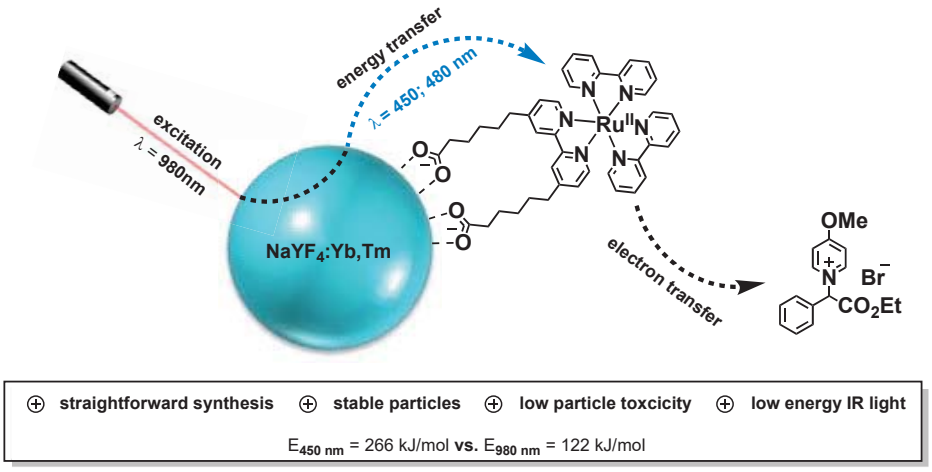
Within the last years, photoredox catalysis has become a powerful tool for mild transformations in organic synthesis. Mostly, Ruthenium and Iridium-based photoredox catalysts are used in these reactions due to their ability of absorbing light in the visible region, long excited state lifetimes and chemical stability, but with limitations in the near IR-light region because of ineffective two-photon absorption processes. Upconversion nanoparticles like $NaYF_4$: Yb^{3+}, Tm^{3+} show a sharp absorption at 980 nm and emission in the absorption area of the Ruthenium-photocatalysts. To date, there are only a few examples where Ruthenium-based photocatalysts were used in combination with upconversion nanoparticles for generation of reactive oxygen species or in nanosensors.[1,2] Moreover, these systems were used to generate bioactive Ru-complexes due to a near IR-induced ligand cleavage.[3] However, in all these examples the Ru-complex acts as a photosensitizer. No precedent examples are known, where the metal-complex acts as a photoredox catalyst after excitation by the upconversion nanoparticles.



In this work, a $Ru(bpy)_3$ derivative was synthesized and attached to upconversion nanoparticles via a ligand-exchange process.[4,5] The particle-catalyst system showed excellent stability in solvents like acetonitrile and biocompatible solvents like DMSO over month with comparable photochemical properties to $Ru(bpy)_3$. Besides other reactions, a straightforward aerobic oxidation reaction of Ethyl-2-bromo-2-phenylacetate was conducted, resulting in 50% yield after 24 h near IR-laser irradiation at 980 nm, while a variety of blind reactions resulted in no product formation.
The presented system might be an excellent in vivo photoredox catalyst with easily tunable properties, harnessing the permeability of the human skin for near IR-light. Moreover, photoredox catalysis, which tolerates light-sensitive functional groups, could depict new synthetic pathways to complex molecules.

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Deoxygenative Borylation of Secondary and Primary Alcohols

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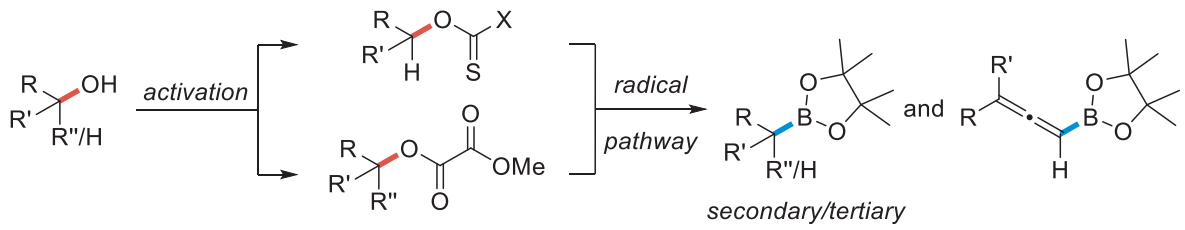
Alkyl boronic esters are highly valuable building blocks in chemical synthesis since the C–B-bond is easily transformed into a great variety of useful functional groups. Moreover, these boronic esters are excellent substrates in transition-metal catalysed C–C coupling reactions.[1,2] Therefore, synthetic methods for their preparation are of great importance. Along these lines, methods for the radical borylation of alkyl halides[3], carboxylic acids[4] and amines[5] have been reported recently. One missing link in this area remains in the borylation of highly abundant and easily accessible alcohols.



Herein, two different approaches for the deoxygenative radical borylation of secondary and tertiary alcohols are presented. Based on the well-known Barton-McCombie reaction, we developed a silyl radical mediated pathway for the borylation of secondary xanthates and O-thiocarbamates. For the even more challenging borylation of tertiary alcohols, we established a photoredox catalyst mediated approach using methyl oxalates. Both protocols show a broad substrate scope and high functional group tolerance and are conducted under mild and practical conditions.

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Poster No.16

Development of Automated Methods for catalytic C-H activation

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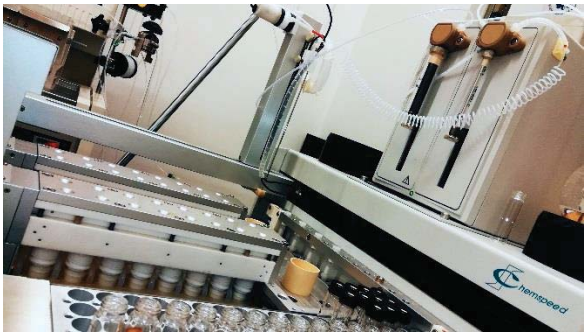
Discovering new chemical reactivities often requires conducting numerous experiments from broader screening to more specific optimization, usually bearing a high proportion of repetitive, non-value-adding tasks like transferring reagents or column chromatography[1]. Nevertheless, these tasks are usually performed manually, without computer- or machine-assisted aid[2]. Furthermore it is often almost impossible to conduct full, exhaustive screenings considering all parameters simply due to the sheer number of possible combinations thereof.[3] Adding the problem of available but unused equipment, there is a risk of losing much time and potential during the research process.



In an effort to minimize that loss of potential in our group, we are developing automated workflows based on a Chemspeed® ASW 2000P parallel synthesizer, which allows for up to 64 reactions being carried out and analyzed at once. Its functions are further enhanced by a custom-made Python/Arduino-based interface, which is used for quantitative TLC evaluation, combination with MPLC, email notifications and general communication between devices. In combination with statistical experiment design, we aim to optimize the entire process from reaction planning through preparation and execution to analysis[4,5]. These methods will primarily be used in our research on Cp^*Co^{III}-catalyzed C-H activation reactions at ferrocene.[6,7]

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Synthesis and evaluation of new heterocyclic compounds as potential antitrypanosomal agents

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ABSTRACT: The present work[1] describes the development and synthesis of 80 new heterocyclic compounds as agents against *Trypanosoma brucei* (*T. brucei*) and *Trypanosoma cruzi* (*T. cruzi*) infections. Several compounds of this series exhibited an *in vitro* EC_{50} ≤ 1μM against *T. brucei* and *T. cruzi* parasites. All potent compounds were furthermore tested for toxicity against human lymphocytes CRL-8155 and human hepatocytes HepG2. Selected compounds were assayed for stability to pooled mouse liver microsomes, their solubility at three different pHs (7.4, 6.5 and 2.0) and their plasma protein-binding. The half-lives of four compounds were greater than 60 min, with a range of 84−100% of the test compounds remaining at the 60 min time point. The most active compound **1** arising from this series, also displayed the greatest plasma protein unbound fraction (FU = 9.9 %; EC_{50} value of 93.32 nM for *T. cruzi*; EC_{50} value of 18.12 nM for *T. brucei*). Furthermore, CNS uptake of compound **1** was determined and displayed a mean brain concentration of 1.12 μM and a mean plasma concentration of 1.31 μM. This gave a brain : plasma ratio of 0.856 for compound **1.** Pharmacokinetic studies were performed in mice to evaluate if compound **1** was suitable for *in vivo* studies. Compound **1** showed an (average ± SEM) C_{MAX} of 5.74 ± 0.86 μM, an average AUC of 3584.95 ± 669.84 min*μM. This C_{MAX} is almost 60 fold higher than the T. *cruzi* EC_{50} and maintained a concentration higher than the EC_{50} well past the 12 h timepoint. This compound was screened further in an acute model against *T.cruzi* TcTC2/*Tulahuen*. It could be demonstrated that through repeated dosing, compound **1** was able to achieve active concentrations in the blood as expected from the single dose PK data. Overall, compound **1** (**Figure 1**) represents a potential lead for the development of novel drugs to treat Trypanosomiasis.

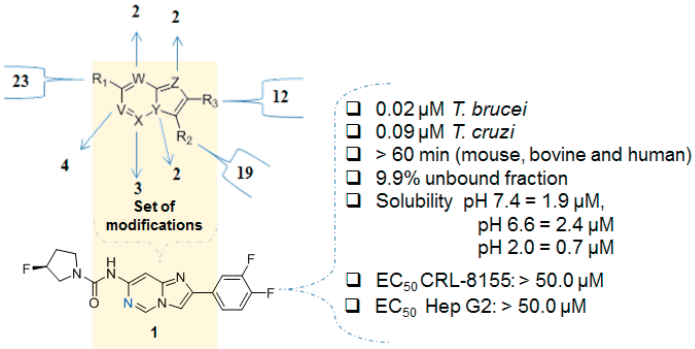

Figure 1. Set of modifications of the core ring. Antitrypanosomal activities, stability, protein binding, solubility and cytotoxicity results for compound **1**.

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Hydrogen Bond Dynamics of N-Heterocyclic Carbenes

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N-heterocyclic carbenes (NHCs) are known as organocatalysts which enable an extensive scope of reactions. In the first step of the reaction the substrate forms a covalent bond to the carbene's hypovalent carbon atom – the NHC's active site. Beforehand, this atom is coordinated via a hydrogen bond to a solvent molecule or a protonated base and therefore blocked. Understanding the influences of the NHC's structure and the solvent's composition on the lifetimes and exchange rates of these hydrogen bonds is an essential cornerstone in the rational design of NHC-solvent systems.
The most precise way to calculate the hydrogen bond dynamics from molecular dynamics simulations is the reactive flux approach, which was already successfully tested for water. [1] In order to study more complicated systems such as NHC-solvent systems, we extended the reactive flux approach to be able to calculate the hydrogen bond dynamics between variable doner-acceptor pairs. [2] To get sufficent deep correlations, long (~10 ns) simulations are necessary, which can only be achieved by classical molecular dynamics simulations. Therefore, we simulated the NHC-solvent systems with our recently developed NHC force field [3] which has been fitted to hydrogen bond potentials and applied the enhanced method on these simulations. We found that carbene rings with a high basicity enable stronger, long living hydrogen bonds, while rings which are found in several reported catalysts form only relatively weak hydrogen bonds with fast exchange rates. [4] During the analyses, we identified two generally different pathways for the exchange of the bonding partner – a dissociative pathway with a carbene in its free form and an associative pathway with a transient three-body assembly as an intermediate, similar to the recently postulated alternative reaction pathway for the catalytic reaction itself. [5] The enhanced analysis shows that a higher occurance of the associative pathway is obviously correlated to shorter lifetimes.

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Photocatalytic activation of alkyl chlorides by assembly-promoted single electron-transfer in microheterogenous solutions

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Photocatalysis emerged as a powerful tool for inducing single electron-transfer to various alkyl C-X bonds.[1] It gives access to carbon-centred, nucleophilic radicals, which are valuable intermediates in the construction of C(sp^3)-C and C(sp^3)-H bonds.[2] However, stable carbon-chloride bonds remain beyond the energetic limits of the outer-sphere photoreductive activation.[3] Herein, we demonstrate that the organization of the reacting species in microstructured, aqueous solutions allows for a direct generation of carbon-centered radicals from non-activated alkyl chlorides in the presence of double bonds via assembly-promoted single electron-transfer (APSET).[4] Photocatalytic systems comprising a surfactant, organic substrates, and additives have been designed, characterized, and applied for radical dechlorination, addition and cyclization reactions. Cheap and commercially available blue LEDs are used as irradiation source for the transformations. Mechanistic studies indicate the accumulation of the energy of two visible light photons in one catalytic cycle.

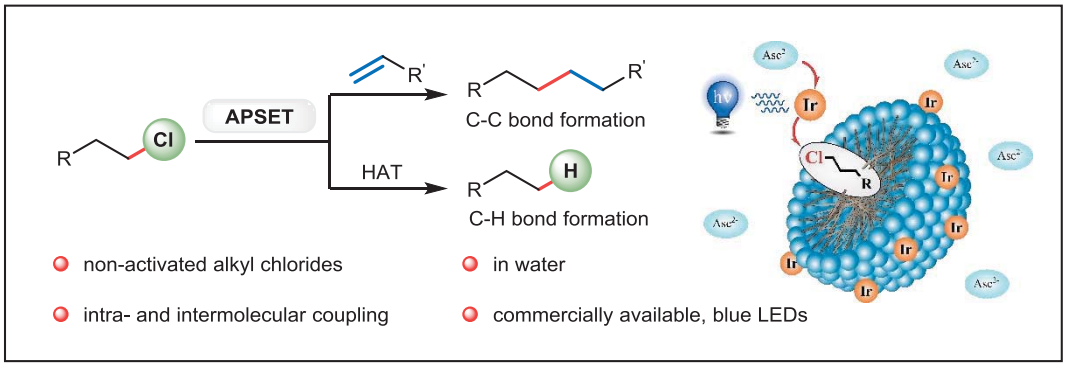

Figure 1. Activation of alkyl chlorides via the assembly-promoted single electron-transfer (APSET).

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Poster No.20

Reversible reconfiguration of catalytic networked machinery

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The present work demonstrates how the workflow of two multicomponent rotary machineries can be interlinked by the simultaneous shuffling of two components (metal and ligand) requiring perfect signaling in a multi-component networked[1] system. Addition and removal of zinc(II) ions trigger three distinct events in parallel: (i) self-assembly of three-component nanorotors and two-component parallelograms by resorting components, (ii) toggling between different rotational exchange rates in the assembled rotors, and (iii) toggling between two diverse catalytic reactions.

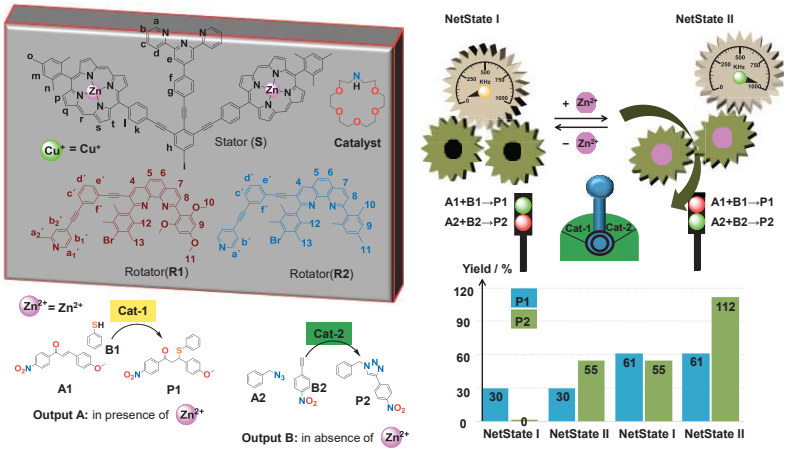

Figure 1: Multifunctional chemical network to control over three distinct events.

In the zinc-free state, the multi-component network contains the self-assembled dimeric architecture $[Cu_2(\mathbf{R1})_2]^{2+}$ (parallelogram) and the three-component nanorotor $[Cu(\mathbf{S})(\mathbf{R2})]^{+}$ with **S** serving as stator and **R2** as rotator. Upon addition of zinc(II), ligands **R1** and **R2** exchange their position in rotor and parallelogram and due to formation of rotor $[Zn(\mathbf{S})(\mathbf{R1})]^{2+}$ one equivalent of copper(I) is released (NetState II). Ligand **7** serving as catalyst for a conjugate addition in NetState I captures the released copper(I) in NetState II to form complex $[Cu(\mathbf{7})]^{+}$ that operates as catalyst for a click reaction. Parallel the newly formed rotor $[Zn(\mathbf{S})(\mathbf{R1})]^{2+}$ is 25-times faster (980 kHz) than the initial rotor $[Cu(\mathbf{S})(\mathbf{R2})]^{+}$ (38.0 kHz). Removal of zinc(II) ions from NetState II regenerates the zinc-free state. This twelve-component network was then reversibly toggled over three cycles as documented by ^{1}H-NMR, UV-Vis, fluorescence spectroscopic and ESI-MS data.

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Metal-Free *gem* Selective Dimerization of Terminal Alkynes Enabled by Boron-Ligand-Cooperation

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We report the first example of a metal-free *gem* selective dimerization of terminal alkynes catalysed by a pyridonate borane complex. This catalyst was previously shown to activate molecular hydrogen.[1] We now found that it is also able to cleave the C-H bond of a terminal alkyne. This C-H activation is accompanied by a change of the covalently bound pyridonate moiety to a neutral pyridone ligand. This change in bond modality enables the dissociation of the newly formed alkynylborane and precedes an unprecedented 1,2-carboboration as key step for the dimerization of the alkyne. In analogy to the concept of metal-ligand cooperation, this mode of action is referred as boron-ligand cooperation.

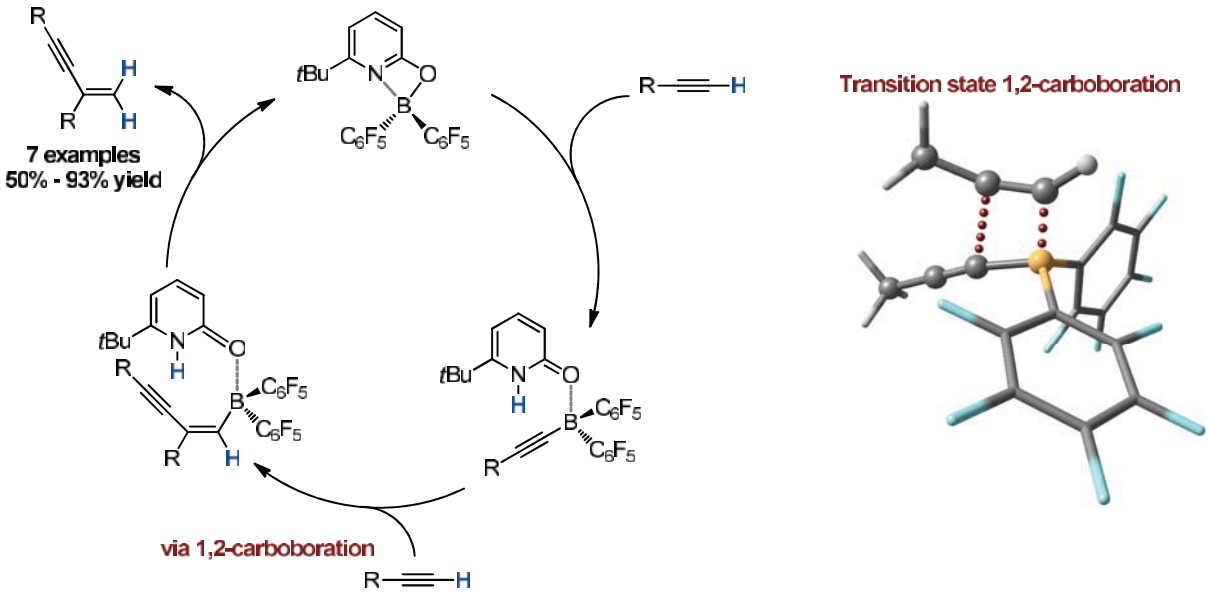

Figure 1: Mechanism of the metal-free *gem* selective dimerization of terminal alkynes and the computed transition structure of the 1,2-carboration.

The mechanism of this transformation was investigated by substantiating every individual step of the catalytic cycle experimentally and by DFT and accurate DLPNO-CCSD(T) computations.[2] Based on these investigations, a synthetic protocol was devised. Besides pure aromatic and non-aromatic hydrocarbons, weakly coordinating groups like arylethers or sterically demanding alkynes are dimerized in fair to excellent yields.

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Aggregation-Induced Emission as a versatile read-out Tool for Biomolecule Recognition

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It is often a challenge to identify small ligands for the inhibition, activation or simple binding to a protein pocket or surface. The well-known organic fluorophores work as fluorescence "off" sensors which fluorescence can be quenched via different unspecific pathways giving false positive binding signals in this context. The new class of luminophores with the fluorescence phenomenon called aggregation-induced emission (AIE)[1] shows an fluorescence "on" behavior by the restriction of their movement. This happens upon simple aggregation or binding to a specific target, which can be used as a versatile readout tool for the evaluation of binding events[2]. We developed novel luminophores with AIE properties as small ligands for recognition of specific bioamines.[3] Therefore, several bioamines were tested and analysed by UV/Vis-, fluorescence spectroscopy, ITC and DLS measurements. We screened three different classes of amines: amino acids, linear amines and aromatic amines. This screening was done in pure water as well as in buffer at pH 6 and 7. Our compounds were able to recognize specific linear amines such as spermine and spermidine via electrostatic interactions. These results presented a novel approach for the selective molecular recognition of spermine using a novel AIE active luminophore.

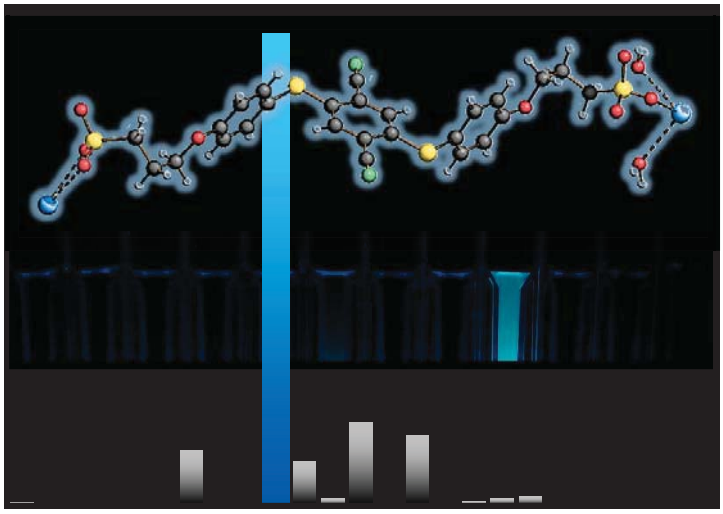

Figure 1: X-ray crystallography of our compound and the selective binding event under UV-light.

References:

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Total Synthesis of Putative Chagosensine

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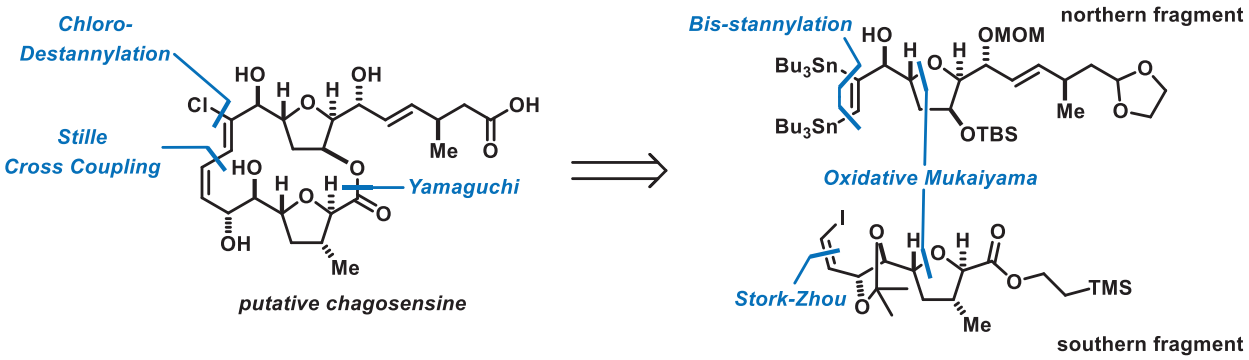
Chagosensine was isolated in 2003 from the Red Sea calcareous sponge *Leucetta chagosensis* collected in the Gulf of Aqaba, Israel.[1] To date, no synthetic efforts towards this novel marine macrolide have been reported and its biological activity remains unevaluated. Structurally, chagosensine is a highly functionalized 16-membered macrolactone containing two *trans*-configured tetrahydrofuran moieties and an unprecedented (*Z*,*Z*)-chlorodiene. The highly oxygenated macrolide bears a total of eleven stereogenic centers. Its unusual structure combined with an unknown biological activity renders the polyketide an interesting target for total synthesis.



Scheme 1: Retrosynthetic Analysis of Putative Chagosensine.

In the retrosynthetic analysis the macrolide was divided into two fragments: a ‘northern’ alcohol section and a ‘southern’ carboxylic acid. The strained macrocycle is furnished via a Yamaguchi macrolactonization. The corresponding *seco* acid derives from an unprecedented sequence of bis-stannylation, regioselective Stille cross coupling and tin-chloride exchange in order to install the (*Z*,*Z*)-chlorodiene moiety in a highly convergent manner. Employing an oxidative Mukaiyama cyclization to access both of the tetrahydrofuran subunits, the synthesis of the two fragments contain a longest linear sequence of 15 steps. In total the first total synthesis of putative chagosensine is achieved in only 22 steps from commercial starting materials.[2] Because of the many discrepancies in the ^{1}H- and ^{13}C-NMR, the isolation team mis-assigned the stereochemistry of chagosensine and future work will focus on the stereochemical reassignment.

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Poster No.24

Photomediated Iodo Perfluoroalkylation of Alkenes with Visible Light Using Phosphine Catalysts

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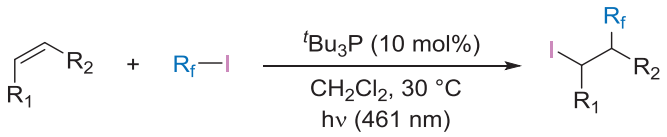
Photocatalysis has an increasing attention in organic synthesis. In recent years a large number of catalysts have been published, that allow the generation of highly reactive intermediates through the excitation of light.[1] Furthermore photocatalysis also resonated in the synthesis of fluoroorganic compounds due to the development and interest in fluorination and perfluoroalkylation of substrates.[1] The activation of perfluoroalkyl halide through the formation of an electron donor-acceptor complexes (EDA) with a Lewis base shows another possibility to synthesize perfluoroalkylation products. [2]

A photochemical iodo perfluoroalkylation, by using amines as Lewis base, was published recently. In a typical reaction 3 equiv of *N*,*N*,*N*′,*N*′-tetraethylethylene diamine (TEEDA) over the course of 36 h were required. A compact fluorescent lamp (CFL), low pressure Hg lamp, or direct sun light were used.[3]

Herein, we present a novel development of a mild, metal-free and efficient photomediated iodo perfluoroalkylation of different simple and functionalized olefins.[4]



Scheme 1: Photomediated iodo perfluoroalkylation of alkenes.

Using *tri*-tert-butylphosphine (10 mol%), various perfluoroalkyl iodides (1.1 eq.) and a customary blue light LED (461 nm) within a short reaction time (1-3 h). The formed complex between the perfluoroalkyl iodide and the used phosphine is observable through a substantial shift of the $-CF_2I$ moiety of the perfluoroalkyl iodide and the phosphine in the corresponding NMR-spectra[5] and a substantial increase of the absorption coefficient in the presence of perfluoroalkyl iodide and a phosphorus-compound. However, the absorption band of $^tBu_3P$ expands marginal wider unto the region of visible light then other screened amines and phosphines. Hereby less harmful light sources can be used for the reaction. As reaction setup a modular and convenient 3D printed photoreactor was constructed and various olefins with different functionalities were converted.[4]

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Tailoring The Generalized Spectral Overlap Integral For Advanced Plasmon-Coupled sm-FRET Pair Investigations

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Energy Transfer mechanisms enable fundamental processes such as energy migration, location, storage and conversion. Resonant energy transfer (RET) based on dipole-dipole coupling is a process widely found in natural materials and artificially designed devices. Furthermore, the principle of RET is also important for multiple sensing applications. Due to its near-field character, RET is limited to the nanometer scale, which also limits the achievable sensitivity and accuracy. Boosting the light matter interaction by improving the near-field coupling efficiency has been shown to bypass these limitations. However, different studies yield contradictory results on the enhancement of the energy transfer rate and efficiency.

We approach this issue by exploiting tailored plasmonic nanoantennas [1], which are coupled to defined donor-acceptor pairs with sub-nanometer position accuracy. Plasmonic nanoantennas composed of noble metal nanoparticles are utilized [1-3]. Individual AgNPs and AuNPs as well as AuNP dimer antennas are used to probe the energy transfer rate and efficiency by means of static and time-resolved fluorescence measurements. In order to avoid ensemble average effects, all investigations are carried out on single donor-acceptor pairs. This approach enables us to adjust the LSPR of the antenna with respect to the spectral overlap integral of the donor-acceptor pair, and thus, to tailor the generalized spectral overlap integral (GSO) [4]. The presented study reveals the effect of the GSO on the ET rate enhancement. Furthermore, influences affecting the ET efficiency are addressed. For all utilized antennas we observe an enhancement of the ET rate, with the largest impact imposed by a dimer antenna with a red-shifted LSPR from the donor emission peak. Despite of the ET enhancement imposed by the plasmonic nanoantenna, the energy transfer efficiency may not be increased necessarily. This can be explained by means of the influence of quenching mechanisms and the spectral dependence of the transition rate modification for the donor and the acceptor imposed by the optical antenna [5].

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Enantioselective Conjugate Azidation of α,β-unsaturated Ketones

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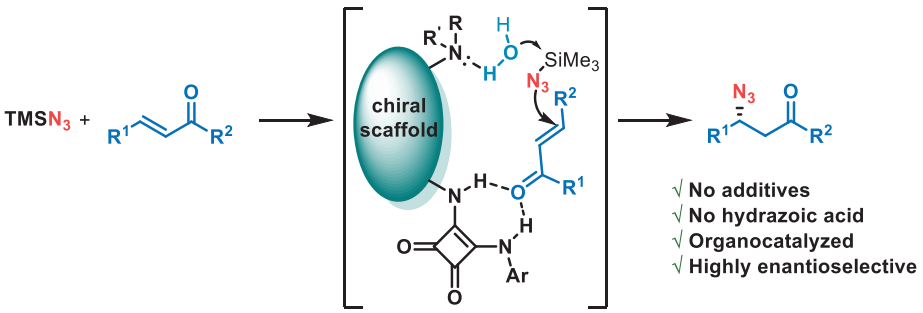
Since the discovery of phenyl azide in 1964 by Peter Griess,[1] organic azides have attracted chemists due to its extensive applications. They are important intermediates in organic synthesis, as they can be transformed in valuable functional groups, such as amines, amides, carbamates, 1,2,3-triazoles, tetrazoles, etc.[2] Therefore, the incorporation of the azide moiety, specially in an enantioselective manner, is of great interest. In this context, *β*-azidation of electron deficient alkenes has been explored as a tool for their enantioselective installation. In the literature, few organocatalytic methodologies for the conjugate azidation can be found, and all of them describe the formation of highly toxic and explosive HN_3 *in situ*.[3]

In our research group, thiourea- and squaramide-based organocatalysts have been widely studied due to their versatility in terms of interactions with different species.[4] We envisioned that a neutral coordinate organocatalyst of this class would be able to activate directly the organosilyl nucleophile. This will trigger the enantioselective conjugate addition of the azide group to the α,β-unsaturated ketone, which to the best of our knowledge have never been utilized as platform in a organocatalytic azidation processes. Through this strategy, we access to a set of enantioenriched azides, which are key intermediates in the preparation of synthetically relevant products.



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Extension of Dynamic Polymer Networks *via* Nitroxide Mediated Polymerization

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Recently we reported the synthesis of dynamic covalent porous organic polymers *via* the nitroxide exchange reaction (NER), directly from multitopic alkoxyamine and nitroxide precursors.[1] The dynamic nature of the NER allows tuning, recycling and self-healing of the networks as well as following the exchange process *via* electron paramagnetic resonance (EPR).[1-2] In the NER, thermal C-O bond homolysis of alkoxyamines leads to transient carbon-centered radicals and persistent nitroxide radicals. If homolysis of an alkoxyamine is performed in presence of additional nitroxide radicals, the thermodynamically favored mixed derivatives are obtained.[3-4]
The alkoxyamine functional groups can not only be utilized as dynamic bonds, as in the described NER, but also act as initiators for nitroxide mediated polymerization (NMP).[5] In this presentation we will introduce our ongoing investigation to form nitroxide exchange networks with extended strands by combining NER and NMP.
We followed three possible approaches: (i) first network formation, followed by monomer addition to extend the network; (ii) first polymerization using multitopic alkoxyamines and monomers, followed by addition of multitopic nitroxides to crosslink the structure; (iii) polymerization and network formation in a one pot approach. The three approaches are summarized in Fig. 1. The different approaches are discussed in terms of network homogeneity and strand polydispersity.

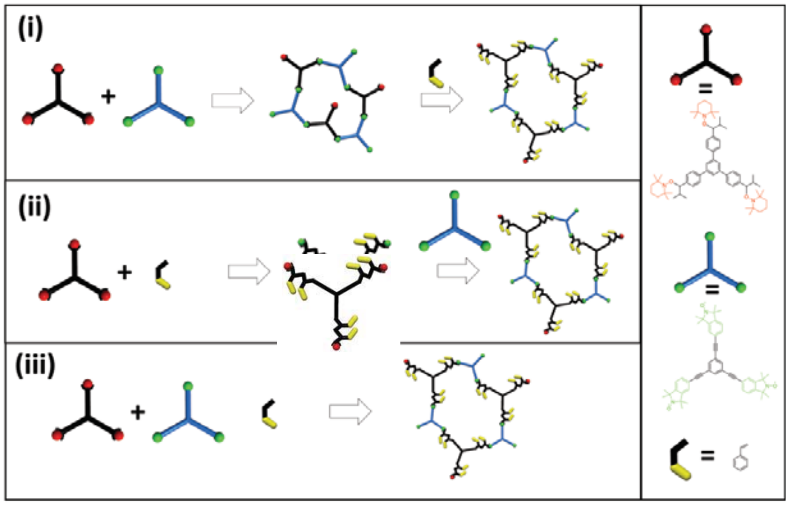

Fig. 1: Different approaches in the synthesis of polymer networks with strand extension *via* combination of NMP and NER.

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Poster No.28

Triazole-based XB donors and their application in catalysis

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The number of applications that utilize the attractive interaction between a Lewis acidic halogen atom and a Lewis base, *i.e.* the halogen bond (XB), is growing.[1] Many of these applications describe the use of XB-based catalysts.[2] As of now, no examples of asymmetric catalysis based solely on XB activation have been reported, although enantiodiscrimination utilizing XBs is possible.[3] We envisioned that asymmetric XB catalysis could be achieved by using chiral halo-triazoles (Figure 1, A), which are readily accessible via a copper-catalysed click reaction between haloalkyne and organic azide.[4] Herein we characterise the XBs formed by these donors in the solid state to the counterion or a second triazole molecule (Figure 1, B). Next, association constants in solution to (thio)ureas, amines and imines are described, with values of up to 1.1 x 10^4 M^{-1} in the case of quinuclidine (Figure 1, C).[5] Additionally, the enantiodiscrimination ability of the donors is explored. Finally, the catalytic potential of the triazoles in an aza-Diels-Alder reaction is described with catalyst loading as low as 2 mol% (Figure 1, D).

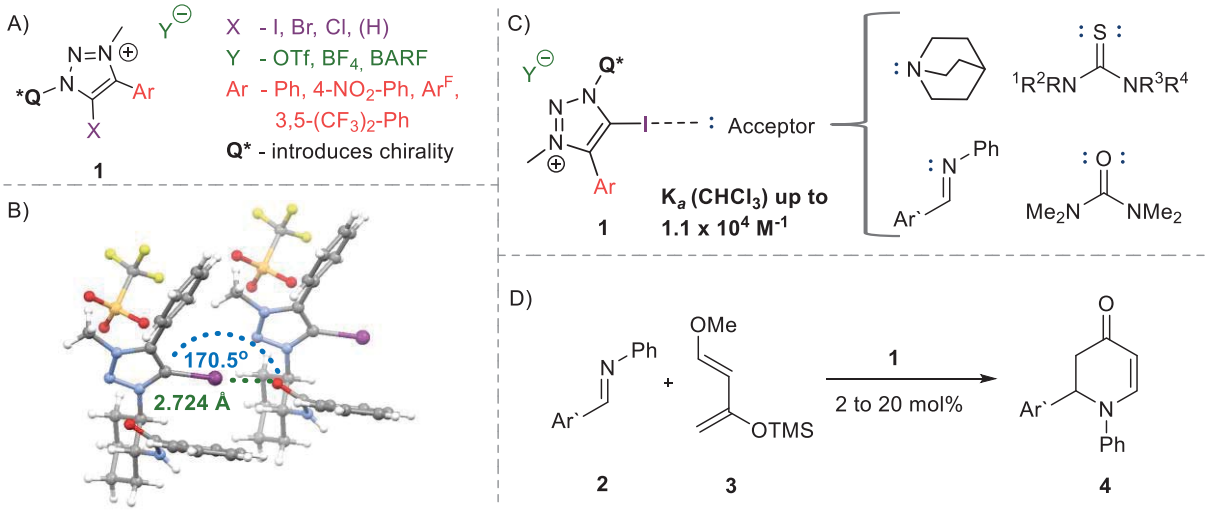

Figure 1: A) Triazole-based XB donors, B) a XB in the solid state, C) studies in solution, D) model reaction under study.

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Late-Stage Diversification through Manganese-Catalyzed C−H Activation: Access to Acyclic, Hybrid, and Stapled Peptides

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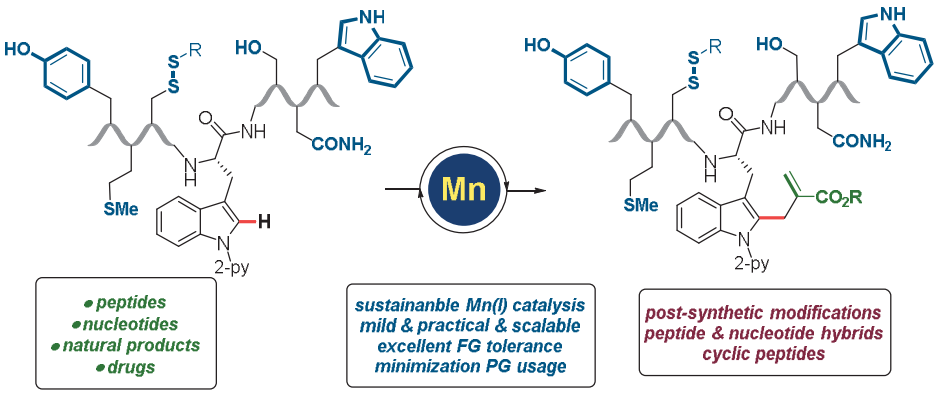
Non-natural peptides have emerged as increasingly potent scaffolds in medicinal chemistry and the pharmaceutical industry. As a consequence, the chemoselective assembly and modification of structurally complex peptides continues to be of utmost importance.[1] Significant recent momentum was gained through the development of palladium-catalyzed cross-couplings of peptides. A significantly more atom- and step-economic strategy relies on the direct activation of otherwise unreactive C–H bonds,[2,3] with recent transformative applications towards peptide modification.[5] As part of our program on sustainable C–H activation,[5,6] we reported on the first manganese-catalyzed C–H allylation of structurally complex peptides with easily accessible Morita–Baylis–Hillman adducts.[7] Notable features of our strategy include 1) an unprecedented manganese(I)-catalyzed peptide C–H alkylation, 2) the first metal-catalyzed peptide modification that installs synthetically useful α,β-unsaturated esters, 3) orthogonal late-stage diversification, and 4) a uniquely versatile manganese catalyst that proved applicable to C–H fusion with peptides, natural products, steroids, drug molecules, and nucleobases, among others.



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Poster No.30

Mechanistic Insights on CO_2 Reduction Reactions at Pt/[BMIM][BF_4] Interfaces from In Operando Spectroscopy

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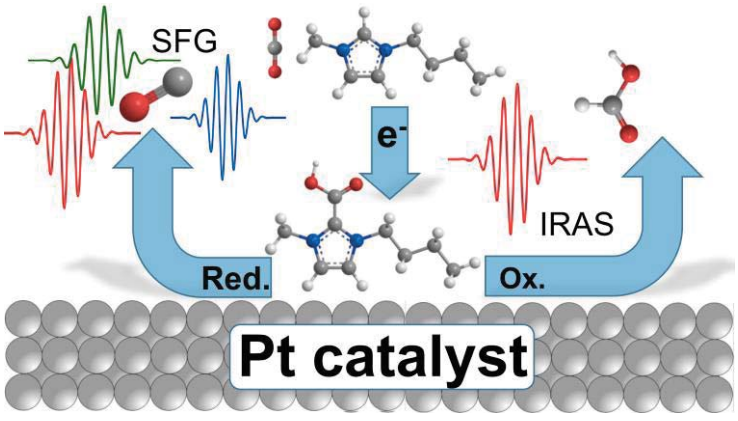
Electrochemical CO_2 reduction reactions (CO_2RR) at Pt(poly) and Pt(111)/electrolyte interfaces were studied with cyclic voltammetry (CV), FTIR and vibrational sum-frequency generation (SFG). Using room-temperature ionic liquids (RTIL) such as [BMIM][BF_4] and [EMIM][DCA] as electrolytes, we have investigated the influence of both water as proton source and the chemical identity of the RTIL as a co-catalyst on the activity for CO_2RR. Water concentrations of up to 0.5 M lead to a substantial rise in activity for CO_2RR. Also the chemical structure of the electrolyte seems have a strong impact on the reactivity as higher reduction currents have been observed for [EMIM][DCA] compared to [BMIM][BF_4] and [EMIM][BF_4].

To study mechanistic details of the CO_2RR we applied electrochemical IR absorption spectroscopy. Potentiodynamic measurements in [BMIM][BF_4] revealed a vibrational mode centered at 1670 cm^{-1} which rises during the cathodic sweep. We attribute the latter to the C=O stretching mode of a zwitterionic imidazolium carboxylate species. The latter is generated via a carbene intermediate, for which we present spectroscopic evidence.

In order to study the molecular structure of Pt/[EMIM][DCA] interfaces in operando, we have performed potentiodynamic SFG spectroscopy. SFG spectra were recorded in situ during potential sweeps from 0.6 to -1.4 V vs SHE and reveal formation of CO on atop surface sites and a Stark shift of 24 cm^{-1}/V. This Stark shift is indicative for a relatively high surface coverage of CO.

Strongly adsorbed CO molecules cause a poisoning of the Pt catalyst surface and lead to a deactivation over many cycles (>20).



Micellar Brønsted Acid-Mediated Synthesis of DNA-Tagged Heterocycles

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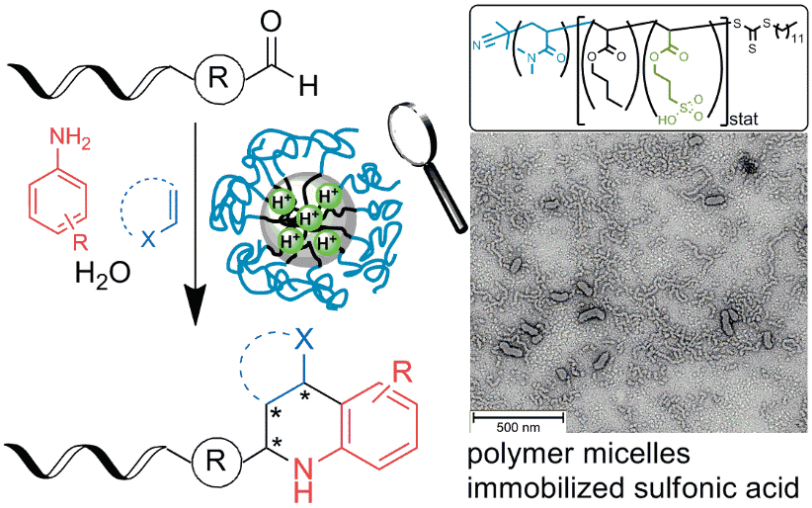
Methods for selectively reacting DNA-tagged small organic molecules to target compounds are sought not the least since DNA-encoded compound collections have found broad use as screening technology. DNA-encoded libraries (DELs) are synthesized through combinatorial strategies with alternating organic preparative synthesis, and enzymatic DNA-encoding steps.[1] DNA-encoded compound synthesis must take into account the chemical lability of DNA, for instance the risk of cleavage of purine bases from the oligomer under acidic conditions. To circumvent this impediment, we utilized a hexathymidine sequence “hexT” as an adapter oligonucleotide in the initial step of DEL synthesis.[2,3] From the other side, micellar catalysis holds much promise for encoded chemistry as it facilitates compound synthesis under often mild conditions in aqueous dispersions. Amphiphilic block copolymers consisting of a hydrophilic polyacrylamide portion, and a hydrophobic poly(butyl acrylate) portion statistically functionalized with sulfonic acid moieties, assemble in water to micellar aggregates. These micelles confine the acid catalyst in their hydrophobic compartment. DNA strands could be incubated for prolonged time with up to millimolar concentrations of these acidic nanoreactors. They enabled the reaction of DNA-conjugated aldehydes to diverse substituted tetrahydroquinolines and aminoimidazopyridines by Povarov, and Groebke-Blackburn-Bienaymé reactions, respectively, and the cleavage of *t*Boc protective groups.



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Host-Guest-Interactions Between a Novel Metallacycle and Goldclusters

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The synthesis of a novel supramolecular coordination oligomer can readily be performed by C_3-symmetric triaminoguanidinium based ligands and zinc(II) precursors.[1] These metallacycles show rapid complexation of fullerenes C_{60} and C_{70} due to stabilizing π-π-interactions and entropic effects.[2]

For goldclusters $Au_9(PPh_3)_8(NO_3)_3$[3], $Au_{11}(PPh_3)_7Cl_3$[4] and $Au_{55}(PPh_3)_{12}Cl_3$[5] interactions with the metallacycle are observed. Au_{55} and Au_9 are "digested" to form Au_{11}. Synthesis and stabilization of new goldclusters shall be performed in the oligomer cavity by utilization Au-π-interactions.

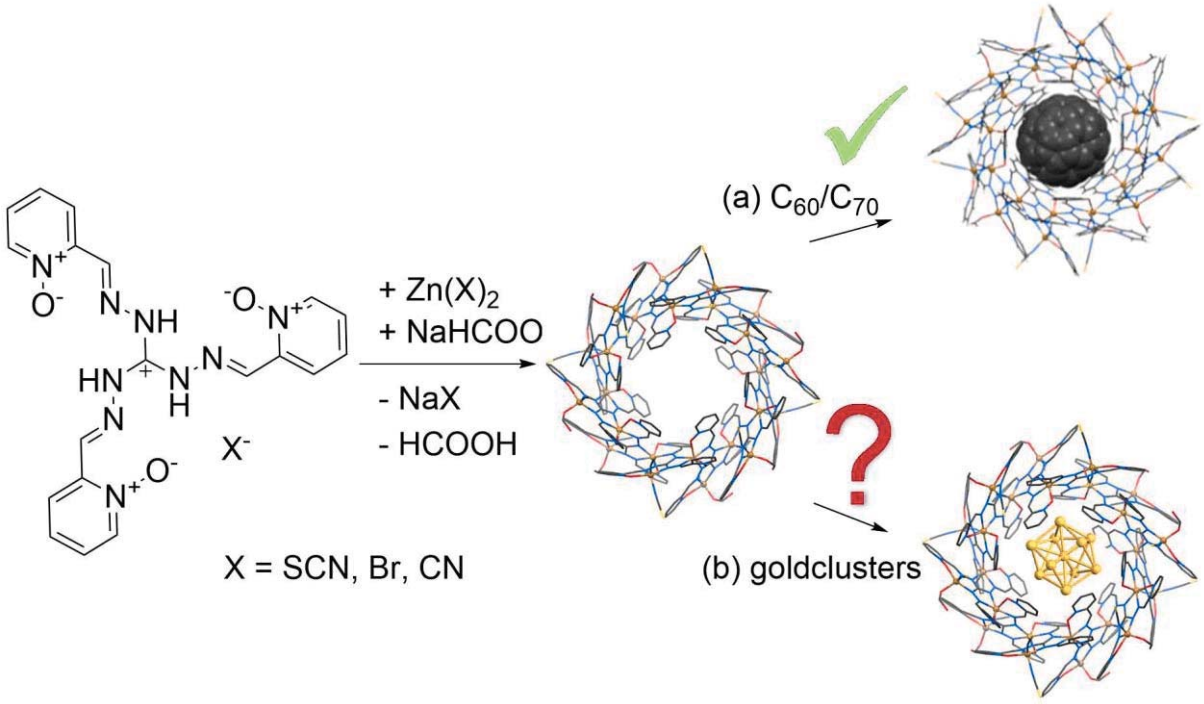

Figure 1: (a) Host-guest chemistry; the storage of fullerene into the cavity proved by SCXRD (b) Supposed: host-guest chemistry with a goldcluster stabilize cavity.

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Iodine-Catalyzed Nazarov Cyclization[1]

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Molecular iodine – an earth abounded, cheap and easy to handle solid – is a versatile and very effective catalyst for the activation of carbonyls.[2] Its catalytic activity is most likely due to halogen-bond interactions with the substrate.[3]

The Nazarov reaction is a conrotatory 4-π-cyclization leading to the formation of cyclopentenones (Figure 1), which can be found in various natural products and pharmaceuticals.[4] So far, different approaches with Lewis acids or chiral Brønsted acids are reported.[5]

We were now able to apply molecular iodine in the cyclization of a brought variety of substrates under very mild conditions. The Nazarov products could be obtained in good to excellent yields (17 substrates, up to 99% yield) within short to reasonable times. Besides aromatic and alkyl moieties, different functional groups were tolerated, and both activated as well as non-activated double bonds underwent the cyclization. Furthermore, computational and kinetic investigations indicate that the active catalyst is in fact molecular iodine and that other modes of activation (Brønsted-acid or iodonium-ion catalysis) are very unlikely.

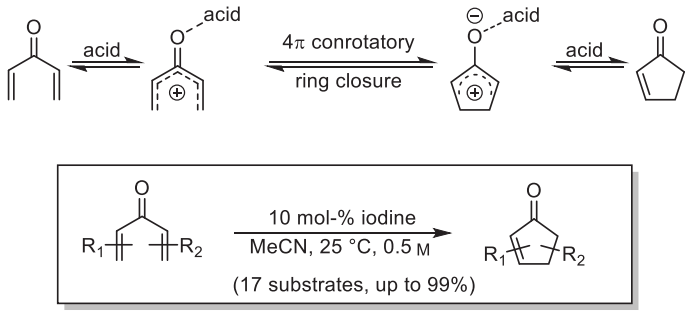

Figure 1: Development of an iodine-catalyzed Nazarov cyclization.

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Poster No.34

Palladium-Catalyzed Decarboxylative Heck-Type Coupling of Aliphatic Carboxylic Acids Enabled by Visible Light

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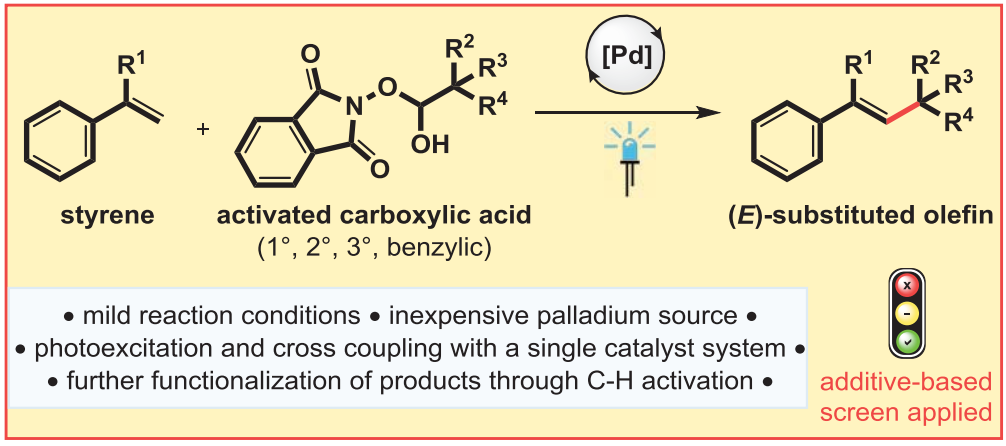
Olefins represent a widely-used class of functional groups in organic synthesis and material science. Thus, the development of new methods for the preparation of multisubstituted alkenes with complete stereocontrol is highly desirable. The Heck reaction is among the most fundamental reactions in the portfolio of synthetic organic chemists to create substituted carbon-carbon double bonds. While the formation of $C(sp^2)$–$C(sp^2)$ bonds is largely established, analogous assembly of $C(sp^2)$–$C(sp^3)$ connectivity is more challenging with traditional methods.[1] Typically, aliphatic carboxylic acids are cheap, stable and non-toxic and their activation can be achieved in a single, operationally simple and high yielding step, which makes them an attractive alternative to organic halides.[2]

Here, we present the coupling of *N*-hydroxyphthalimide esters derived from aliphatic carboxylic acids with electronically diverse styrenes to deliver substituted olefins with perfect (*E*)-selectivity.[3] This method is exceptionally mild and relatively inexpensive $Pd(PPh_3)_4$ is used as the catalyst. Mechanistic studies for this process revealed a radical process initiated through excitation of a Pd(0) species with visible light. To showcase the utility of the products obtained through this methodology, they were further functionalized through a new C–H activation approach.[4]



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Reductively Degradable Polymer-Nanocontainers for Intracellular Delivery of labeled Phospholipids

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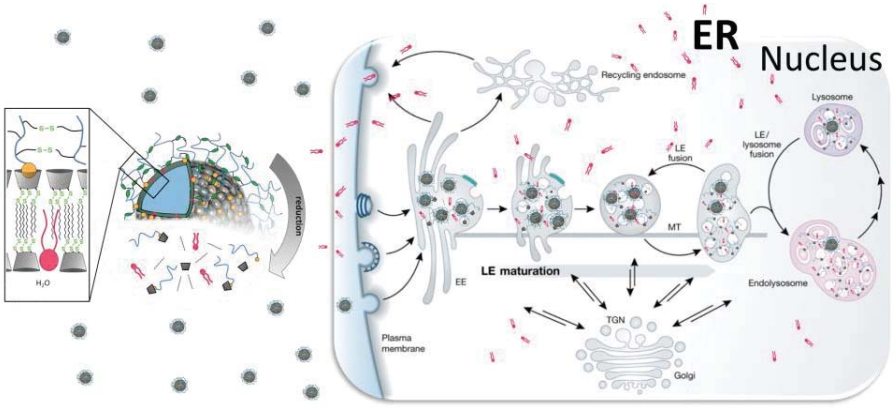
The specific transport of fluorescently labeled phospholipids into intracellular regions offers significant potential to answer fundamental questions about highly dynamic membrane-related processes like e.g. intracellular distribution of lipids, the formation of lipid microdomains and the interaction of specific lipid subsets with membrane proteins. An essential biotechnological challenge in live cell experiments is to introduce fluorescent cargo into intracellular regions without affecting the physiological integrity or morphology of the cell membrane. Therefore we synthesized redox-responsive cyclodextrin amphiphiles for establishing polymer-nanocontainers which are able to deliver fluorescently labeled phospholipids (PC, PA, PI, PIP_2) to intracellular membrane compartments (endosomes, ER). We show here that reductively degradable cyclodextrin amphiphiles[1-3] and different phospholipids can form liposome-like cyclodextrin vesicles (CDL_{SS}) with a homogeneous distribution of each lipid. Host-guest-mediated self-assembly of a cystamine-crosslinked adamantane polymer shell on the CDL_{SS} then produced reductively degradable polymer shelled liposomes (PSL_{SS}). The PSL_{SS} showed very high stability in biological medium and efficient endocytic uptake into primary endothelial cells (HUVEC). The release of the amphiphilic cargo via reductive degradation of the PSL_{SS} was verified by DLS, TEM and FRET experiments. Importantly the reductive microenvironment of endosomes also triggered the release of the amphiphilic cargo, i.e. the fluorescently labeled phospholipids. Our data also show that the release of phospholipids from endosomes depends on the type of lipid. PC and PA derivatives escaped endosomes and localized in the ER, while for PI only a slow release from endosomes was observed. Thus PSL_{SS} represent a highly efficient transport system for lipid-like amphiphilic cargo into the intracellular environment.



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Abstract Picture modified: Huotari et al., *EMBO Journal*, **2011**, *30*, 3481–3500.

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Poster No.36

Rotating Catalysts Are Superior: Suppressing Product Inhibition by Anchimeric Assistance in Four-Component Catalytic Machinery

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Three distinct four-component supramolecular nanorotors, prepared by varying the rotator's structure and keeping all other components constant, exhibit rotational frequencies that differ by almost a factor of 100. When the rotors were used as catalyst for a click reaction, the product yield correlated with the speed of the machine, i.e. 20% at 0.5 kHz, 44% at 20 kHz and 66% at 42 kHz. The kinetic effect on the product yield is attributed to the ability of a rotating catalyst to displace the product more efficiently from the active site the higher the speed. This mechanistic hypothesis was convincingly corroborated by a linear correlation between product yield and product liberation.

(a) (b)

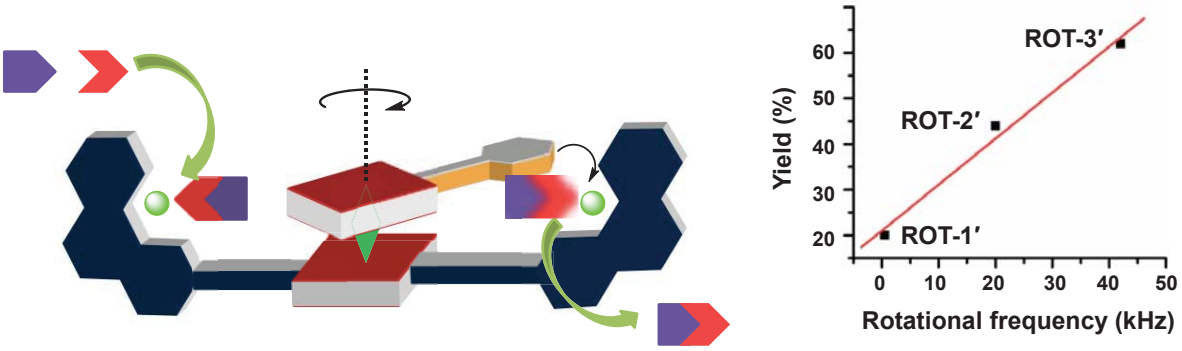

Figure 1: (a) Faster rotary motion leads to reduced product inhibition. (b) Yield of product vs rotational frequency of rotors.

The present work demonstrates that catalytic machineries with particular features for suppressing product inhibition can be prepared by simply mixing four distinct components. Analogous to multicomponent enzymatic systems, such as the ATP synthase, the catalytic activity depends on the nanomechanical liberation of the product, presum-ably by an SN2-type displacement reaction. It is one of the rare non-biological examples, where the
machine speed correlates with the catalytic activity.

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Short and Efficient Preparation of Mono- & Tri-functionalized Resorcin[4]arenes

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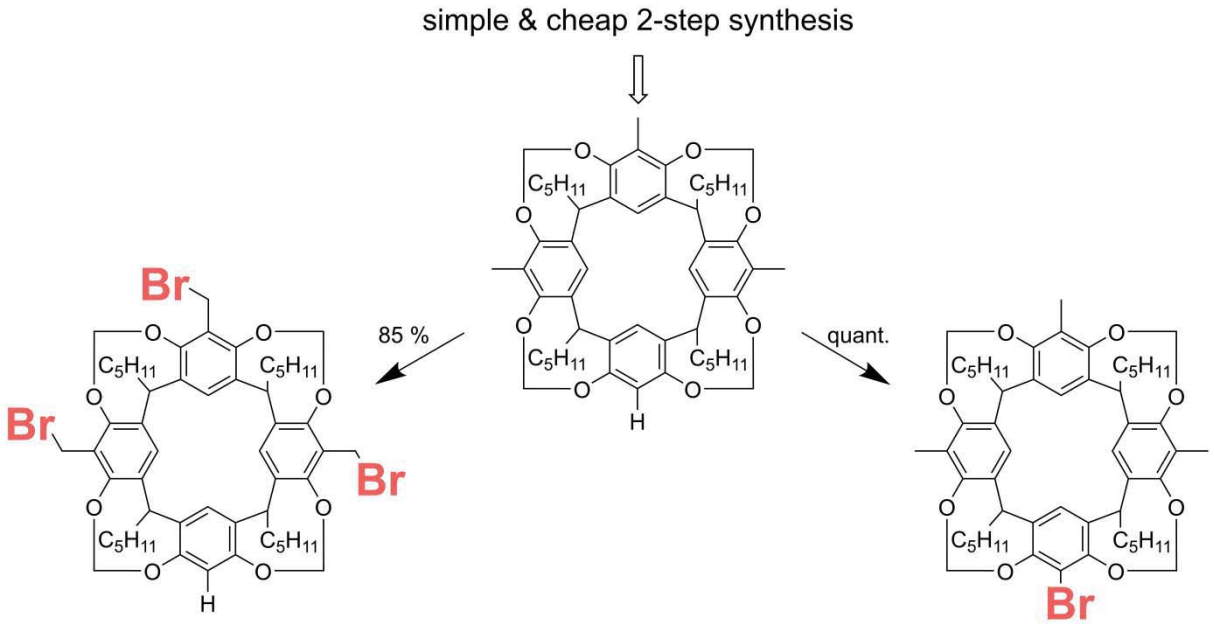
Resorcin[4]arenes are manifold building blocks for supramolecular motifs like molecular bowls[1], (hemi-)carcerands[2], molecular reactors[3],[4] or molecular machines[5]. For higher selectivity in molecular recognition a more specific derivatization of the resorcin[4]arene upper-rim is helpful.

Herein, we present the simplified synthesis of mono- & tri-functionalized resorcin[4]arenes and the elegant use of different reaction conditions towards the selective mono-& tri-halogenation, enabling further derivatization with coordinating motifs.

Through tuning and refining reaction conditions for the co-condensation of hexanal, 2-methyl-resorcinol and resorcinol we were able to easily collect a well-defined mixture of tetramethyl- and trimethylresorcinarenes, which - after further bridging - provided the bowl-shaped structure. Highly selective protocols for the radicalic tris-bromination, as well for the electrophilic mono-halogenation were developed, setting the stage for subsequent functionalizations.

Paper in preparation.



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DNA-Supported Bimetallic Photoredox Catalysis

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In the era of climate change and limited fossil resources, the generation of energy or the synthesis of materials from renewable resources is particularly important. Over the last years, catalytically active bimetallic photoredox-systems have been developed, which allow the use of solar energy for the generation of hydrogen from aqueous solutions or the formation of new C-C bonds.[1,2] However, the rational design of effective photoredox-catalysts is still difficult, which has limited the success in generating highly active and stable systems. For this reason, novel approaches that allow for the fast generation of catalyst libraries are highly sought after, since these might allow the identification of promising new catalyst structures.

We herein present our experiments for the generation of novel bimetallic photoredox-catalysts based on DNA-templation. The synthesis of such photoredox catalysts is being accomplished by tethering organometallic complexes (a photosensitizer and a reaction center, see figure 1) to complementary oligonucleotide strands. Coupling worked best via strain-promoted copper-free click reaction. The resulting functionalized DNA-strands can then undergo hybridization to generate the corresponding double-helical structures, thereby bringing the respective metal-complexes into close proximity and giving the desired bimetallic catalysts. Combination of differently functionalized strands thus allows the easy generation of a library with a plethora of photoredox catalysts. These are then compared in terms of hydrogen-yield and efficiency to the non-supramolecularly coupled complexes in aqueous solution via gas-chromatography.

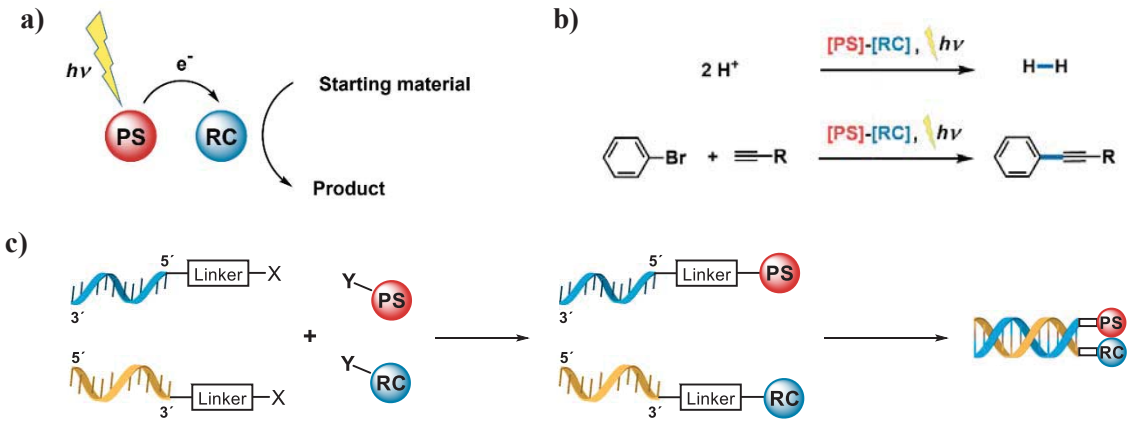

Figure 1: **a)** Concept of photoredox-catalysis via photosensitizer and reaction center,
b) Possible reactions via photoredox-catalysis,
c) Generating a bimetallic catalyst-library by hybridization of differently functionalized oligonucleotides.

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Ni-catalyzed Reductive Liebeskind-Srogl Alkylation of Heterocycles

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The functionalization of heterocycles via cross-coupling has become a powerful tool towards the rapid diversification of biologically active compounds.[1] In this context, the venerable Liebeskind-Srogl coupling opened the door to the use of robust and stable C(sp^2)–SMe bonds as electrophilic partners[2] in combination with a variety of nucleophiles.[3] Despite the great progress in this area, the coupling of thioethers is still limited to the use of an organometallic reagent partner, which is often sensitive to air, incompatible with several functionalities and require several steps of synthesis. Recently, reductive cross-couplings between two electrophiles have arisen as powerful, simple and practical strategies to circumvent the preparation of such reactive organometallic reagents.[4] However, most of examples reported have focused on the use of aryl halides or pseudo-halides where the C(sp^2)–X bond is polarized due to the electronegative nature of the X element (inductive effect).[4] Herein we present a Ni-catalyzed alkylation of C–SMe with alkyl bromides for the decoration of heterocyclic frameworks (Figure 1).[5] The protocol, reminiscent to the Liebeskind-Srogl coupling, makes use of simple C(sp^2)–SMe to be engaged in a reductive coupling. The reaction is suitable for a preponderance of highly value heterocyclic motifs. In addition to cyclic bromides, non-cyclic alkyl bromides are well accommodated with exquisite levels of retention over isomerization. The protocol is scalable and permits orthogonal couplings in the presence of other functionalization handles.

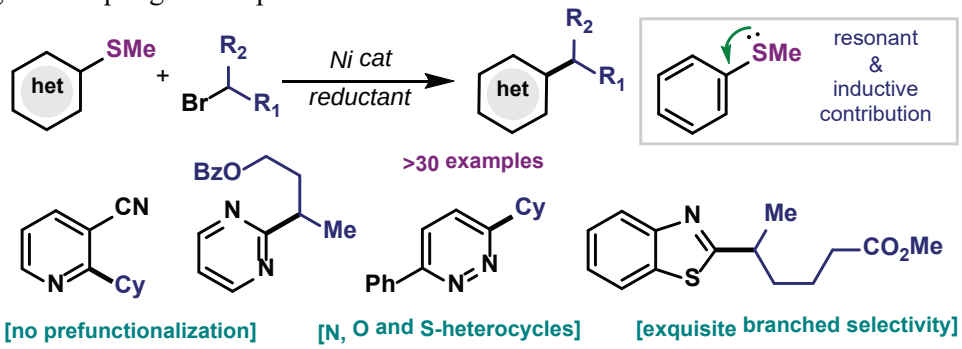

Figure 1. Reductive Liebeskind-Srogl Alkylation of Heterocycles

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Poster No.40

Insights into the Immobilization of Enzymes onto Hybrid Hairy Isotropic and Janus Particles

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The design of colloidal core-shell particles with advanced architectures and tailored properties provides an excellent base for the immobilization of catalytically active species, such as enzymes [1,2] and metal nanoparticles [3], which may enhance their structural and catalytic stability, reducing product inhibition and facilitating their recovery.
Herein, we report on the synthesis of hybrid isotropic and Janus particles with controllable size, geometry, grafting density, polymer chain length, and chemical functionality to control the interfacial properties of the particles (Fig. 1a,c).[1,2] We propose the immobilization of laccase from *Trametes versicolor* onto these particles as an application that would benefit from the unique properties and as well as chemical and geometrical anisotropy of these carrier materials (Fig. 1b).[1,2] Further, we discuss the correlation between the controlled design of polymeric interface and its impact on the immobilization yield and enzymatic structure of laccase, as well as occurring changes in the surface morphology, charge and adhesion performance of the final polymer-enzyme layer.[1,2] Moreover, the best performing system offering an immobilization yield of 92% and activity of 5.7 kU/(g particle) was successfully used for the decolorization of Cibacron Blue P-3R in up to 18 cycles.[2] To exploit the superior interfacial activity and recovery of Janus particles, we selectively modify one of their sides with enzyme, and the other hemisphere with a thermo-switchable adhesive polymer. This detailed study contributes to the understanding of the rational design of catalytically active and easily recoverable hybrid materials for applications in textile industry and environmental technologies.[1-3]

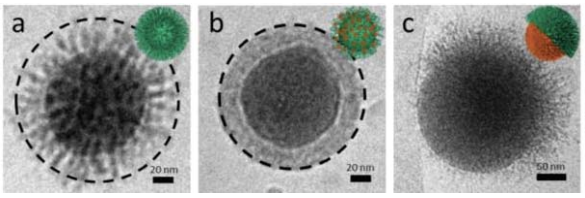

Figure 1: (a) Representative cryo-TEM images of (a) an isotropic hybrid particle without immobilized enzyme, (b) an isotropic hybrid particle with immobilized laccase from *Trametes versicolor*, and (c) a hybrid Janus particle. Insets show schematic illustrations.

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Competing Pathways in a BODIPY-based Metallosupramolecular Polymer

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BODIPY dyes have attracted considerable attention in the past decades due to their excellent optical, photochemical and electronic properties as well as physiological stability, which have enabled their application in fields as diverse as optoelectronics and biomedicine. [1] Some of these applications require an organized dye arrangement into well-defined aggregates, which can be achieved by molecular design. [2] In addition, BODIPY-dyes have the ability to self-assemble in an H- or J- type fashion, because of the presence of π-π interactions and the small size and planarity of the BODIPY core. [3]

In this abstract, a new Pd(II)-BODIPY complex that self-assembles into three different aggregates depending on various external parameters is presented. Upon cooling a hot solution of the molecularly dissolved state, an H-type aggregate (**Agg II**) is formed through a cooperative self-assembly process. On the other hand, when a solution of **Agg I** is subjected to high temperatures, sonication, or kept at room temperature over time, a J-type aggregate is formed (**Agg III**) involving a complex aggregation pathway.

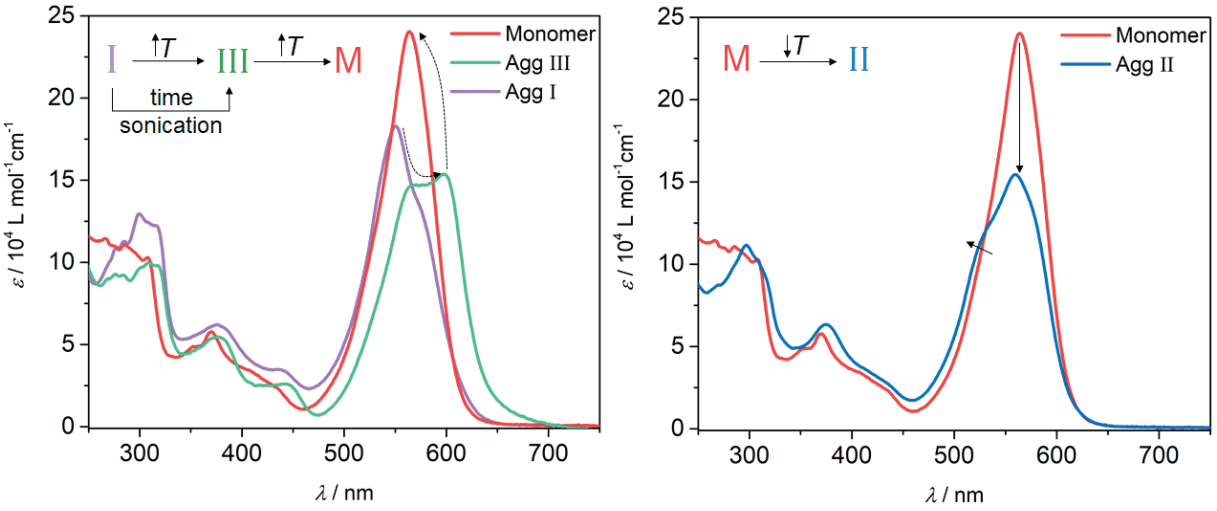

Figure 1. Comparison of the UV/Vis spectra (2 x 10^{-6} M, methylcyclohexane) of **Agg I**, **Agg III** and **Monomer** (left) and **Agg II** and **Monomer** (right). The arrows indicate the spectroscopic changes upon heating, over time or sonication (left) or upon cooling (right).

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Poster No.42

Genetically Encoded Homocysteine Derivatives Carrying Enzymatically Removable Protecting Groups

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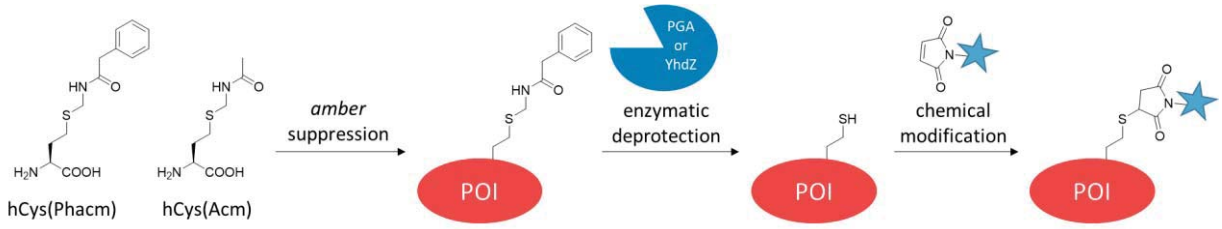
The chemical modification of proteins is of great importance for numerous applications. In biochemical research fluorophores can be attached to visualize proteins in live cells or protein-protein interactions can be chemically stabilized for investigation. For medicinal purposes bioconjugates, like antibody-drug conjugates, can be formed, which represent a highly promising class of therapeutics. Cysteine maleimide chemistry has become the most widely used modification strategy due to its mild reaction conditions, the avoidance of toxic or highly reactive reagents and the commercial availability of many maleimide reagents.[1] However, for some applications it is necessary to label two different positions orthogonally, for instance in FRET studies. Therefore the development of novel modification strategies is of great interest.

Here we present two new genetically encoded homocysteine (hCys) derivatives, phenylacetamidomethyl (Phacm) and acetamidomethyl (Acm) protected hCys. Both can be enzymatically deprotected under mild conditions by Penicilin-G amidase (PGA) or the deacetylase YhdZ from *Bacillus subtilis*[2] and subsequently modified using maleimide reagents. This strategy enables the orthogonal modification of a homocysteine and a cysteine residue to dually modify a protein.



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Photocatalytic Oxidative Iodination of Electron-Rich Arenes

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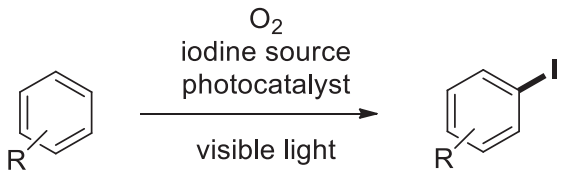
Aryl iodides are valuable building blocks in organic chemistry, as they are widely used as synthetic intermediates in various C–C couplings, and for the preparation of hypervalent iodine reagents. Furthermore, they are also used as radiopharmaceuticals. Consequently, the preparation of iodoarenes attracts attention within the synthetic community and the development of new methods for their synthesis is highly desired. Iodination with molecular iodine is challenging because iodine is quite unreactive towards most organic compounds and hence some additional activation is necessary to achieve efficient iodination. Usually, acids and oxidizing agents are employed to facilitate the process. [1]



Scheme: Photooxidative iodination.

Photoinduced oxidation is a very efficient method, as aerobic oxygen can often be used as the terminal oxidant. A photoinduced single-electron oxidation of an arene was used to facilitate bromination, [2] chlorination [3] and fluorination [4] reactions. Moreover, another approach with the light-induced generation of hydrogen peroxide was demonstrated to also facilitate the chlorination process. [5] However, reports of photochemical reactions utilizing the iodine I^-/I_2 manifold are only scarce and to this date, no effective photochemical oxidative iodination of arenes was reported. In this manifold I^- gets readily oxidized to I_2 that is very colored and consequently causes light penetration issues.

We will present our results of the development of the light-driven oxidative iodination method (**Scheme**) and its mechanistic investigation. A special emphasis will be put on overcoming the poor light penetration issues.

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Poster No.44

A Highly Reduced Ni–Li–Olefin Complex for Catalytic Kumada–Corriu Cross-Couplings

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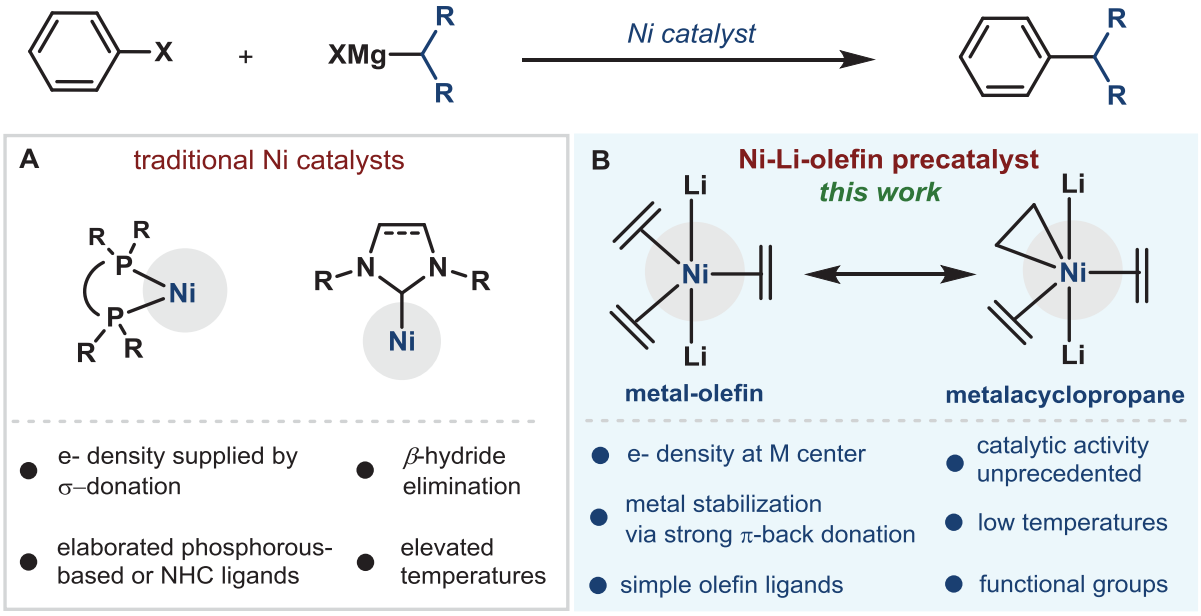
The ability of nickel catalysts to efficiently maneuver across different oxidation states (Ni(0), Ni(I), Ni(II), Ni(III) or Ni(IV) species) has endowed it with distinctly attractive features, many of which have enabled a wealth of consequent synthetic utility.[1] Despite this rich history, efforts to probe the catalytic activity of low-valent —formally negative Ni complexes— remain literally nonexistent.[2] A formally Ni(-II) complex was reported by Pörschke and Jonas in 1975.[3] Subsequent investigations to explore the catalytic behavior of this interesting complex were undertaken by us in the context of Kumada-Corriu couplings. Our work suggests the ability to engage various C(sp^2)-X electrophiles (X=Br, Cl, F, OTf) with alkyl Grignard reagents. The transformation is tolerant with Grignard-sensitive functionalities, which is underpinned by the extremely low temperatures permissible with the Ni-catalyst.



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Halogen-bonded boxes employing azobenzenes

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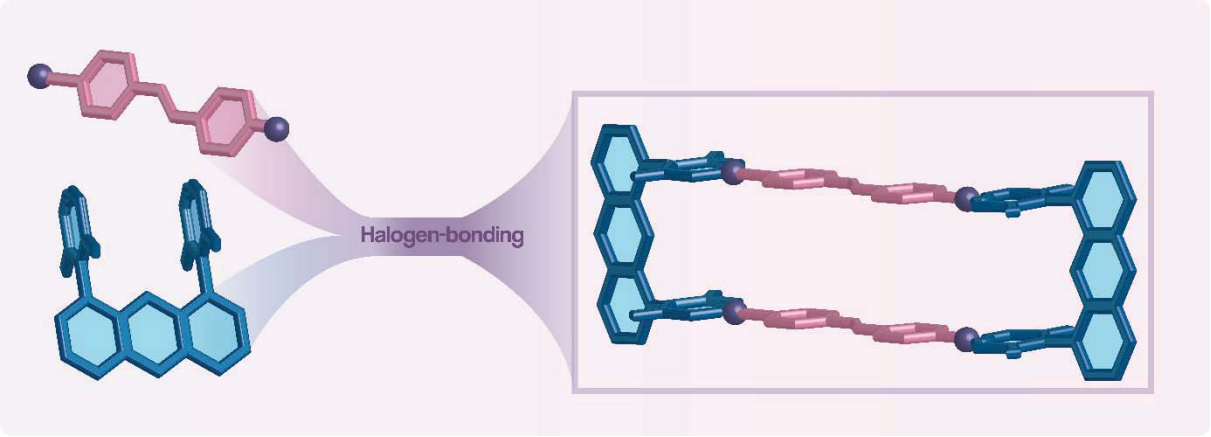
The halogen bond is an attractive non-covalent interaction between a polarized halogen atom (donor) and a Lewis base (acceptor).[1] Herein, we report the synthesis and crystal structures of three [2+2] supramolecular boxes assembled by halogen bonding. The discrete, two-dimensional boxes with a length of 25 - 30 Å are based on rigid u-shaped anthracene and anthracene-9,10-dione building blocks bearing two 3,5-lutidine acceptors in 1 and 8 position combined with *E*-4,4'-di(iodo)perfluoroazobenzene (**A1**) and novel *E*-4,4'-di(iodoethynyl)perfluoroazobenzene (**A2**) acceptors. Solvent-free single-crystals of **U1**···**A1** and **U2**···**A1**, as well as a chloroform adduct of **U1**···**A2** could be obtained and the solid-state structures were studied by single-crystal X-ray analysis. The **U1**···**A1** box has a length of approximately 25 Å (anthracene-anthrance distance) and a height of 5 Å (distance between the *ipso*-carbons of the lutidines). The lutidine units are curved inwards slightly possibly to maximize the short halogen bonding interactions (N···I distances 2.76 and 2.78 Å) between the stacking azobenzenes **A1**. In contrast to **U1**···**A1**, the azobenzenes in **U2**···**A1** are rotated by almost 90°. To our surprise, it was challenging to observe and quantify the assemblies in solution. Association constants were determined to be $K_a < 10^2$ M^{-1} for the strongest binding **A2** and are on the lower detection limit with errors conservatively estimated to be in the same magnitude as the actual binding constant. Although precise NMR analysis was not possible, the change of the geometry of azobenzenes upon switching must necessarily be followed by an overall change of the geometry of the halogen bonded systems. To the best of our knowledge, no switchable halogen-bonded monodisperse boxes are known to this date and the principles disclosed here may pave the way towards the design and realization of more complex and potentially responsive, halogen-bonded supramolecular systems.



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Poster No.46

Heterobifunctional rotaxane catalysis: Cooperative effect of alkali metal phosphate and amine.

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The particular nature of mechanically interlocked molecules makes them suitable as artificial receptors or sophisticated chemical catalysts.[1] Recently, a bifunctional chiral homo-[2]catenane based on 1,1'-binaphtyl-phosphoric acids has been synthesized.[2] It has been used as receptor for dicationic molecules and as asymmetric organocatalyst for the stereoselective transfer hydrogenation of quinolines by Hantzsch-esters.[3] Here is presented the synthesis and application for *Asymmetric Counteranion-Directed Catalysis*[4] of a new heterobifunctional rotaxane based on mechanically linked ammonium-phosphate zwitterion (see Fig. 1.a). In its basic form, this system catalyzes the Michael addition of diethyl malonate on *trans*-cinnamaldehyde *via* its active amine through an iminium intermediate (see Fig. 1.b).

In this study, a cooperative effect is demonstrated between the phosphate salt and the amine moiety leading to an enhancement of the conversion yield and reaction rate when compared to amine catalyst alone (see Fig. 1.c). Interestingly, this effect is more expressed when both active components are mechanically linked into a rotaxane architecture allowing a high and constant local concentration of catalytic units. Indeed, reactions based on non-interlocked amine-phosphate catalysts only give worst results. Finally, it has been proved the reaction efficiency is correlated to the employed countercation as the conversion and rate increase in order with alkali metal electronegativity (Li > Na > K).

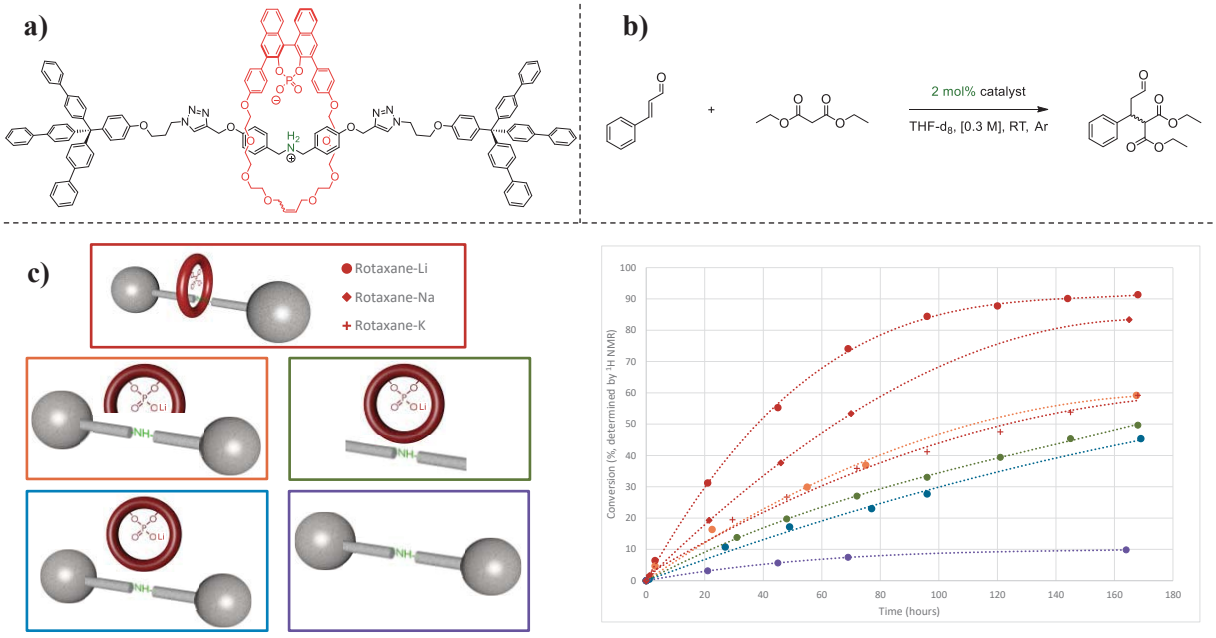

Figure 1.a) *Structure of [2]rotaxane,* ***b)*** *Application to Michael addition reaction,* ***c)*** *Conversion based on catalyst structure*

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Bi(I)-Catalyzed Transfer Hydrogenation with Ammonia-Borane

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Bismuth (Bi) represents the last stable element in the periodic table, with properties at the interface of metalloids and main group elements.[1] Importantly, Bi has been considered nontoxic and largely more abundant than commonly employed transition metals such as Pd, Rh or Ir,[2] thus highlighting its potential toward developing truly sustainable catalytic strategies. In contrast to the wealth of methods using high-valent Bi species, attention to its low-valent counterparts has been scarce. Low-valent Bi(I) compounds are known in the literature,[3] yet seldom monomeric Bi species have been isolated.[4] Generally, the formation of Bi(I) compounds is achieved through a highly unstable Bi(III) dihydride, which rapidly extrudes H_2 upon ligand coupling.[4] Inspired by these results, a catalytic transfer-hydrogenation utilizing a well-defined Bi(I) complex as catalyst and ammonia-borane as transfer agent has been developed.[5] This transformation represents a unique example of low-valent pnictogen catalysis cycling between oxidation states I and III, and proved useful for the hydrogenation of azoarenes and the partial reduction of nitroarenes (Figure 1). Mechanistic investigations suggest the intermediacy of an elusive bismuthine species, which is proposed to be responsible for the hydrogenation and the formation of hydrogen.

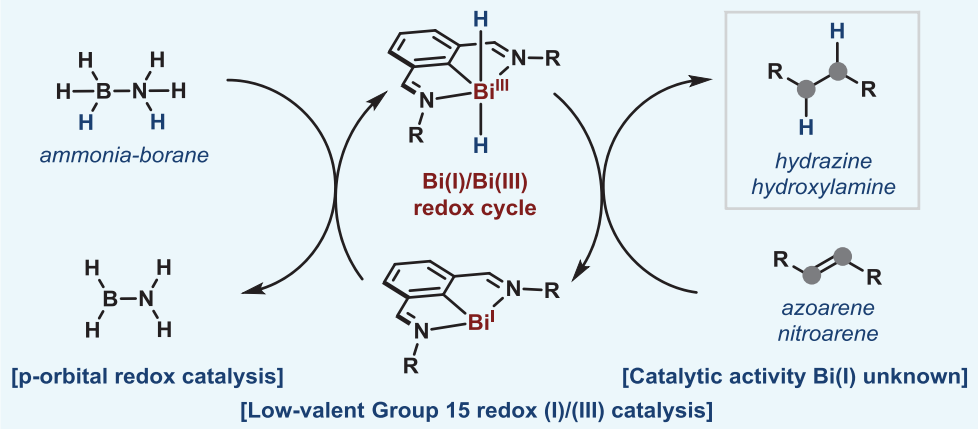

Figure 1. Redox catalysis at a low valent Bi(I) center in transfer hydrogenation.

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Visible Light-Mediated Synthesis of γ-Cyclobutane Amino Acids and their Application as Foldamers

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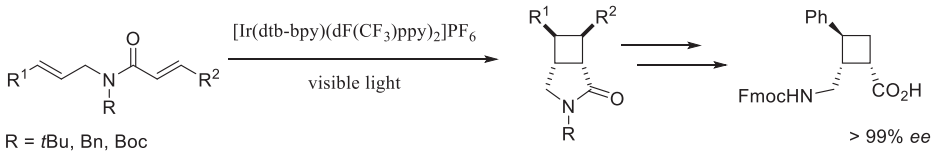
Incorporation of unnatural cyclic amino acids into peptide sequence affords foldamers with useful properties, such as stabilized secondary structure and stability against enzymatic degradation. Thus, cyclic amino acids as building blocks in relevant peptides have emerged as promising compounds in medicinal chemistry.[1-2]

We investigated the synthesis of γ-cyclobutane amino acids with an intramolecular visible light-mediated [2+2]-cycloaddition as the key step.[3] Starting with amide-linked dienes, cycloaddition proceeds through energy transfer mechanism and furnishes corresponding bicyclic compounds in good yields and with excellent diastereoselectivity. After the transformation of the obtained bicyclic compounds into racemic *N*-Boc-*cis*-γ-cyclobutane amino acids and the chiral resolution of latter, enantiomerically pure corresponding amino acids were prepared. Newly synthesized *N*-Fmoc-*cis*-γ-cyclobutane amino acids were subsequently incorporated in NPY-analogues in order to develop new selective ligands for Y_4R receptors.



R = *t*Bu, Bn, Boc
R^1 = H, Ph, 4-MeOPh, CO_2Me
R^2 = H, Ph, 2-furanyl, 2-thiophenyl, *N*-acetyl-3-indolyl

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Solid-phase bound DNA – Less instable than expected

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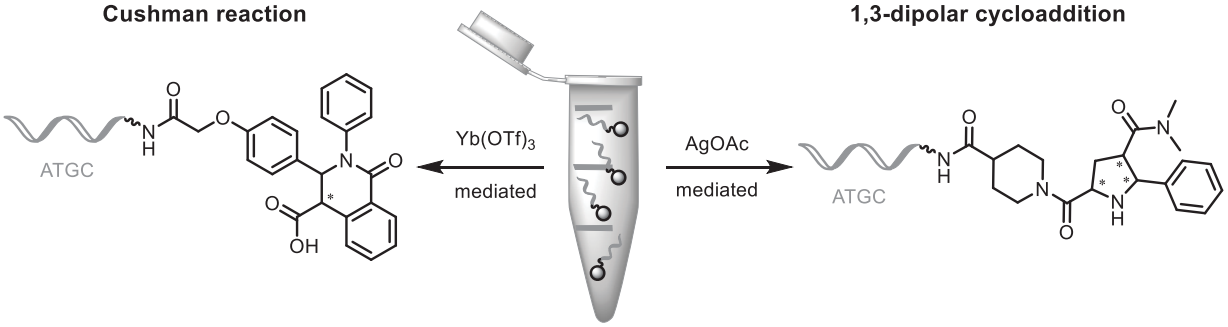
Selection of DNA-encoded small molecule libraries (DELs) is a fast and economic alternative to brute force screening of discrete compound collections. Nevertheless, the preparation of structurally diverse DELs is still a formidable challenge due to the low stability of DNA under many standard reaction conditions in organic synthesis.[1] The trifluoroacetic acid-mediated Pictet-Spengler reaction for example is a reaction that leads to a significant DNA degradation due to cleavage of purine bases from the barcode oligomer.[2] However, a screening campaigning assessing the stability of DNA in the presence of 40 metal salts that are commonly used as catalysts in organic synthesis, revealed to our surprise that fully protected, solid-phase bound DNA tolerated several of the catalysts under mild conditions. Based on these findings, we have selected metal catalysts and reaction conditions that can be used in reactions on solid-phase bound DNA.



Scheme 1. Cushman reaction and 1,3-dipolar cycloaddition on solid-phase bound DNA-conjugates.[3]

To expand the chemical space for DNA-encoded libraries we focused on heterocyclic chemistry and established the $Yb(OTf)_3$-mediated Cushman reaction[4] and the AgOAc-mediated 1,3-dipolar cycloaddition[5] (Scheme 1). In both cases we found good compatibility of the reaction conditions with a 10mer ATGC-oligonucleotide and were able to synthesize a collection of DNA-tagged, diverse substituted heterocycles. A novel encoding scheme was developed for tagging these heterocycles.

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Poster No.50

Catalysis in Confined Space – From Metal-Organic Frameworks to Supramolecular Coordination Cages

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In enzymes, catalytic reaction centers are placed in discrete cavities that allow for specific substrate binding and activation. It has been demonstrated that the placement of biomimetic catalysts into metal-organic frameworks (MOFs) as artificial cages leads to stabilization of reactive intermediates and thus improves their overall performance. However, the accessibility of incorporated catalysts strongly depends on pore size and diffusion within the MOF crystal.[1]

Metal-mediated self-assembly on the other hand is a powerful tool for the preparation discrete metal-organic cages (MOCs) featuring single nano-scale pores.[2] We are currently developing strategies for introduction of organometallic catalysts into discrete MOCs. In this contribution, I will give a detailed comparison between MOFs and MOCs for catalysis applications. This will be followed by a detailed structural analysis of our newest systems, as well as a study on catalytic.

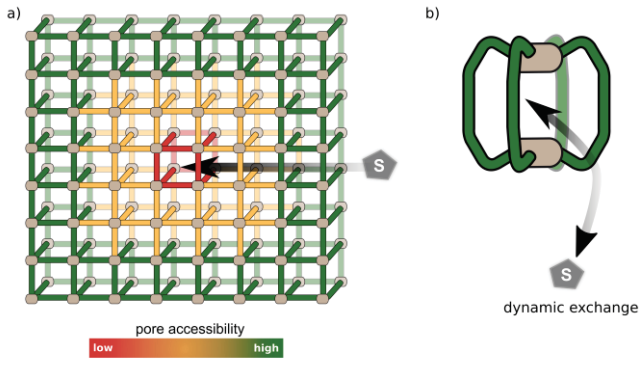

Fig. 1: Comparison of pore accessibility in MOFs and MOCs.[2]

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Synthesis of Trifluormethylated Pyridines via Rearrangement of Propargyl Vinylamines

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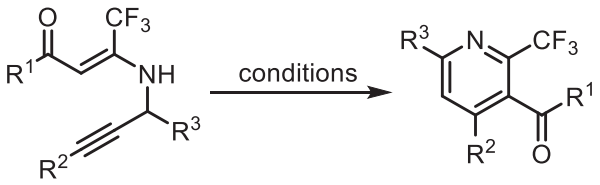
The pyridine scaffold is a very common structural motif among a variety of bioactive natural products and one of the most important heterocycles in modern drug discovery.[1] Because of this the investigation of new and alternative synthetic protocols towards highly functionalized pyridines is an ongoing field of interest in modern organic chemistry.[2]

Over the last decades the number of fluorine-containing drug molecules is rapidly increasing. Nowadays 30% of all new approved drugs contain at least one fluorine atom.[3] Because of its unique properties this element is of great interest and value for the design and development of new drugs, urging the synthetic research to enable new ways towards fluorinated or trifluoro-methylated compounds.[4]

Herein we present an opportunity for the synthesis of trifluormethylated pyridines via transition metal catalysis, starting from commercially available fluorine-containing materials. We furthermore contribute to Green Chemistry by establishing the transformations in a water-based micellar catalytic system.



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Design of a photo-controlled mRNA-cap guanine-*N*7 methyltransferase

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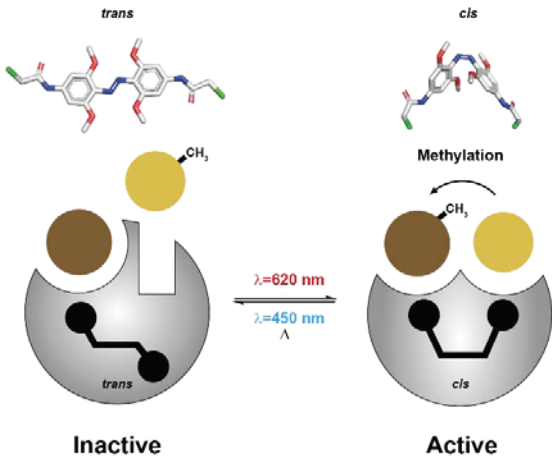
Optogenetics and photopharmacology are powerful tools to investigate biochemical systems. Besides approaches using photocaged amino acids, or photoactive protein domains, the modification of biomolecules with synthetic azobenzene-photoswitches offers an attractive option to implement subsequent light dependent properties.

An important cellular target is the eukaryotic mRNA 5′ cap due to its diverse roles in mRNA life cycle. Previously, we established a chemo-enzymatic approach for the modification of the mRNA 5′ cap based on a highly promiscuous methyltransferase from *Encephalitozoon cuniculi* (Ecm1).[1] In order to extend the application of the system by enhancing its specificity, it would be desirable to control the enzymatic activity with an external trigger.

Here we report the design of a photo-controlled Ecm1 for the *in vitro* modification of mRNA 5′ cap analogs. In this work, we use a computational approach to find a suitable position for the conjugation with *ortho*-substituted azobenzene derivatives to increase the impact of light-induced *trans* to *cis* conformational change on the protein structure.[2]



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Münster Symposium on Cooperative Effects in Chemistry 2019

Poster

Titanium-Catalyzed Hydroaminoalkylation of Ethylene with Secondary Amines

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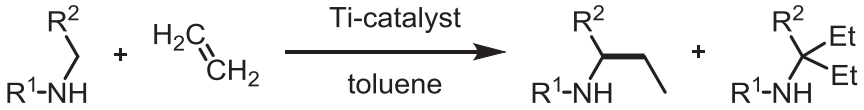
Keywords: ethylene, amines, hydroaminoalkylation, titanium

Content of Abstract:

The transition metal-catalyzed hydroaminoalkylation of alkenes[1] allows the direct addition of α-C(sp^3)–H-bonds of primary or secondary amines across C-C double bonds. While the use of liquid alkenes such as 1-octene or styrene has been common practice for a long time, the simplest of substrates, ethylene, has largely been ignored. Although the conversion of ethylene in the presence of Ta, Zr or Nb catalysts was among the first hydroaminoalkylation reactions reported,[2] the successful conversion of ethylene using titanium catalysts remains unprecedented so far. We now present the first examples of titanium-catalyzed hydroamino-alkylation reactions of ethylene with several secondary amines in good to excellent yields.



R^1 = Aryl, Alkyl
R^2 = H, Alkyl, Aryl

up to 95 % yield

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Switching the Electron-Donating Ability of Phosphines through Proton-Responsive N-heterocyclic Imine Substituents

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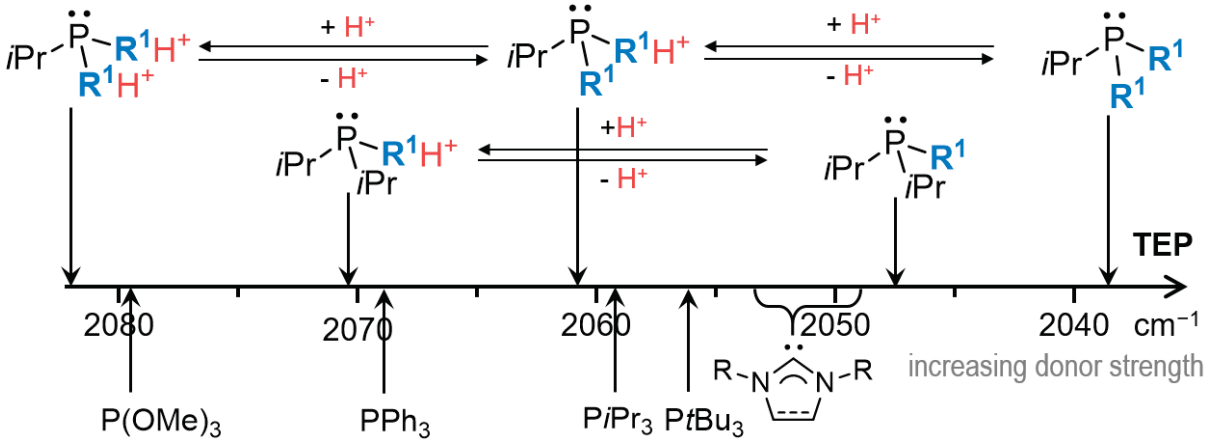
Design, modification and tailoring of ancillary ligands are key tools to tune the activity and selectivity of transition-metal catalysts. Modulating the electronic and steric properties of tertiary phosphines, while coordinating to a transition-metal, in a reversible fashion by using an external stimulus is particularly intriguing. The various methods for (photochemical, redox or chemical) switching differ with respect to their influence on the electron-donating character of the ligand.[1] Herein, we report the synthesis and characterization of a series of metal complexes containing phosphines with proton-responsive imidazolin-2-ylidenamino substituents. Determination of the ligand-donor properties revealed that protonation of each substituent increases the Tolman electronic parameter (TEP) of the phosphine by 22 cm^{-1}, hence allowing for switching of the electron-donor power of particularly electron-rich phosphines within an unprecedented range (ΔTEP = 43.4 cm^{-1}).[2] Furthermore, we report the one-pot, scalable synthesis of a series of electron-rich α-basic phosphines carrying pyridinylidenamino substituents.



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Self-Assembled Functionalized Coordination Cages

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Self-assembly of square-planar Pd(II) cations with four banana shaped bis-monodentate pyridyl ligands leads to the formation of supramolecular, homoleptic coordination cages of the [M_2L_4] type. Modifications of the ligands led to a high number of functionalized guest binding compounds.[1] The synthesis of heteroleptic cage structures of the [$M_2L_2L'_2$] type is challenging because the classical cage synthesis with using two different ligands would give a statistical mixture of cage structures.[2] Through targeted ligand design, which leads to a shape complementary, our group obtained the first configurationally stable heteroleptic Pd(II) cages of the [$M_2L_2L'_2$] type (Figure 1c)).[3]

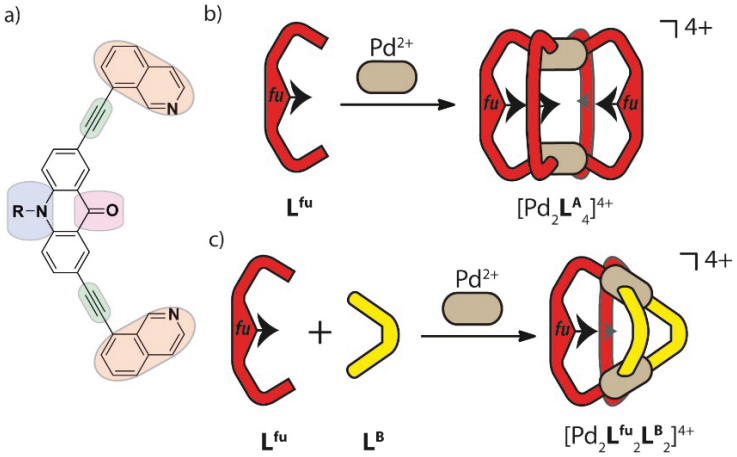

Figure 1. Influence of the ligand design on the cage self-assembling (a) modifiable structural elements exemplified by an acridone ligand; (b) scheme of the self-assembly of homoleptic cages with inward pointing functional units (*fu*) at $\mathbf{L^{fu}}$; c) combining functionalized ligand $\mathbf{L^{fu}}$ with ligand $\mathbf{L^{B}}$ for integrative self-sorting to form heteroleptic *cis*-[$Pd_2\mathbf{L^{fu}}_2\mathbf{L^{B}}_2$]$^{4+}$.

The modification of inward the cavity pointing functions of the backbone leads to new properties. Usage of aniline or phenol based ligands would give a good synthetic starting point for the implementation of functional units or for post-synthetic modification of the cage. A combination of complementary entities (e.g., electron-donor-acceptor system) based on these structure motifs may lead to novel series of functionalized heteroleptic cages of the [Pd_2L_4] type.

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Poster No.56

Pd-catalyzed Decarboxylative γ-Arylation for the Synthesis of Tetrasubstituted Chiral Allenes

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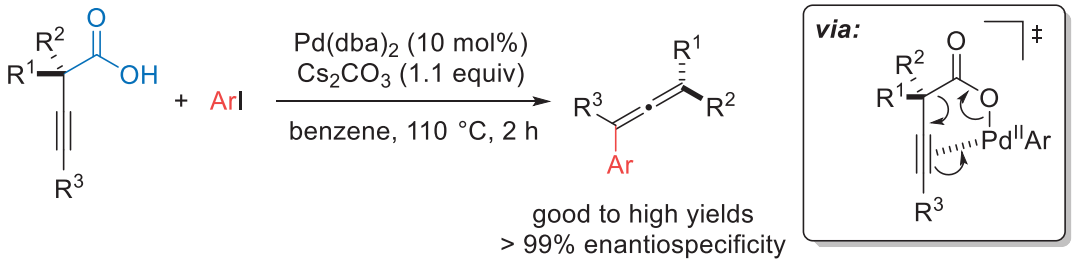
Allenes have become highly important as valuable and versatile building blocks in organic synthesis.[1] As a result, great efforts have been devoted to the development of synthetic routes for the preparation of enantiomerically pure allenes. However, the synthesis of chiral tetrasubstituted allenes remains challenging. In 2013, Maruoka and co-workers described the asymmetric functionalization of ester-substituted allenes in a deprotonation/alkylation sequence by phase-transfer catalysis.[2] Recently, Aggarwal and co-workers presented an enantiodivergent method to access highly substituted allenes, including tetrasubstituted allenes, by point-to-axial chirality transfer with chiral allyl boronic esters as substrates.[3]

Encouraged by our studies on the decarboxylative γ-arylation of acyclic β,γ-unsaturated carboxylic acids providing diaryl vinyl methanes by C(sp^2)–C(sp^3) bond formation,[4] we questioned whether such a valuable decarboxylative γ-arylation can also be performed with alkynoic acids. Herein, we present our first results on the highly stereospecific decarboxylative γ-arylation of α,α'-disubstituted β,γ-alkynoic acids with aryl iodides under Pd catalysis, which generates chiral tetrasubstituted allenes with excellent yields.[5] The key steps of the decarboxylation strategy comprise an oxidative addition, ligand exchange with *in situ* generated Cs-carboxylate followed by a concerted decarboxylative γ-palladation/CO_2 extrusion, which ensures perfect point-to-axial chirality transfer. As the subsequent reductive elimination step is also a stereospecific reaction, the overall sequence proceeds with complete enantiospecificity. The absolute configuration of the allenes was determined by circular dichroism (CD) spectroscopy. Our novel approach is complementary to existing methods for the asymmetric synthesis of tetrasubstituted allenes, which are interesting and valuable compounds in various fields.



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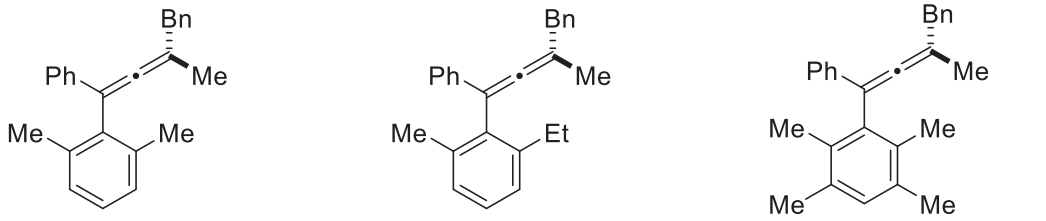

(*P*)-allene
75%, > 99% enantiospecific

(*P*)-allene
72%, > 99% enantiospecific

(*P*)-allene
75%, > 99% enantiospecific

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Enantioselective Nucleophilic Dearomatization of Quinolines *via* Triazole-based Anion-Binding Catalysis

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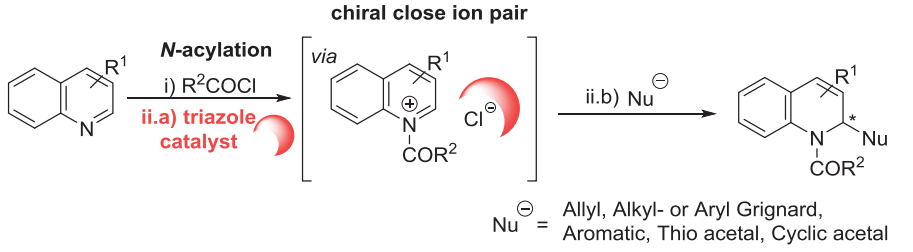
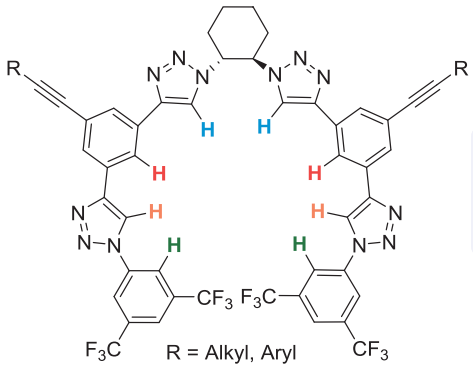
Chiral 1,2-dihydroquinolines are interesting motifs for pharmaceutical and medicinal chemistry due to their antibiotic, antiviral, antitumor as well as antioxidative activities.[1] In the last years, notable asymmetric synthetic approaches have been developed. However, they are mainly limited to metal-catalyzed conditions or require elaborate steps.[2] Thus, the development of new, mild and easily accessible enantioselective metal-free methods is still highly desirable.

Motivated by our work in the field of enantioselective dearomatization of *N*-heteroarenes with silyl ketene acetals and phosphites employing our designed triazole-based H-donor as anion-binding catalyst,[3] we decided to extend this chemistry aiming at providing a general route for optically active 2-substituted 1,2-dihydroquinolines under mild conditions.

Herein we present the enantioselective dearomatization of quinolines in a facile one-pot approach by using different nucleophiles with a broad range of nucleophilicity strength.





Anion-Binding Catalyst TetraTri*

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Poster No.58

Photochemically Driven Reverse Water-Gas Shift Reactivity

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Hydrogen transfer from transition metal hydride (TMH) complexes is pivotal as elementary reaction in many catalytic chemical and biochemical transformations. Combination of formal proton and electron transfer can result in net proton, hydrogen atom or hydride transfer.[1] While ground state hydrogen transfer reactions are well examined, photochemical reactivity of group 10 TMH complexes is rare.[2]

Herein we report carbon dioxide activation by PNP Nickel(II) hydride **1** (PNP = N(CHCHP*t*Bu$_2$)$_2$). giving formate **2** under thermal conditions and hydroxycarbonyl **3** via unprecedented abnormal CO_2 insertion upon photolysis (figure 1).[3] Mechanistic investigation by transient UV/Vis and infrared spectroscopy, DFT calculations, kinetic studies and trapping experiments suggest rapid intramolecular formation of a Ni(0) intermediate by proton transfer of the hydride ligand to the PNP pincer nitrogen.

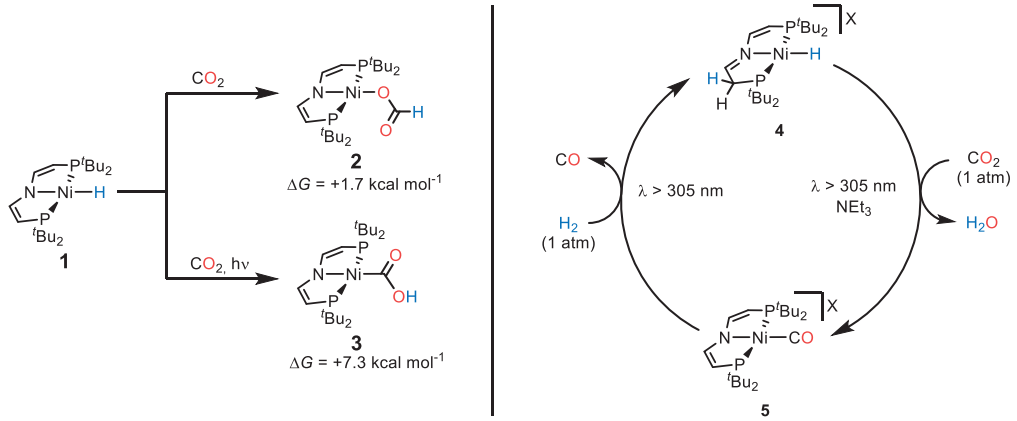

*Figure 1: Based on the photochemical reduction of carbon dioxide by Nickel(II) hydride **1**, a synthetic cycle for the reverse water-gas shift reaction is established.*

Reformation of hydride **1** via carbonyl **5** is a net $2H^+/2e^-$ process and can be performed by stepwise addition of acid and hydride donors or reductants, respectively, showing formation of a rare Ni(II) formyl as intermediate in both cases. Using H_2 as electron and proton source, starting from imine hydride **4** a two-step synthetic cycle for the reverse water-gas shift reaction on a PNP Ni(II) platform is established (figure 1).[4]

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1,3-Diaza-2-oxophenoxazine as a luminescent cytosine analog in silver(I)-mediated base pairing

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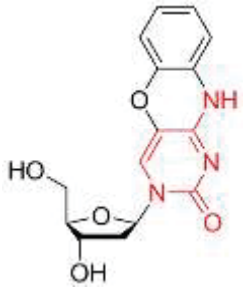
Recently, metal-mediated base pairing has become a convenient approach to functionalize nucleic acids site-specifically [1]. Parallel-stranded DNA which only rarely occurs in nature even expands the possible binding geometries for transition metal ions due to the transoid orientation of the glycosidic bonds [2]. Fluorescent nucleobase analogues are of special interest as they could be used as sensitive metal ion sensors when the incorporated metal ion tailors the fluorescence intensity and absorption maxima [3].
In parallel-stranded DNA duplexes, 1,3-diaza-2-oxophenoxazine (**X**) forms stabilizing **X**–Ag(I)–**X** and **X**–Ag(I)–C base pairs as was confirmed by temperature-dependent UV spectroscopy and luminescence spectroscopy. The homo base pair **X**–Ag(I)–**X** stabilizes the examined duplex by 5.3 °C whereas the incorporation of silver ions into the hetero base pair leads to a thermal stabilisation of 7.9 °C (**X**:**C**) or 3.6 °C (**C**:**X**), respectively. Upon silver(I)-binding to the **X**:**X** or **X**:C base pairs, the luminescence emission maximum experiences a red-shift from 448 to 461 nm upon excitation at 370 nm. Importantly, the luminescence of the 1,3-diaza-2-oxophenoxazine ligand is not quenched significantly upon binding a silver(I) ion. In fact, the luminescence intensity even increases upon formation of a C–Ag(I)–**X** base pair. As a consequence, the silver(I)-mediated phenoxazinone base pairs represent the first strongly fluorescent metal-mediated base pairs.
In addition, theoretical calculations have been accomplished: DFT calculations of the silver(I)-mediated base pairs suggest the presence of a synergistic hydrogen bond. MD simulations of entire DNA duplexes nicely underline the geometrical flexibility of these base pairs, with the synergistic hydrogen bond facing either the major or the minor groove.
Acknowledgement: Funding by the Deutsche Forschungsgemeinschaft (SFB 858) and the Russian Science Foundation (project no. 18-74-00051 - phenoxazine phosphoramidite and modified oligonucleotides synthesis) is gratefully acknowledged



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Poster No.60

Supercooled Water Droplet Impact on Chemically Heterogeneous Surfaces

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Soft interfaces and materials with freeze-tolerant and ice resistant properties are irreplaceable in life sciences and materials science including engineering applications. Examples include cryopreservation, ice-templating, dispersion stability, and robustness in functional coatings. Current advanced anti-icing strategies based on hydrophilic and hydrophobic materials exist but, have intrinsic disadvantages, which limit their applicability. [1, 2, 3]

In general, our group aims at the development of amphiphilic materials combining advantages of different ice preventing strategies such as supressing of freezing point using colligative properties or kinetic inhibition as well as de-icing strategies using the low surfaces energy components. Specifically, we aim at the fundamental understanding of molecular origins of ice nucleation and formation at chemically heterogeneous interfaces and their correlation to macroscopic ice adhesion. [2] Icing of various interfaces or surfaces is often a result of the collision of supercooled water drops with substrates. Ice formation from supercooled water drops is initiated by nucleation when the size of an ice embryo reaches a critical value. The lack of controlling the inception of heterogeneous nucleation and the rate of solidification, which depend on the properties of the substrate, temperature, and impact parameters of the liquid drop, poses a very serious challenge to the design of effective ice-preventing materials. In this exploratory experimental study, we show how a significant nucleation delay during impact of supercooled water droplets can be achieved by tuning the properties of the substrate and, specifically, by introducing chemical and topographical heterogeneities on the surfaces formed by a mixture of either polymer-coated hydrophilic and hydrophobic particles or Janus particles. [3]

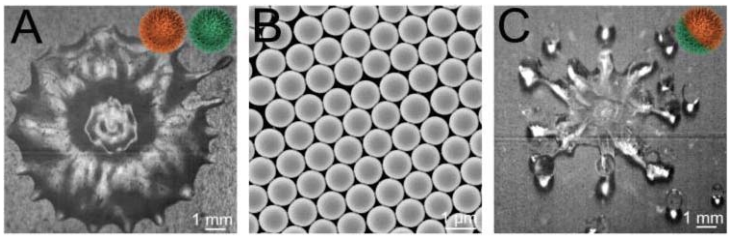

Figure 1: A) Representative optical image of the impact of a supercooled water droplet on a surface based on a mixture of two different particle types, B) SEM image of a particle-based surface, C) representative optical image of the impact of a supercooled water drop on a surface based on Janus particles.

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NHC-based Molecular Motors on Gold Surfaces

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The research on artificial "nanomachines" has come a long way since Richard Feynman's deliberations in 1959 [1]. As a matter of fact, in 2016 Feringa, Sauvage and Stoddart received the Nobel Prize in Chemistry for their design and synthesis of molecular machines (MMs). This, however, did not conclude this research area, but rather opened up research to design nanoscale motors and make them usable. In particular, to really exploit directional motion of MMs in practice, one has to be able to control their orientation. One obvious approach to achieve specific orientations is the assembly of MMs onto metal surfaces [2], which proves non-trivial for usual light-driven motors.
N-Heterocyclic carbenes (NHCs) have gained large attention for their many uses, including the modification and stabilization of surfaces and nanoparticles [3]. Recently, their strong binding to gold surfaces has been explored and shown to be tunable by the choice of N-substituents [4].
In here, a reactive force field [6] molecular dynamics framework is utilized to investigate the rotation of NHCs on a Gold(111)-surface. Through extraction of rotational free energy landscapes, various ligands can be screened to identify NHCs exhibiting highly asymmetric, "ratchet-like" rotational barriers.
Theoretical investigations predict that such asymmetric potentials can be exploited to create "Brownian ratchets", which exhibit directional motion under periodic temperature oscillations [5]. Using a one-dimensional model system, we show that our rotational potentials can be used in a similar way.
In a last step, we devise a model system to show that external perturbations by an STM tip can lead to similar temperature oscillations. This completes the picture of NHC-based molecular motors: we designed surface-bound NHCs with asymmetric rotational potentials, which can then be driven by temperature oscillations, which are predicted to be achievable in experiment by utilization of STM tips.

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Poster No.62

Glycomimetic polymers with brush-like structures

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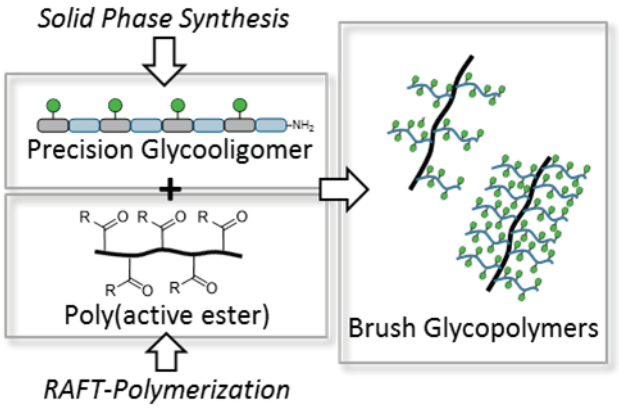
Glycopolymers have been established as glycomimetics using the multivalent presentation of single carbohydrate ligands on a macromolecular scaffold to achieve high affinity binding. Thus they serve as model systems to investigate the effects and mechanisms of multivalency in ligand-receptor interactions but have also shown their potential in biomedical applications such as antiviral and antibacterial therapy.



Previously, our working group has introduced the synthesis of a new class of glycopolymers, the so-called precision glycomacromolecules. Precision glycomacromolecules are monodisperse and sequence-defined – much like their natural analogues, the glycopeptide and –proteins and thus allow for detailed structure-activity studies on the binding of glycomacromolecules to protein receptors. In this study we extend the platform of precision glycomacromolecules towards proteoglycan-like structures.

Proteoglycans consist of a protein core and oligosaccharide sidechains giving highly dense brush structures that seem to directly affect their biological function e.g. in binding to pathogens. Here we present a synthetic method to obtain brush-like glycopolymers with monodisperse, sequence-defined sidechains. Using solid phase polymer synthesis, glycooligoamides are assembled carrying Mannose ligands in varying number and density along the scaffold. These glycooligomers are then coupled to a poly(active ester) as second scaffold giving the final brush-like glycopolymer. Overall, a series of brush-like glycopolymers varying in different structural parameters such as number of Mannose ligands per sidechain or per polymer, number of side chains and overall chain length of the polymer was obtained. First studies with model lectin Concanavalin A showed effects of both, sequence-control of the side chains as well as brush-like structure on the resulting lectin binding properties.

Soft matter interfaces with controllable underwater adherence: Influence of polymer molecular architecture and charge density

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In this work we aim to fundamentally understand the adhesive contact and the molecular interactions between smart synthetic adhesive systems in wet conditions. Specifically, we are addressing key questions concerning how the polymer architecture (random vs side graft chains, Figure 1A), the degree of functionalization and the ratio between charged and uncharged moieties affect the microscopic adhesive performances underwater, using polymer brushes as model system[1]. We report the design, the investigation and the comparison of adhesive properties of thermo- and pH-responsive adhesive systems based on random and graft copolymer brushes containing poly(N-isopropylacrylamide) (PNIPAm) and poly(acrylic acid) (PAA) units. Swelling properties and surface charge density at the interface were investigated using spectroscopic ellipsometry and streaming potential/streaming current measurements, respectively[2]. The change in wetting properties in the designed systems upon variation of temperature and ionic strength has been studied by captive bubble technique underwater. Multi-responsive adhesion properties were studied in situ in aqueous solutions at different temperatures and at different ionic strength using AFM colloidal probe (Figure 1B) against substrates with varied wetting properties as well as surface charge.

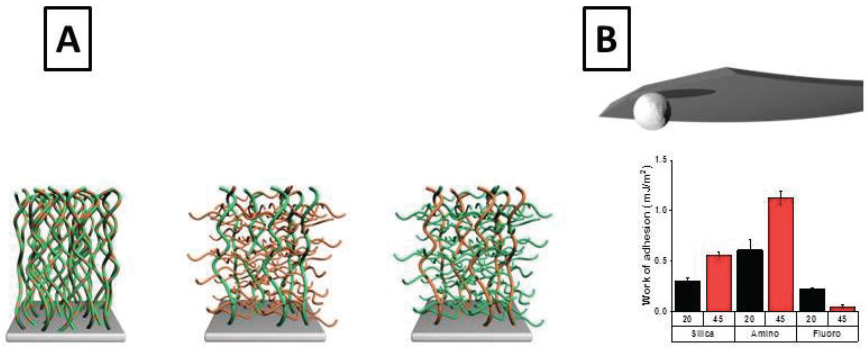

Figure 1. A sketch of structural architectures (A) and principle of adhesion measurement via AFM-CP (B)

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Supramolecular host-guest complexes – biocompatible-, stabilizing- and spacing unit in green nanoparticles for biomedical applications

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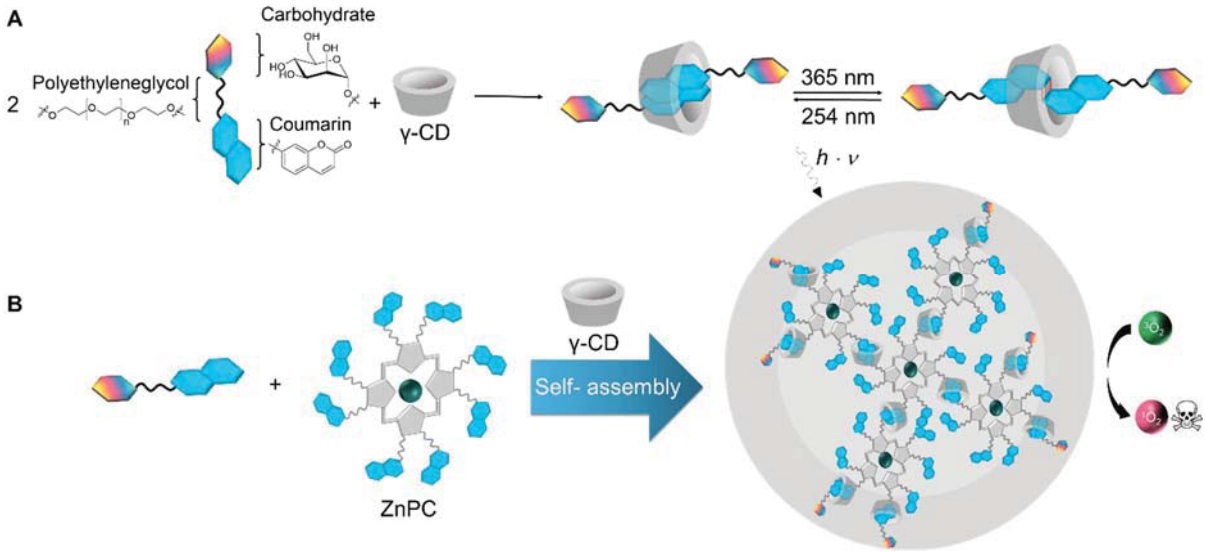
Photosensitizers like porphyrins (PORs) and phthalocyanines (PCs) are common drugs for the photodynamic therapy (PDT) to fight cancer or kill antibiotic resistant pathogens.[1] For the PDT a photosensitizer is distributed in the human body and the tumour or infected region is illuminated with light of long wavelength.[2] This leads to a conversion of triplet ($^3O_2$) into cell toxic singlet oxygen ($^1O_2$).[2] Due to the precise activation by light side effects are reduced.[3] The main challenge for the use in the human body is to prevent the photosensitizers from π-π stacking which leads to a decrease of the fluorescence and $^1O_2$ production.[4]

In this project, we use a supramolecular 2:1-host-guest complex based on umbelliferon and biocompatible γ-cyclodextrin (γ-CD) as a spacer (**Scheme 1A**) between the photosensitizers to increase the $^1O_2$ formation. This complex can be stabilized due to uv-light induced [2+2]-cycloaddition of the umbelliferon double bond. The photosensitizer of choice is umbelliferon functionalized zinc phthalocyanine (ZnPC) (**Scheme 1B**). Together with monofunctional biocompatible compounds sizetunable nanoparticles can be formed.



Scheme 1: Self-assembly of monovalent bioactive compounds with γ-CD and light induced [2+2]-cycloaddition (**A**). Formation of supramolecular nanoparticles with monovalent bioactive compounds, ZnPCs and γ-CD to convert $^3O_2$ into cell toxic $^1O_2$ (**B**).

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Carboxylate Linked Dimeric and Polymeric Coordination Compounds

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C$_3$-symmetric triaminoguanidinium based ligands are able to coordinate hard metal ions like Ti(IV) or Zr(IV) as well as soft metal ions like Cd(II) or Zn(II) in their *tris*-chelating binding pockets. A variety of discrete supramolecular coordination cages, such as tetrahedra, octahedra and trigonal bipyramids, are accessible.[1] The modification of salicylic aldehyde into pyridine-*N*-oxide based ligands reduces the negative charge of the deprotonated species.[2] Coordination of Zn(II) in the presence of carboxylates and pseudohalides like azide or thiocyanate gives cyclic coordination oligomers, which can function as supramolecular host molecules for fullerene $C_{60/70}$ encapsulation.[2,3] The absence of (pseudo)halides leads to the formation of a series of different dimeric and polymeric structures, that are further discussed on the poster.

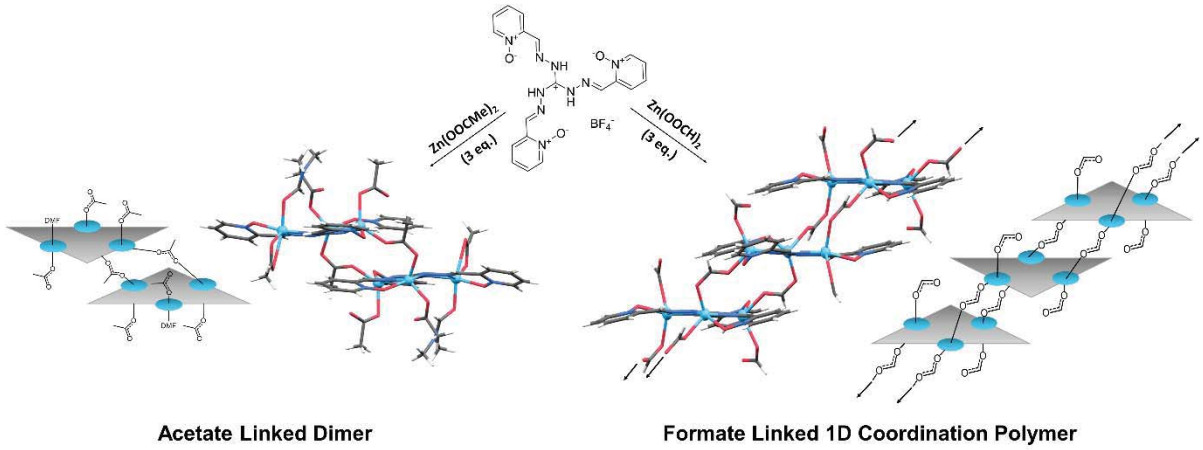

Figure 1. Coordination of different Zn(II) carboxylates results in a variety of dimeric and polymeric structures depending on the carboxylate chain length only. Exemplarily, a formate linked coordination polymer and an acetate linked dimer are selected.

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Chiral Receptors for Lysine Based on Covalently Linked Bis- and Trisbinaphthylphosphoric Acids

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The development of synthetic receptors capable of recognizing α-amino acids has been of considerable interest for several decades due to their biological relevance, as it provides insight into the mechanistic processes involved in molecular recognition in biological systems. Different types of receptors for amino-acids have been developed,[1] however the stereoselective detection of amino acids with chiral receptors remains a considerable challenge.

Therefore, we have used enantiopure 1,1'-binaphthyl-phosphates (see figure 1) as receptors for the molecular recognition of the enantiomers of the amino acid lysine,[2] since they can form strong interactions based on multidentate ammonium-phosphate interactions.

Using the series of receptors 1**a**−**c** in comparison to the simple 1,1′-binaphthylmonophosphoric acid [(*R*)-BNPA)], we were especially interested to see the influence of the number of binding sites (one vs two vs three phosphate groups for BNPA vs 1**a**,**b** vs 1**c**) and varying receptor geometries (1**a** vs 1**b**) on guest binding affinities. Initial binding studies using the lysine enantiomers showed that the ditopic receptors (*R,R*)-1**a**,**b** exhibit not only high association constants in DMSO but also a strong preference for binding of D-lysine.

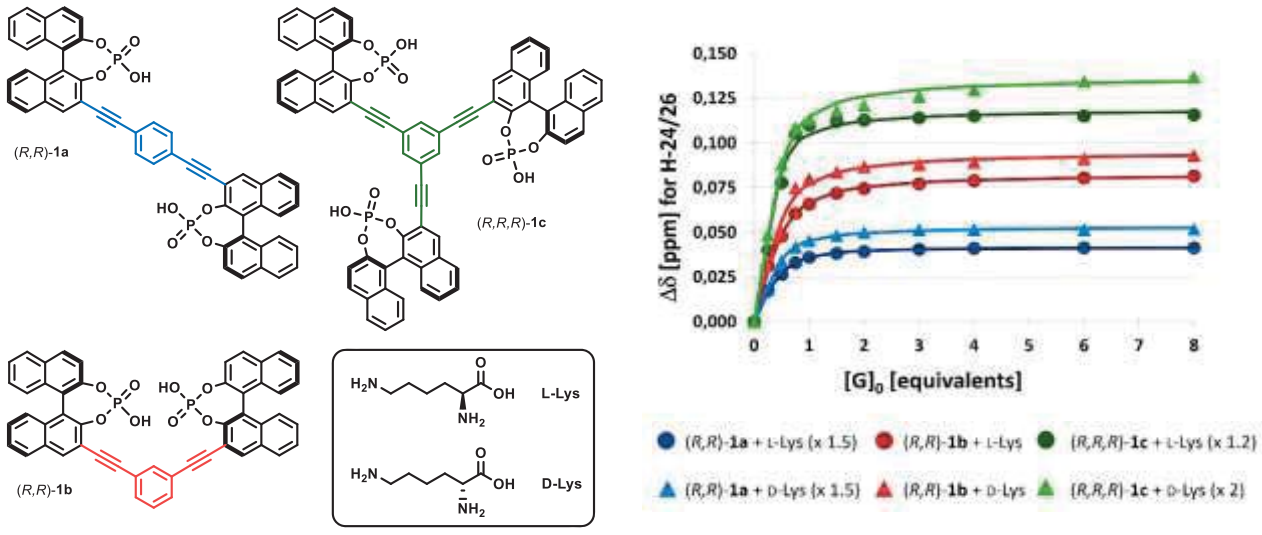

Figure 1: Investigation of the binding of D- and L-lysine with phosphoric-acid-receptors **1a-c**.

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Cobaltaelectro-Catalyzed C–H/N–H Activation by Water-Tolerant Cobalt Complexes at Room Temperature

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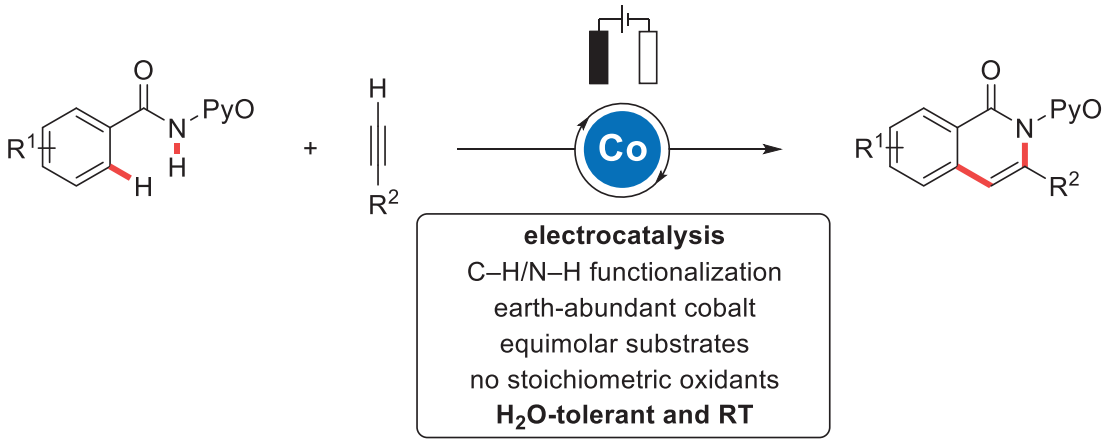
C–H activation has emerged as an increasingly potent platform for molecular syntheses, with transformative applications to natural product chemistry, pharmaceutical industries, and material sciences, among others.[1] Versatile cobalt catalysis has proven powerful for the functionalization of otherwise inert C–H bonds, thus enabling inter alia step-economical heterocycle syntheses by C–H/N–H functionalizations.[2] Despite indisputable advances, these C–H/N–H alkyne annulations were as of yet strongly limited to high reaction temperatures and stoichiometric amounts of toxic metals as the sacrificial oxidants.[3] In sharp contrast, we have now unraveled the power of electrochemical[4] C–H activation to enable the first cobalt-catalyzed C–H/N–H alkyne annulation at ambient temperature, on which we report herein.[5] Salient features of our approach comprise 1) unprecedented electrochemical C–H/N–H activation/annulations, 2) isoquinolone syntheses without toxic sacrificial metal oxidants, 3) fully H_2O-tolerant electrochemical C–H activation, and 4) cobalt-catalyzed C–H functionalizations, under ambient conditions, enabled by sustainable electricity.



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Synthesis of Cyclodextrin-based NHC-Gold Complexes

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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.[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]

Cyclodextrins (CDs) are readily accessible, water-soluble and non-toxic compounds. Due to their unique structure, cyclodextrins can form host-guest complexes with lipophilic substrates. The chirality of CD moieties renders them useful for application in enantioseparation processes.[5]

The combination of NHC precursors bearing a cyclodextrine moiety and gold leads to highly reactive, water-soluble NHC-gold complexes. Herein, we report the synthesis of cyclodextrin-based NHC-gold complexes. One of the key steps is the coupling of an azido-substituted cyclodextrin derivate with an acetylenic imidazolium salt by ruthenium-catalyzed azide-alkyne cycloaddition (RuAAC).

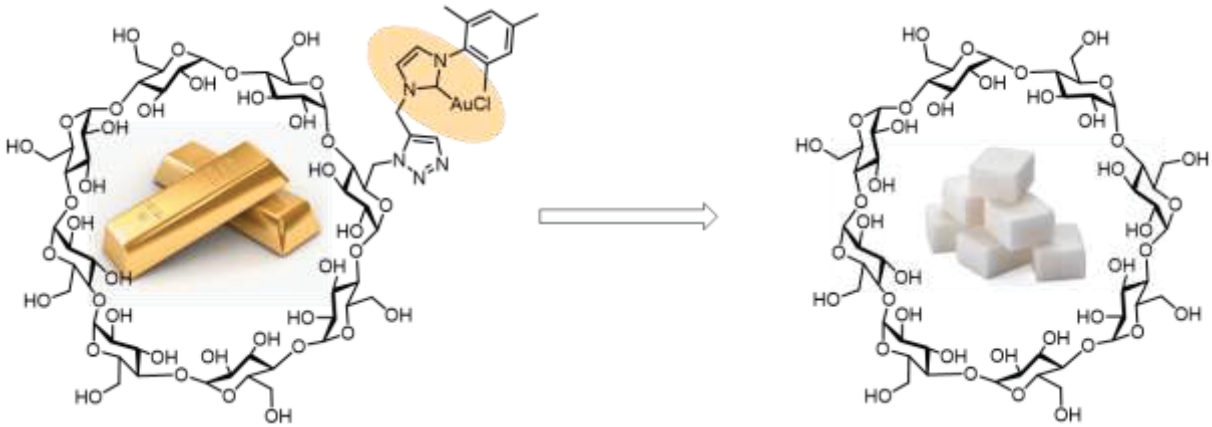

Fig. 1: γ-Cyclodextrin-based NHC-gold complex.

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Regioselective Hydroaminoalkylation of Alkyl-Substituted Alkenes with Secondary Amines

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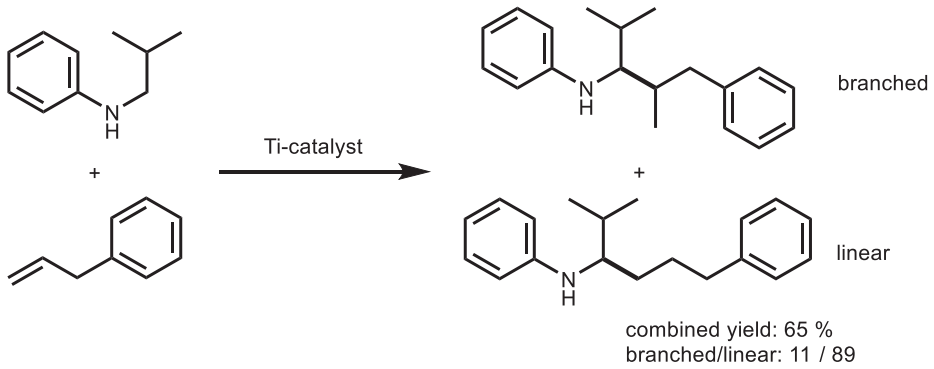
Content of Abstract:

Hydroaminoalkylation reactions[1] of alkenes with secondary amines which in principle deliver branched or linear products can be achieved in the presence of a variety of group 4 and group 5 metal-catalysts. While the latter catalysts are known to selectively form the branched products, titanium catalysts have already been used successfully for the formation of linear hydroaminoalkylation products from aryl-substituted alkenes. We now present the first examples of titanium-catalyzed hydroaminoalkylation reactions of alkyl-substituted alkenes which deliver the linear isomers as the major product. Due to the fact that the regioselectivity of the hydroaminoalkylation strongly depends on steric effects, a simple use of *N*-methylanilines as substrates is not successful. For that purpose, a new two-step procedure that includes the use of a temporarily silylated substrate was developed.



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Poster No.70

To Investigate the Magic Behind the Design of Layered Structures

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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(II) and Cd(II) as well as hard ions like Ti(IV).[1,2]

Coordination of Ga(III)-ions leads to different layered structures consisting of either one, three or four ligands. Through modification of the ligand and metal-precursor as well as the reaction conditions series of compounds can be obtained.

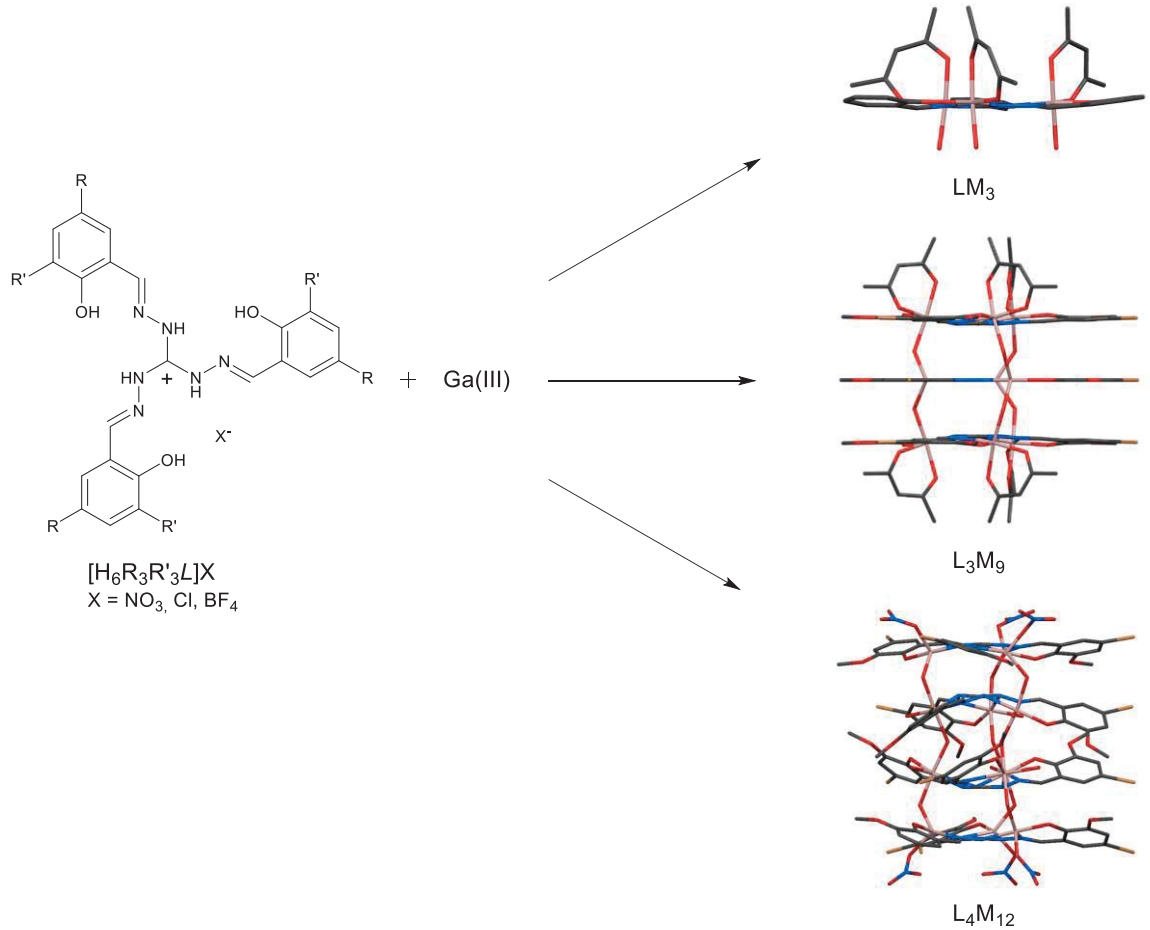

Figure 1. Three examples for layered coordination compounds consisting of a different number of ligands, which can be obtained by coordination of Ga(III)-ions.

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A SECOND GOLD ATOM STABILISES INTERMEDIATE IN GOLD CATALYSED RING OPENINGS OF CYCLOPROPENES

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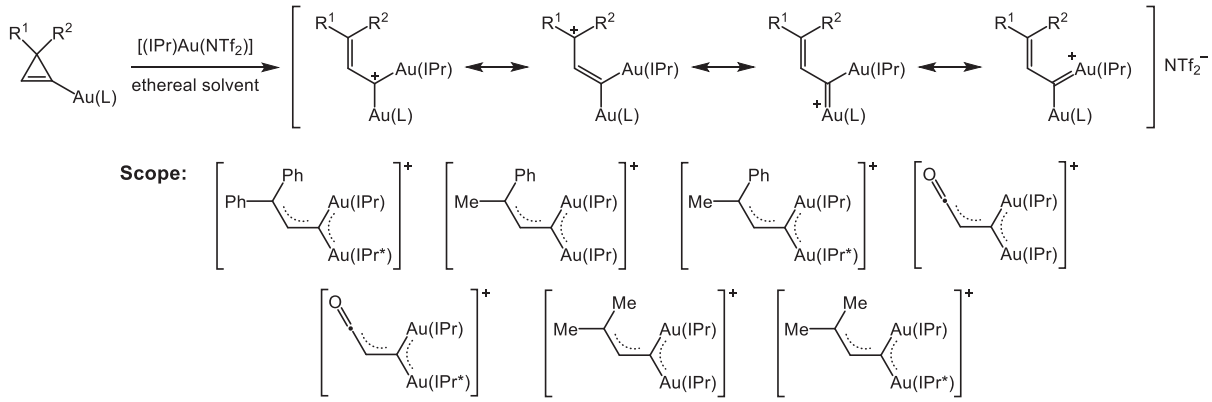
Abstract:

Cyclopropenes are perfect substrates for gold catalyzed ring openings due to their high ring strain.[1] This is thought to transition through cationic allyl gold species that have so far only been observed when bearing strong oxygen donor substituents.[2] Our recently published 3,3-disubstituted cyclopropen-1-ylgold(I) complexes are highly reactive towards gold-mediated ring-opening.[3,4] With cationic [(NHC)Au^{I}] complexes in ethereal solvents at low temperatures, the occurrence of bridged m-allylium-1,1-diyl digold(I) complexes is observed. We found that the second gold atom stabilizes these important intermediates enough to perform spectroscopic experiments at low temperatures. Seven examples were characterized by NMR, CID ESI FT-ICR MS/MS, and UV-Vis-NIR experiments at low temperatures.



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Poster No.72

Experimental Insights into Dispersion Interactions in Self-Assembled Supramolecular Host-Guest Systems

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London dispersion interactions are weak non-covalent interactions, but these attractive interactions can also play important roles in structural stability with a large number of interacting atoms. The Clever group collaborates with Mata group, focus on studying control of London dispersion interactions in self-assembled supramolecular system. Recently, we published a work about triggered neutral guest binding in an interpenetrated coordination cage, influence of shape, size, heteroatom content and dispersive contributions of guest binding were thoroughly investigated and discussed. [1][2] Currently, a series of endohedral dispersion energy donor functionalized coordination cages has been designed and synthesized, investigation of their guest binding behaviors is underway through various means include NMR analysis, ITC and theoretical calculation (Figure 1).

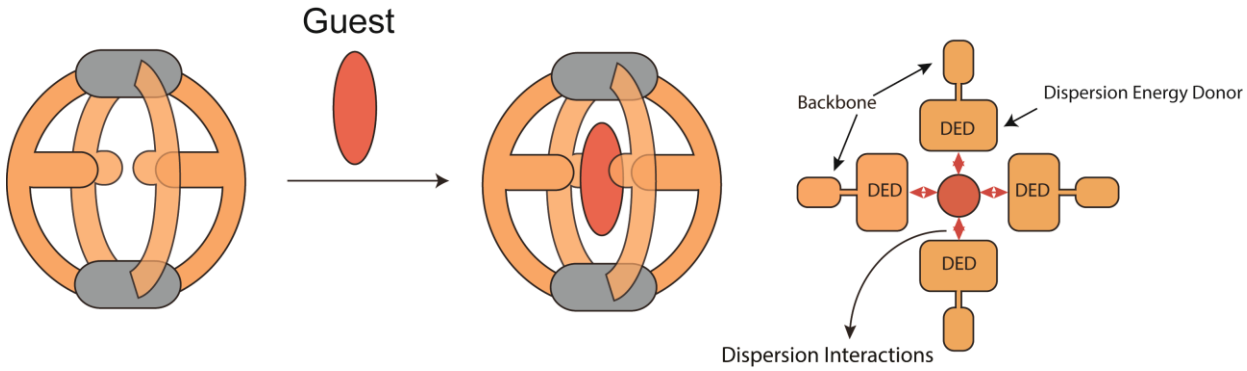

Figure 1. Guest Binding in Self-Assembled [$Pd_2Ligand_4$] Coordination Cages with Endohedral Dispersion Energy Donors

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