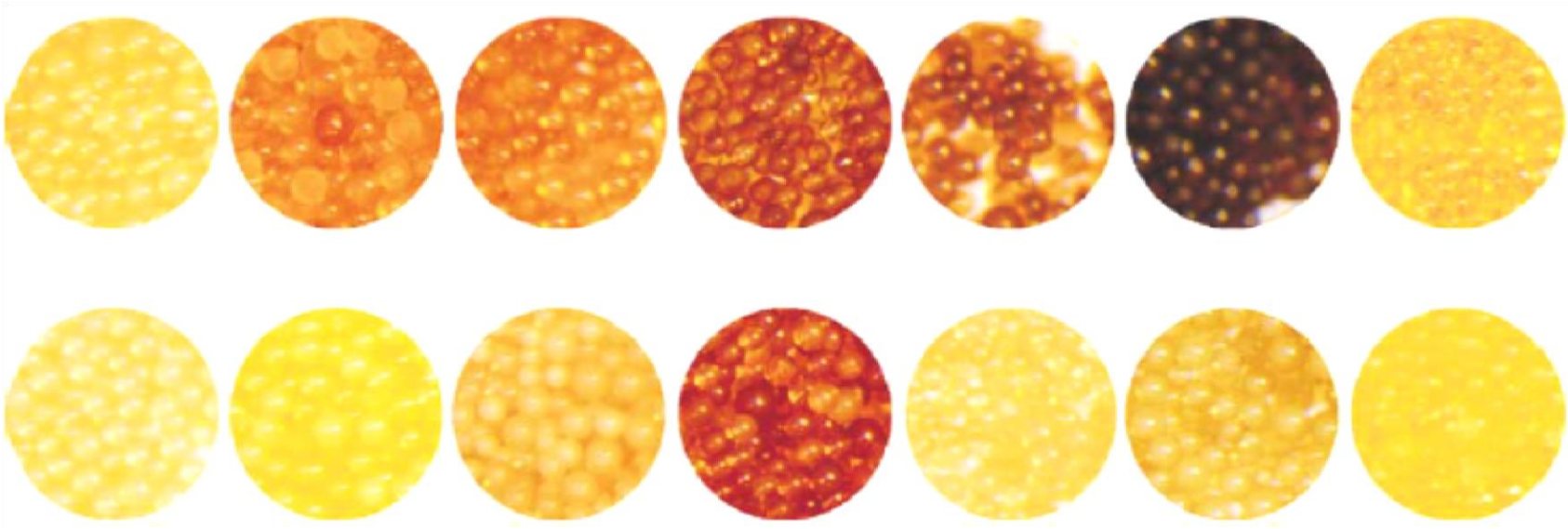
Heterogenisierung von Homogenkatalysatoren durch organische Trägermaterialien – Design, (Kombinatorische) Synthesen und Anwendungen

Stefan Bräse

Institute of Organic Chemistry & Institute of Toxicology and Genetics



Chemistry of the Bräse group: Functionalities and Function

Drug delivery
Bioconjugation
Peptoids

Bioactive entities
Natural products
Medicinal chemistry
Combinatorial chemistry
Pesticides

Organic Synthesis of Functionalized Organic Structures

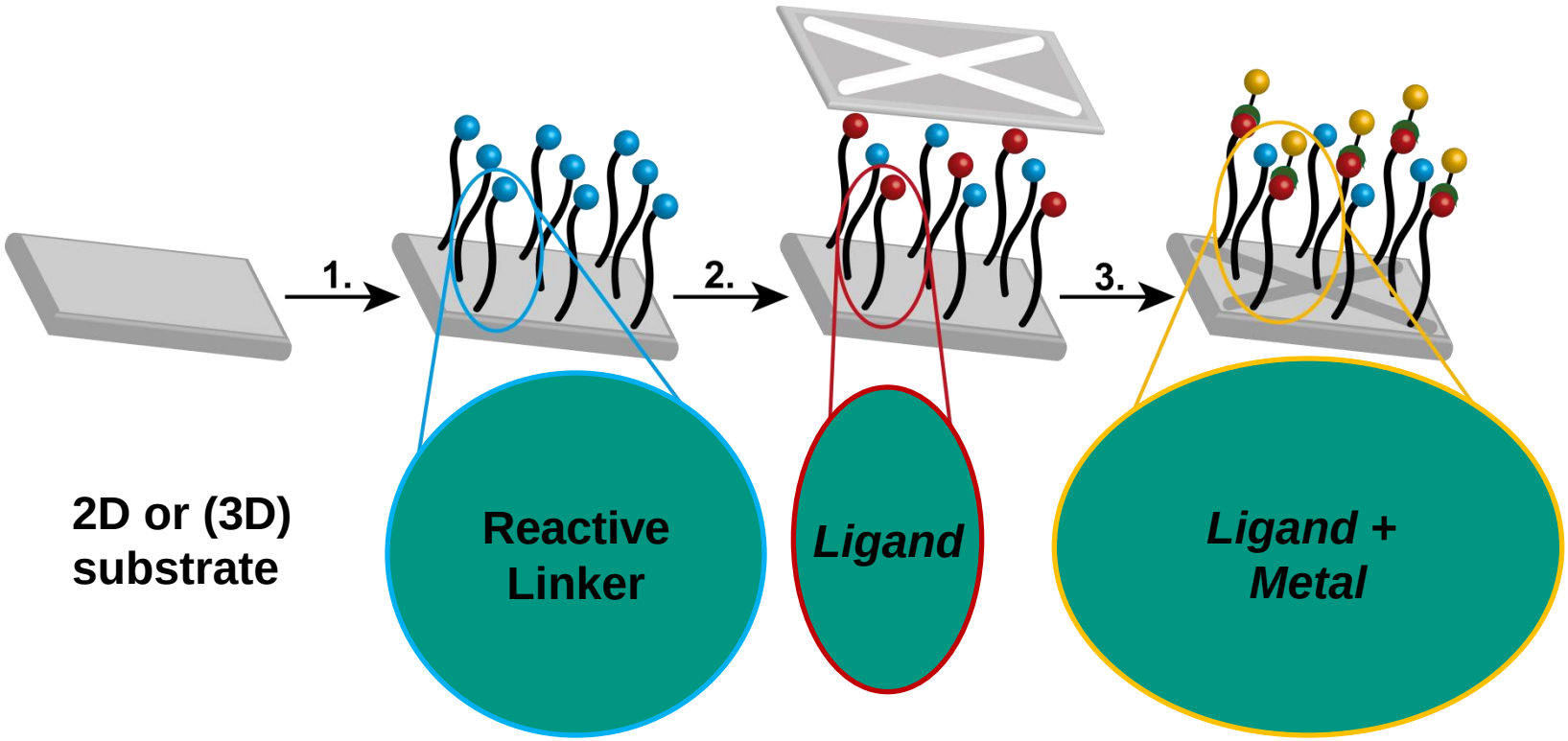
Organometallic Chemistry and Catalysis

Material Chemistry Nanostructures

Today‘s menu

- Aperitif: Immobilization of Homogeneous Catalysts
- Amuse-bouche: Asymmetric Catalysis
- Entrée: Immobilization of Catalysts
- Main course: Combinatorial Chemistry
- Dessert: Diversity through Multifunctional Linker
- Cheese: Auto-Click Reactions

Immobilization of Homogenous Catalysts
Prinziples and Opportunities



Immobilization of Homogenous Catalysts
Pro‘s and Con‘s

Pro‘s:

- Many designed ligands available
- Optimization of catalysts possible
- Asymmetric catalysis
- Reversible binding
-

Con‘s:

- Metal leaching
- Time/space
- Lower catalyst loading
- Bimetallic catalysis/alloys difficult

Immobilization of Homogenous Catalysts
Suitable Substrates

- Polymers
  - Cross-linked polymers (e.g. Merrifield-type)
  - Hyper-cross-linked polymers and related systems
  - New: SURMOF and SURGELs
  - Nanoparticles for nanofiltration

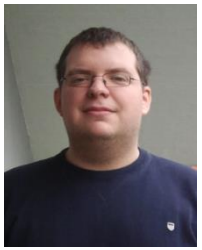
- Hybrid system
- Inorganic substrates

Three-dimensional polymers („Organic Frameworks“)

- The rigid structures are able to form
  - Hydrogen-bonded molecular networks
  - **C**ovalent-**O**rganic **F**rameworks (COFs)
  - **H**yper-**C**rosslinked **P**olymers (HCPs)
  - **Sur**face-mounted **M**etal **O**rganic **F**rameworks (SURMOFs, with C. Wöll)
- Organic frameworks have high porosity and large surfaces
  - Specific Surface Area > 500 m^2/g
- Applications
  - Gas storage and gas separation like zeolites
  - Bio-applications
  - **Catalysis**

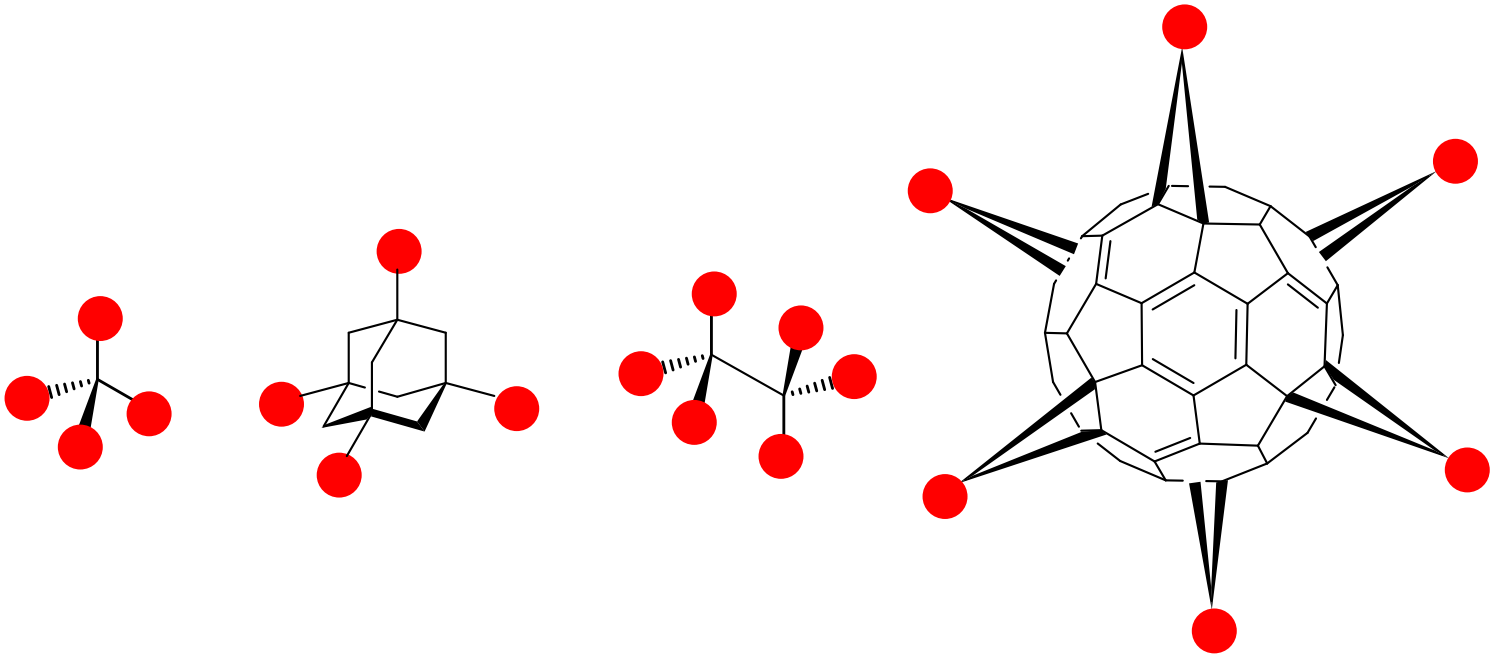

A. Schade

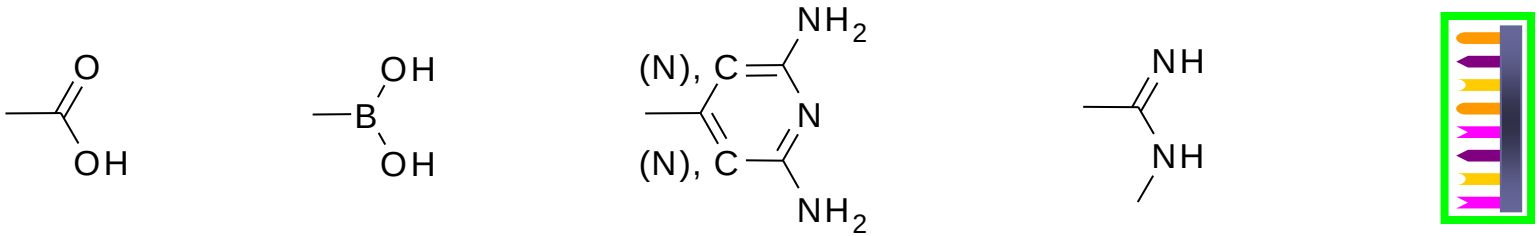

I. Wessely


M. Lang


S. Grosjean

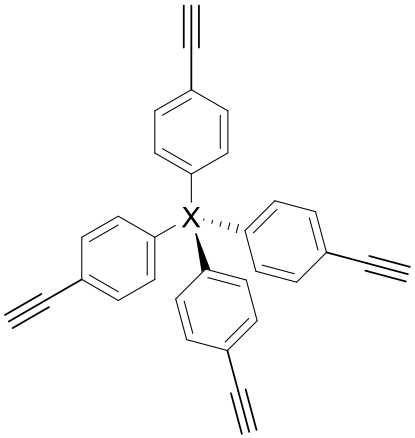
Tetra- and (pseudo)octahedral organic cores



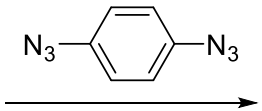


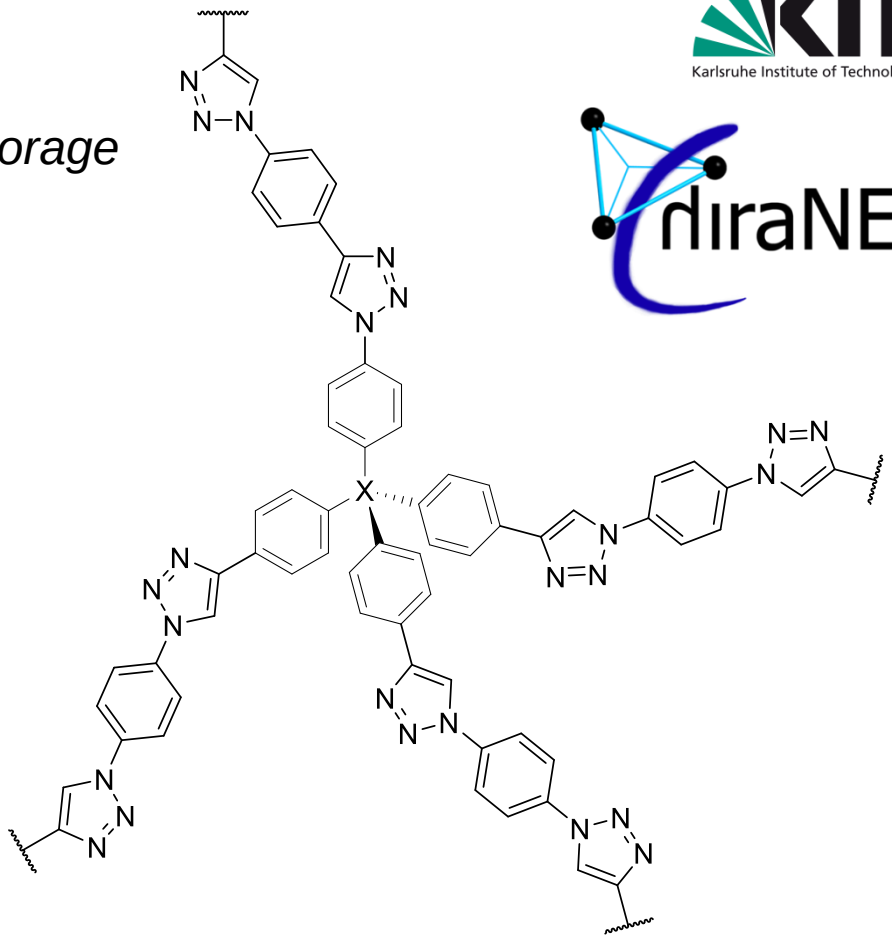
Tetrahedral cores

*Materials for gas storage and **catalysis***



X = C or adamantyl-1,3,5,7-tetrayl

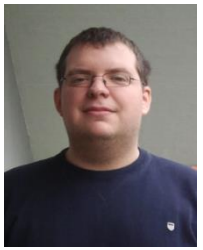




New J. Chem. **2011**, 15, 1577–1581
Chem. Mater. **2010**, *22*, 5964–5972
(Eglington etc.)

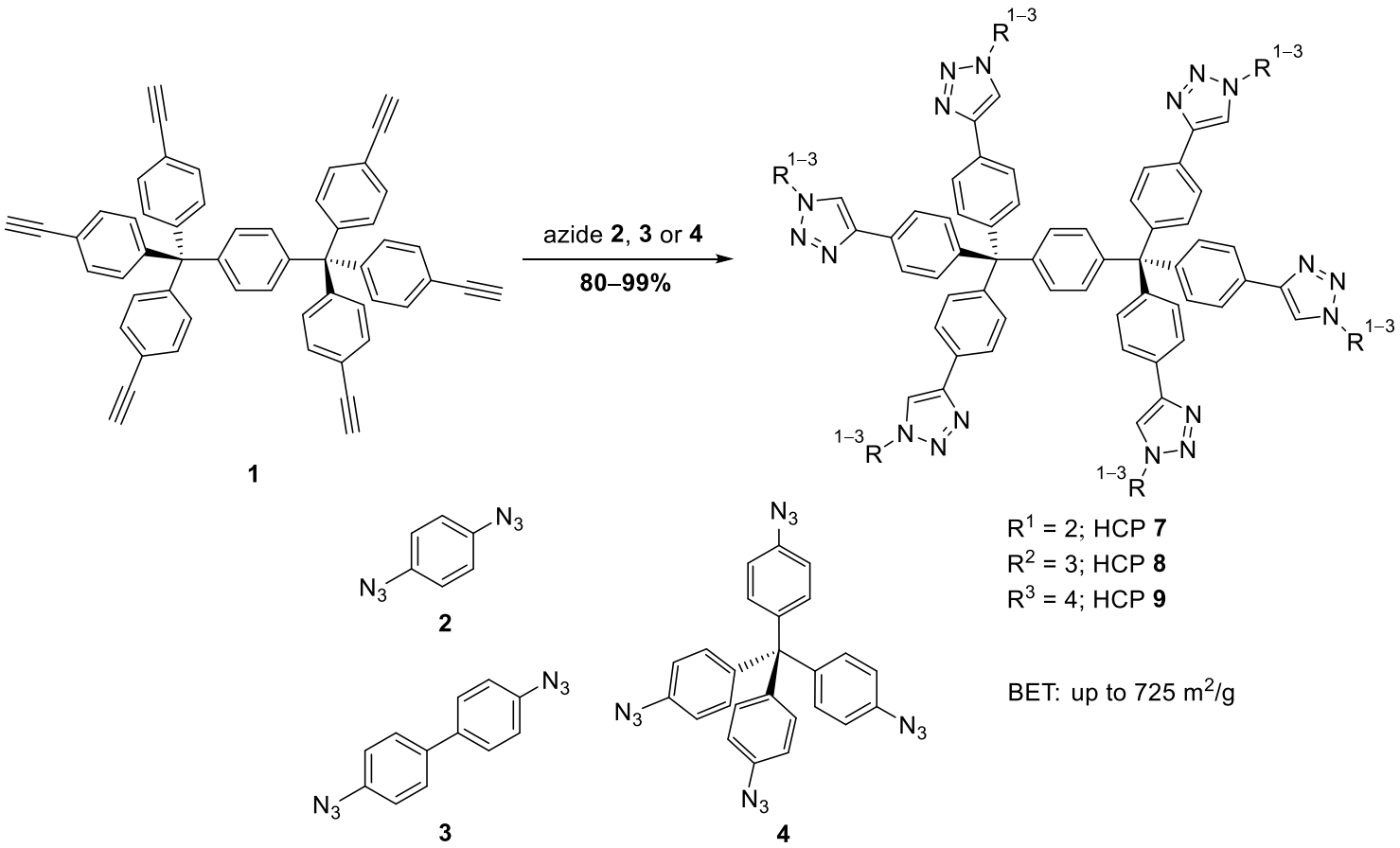

A. Schade


I. Wessely


M. Lang

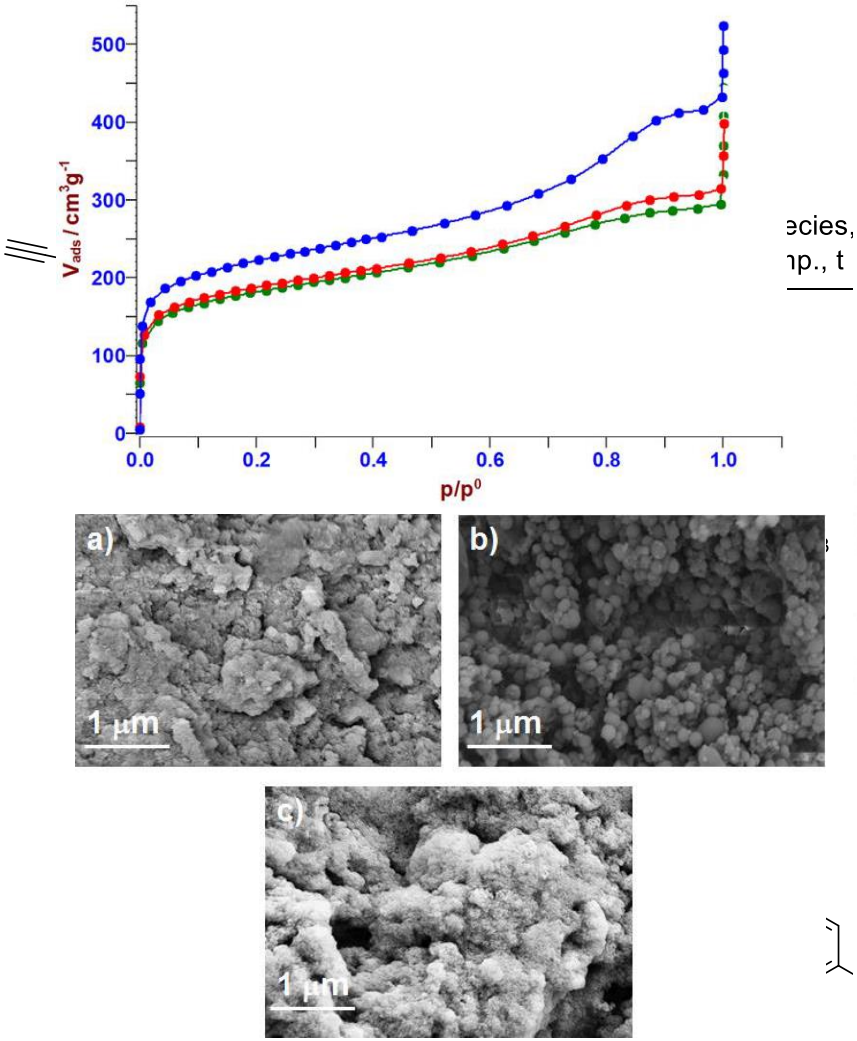

S. Grosjean

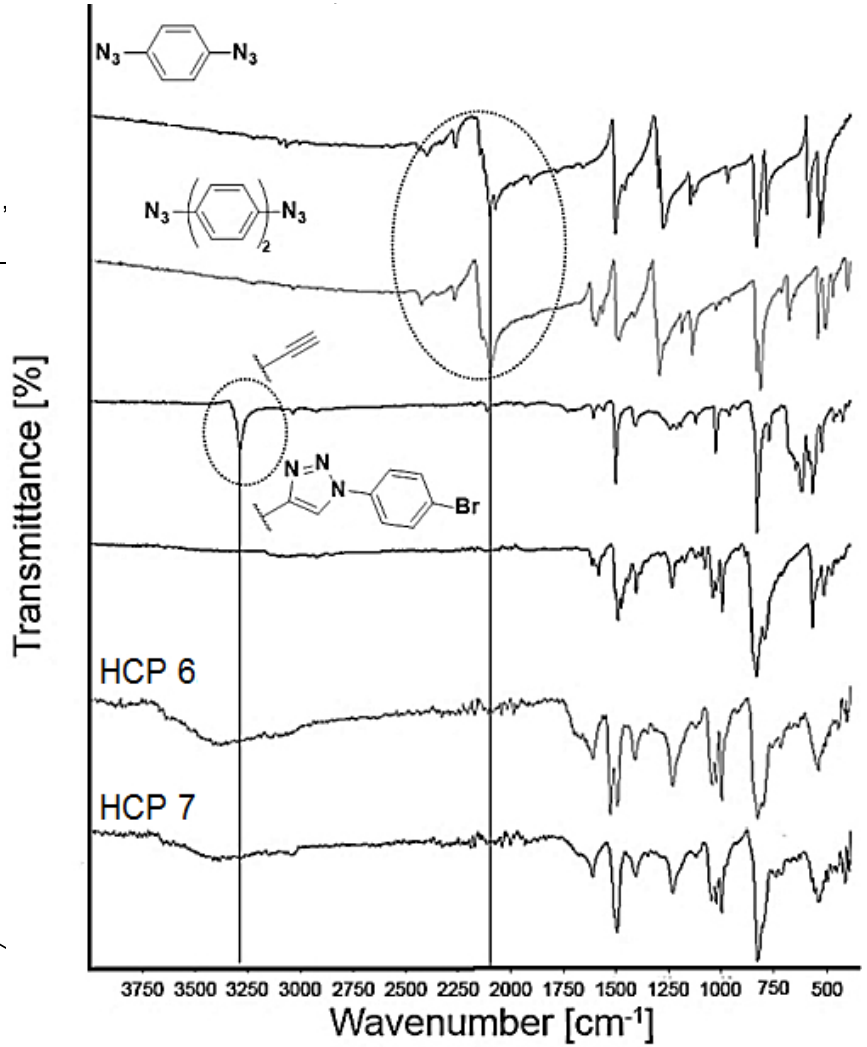
Hexaethynyl bistritylbenzenes as building blocks



A. Schade et al., ChemPlusChem **2014**

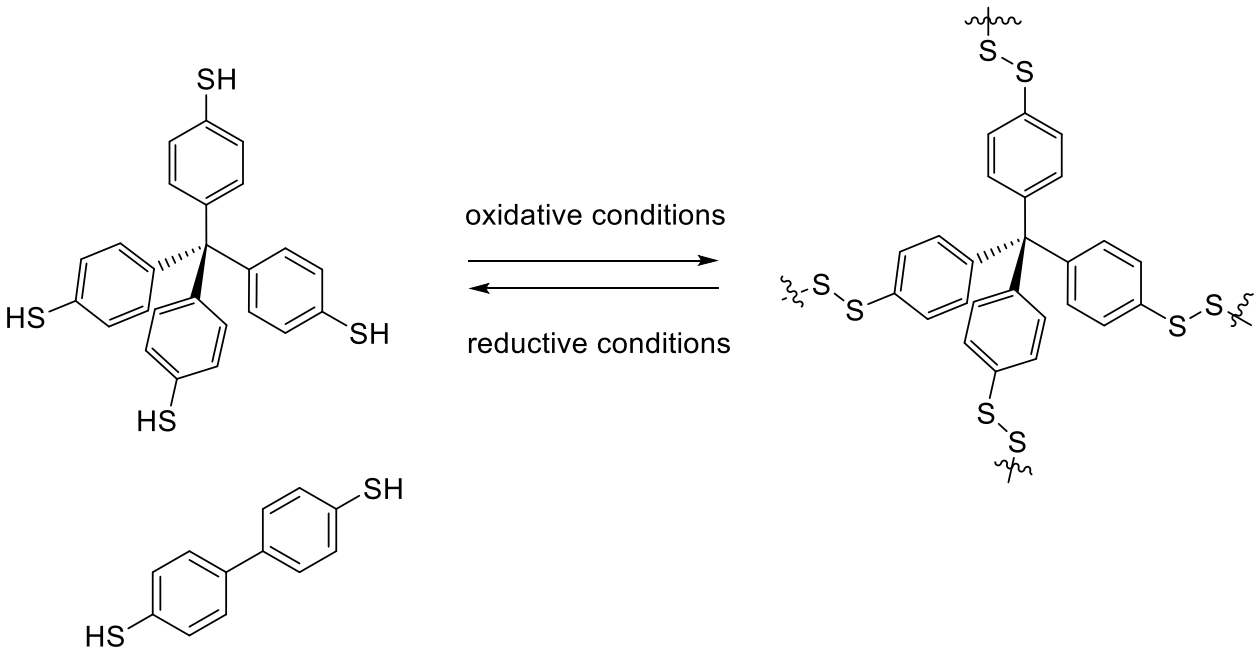
Hexaethynyl bistritylbenzenes as building blocks

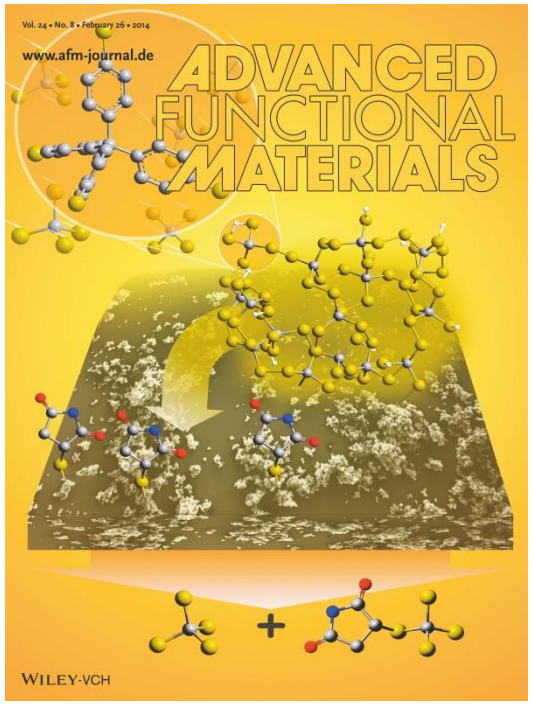




A. Schade et al., ChemPlusChem **2014**

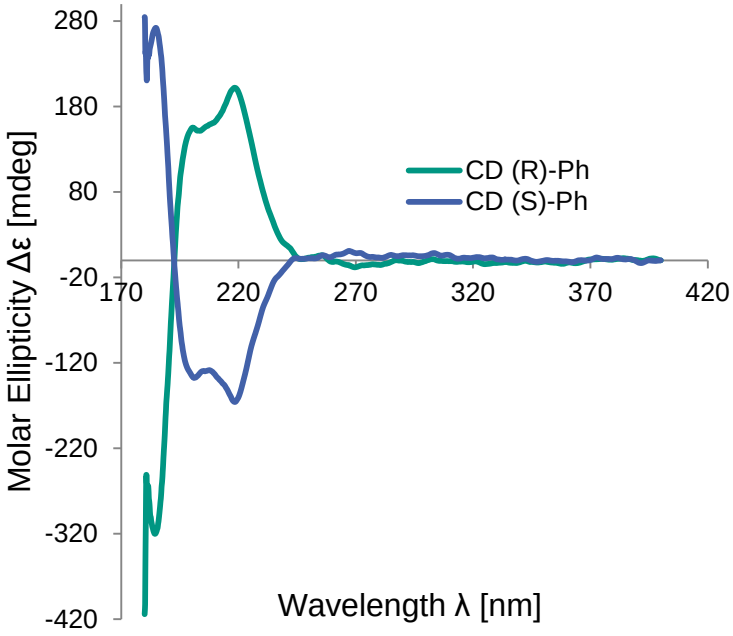
Reversible COFs by Disulfides

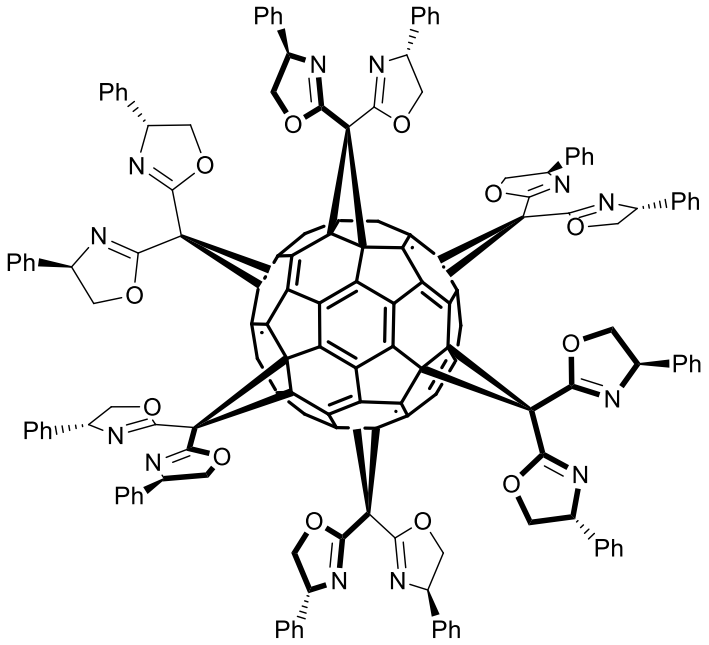


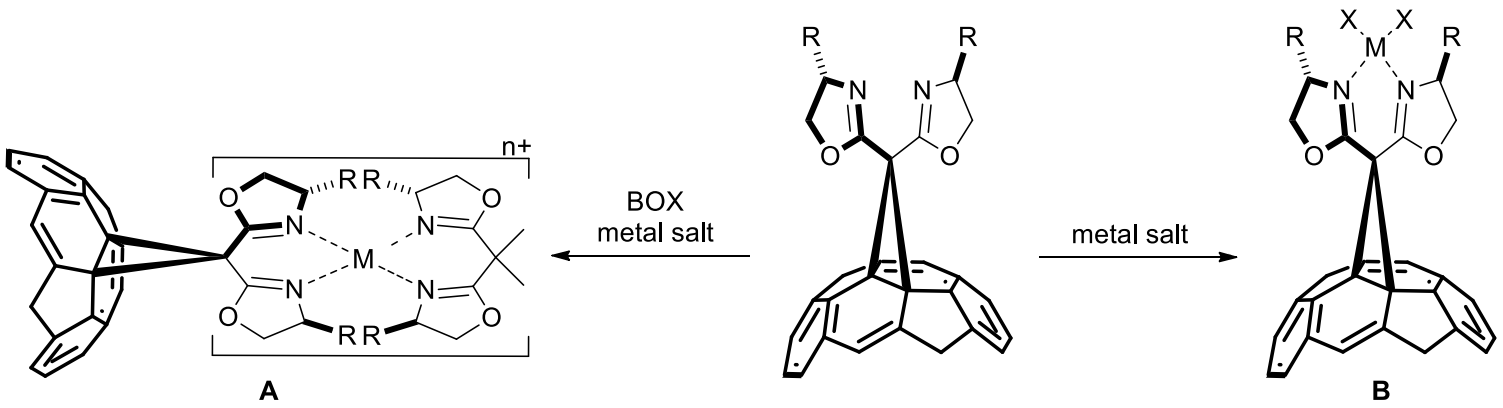


L. Monnerau et al., Adv Funct Mat **2014**

Hexakis Fullerene Adducts of Bisoxazolines
Asymmetric Catalysts for Nanofiltration

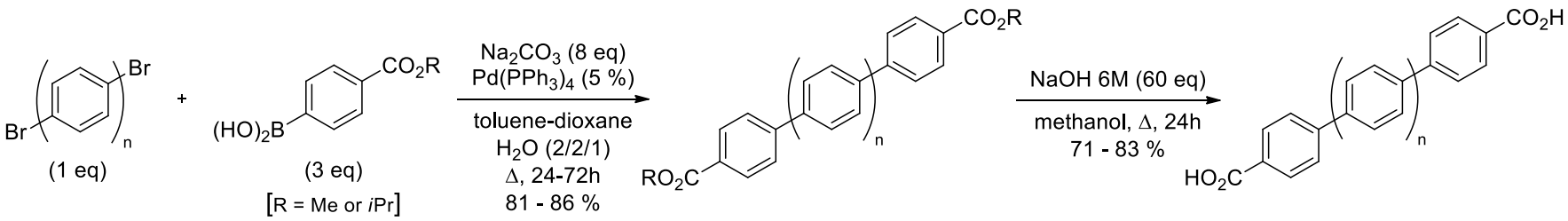




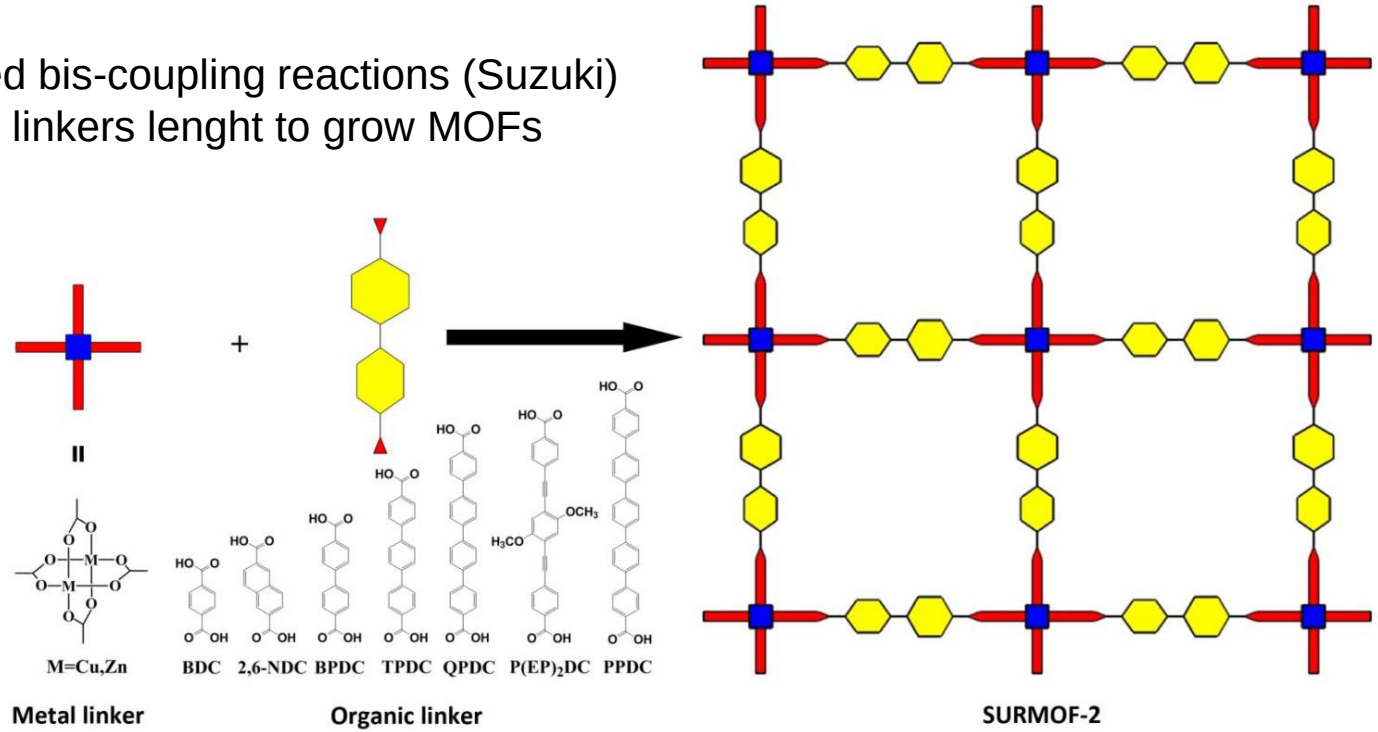


SURMOFs

Surface-mounted Metal-Organic Frameworks (SURMOFs)



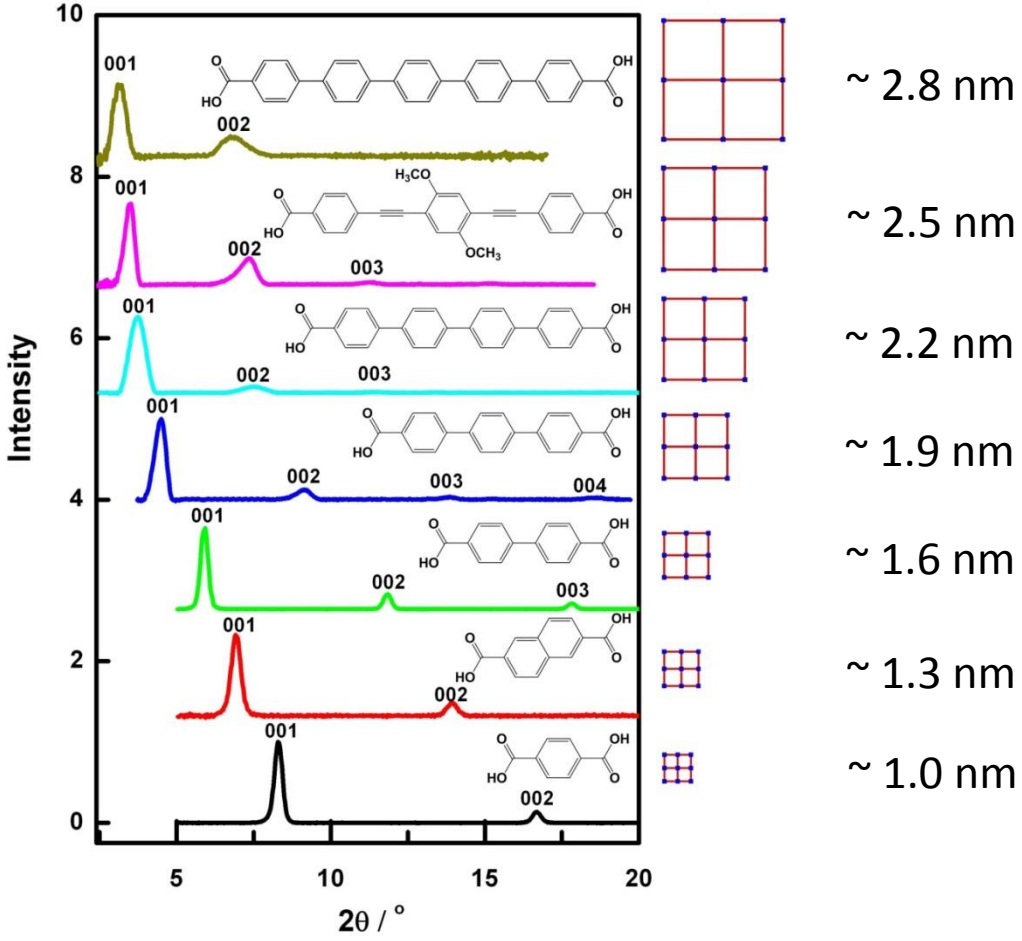
Pd-assisted bis-coupling reactions (Suzuki)
Increasing linkers lenght to grow MOFs

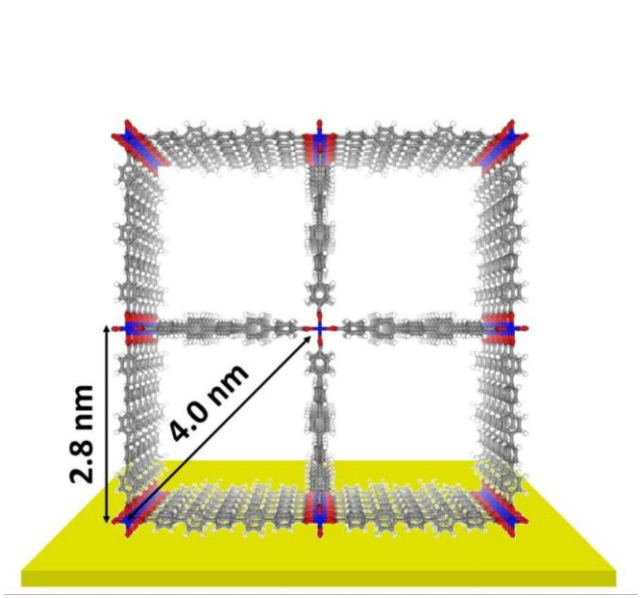


Sci. Rep. **2012**, *2*, 921.

SURMOFs

Surface-mounted Metal-Organic Frameworks (SURMOFs)



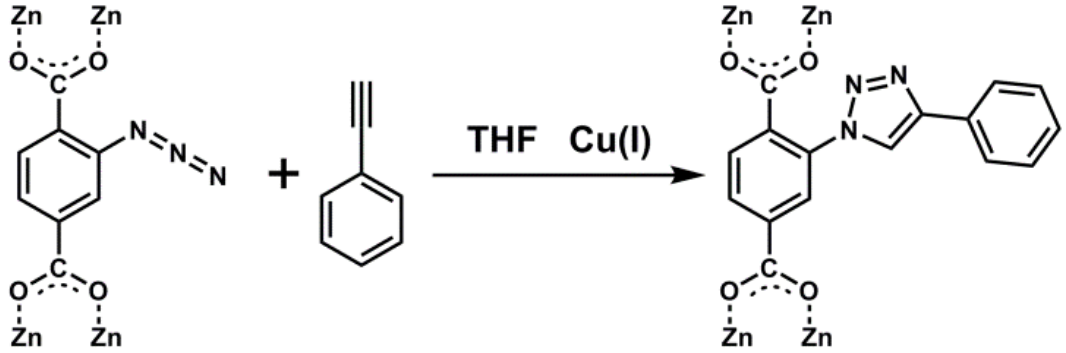


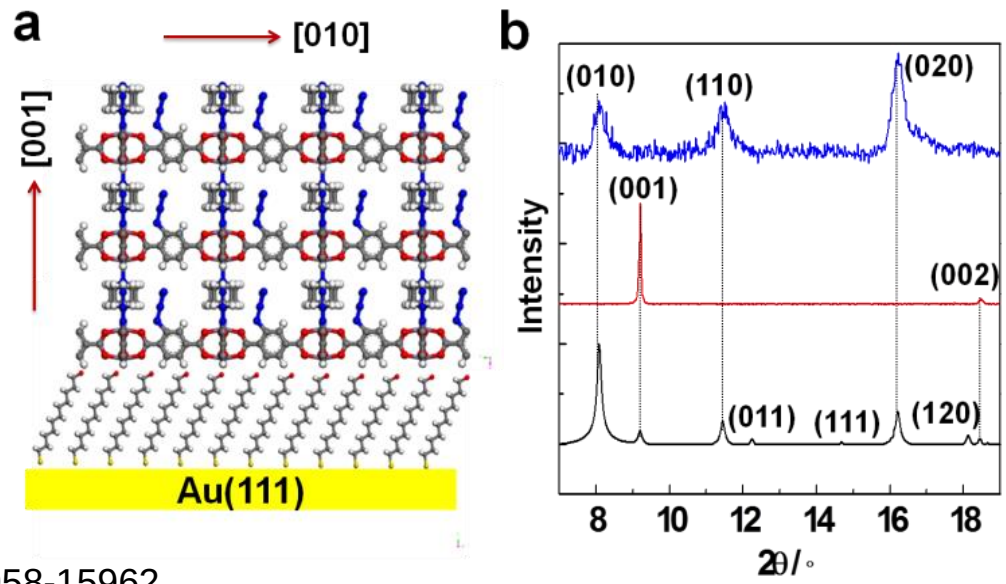
- Increasing linkers length
- Increasing pore size in MOFs

Sci. Rep. **2012**, *2*, 921.

SURMOFs
Postfunctionalization I

- Post-Synthetic Modification of MOFs: Cu(I)-catalyzed Huisgen Cyloaddition

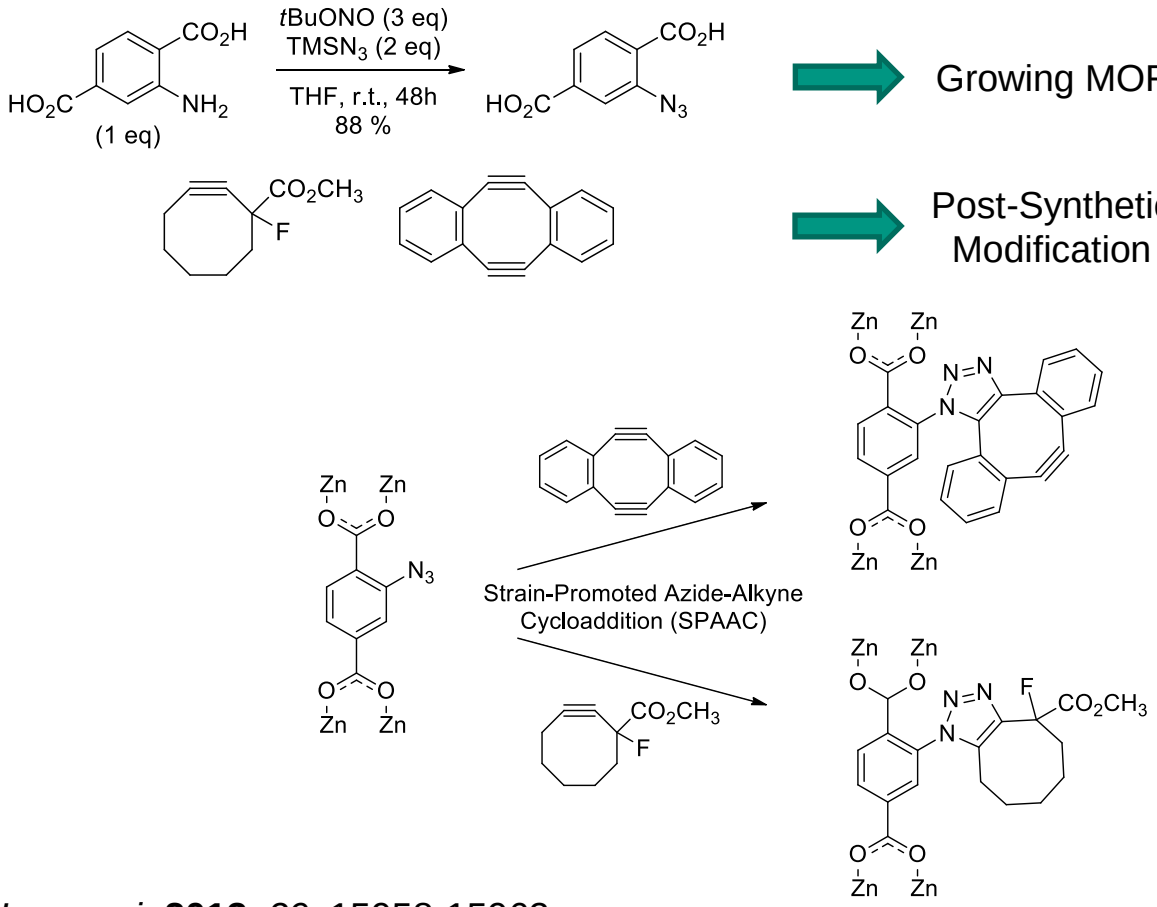




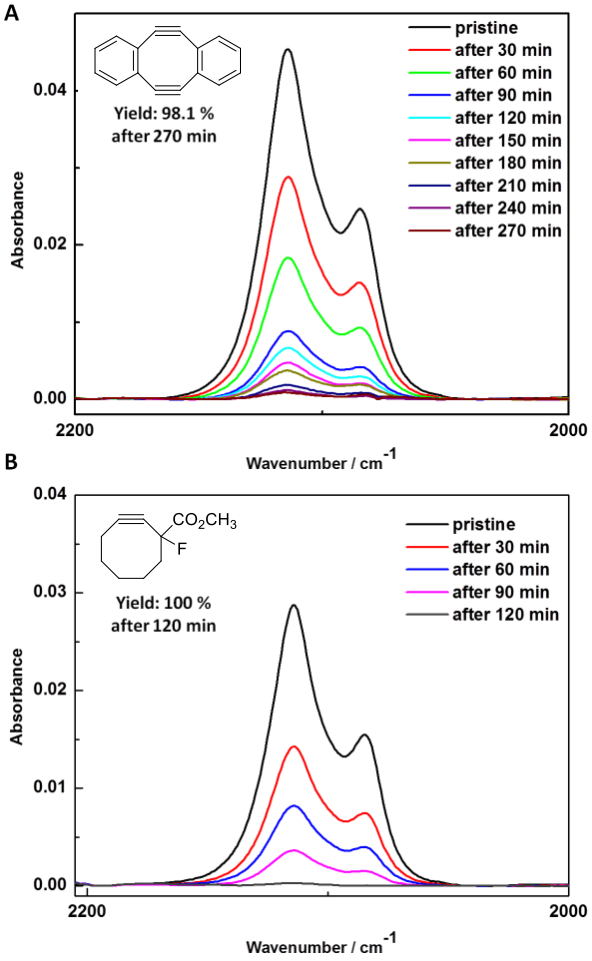
Langmuir **2013**, *29*, 15958-15962.

SURMOFs
Postfunctionalization II

- Post-Synthetic Modification of MOFs:
  Strain Promoted Azide-Alkyne Cyloaddition (SPAAC)

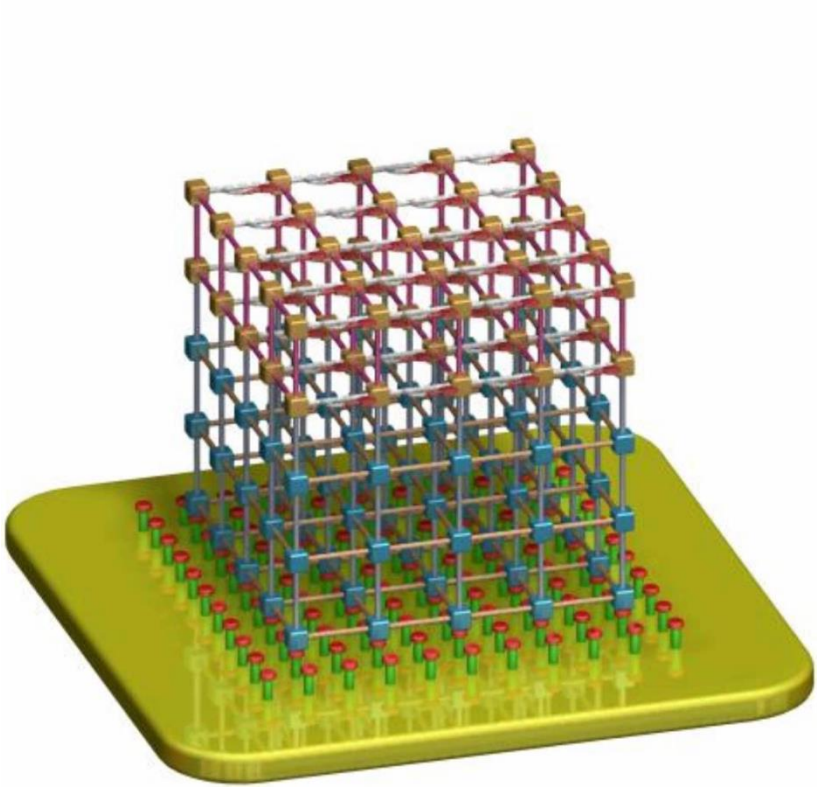


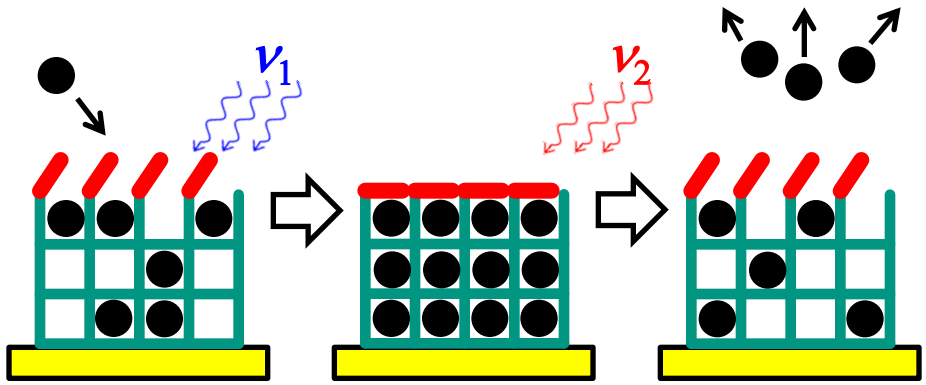
IR monitoring (N_3 vibration)

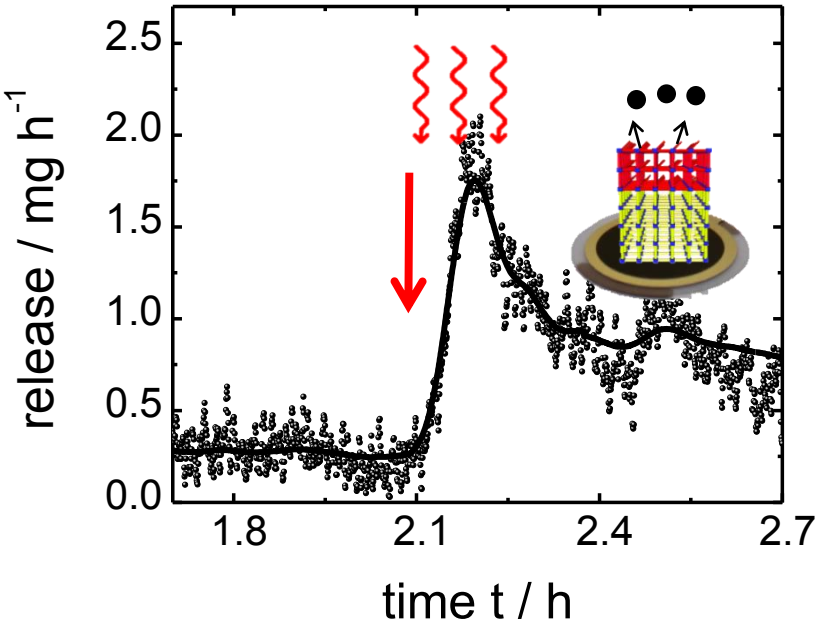


Langmuir **2013**, *29*, 15958-15962.

SURMOFs
Switchable Molecular Container using Azobenzenes



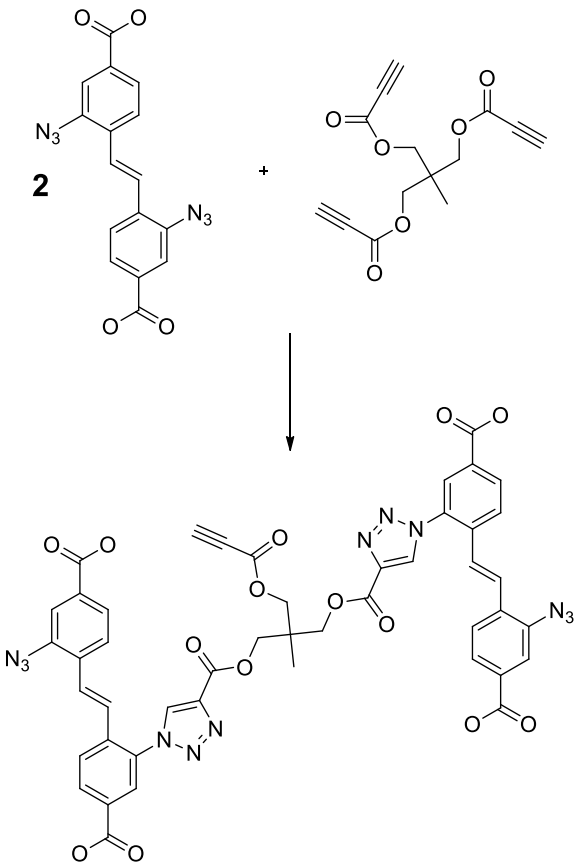


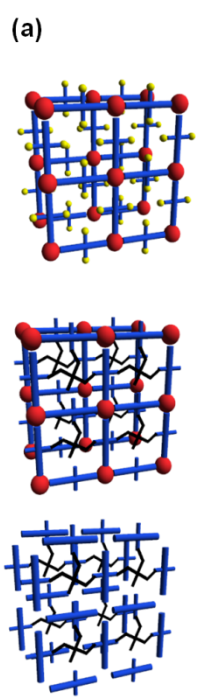


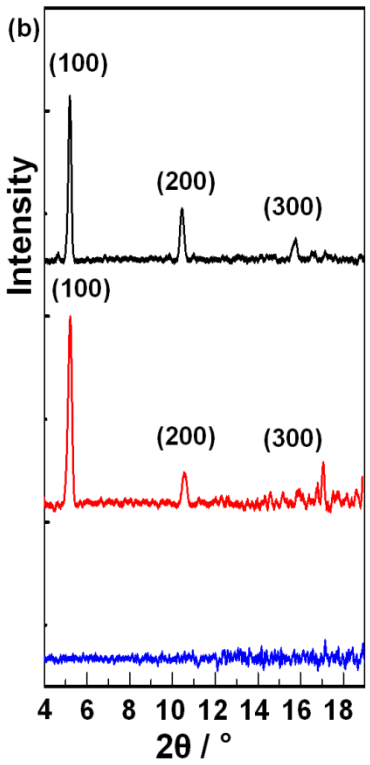
ACS Nano **2014**, *8*, 1463.

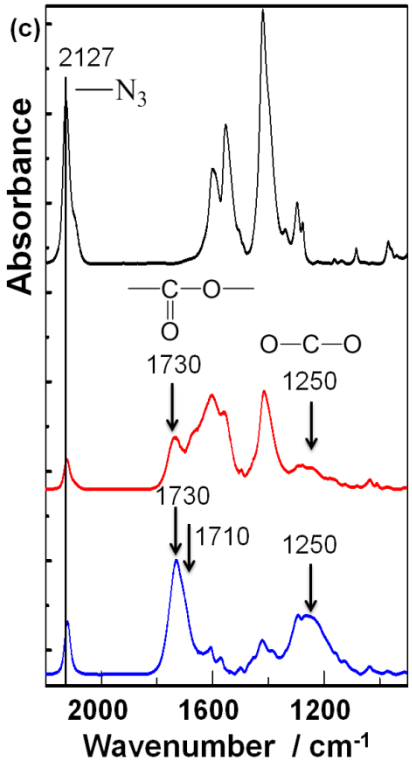
SURGELs

From SURMOFs to Surface Structured Gels (SURGELs)



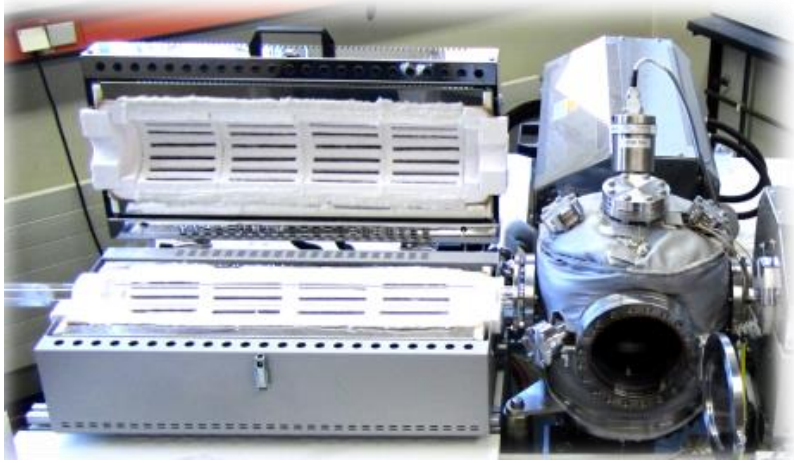






J. Am. Chem. Soc. **2014**, *136*, 8-11.

Functionalized Polymers by Chemical Vapour Deposition Method

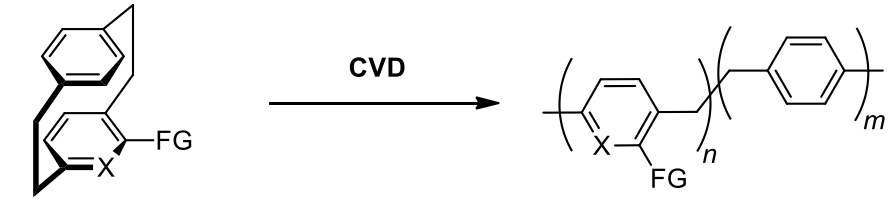


H-Y. Chen, J. Lahann, *Langmuir* **2011**, *27*, 34–48.

Functionalised Paracyclophanes and Pyridinophanes for CVD-Polymerization

Karlsruhe Institute of Technology

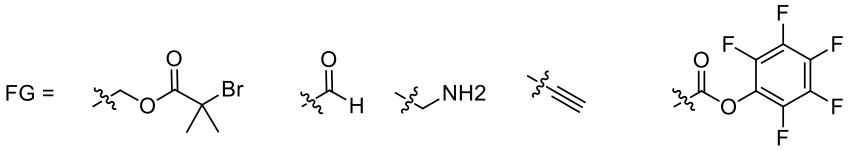
CVD-Process



X = CH: PCP-FG
X = N: PYP-FG

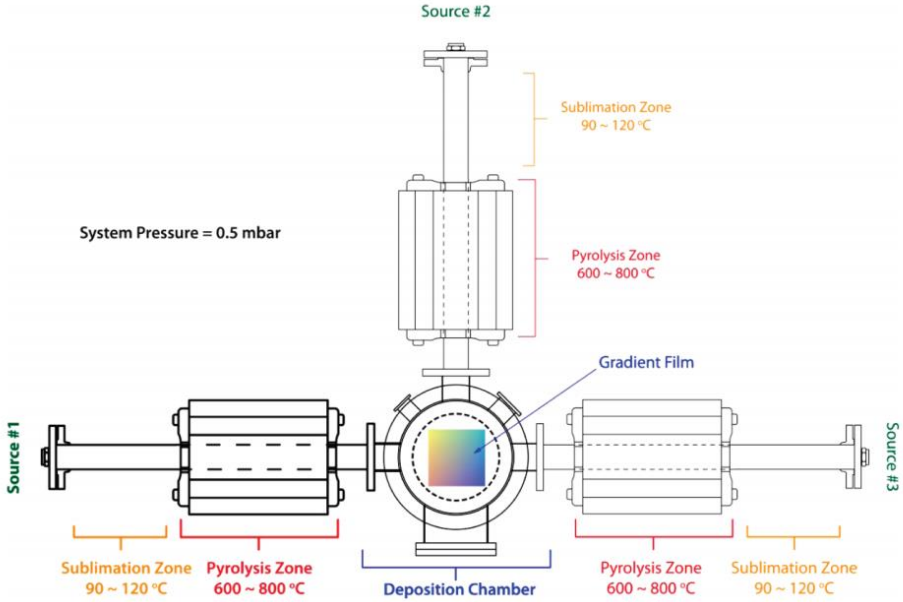
X = CH: PPX-FG
X = N: PPLX-FG

Selection of functional groups used in CVD and possible subsequent chemistry



ATRP | Hydrazide coupling | Click chemistry | Amine coupling

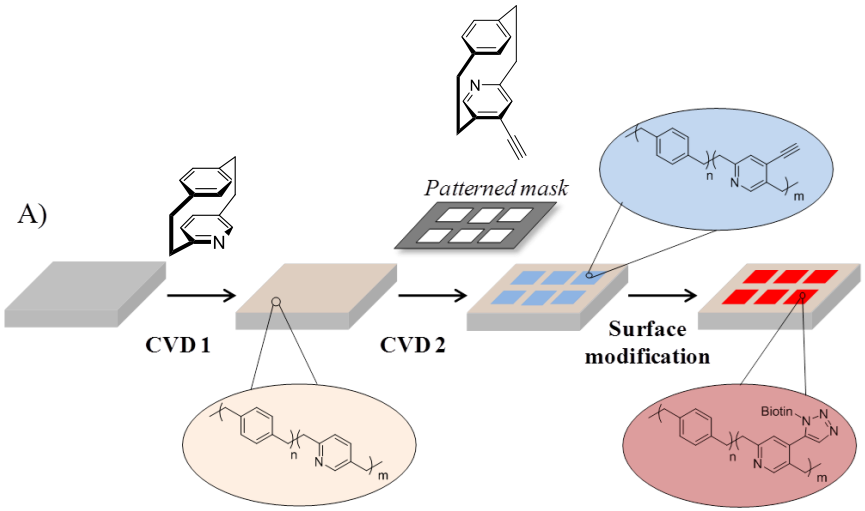
Three-source CVD-system

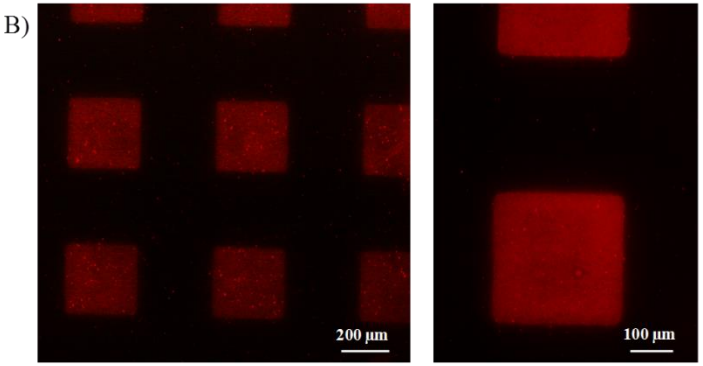


Applications of CVD coatings

- Immobilization of cells
- Thermal bonding: Sensor technology
- Photonics
- ***Metal complexes on surface***
- ***Catalysis***

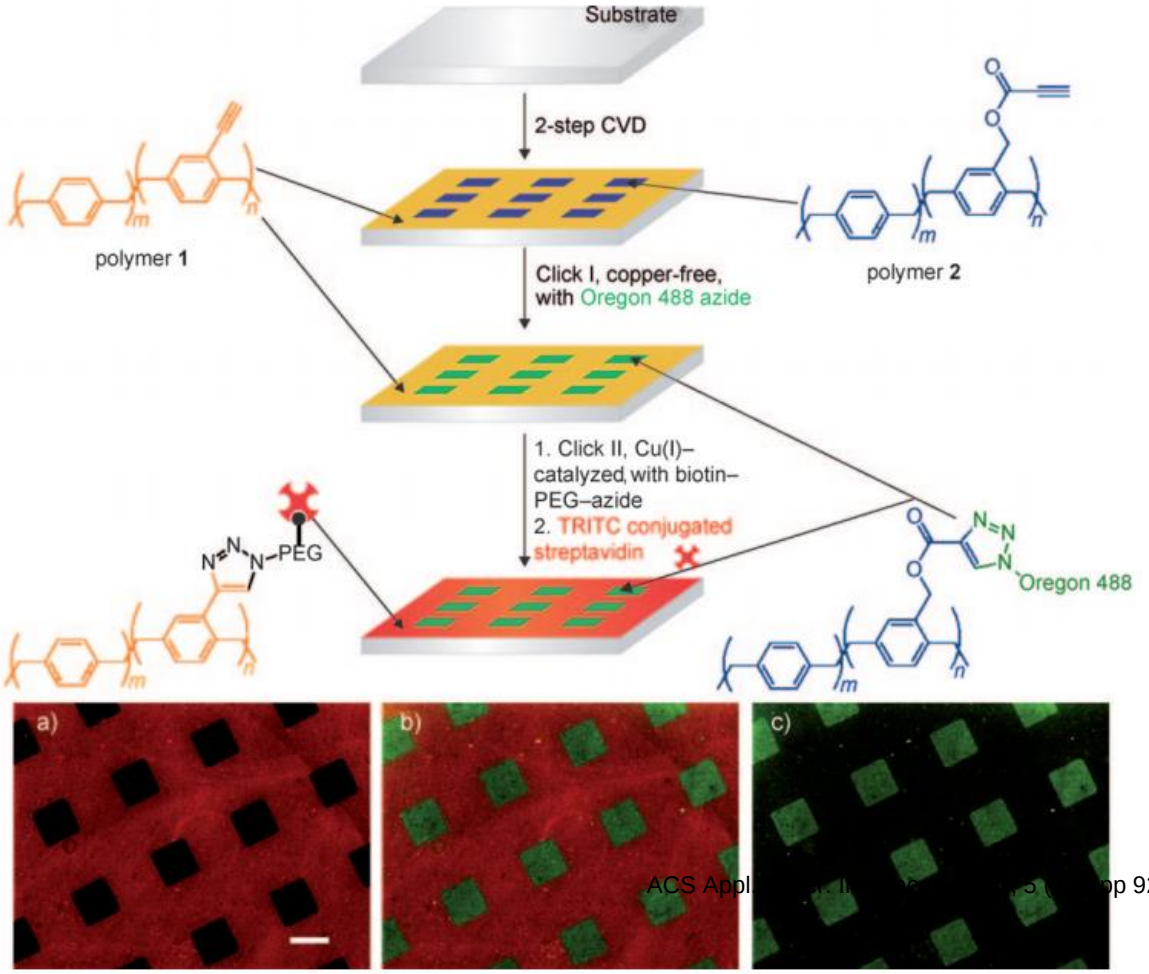
New reactive coatings based on functional pyridinophanes





A) Schematic representation of the protocol used for biotin immobilization on the functional coating and B) fluorescence images after streptavidin incubation.

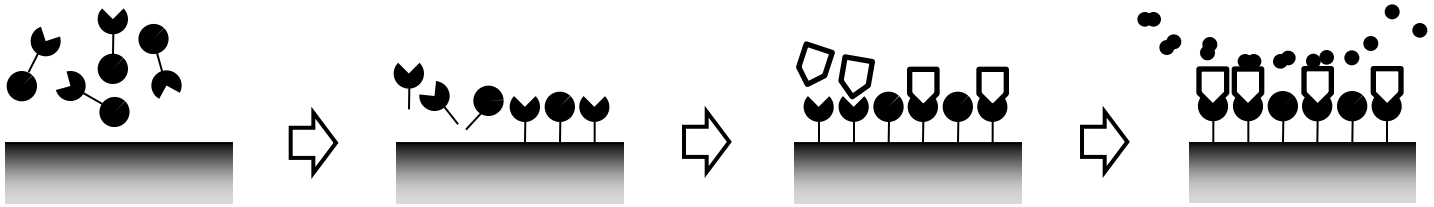
Orthogonal “Double-Click” Chemistry and Co-immobilization of Molecules on CVD films



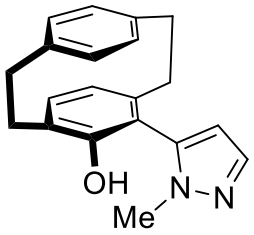
ACS Appl [illegible] p 9262–9268

Deng, X., Friedmann, C. and Lahann, J. (2011), Bio-orthogonal “Double-Click” Chemistry Based on Multifunctional Coatings. Angew. Chem. Int. Ed., 50: 6522–6526

Functionalized Polymers for Catalysis by Chemical Vapour Deposition



7 [2.2]Paracyclophan-Derivate in 25 Experimenten getestet

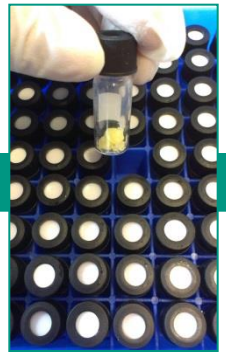


T (Pyrolyse)	**660 °C**	**660 °C**	**750 °C**
T (Ablagerung)	15 °C	15 °C	12 °C
Abscheidungsrate	0.5 Å/s	1.0 Å/s	1.0 Å/s
Monomermasse	23 mg	25 mg	55 mg
Ellipsometer	24.8 +/– 0.1 nm	35.6 +/– 0.1 nm	91.7 +/– 0.2 nm

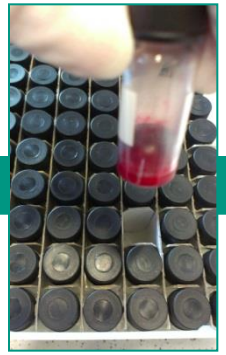
F. Bally, M. Busch, S. Bräse, J. Lahann, *unveröffentlicht.*

Complat as Service Platform for Combinatorial Chemistry at the KIT

Storage/Service



Combined Libraries
Complete analytics
Synthetic protocols available
Scale up
Storage as pure substance AND in stock solution



formatting

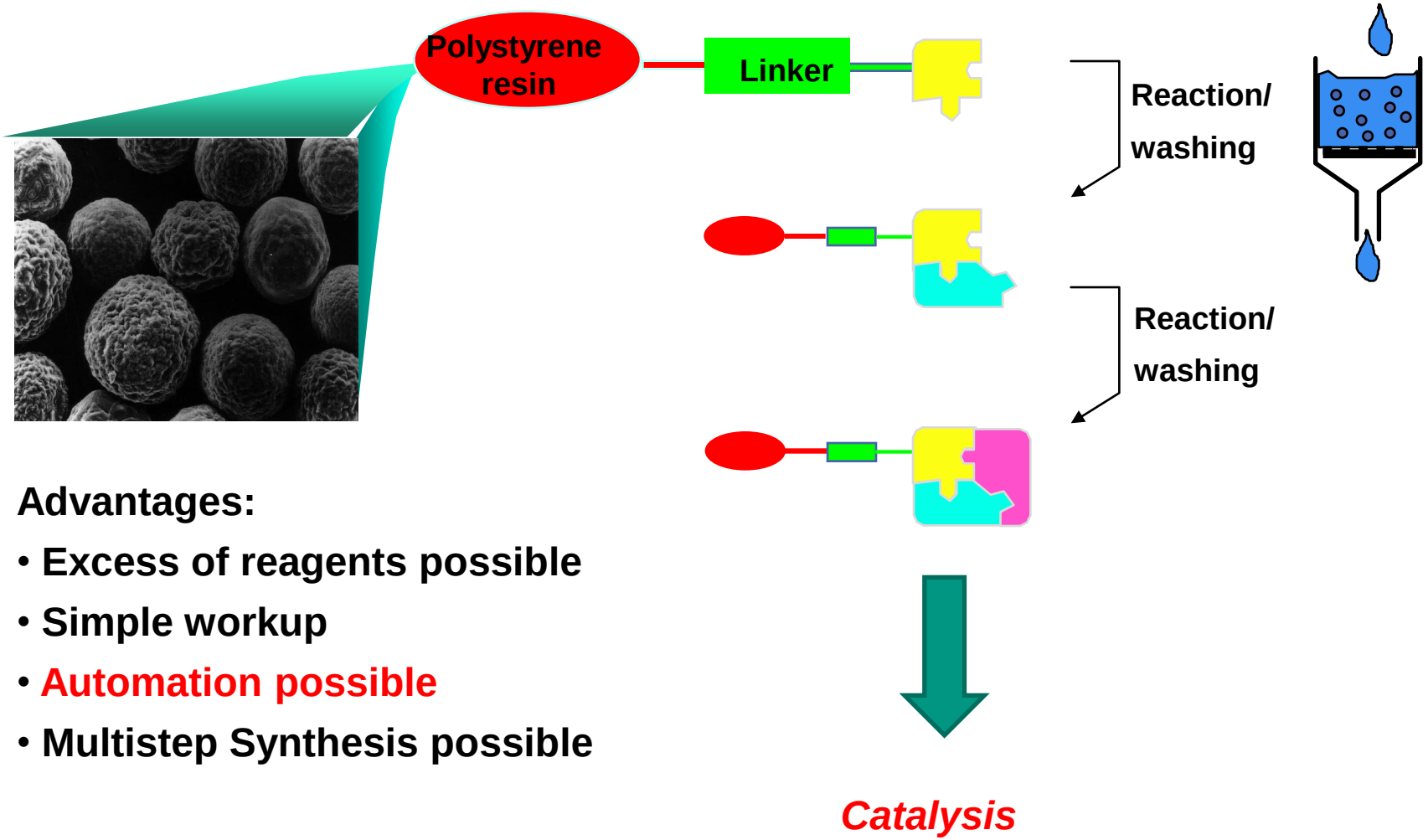
collaborations

KIT internal: biologists, chemists, toxicologists, materials sciences

external: MPI Dortmund, Uni Bonn, Screening facilities EU

complat
Combinatorial Chemistry Platform

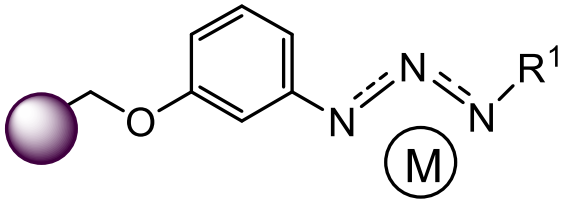
Solid Phase-Bound Catalysts for Combinatorial Catalysis

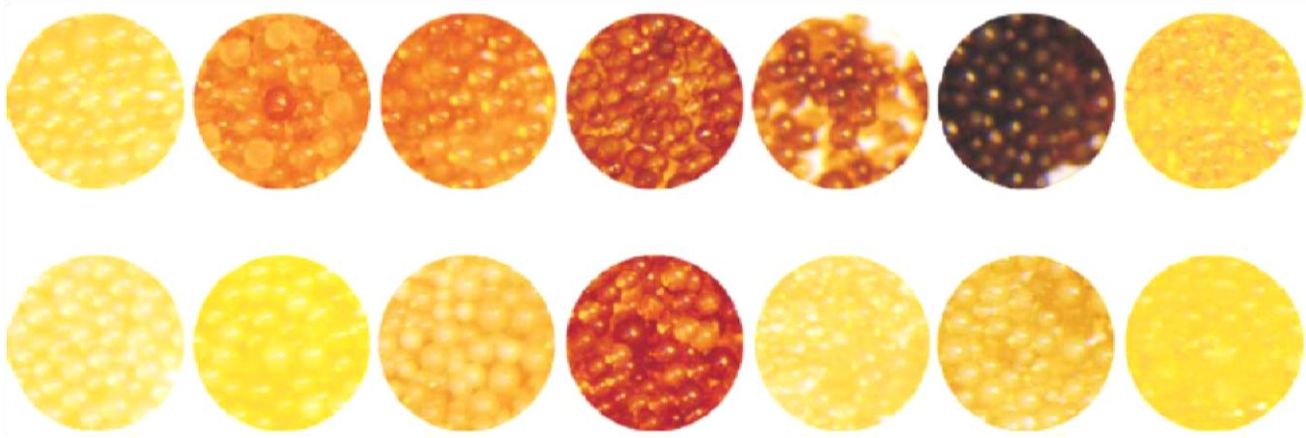


Advantages:

- **Excess of reagents possible**
- **Simple workup**
- **Automation possible**
- **Multistep Synthesis possible**

Triazenes as Linkers for Metal Ions
Metal-Binding





R = indanyl

R = ephedrinyl

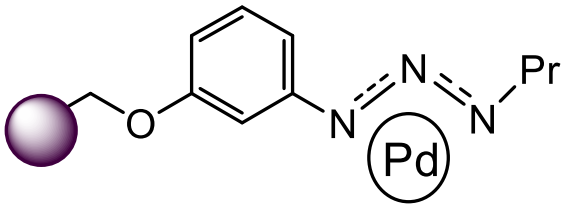
Blank Co Cu Fe Pd Ti Zr

BMCL **2002** (with N. Leadbeater)

S. Bräse, S. Dahmen, *Chem. Eur. J*. **2000**, *5*, 1899-1905.
S. Bräse, *Acc. Chem. Res.* **2004**, *37*, 805–815.

Angew. Chem. Int. Ed. **1998**, *37*, 3413-3415
Angew. Chem. Int. Ed. **1999**, *38*, 1071-1073
Angew. Chem. Int. Ed. **1999**, *38*, 3669-3672
Angew. Chem. Int. Ed. **2008**, 47, 8120-8122
Angew. Chem. Int. Ed. **2010**, *49*, 5986–5988
Angew. Chem. Int. Ed. **2011**, *50*, 11533–11535
Angew. Chem. Int. Ed. **2012**, *51*, 3713–3715

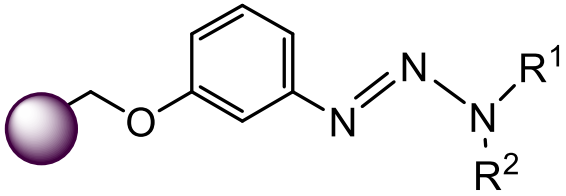
Triazenes as Linkers for Metal Ions Catalysis



very low leaching

Sonogashira

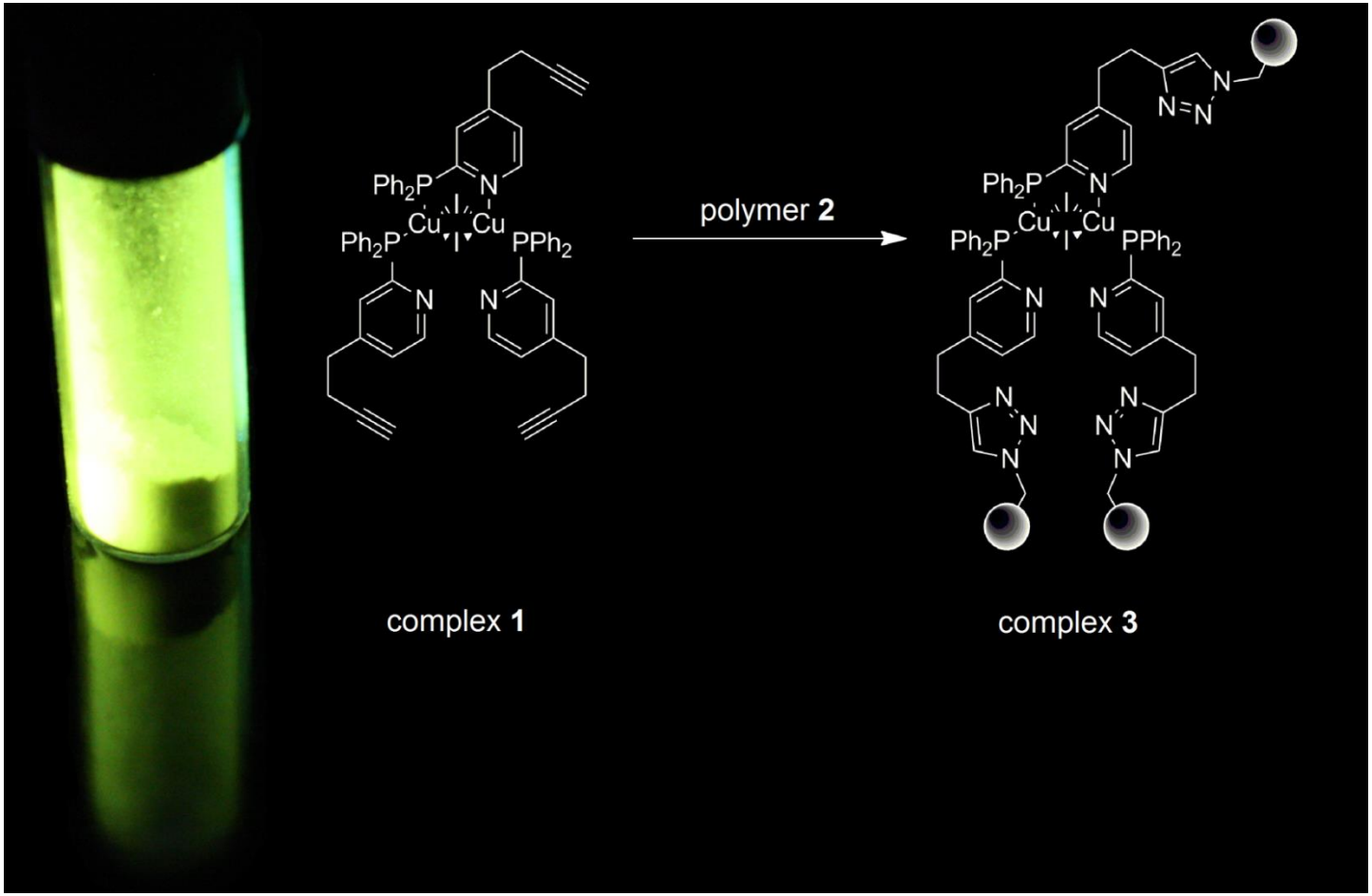
Suzuki



Asymmetric 1,2-additions

BMCL **2002** (with N. Leadbeater)

Concepts for immobilization of Metal Complexes



Volz, D.; Baumann, T.; Flügge, H.; Mydlak, M.; Grab, T.; Bächle, M.; Barner-Kowollik, C.; Bräse, S.
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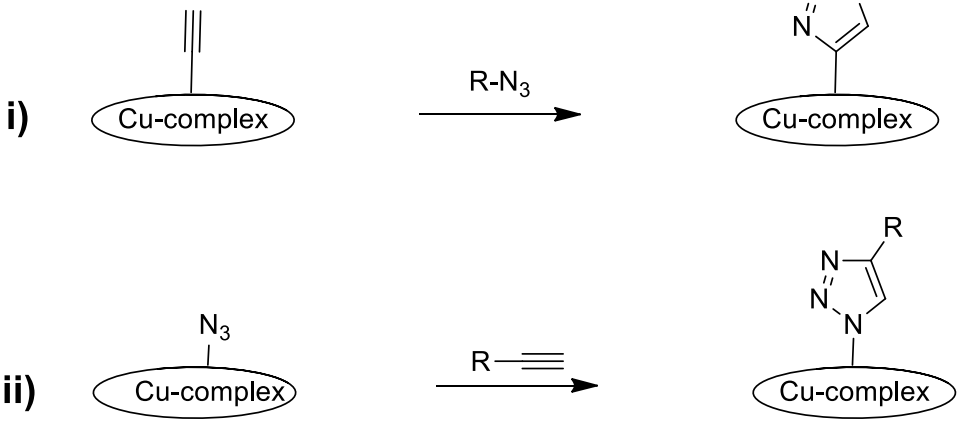
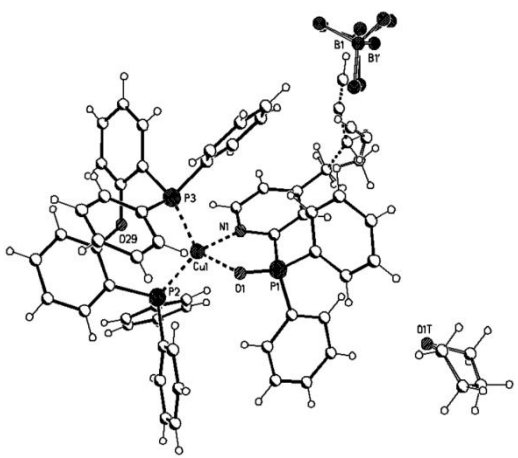
Self-catalyzed Click-reaction of alkyne-Cu(I) complexes

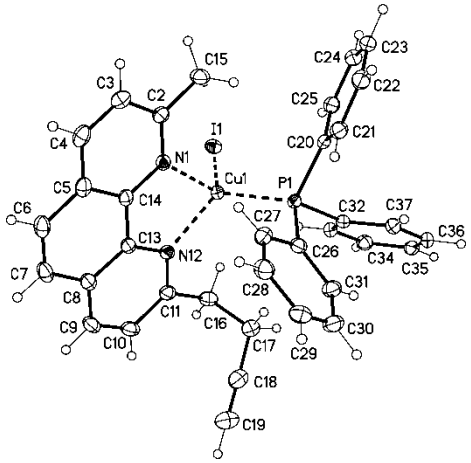
Concept

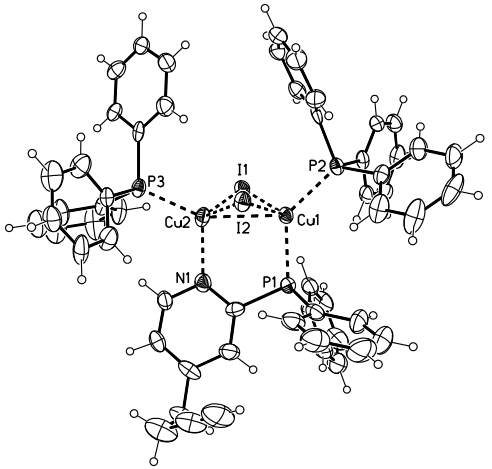
1) **functionalize Cu(I) complex (mononuclear, binuclear..)**

2) **react with small molecule/polymer/functionalized surface**



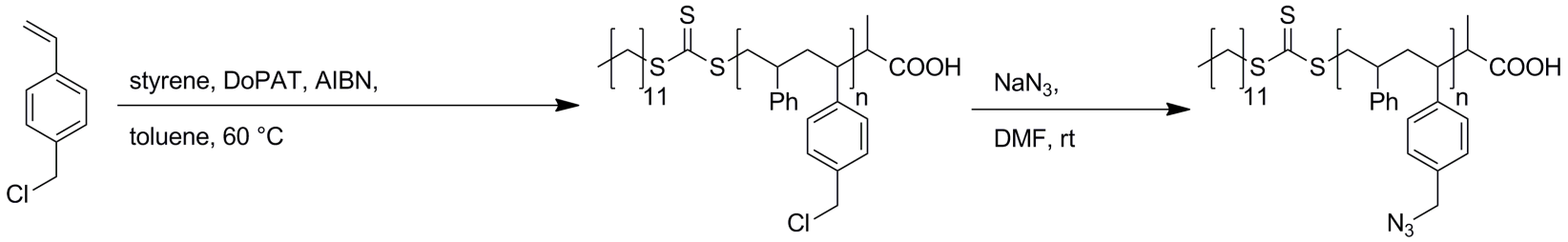






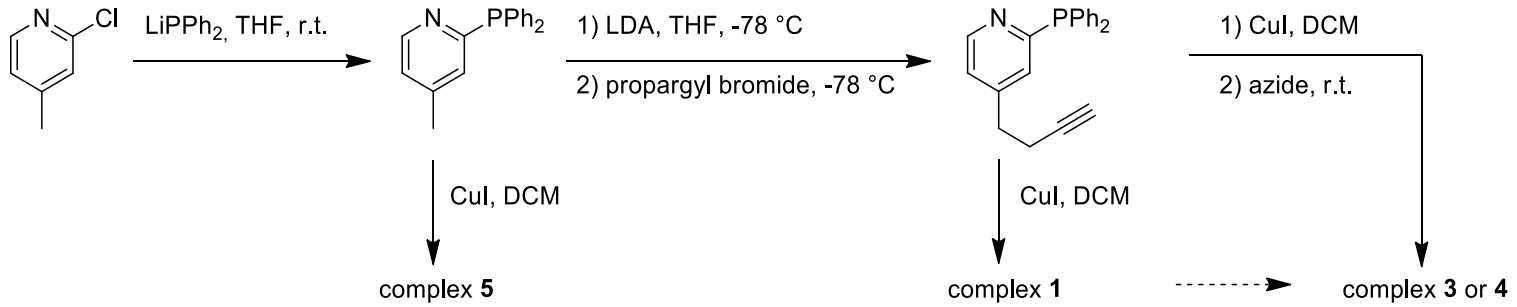
D. Volz, M. Wallesch, S. Bräse, *unpublished results*

Self-catalyzed Click-reaction of alkyne-Cu(I) complexes



10 **11a-d** **2a-d**

b)



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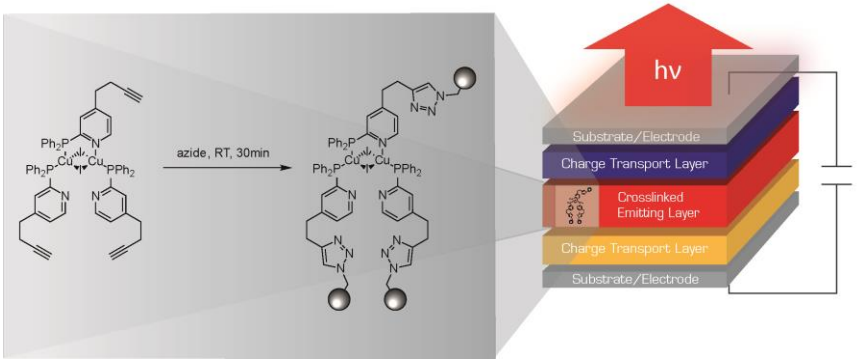
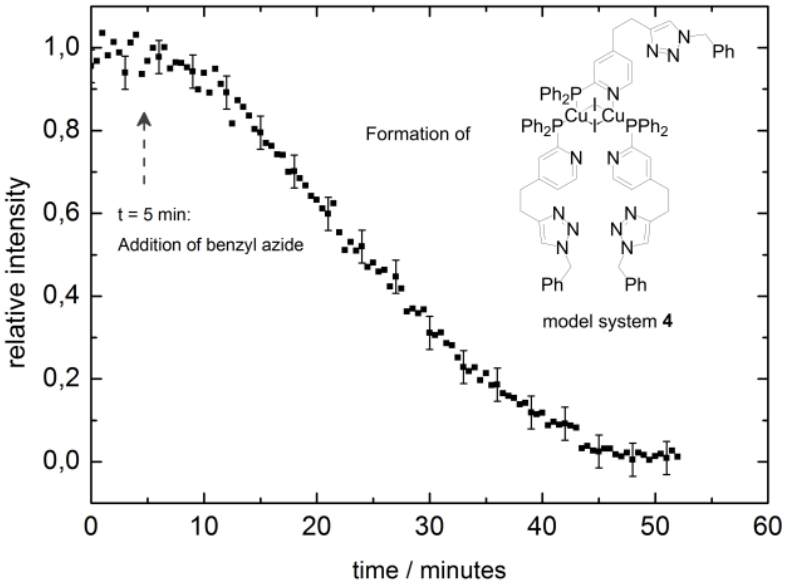
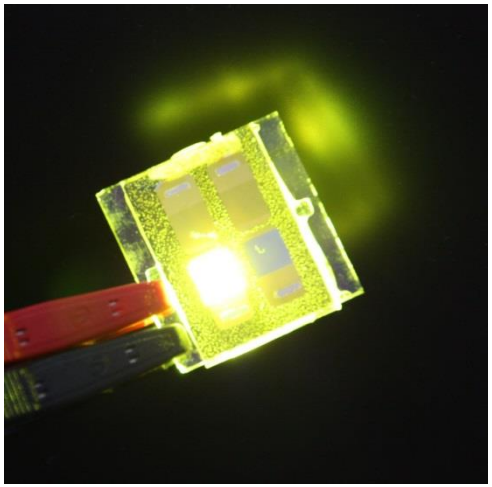
Self-catalyzed Click-reaction of alkyne-Cu(I) complexes





reaction of complex with benzyl azide has been monitored with FT-IR spectroscopy



concept has been demonstrated successfully in a crosslinked OLED device

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Today‘s menu

- Aperitif: Immobilization of Homogeneous Catalysts
- Amuse-bouche: Asymmetric Catalysis
- Entrée: Immobilization of Catalysts
- Main course: Combinatorial Chemistry
- Dessert: Diversity through Multifunctional Linker
- Cheese: Auto-Click Reactions

Bräse group: Current small molecule chemistry team

Secalonic acids/Beticolin
Stephanie Lindner
Larissa Geiger

Cannabinoids
Thomas Hurrle
Sabilla Zhong
Yuling Hu
Christina Retich

Steroids/Wnt-signalling
Vanessa Koch
Serim Murat
Valentin Beyer
Dr. Alicia Dilmac

Biointerfaces/CUBUSLab
Dominic Lütjohann

KIT CombiChemistry Platform
Dr. Nicole Jung
Sylvia Vanderheiden
Irina Protasova
Simone Grässle
Steven Susanto
Tim Wezeman
Nicolai Wippert

Sugars and more
Marco Mende
Paul Sauter
Mirella Wawryszyn
Anna Fellinger
Katharina Peschko
Anna Hörner
Anne Schneider
Stephan Münch
Alexander Braun

Nano structures
Dr. Christin Bednarek
Alexandra Schade
Dr. Sylvain Grosjean
Isabelle Wessely
Mathias Lang
Patrick Hodapp

Metals and more
Larissa Bergmann
Manuela Wallesch
Angela Wandler
Carolin Braun
Ceylan Yildiz
Eduard Spuling

FCI
Alexander-von-Humboldt foundation
DFG: TR 88, KSOP, CFN
BASF
Bayer AG

Thomas Baumann
Daniel Zink
Daniel Volz

Martin Nieger

Ute Schepers
Peter Roesky
Burkhard Luy

Wim Klopper

Clemens Heske
Lothar Weinhardt

Jörg Lahann
Christopher Barner-Kowollik