Strukturierte Oberflächen: Bindeglied zwischen Chemie, Physik und Biologie

H. Gliemann

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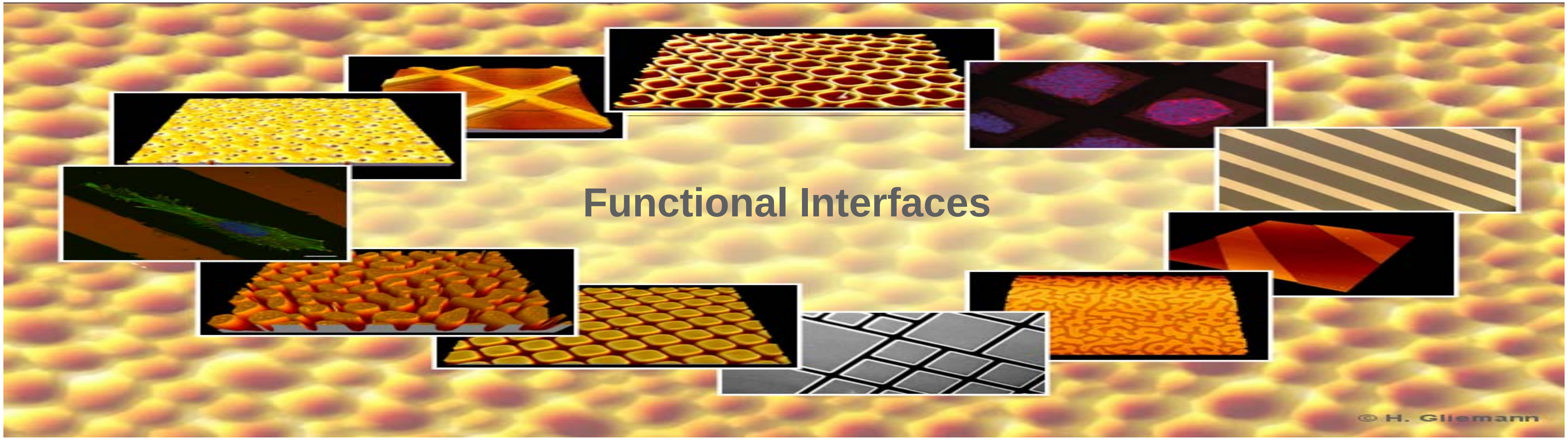
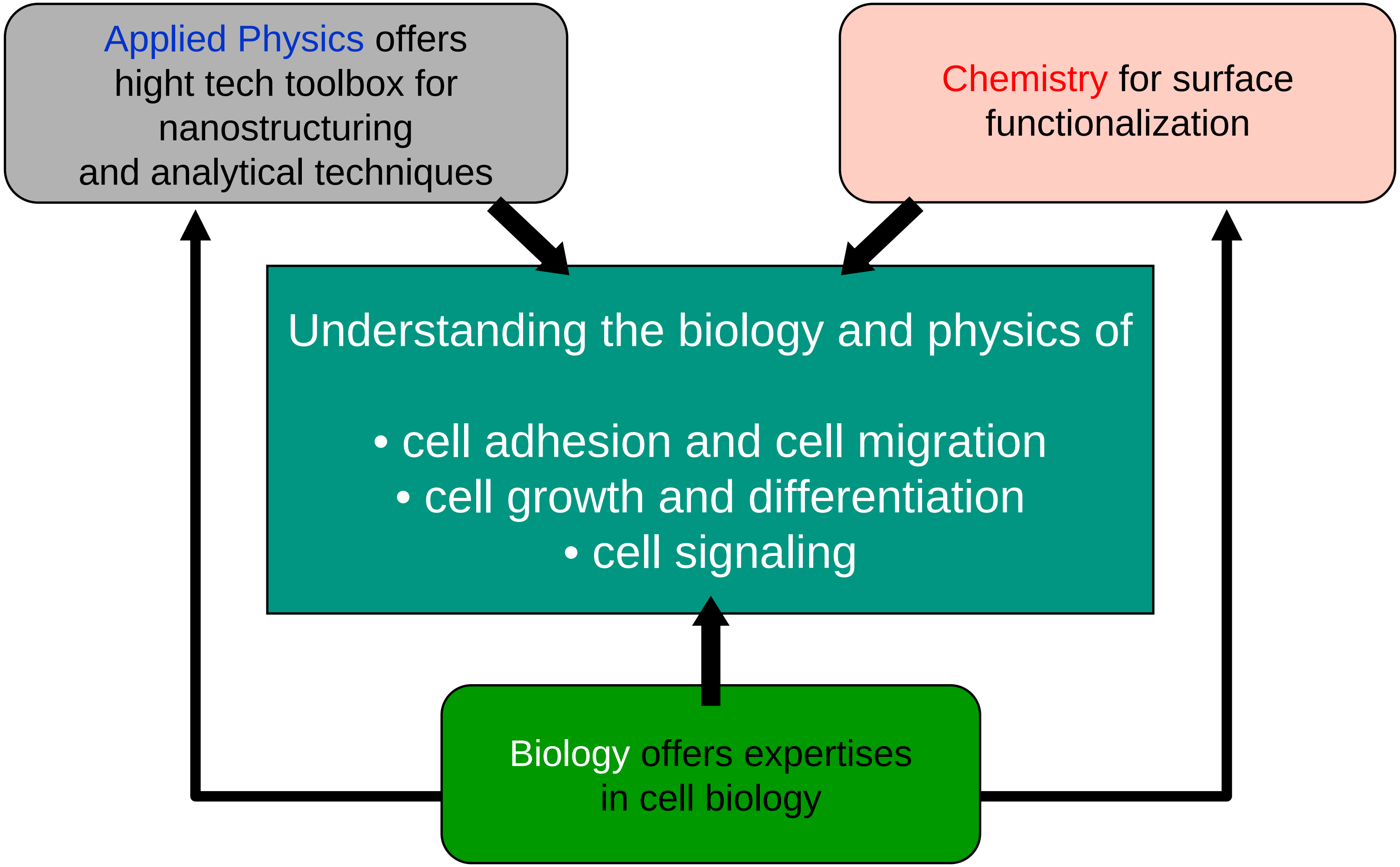
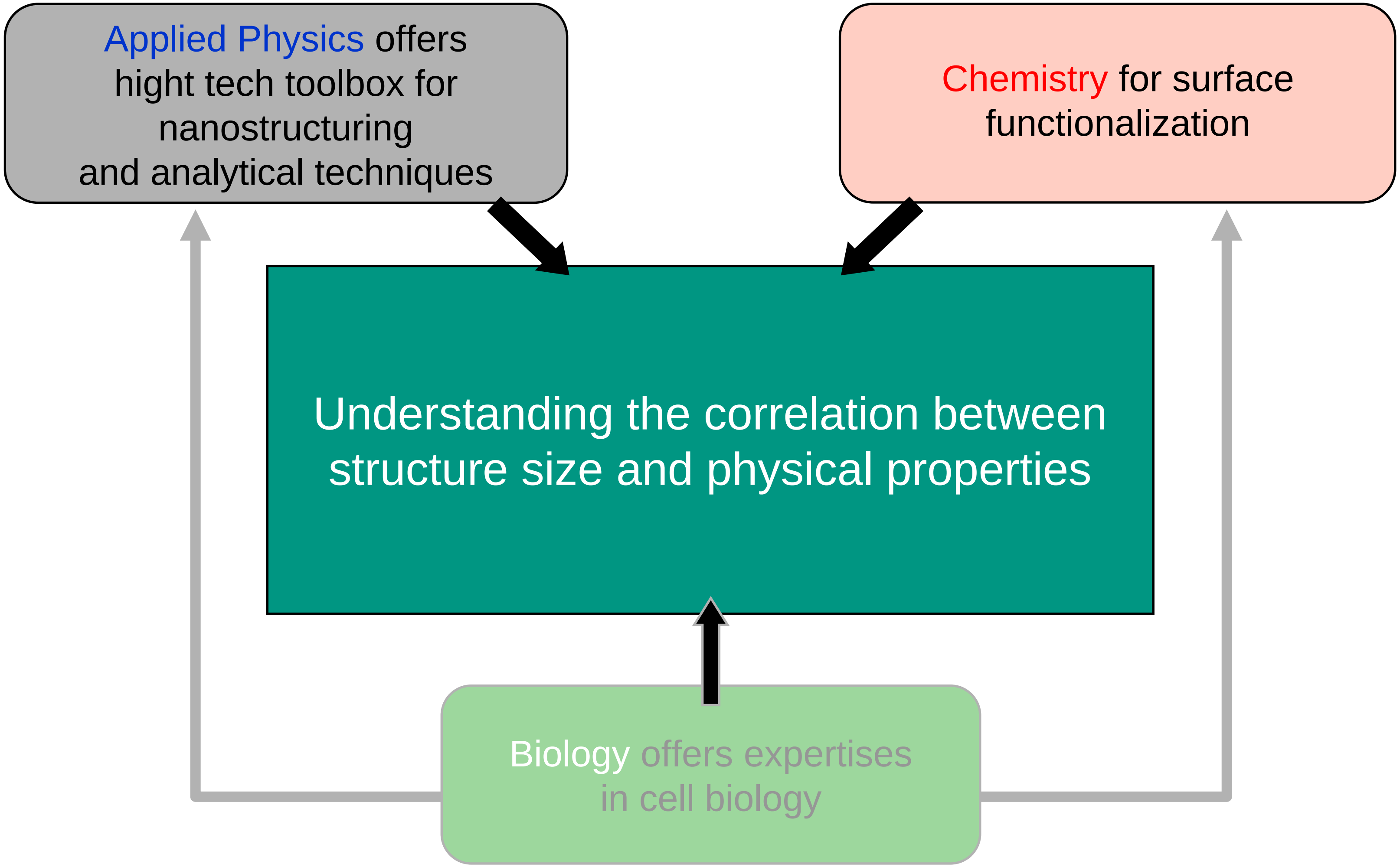


Motivation


Applied Physics offers
hight tech toolbox for
nanostructuring
and analytical techniques
Chemistry for surface
functionalization
Understanding the biology and physics of
• cell adhesion and cell migration
• cell growth and differentiation
• cell signaling
Biology offers expertises
in cell biology

Motivation



Applied Physics offers
hight tech toolbox for
nanostructuring
and analytical techniques
Chemistry for surface
functionalization
Understanding the correlation between
structure size and physical properties
Biology offers expertises
in cell biology

Motivation

Oxidic Interfaces, Metal Interfaces, Polymers		
Chemical Functionalization	**Combination**	**Structuring**
• Basis-SAMs (thiols, silanes) • Coupling reactions and adsorption on interfaces		• AFM-lithography (nm ←→ µm) • Polymer-blend mask lithographie (nm ←→ µm) • UV-lithographie (sub µm ←→ µm) • Micro contact printing (sub µm ←→ µm) • Magnet lithography (µm ←→ mm)
Chemical / Physical Surface Characterization		

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Focus:

→ **Development of a tool box to combine structuring techniques with chemical functionalization methods on different substrates**

→ **Investigation of size-functionality correlation**

Outlook

1. **Structured Surfaces for Specific Cell Adhesion**
    - Fibroblast adhesion on microstructured glass substrates
2. **Selfassembling of Biological Nanotemplates on Structured Surfaces**
    - Site selective assembling of tabacco mosaic viruses (TMV)
3. **Substrate Supported Metal Organic Frameworks (SURMOF)**
4. **Electron Transport in Graphene-based Organic Monolayers**

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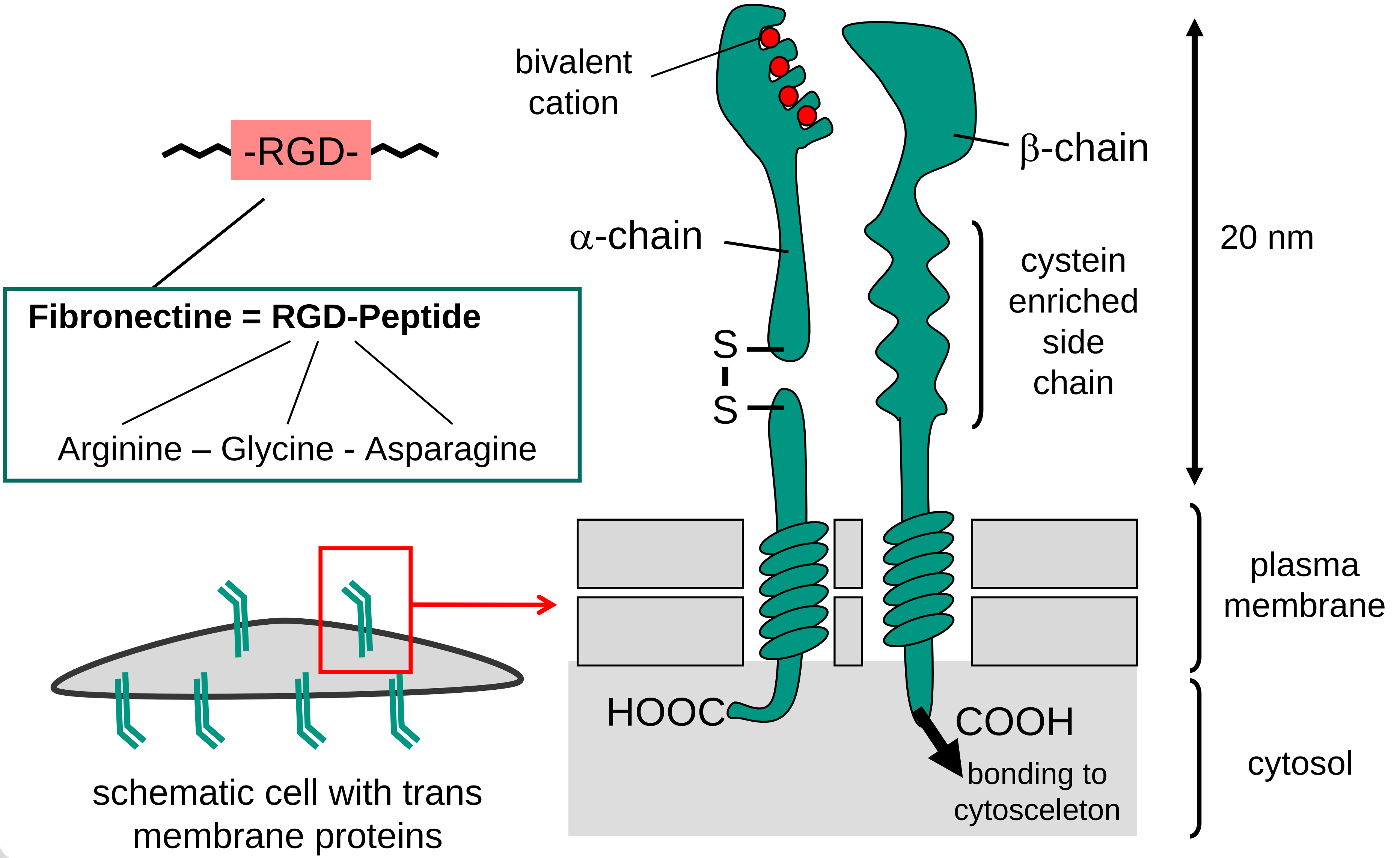
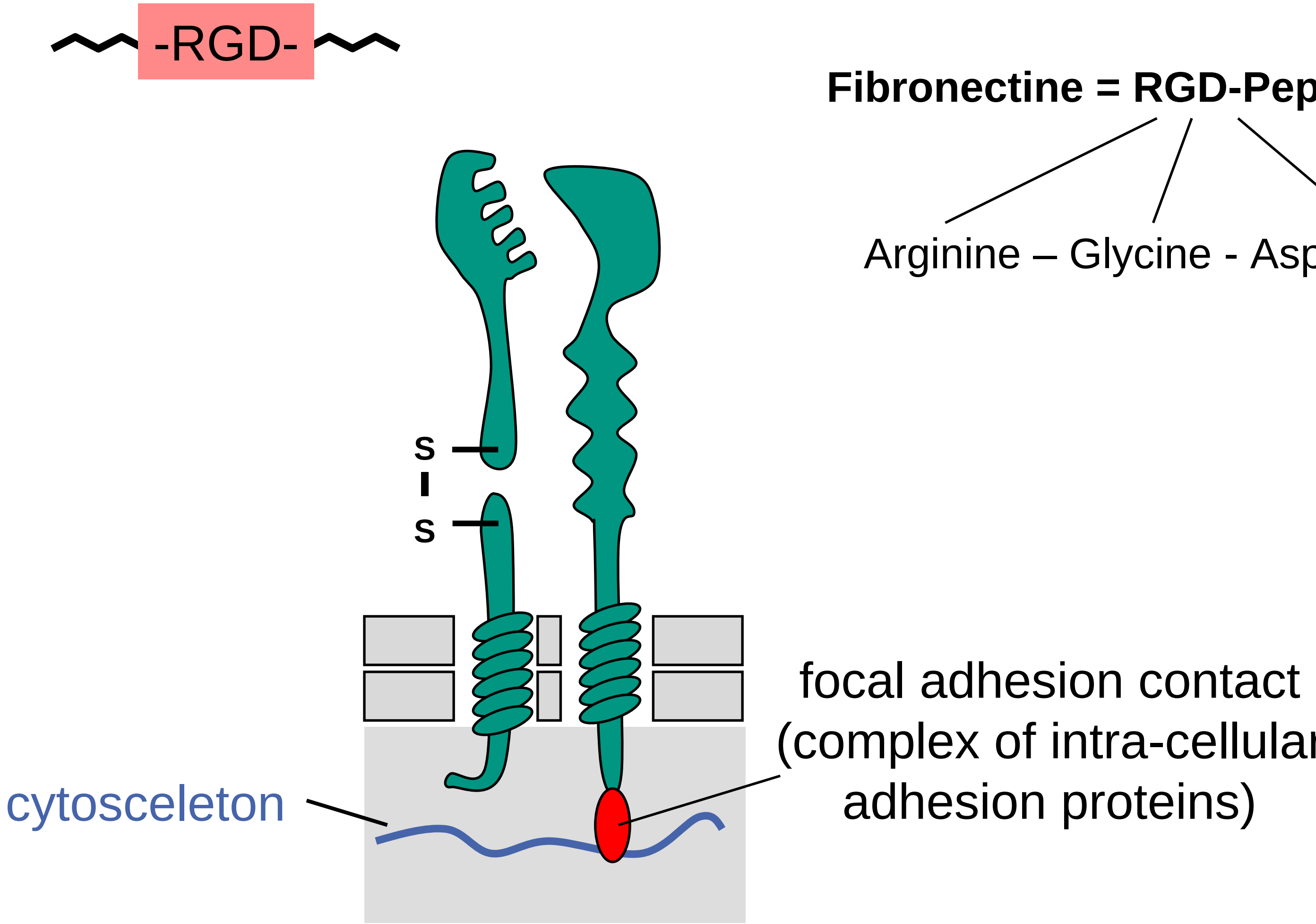
Transmembrane Protein Integrine as Fibronectin Receptor



Adhesion of Fibronectine to Integrine



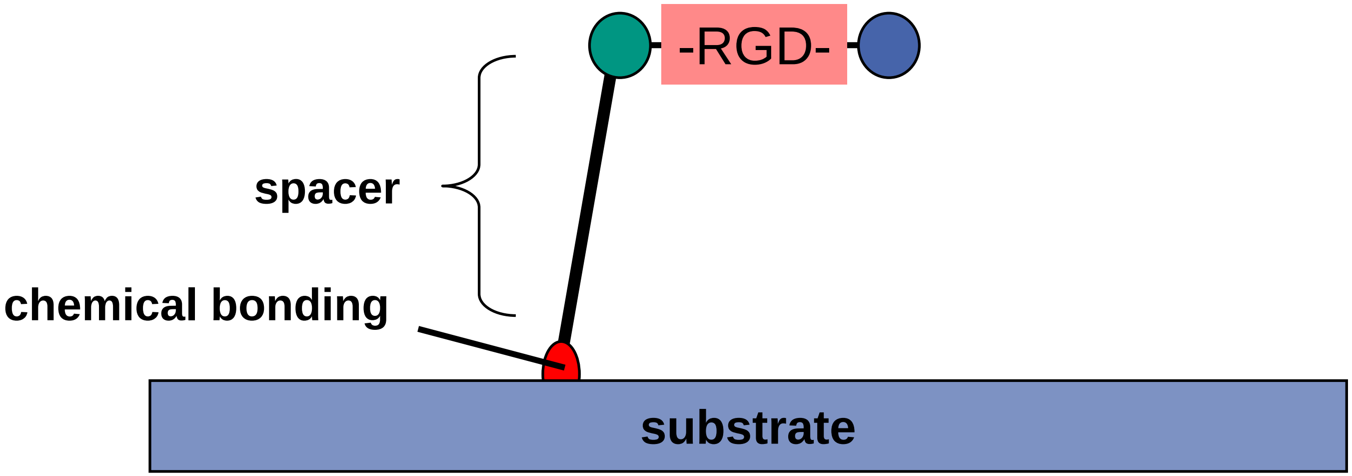
Fibronectine = RGD-Peptide

Arginine – Glycine - Asparagine

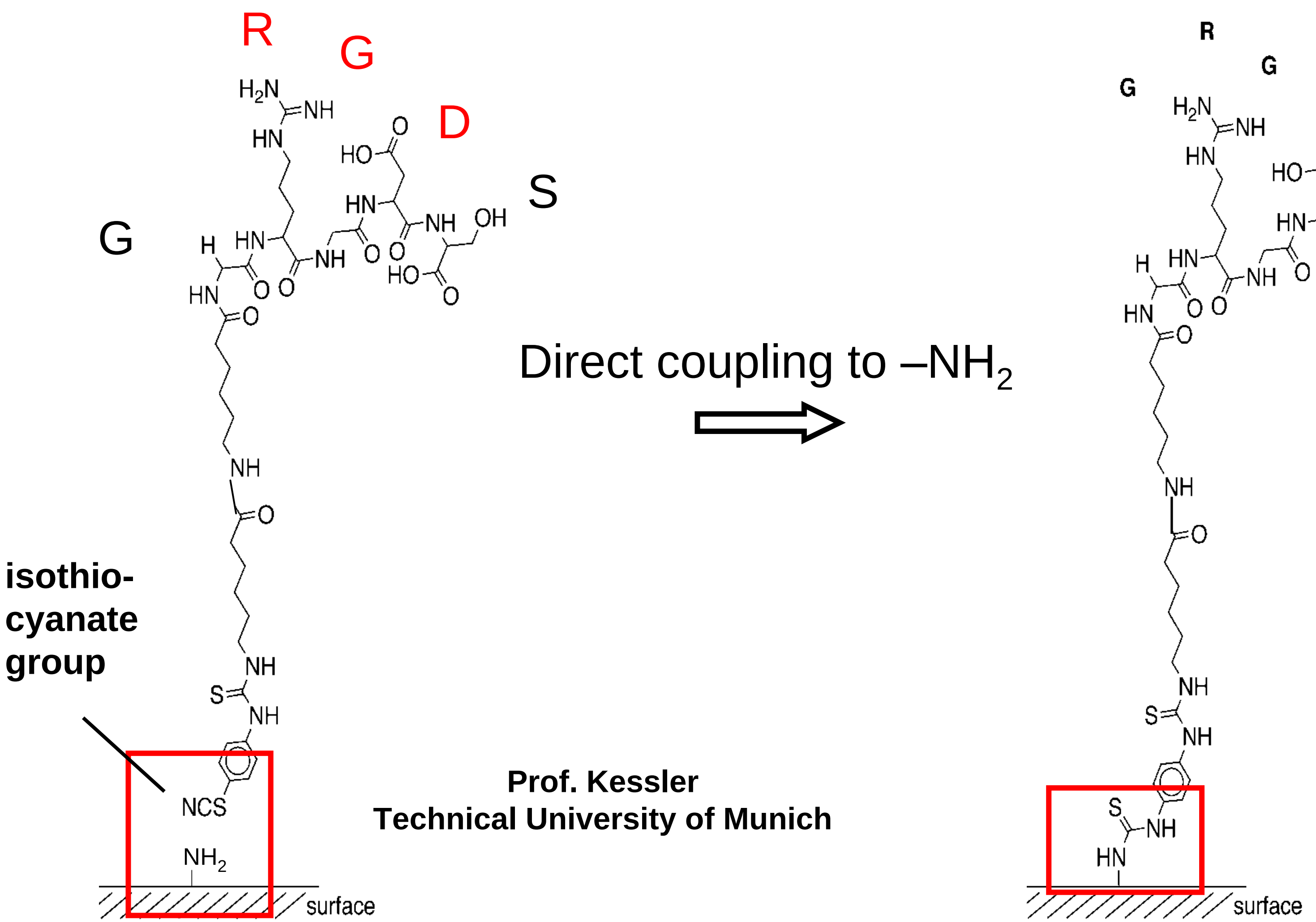
Fibroblast Adhesion on Microstructured Glass Substrates

Challenges:

- **avoid non-specific physisorption of RGD-peptide**
- **spacer between substrate and RGD-motif**
- **chemical bonding of the RGD-peptide to the substrate**

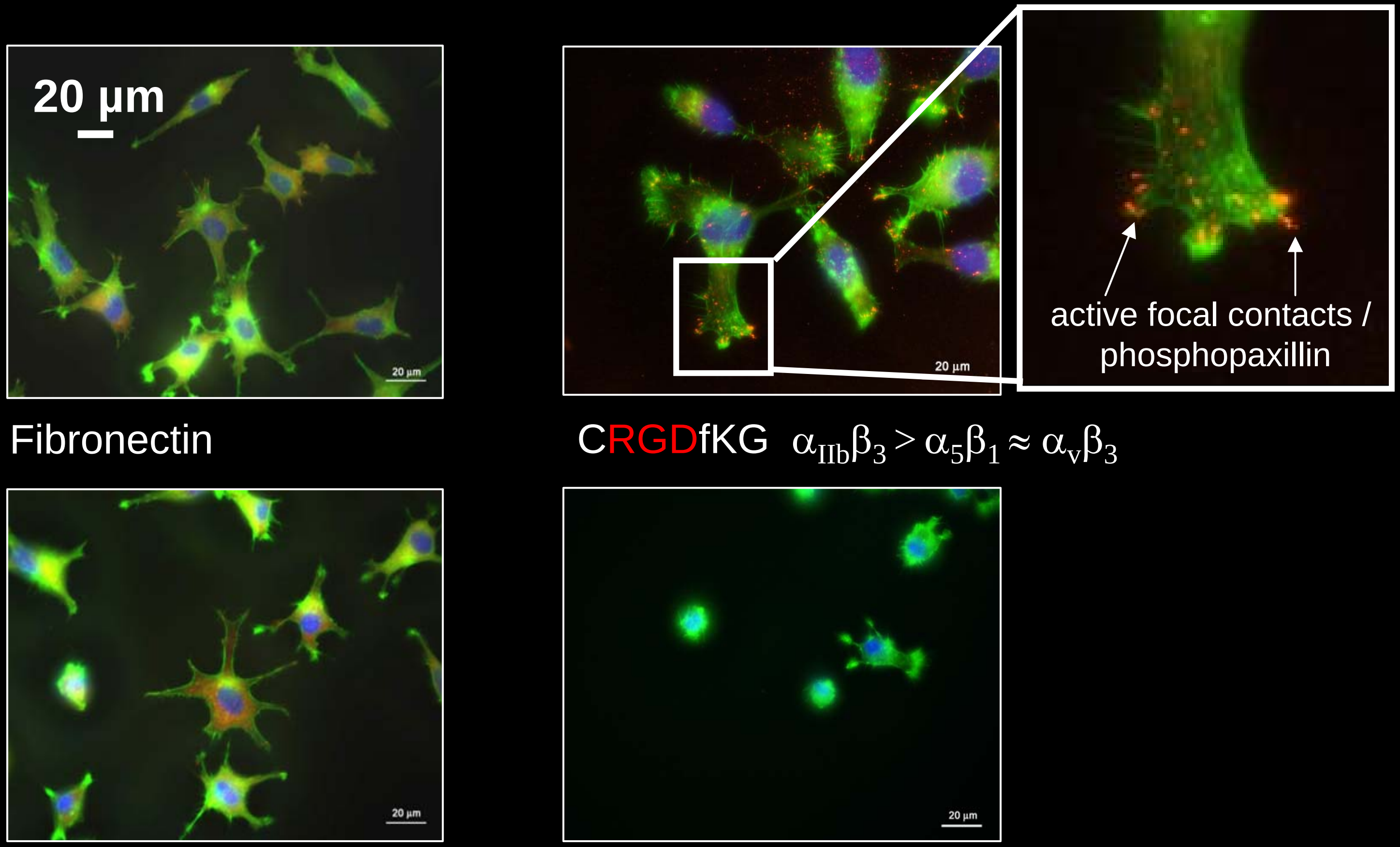


Inanimate Surfaces Functionalised with Artificial RGD-Peptides



Prof. Kessler
Technical University of Munich

Murine Fibroblasts Show Similar Spreading Behavior on RGD-Peptides as on Fibronectin



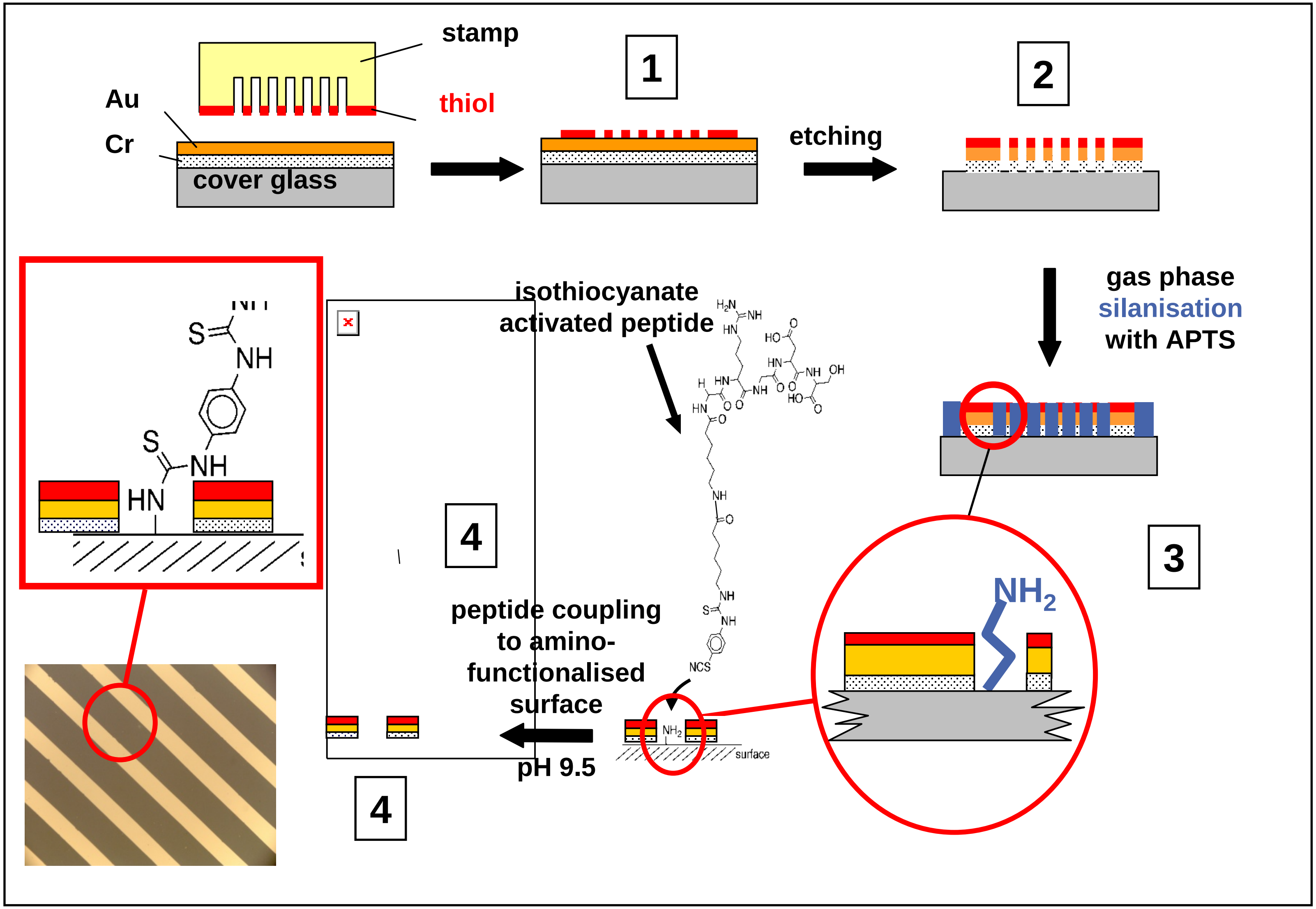
Fibronectin

CRGDfKG $\alpha_{IIb}\beta_3 > \alpha_5\beta_1 \approx \alpha_v\beta_3$

GRGDS: $\alpha_v\beta_3 \approx \alpha_5\beta_1 \approx \alpha_{IIb}\beta_3$

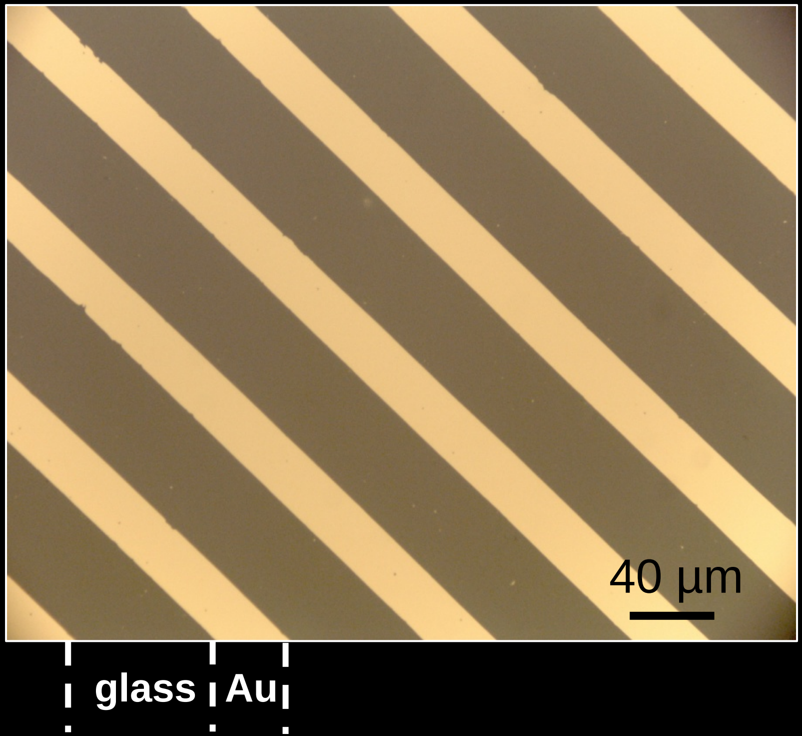
BSA as negative control

Transfer of Surface Chemistry to Microstructures by Micro Contact Printing

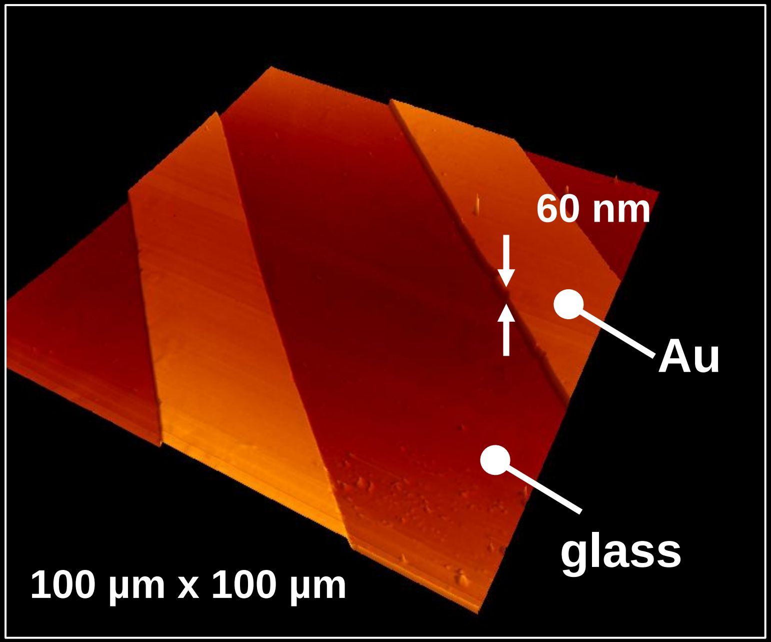


Transfer of Surface Chemistry to Microstructures by Micro Contact Printing

Light microscopy image



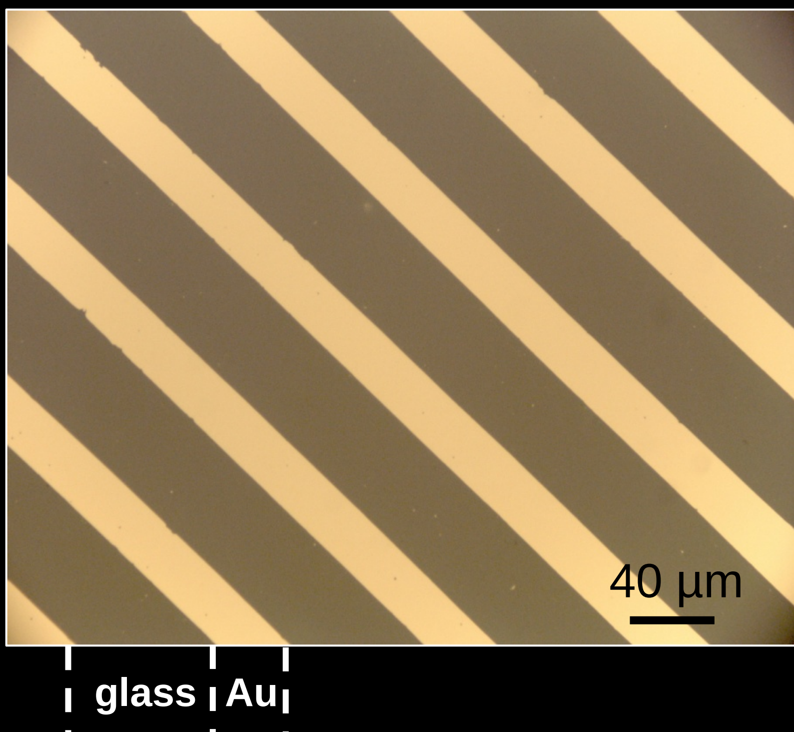
AFM topography image



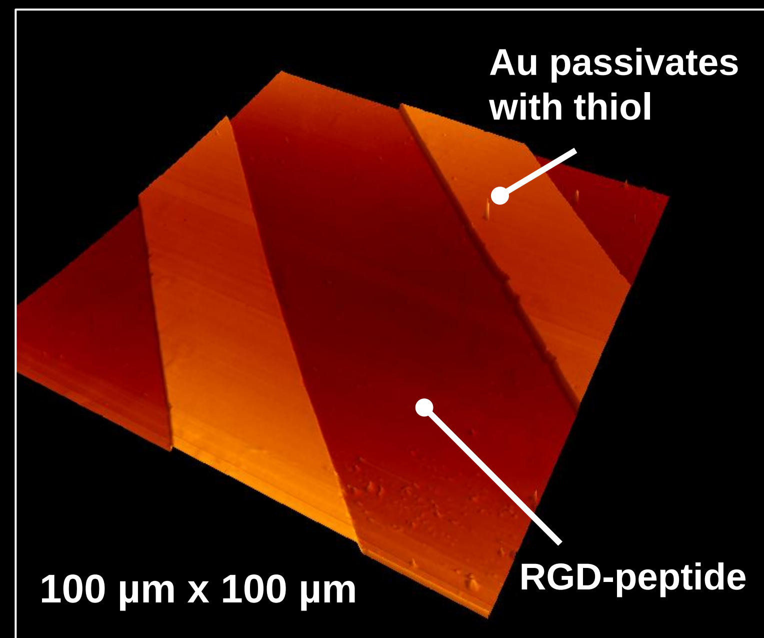
A. Petershans, A. Lyapin, S. Reichlmaier, S. Kalinina, D. Wedlich, H. Gliemann, *J. Coll. Interf. Sci.* **341**, 30 (2010)

Transfer of Surface Chemistry to Microstructures by Micro Contact Printing

Light microscopy image

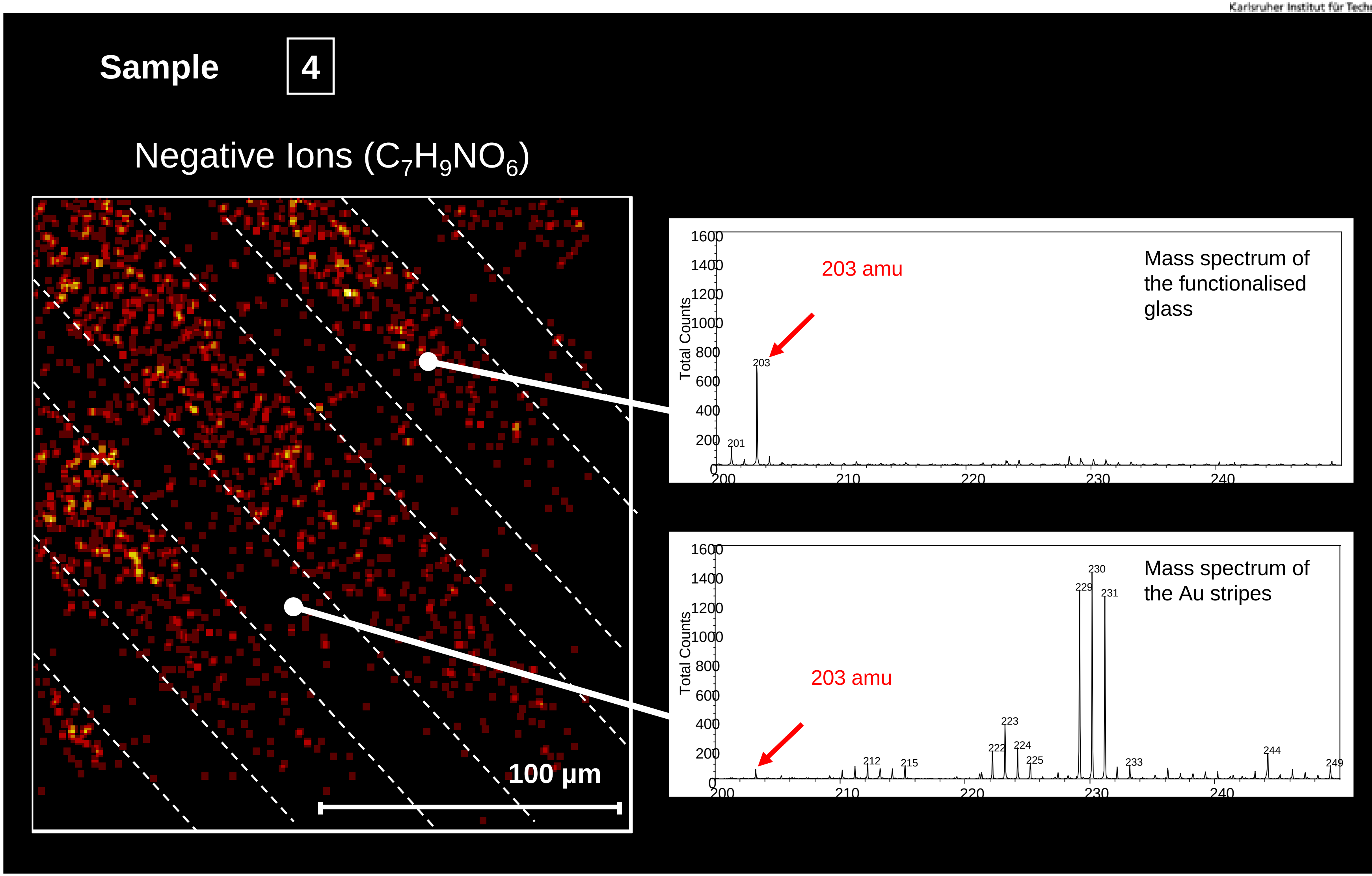


AFM topography image



A. Petershans, A. Lyapin, S. Reichlmaier, S. Kalinina, D. Wedlich, H. Gliemann, *J. Coll. Interf. Sci.* **341**, 30 (2010)

TOF-SIMS Images of GRGDS-Peptide Coupling



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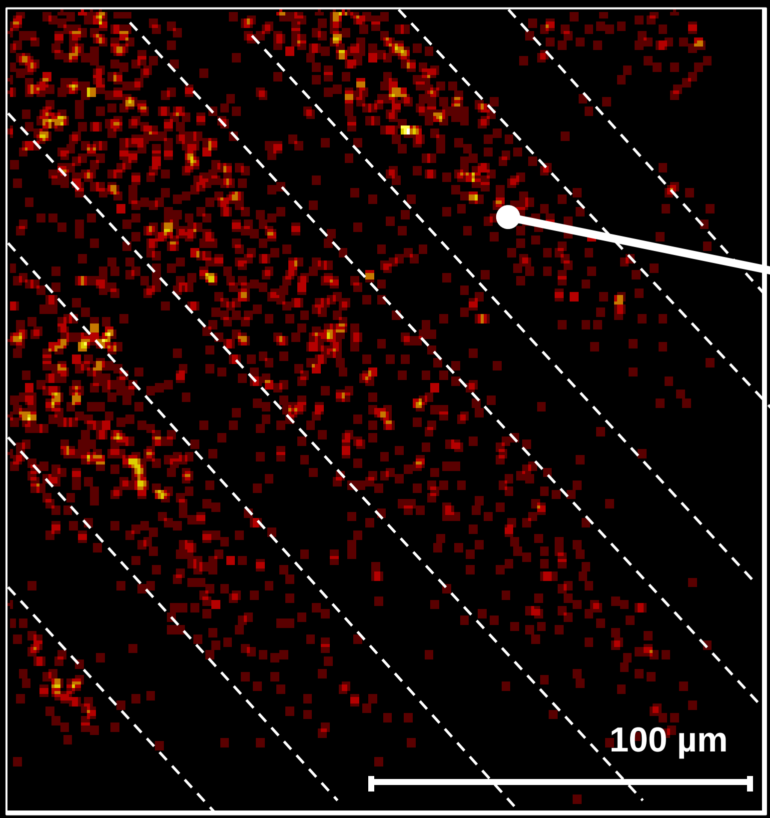
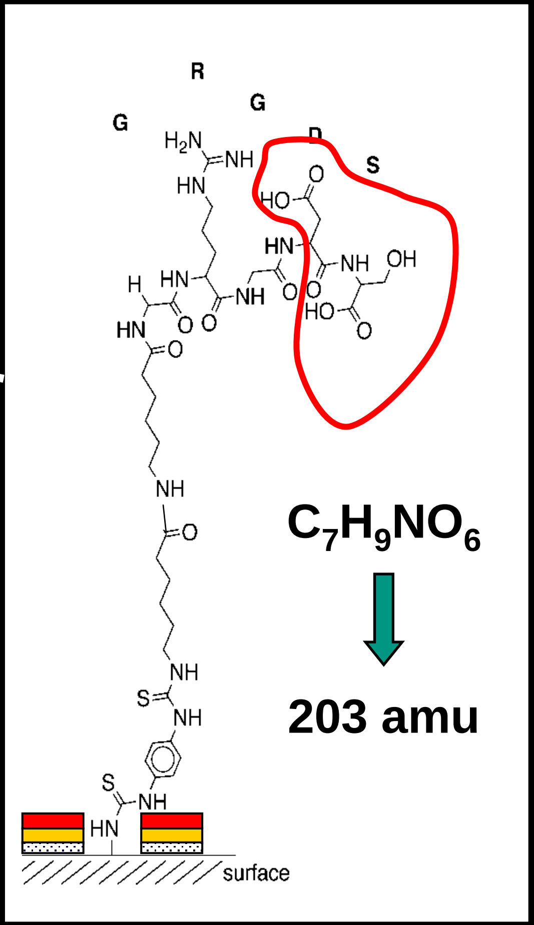
TOF-SIMS Images of GRGDS-Peptide Coupling

Sample 4

Negative Ions ($C_7H_9NO_6$)

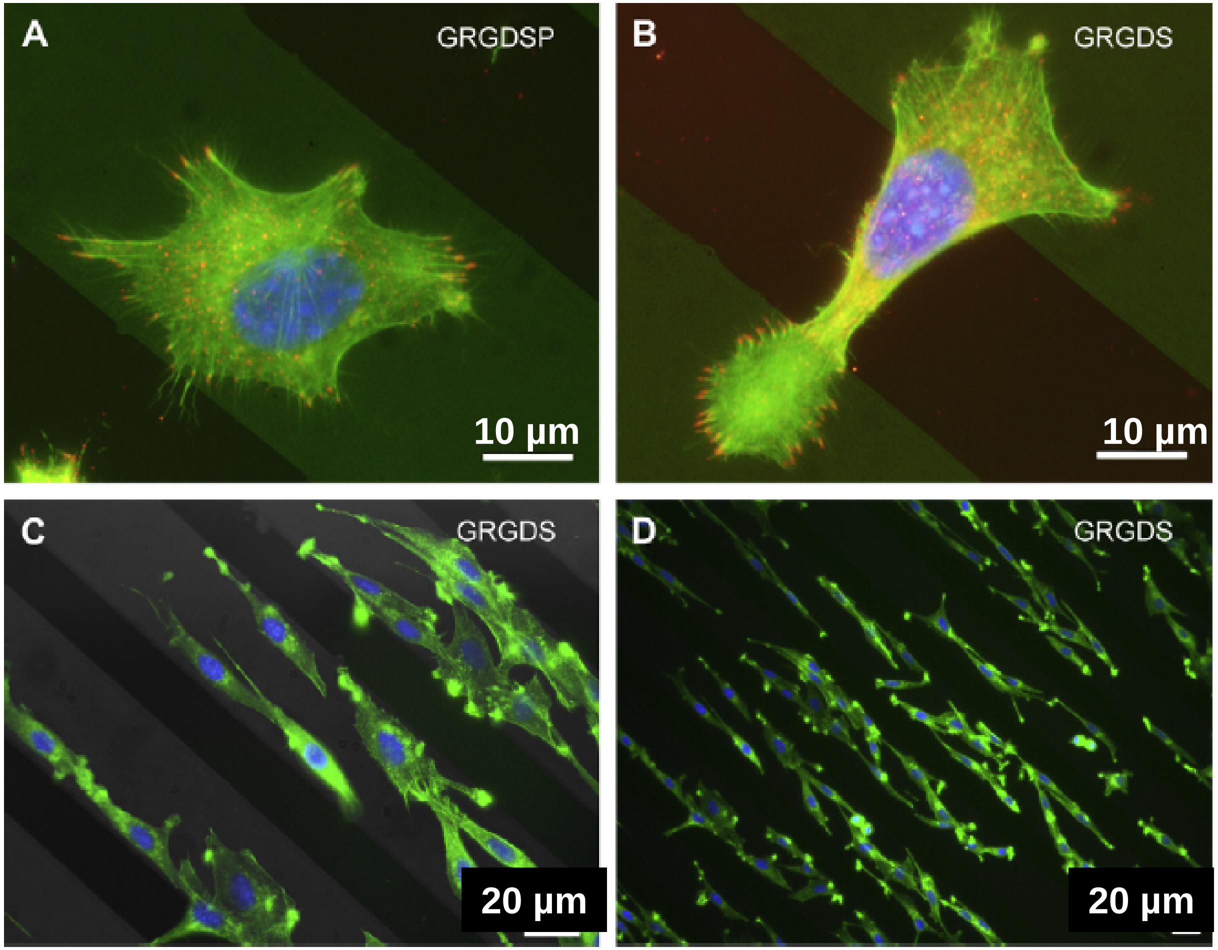




A. Petershans, A. Lyapin, S. Reichlmaier, S. Kalinina, D. Wedlich, H. Gliemann, *J. Coll. Interf. Sci.* **341**, 30 (2010)

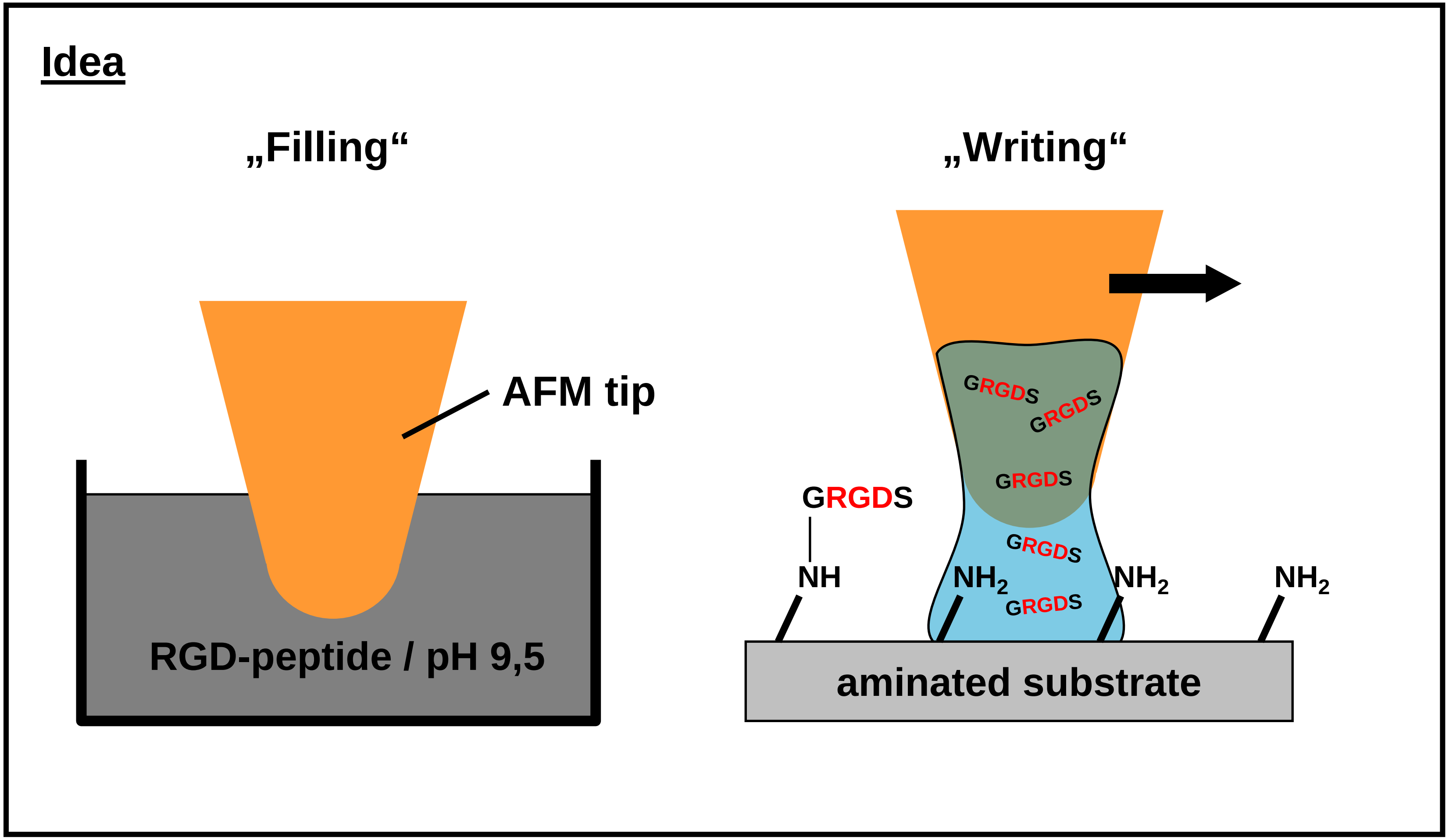
Cell Adhesion on GRGDS-Peptide Functionalised Microstructures

Confocal laser scanning microscope images of fibroplasts on RGD-peptide functionalized surface structures



S. Kalinina, H. Gliemann, M.Lopez-Garcia, A. Petershans, J. Auernheimer, Th. Schimmel, M. Bruns, A. Schambony, H. Kessler, D. Wedlich, *Biomaterials* **29**, 3004 (2008)

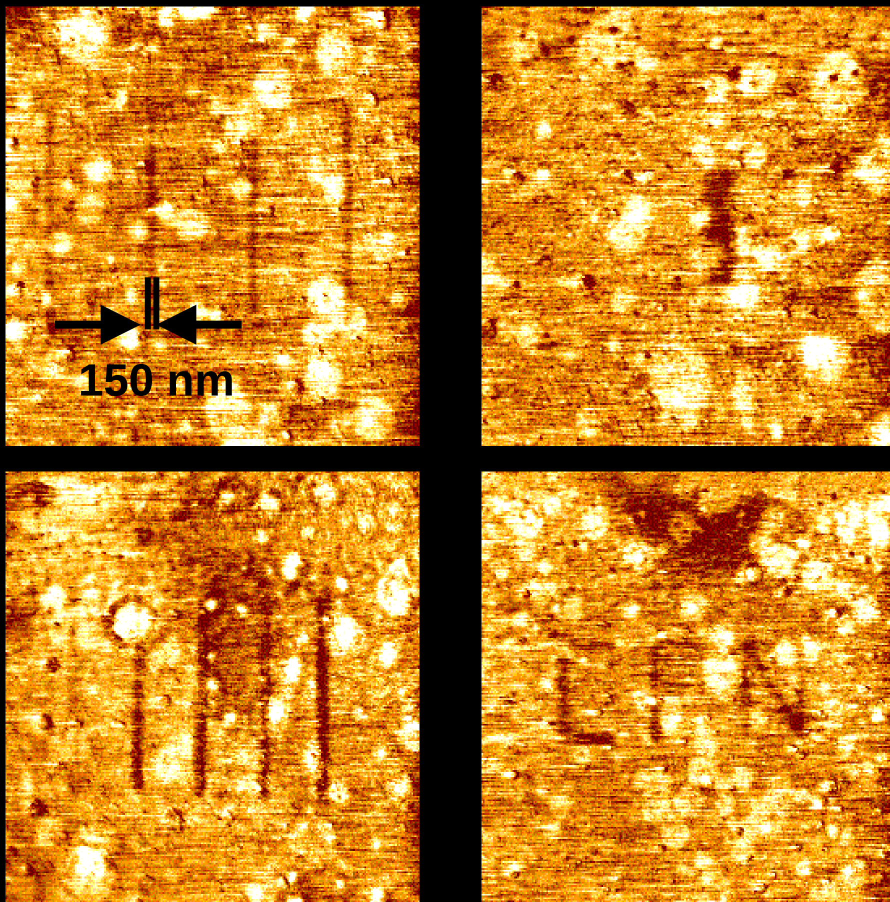
Transfer of Surface Chemistry to the Nanoscale: Dip-pen Lithography



Transfer of Surface Chemistry to the Nanoscale: Dip-pen Lithography

First result

5 µm x 5 µm   5 µm x 5 µm

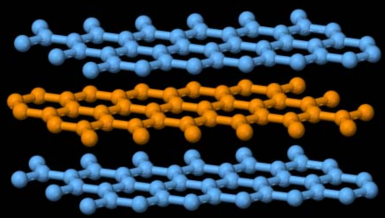
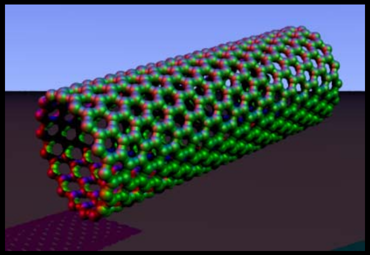
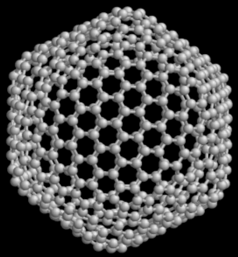
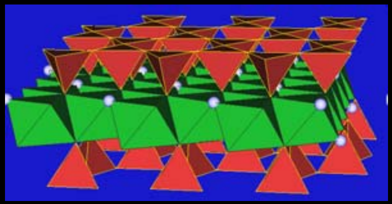
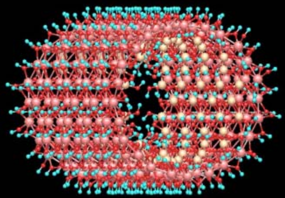
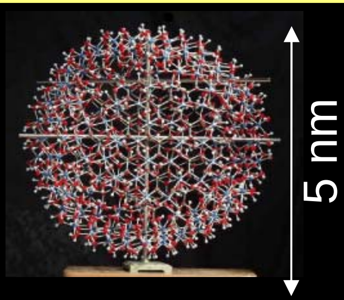


6.7 µm x 6.7 µm   9.13 µm x 9.13 µm

AFM friction contrast images of isothiocyanate-terminated RGD-peptide coupled to aminated surface by dip-pen lithography

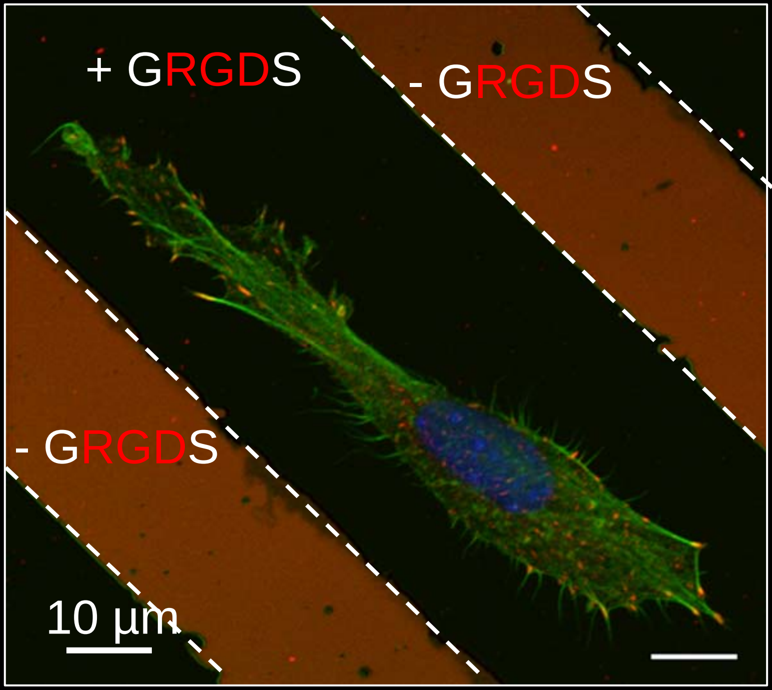
S. Lenhert (INT), Th. Schimmel (INT), H. Gliemann

Transfer of Surface Chemistry to the Nanoscale: Immobilized Oxidic Nanoparticles as Reactive Sites

	Layered System	Tubular System	Particulate System
Carbon	 HOPG	 Carbon Nanotubes	 Fullerene
Silicates	 Layer Silicate	 Imogolite	 Allophane

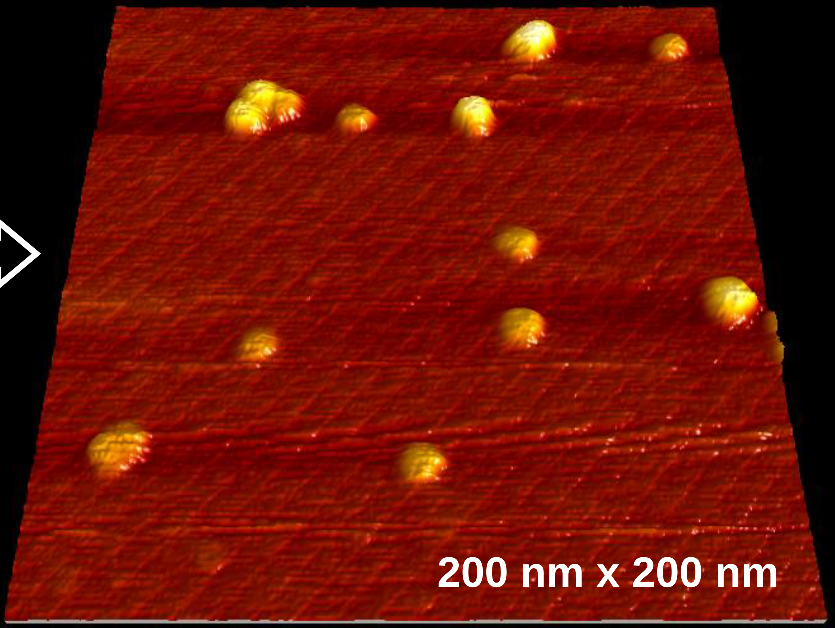
Transfer of Surface Chemistry to the Nanoscale: Immobilized Oxidic Nanoparticles as Reactive Sites

Established chemistry on µm-scale



S. Kalinina, H. Gliemann, M. López-García, A. Petershans, J. Auernheimer, Th. Schimmel, M. Bruns, A. Schambony, H. Kessler, D. Wedlich, *Biomaterials* 29 (2008) 3004

Transfer to nm-scale



AFM image (topography) of allophanes on mica

S. Kaufhold, A. Kaufhold, R. Jahn, S. Brito, R. Dohrmann, R. Hoffmann, H. Gliemann, P.-G. Weidler, M. Frechen, *Clays and Clay Min*erals 57 (2009) 72-81

Transfer of Surface Chemistry to the Nanoscale: Immobilized Oxidic Nanoparticles as Reactive Sites

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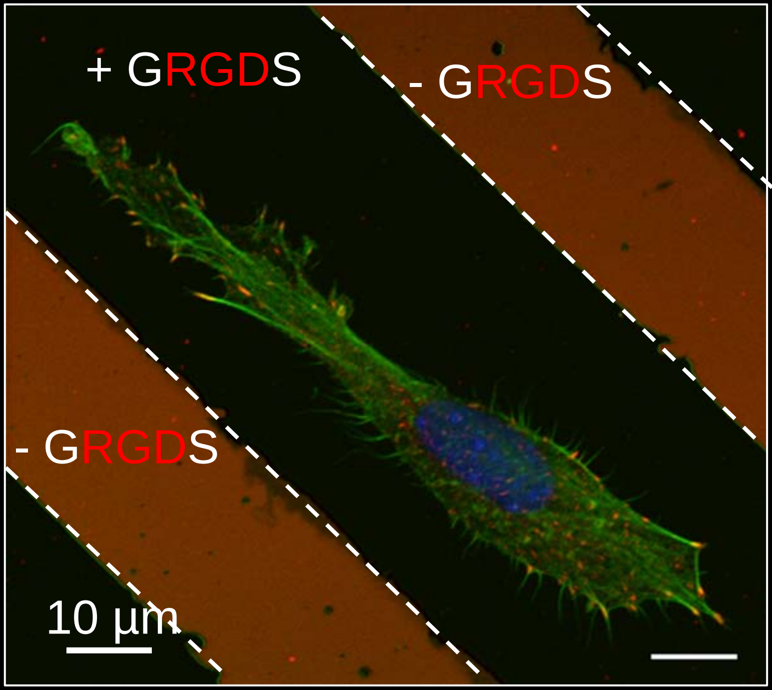

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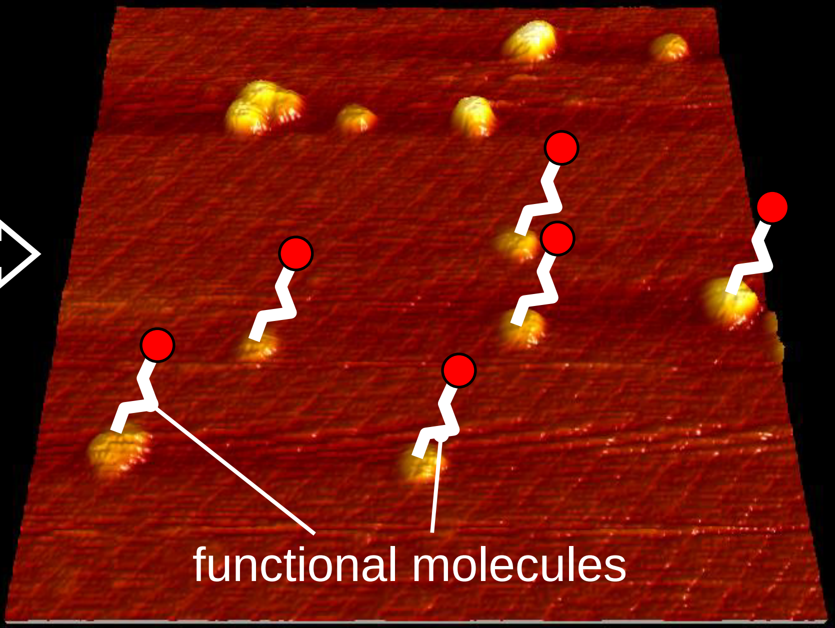

Challange:
Equidistant immobilization of nanoparticles for surface functionalization and patterning

Marco Fuchs

Acknowledgements and Cooperation

A. Petershans / Prof. Bräse
Dr. S. Montero-Pancera

A. Lyapin
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KIT

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— Institute of Organic Chemistry
TU of Munich

V. Trouillet
M. Bruns
— Institute of Material Science III
KIT

Prof. Th. Schimmel
B. Riedel
— Institute of Nanotechnology
KIT

CFN (DFG)
Prof. Bastmeyer

DAAD

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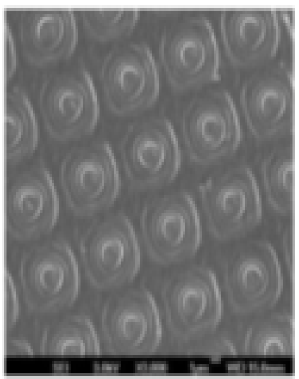
Viruses as Functional, Self-Assembling Building Blocks on the Nanometer Scale

KIT
Karlsruher Institut für Technologie

http://www.elektroniknet.de/home/stromversorgung/stromversorgung-news/n/d/strom-aus-der-virusbatterie/

Strom aus der Virusbatterie

Eine Forschergruppe des MIT hat eine Mikrobatterie entwickelt, die nur halb so groß ist, wie eine menschliche Zelle und teilweise aus Viren aufgebaut wird.



Schluss mit 9-Volt-Batterien und Knopfzellen: Nach Meinung der Wissenschaftler aus dem Team um die beiden Professorinnen Paula Hammond und Angela Belcher vom Massachusetts Institute of Technology sind aus organischen Materialien aufgebaute Mikrobatterien die Energiequelle der Zukunft. Sie sollen einmal vor allem elektronische Mikrosysteme wie z.B. Labs-on-Chip oder implantierbare medizinische Sensoren mit Strom versorgen.

Zur Herstellung der Komponenten der Mikrobatterie setzen die Forscher ein Mikro-Kontakt-Stempel-Verfahren ein. Bei diesem Prozess werden molekulare Strukturen über einen Kunststoff-Stempel auf eine Oberfläche aufgedrückt. »Wir sind die ersten, die diese Methode zur Herstellung von Mikrobatterien einsetzen und auch die ersten, die Viren benutzen, um eine solche Batterie zu bauen«, erklären die beiden MIT-Professorinnen in ihrem gerade publizierten Fachartikel.

Viruses as Functional, Self-Assembling Building Blocks on the Nanometer Scale

Karlsruher Institut für Technologie

Hartmut Gliemann[1], Andre Petershans[1], Stefan Walheim[2], Thomas Schimmel[2], Alexander Bittner[3], Michael Börsch[4], Joachim Spatz[5], Anan Kadri[6], Anna Müller[6], Fania Geiger[5/6], Holger Jeske[6], Christina Wege[6]

[1]: Institut für Funktionelle Grenzflächen (IFG), Forschungszentrum Karlsruhe (FZK); [2]: Institut für Angewandte Physik und Centrum für Funktionelle Nanostrukturen (CFN), Universität Kalrsruhe; und Institut für Nanotechnologie (INT), FZK; [3]: CIC NanoGUNE, San Sebastian, Spain; [4]: Univ. Stuttgart, 3. Physikalisches Institut; [5]: MPI für Metallforschung, Stuttgart; [6]: Universität Stuttgart, Biologisches Institut.

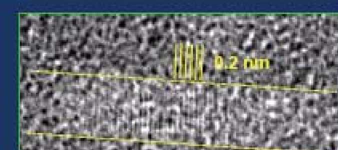
Karlsruhe Institute of Technology

CIC nanoGUNE

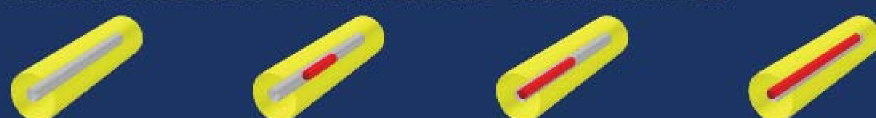
TP A6 des Kompetenznetzes "Funktionelle Nanostrukturen" der Landesstiftung Baden-Württemberg

Künstliche Metalldrähte in natürlichen Viren

Metallische Nanodrähte mit Durchmessern von 3 nm werden in einer einfachen nasschemischen Reaktion im zylinderförmigen Innenkanal des Tabakmosaikvirus erzeugt. Der kleine Durchmesser von nur etwa 10 Atomen erschließt die Quantenwelt.



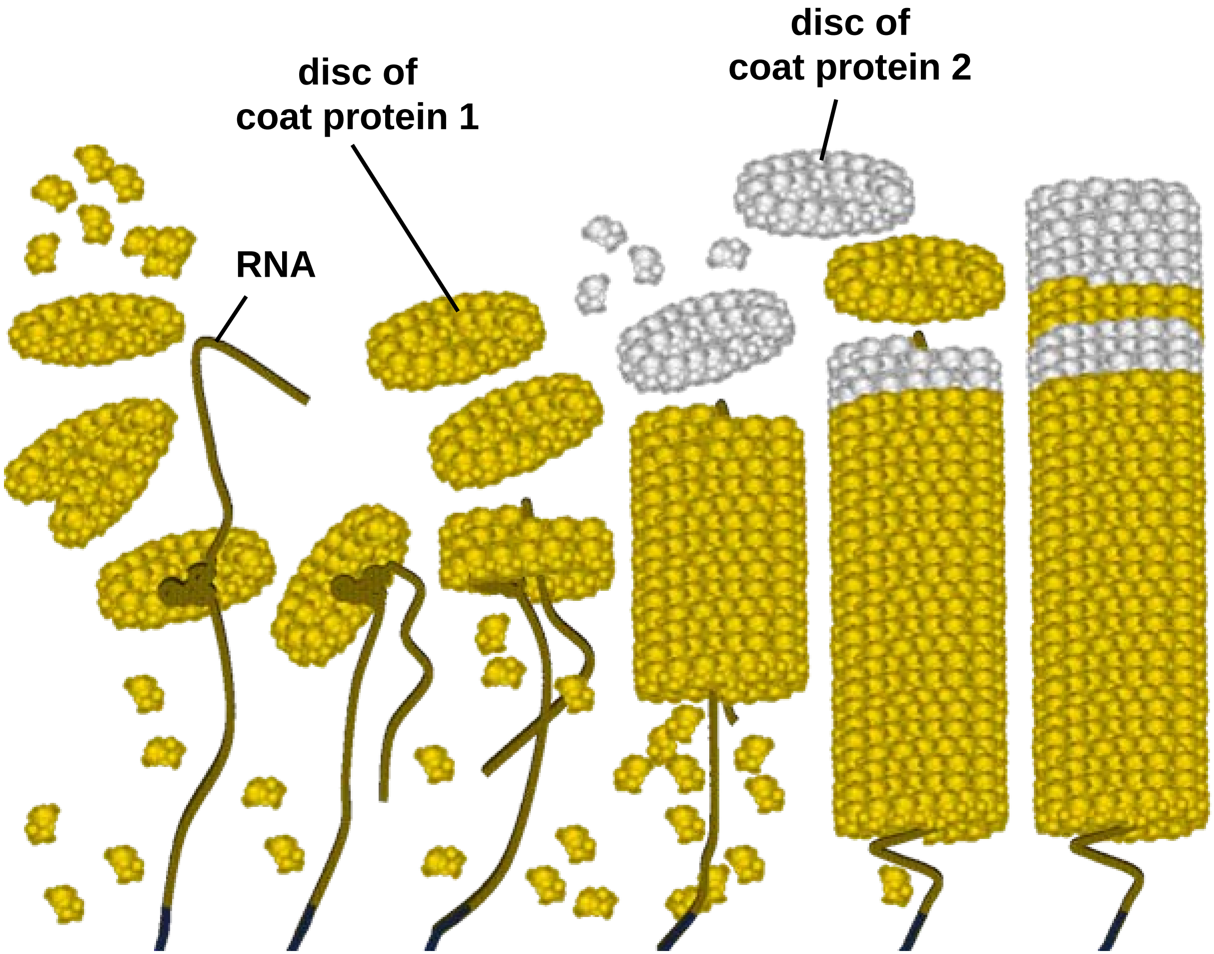
Atomares Gitter des Metalls im Virus



Stromlose Abscheidung von Kobalt (rot) im Palladium-belegten Innen-kanal (grau) des Virus (gelb):

$$3\,Co^{2+} + 2\,BH_3 + 6\,OH^- \rightarrow 2\,H_3BO_3 + 3\,H_2 + 3\,Co$$

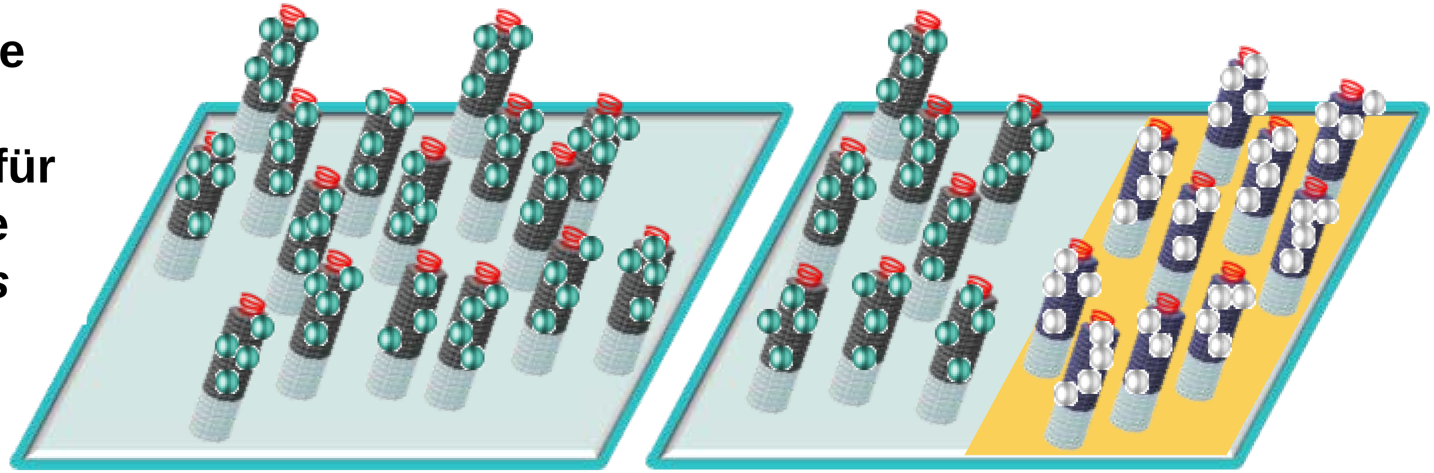
Assembly Mechanism of Tabacco Mosaic Viruses

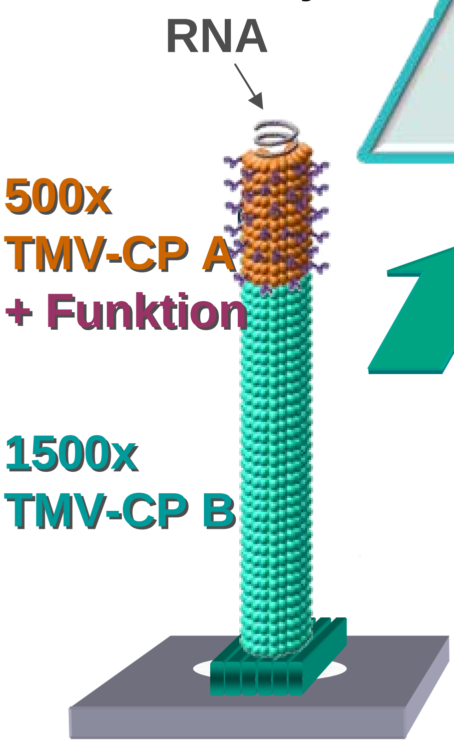


Bioaktive *Nanosticks*: Tabakmosaikvirus-(TMV-)-Derivate

Karlsruher Institut für Technologie

TMV-basierte Nano-Trägersticks für verbesserte *Microarrays*

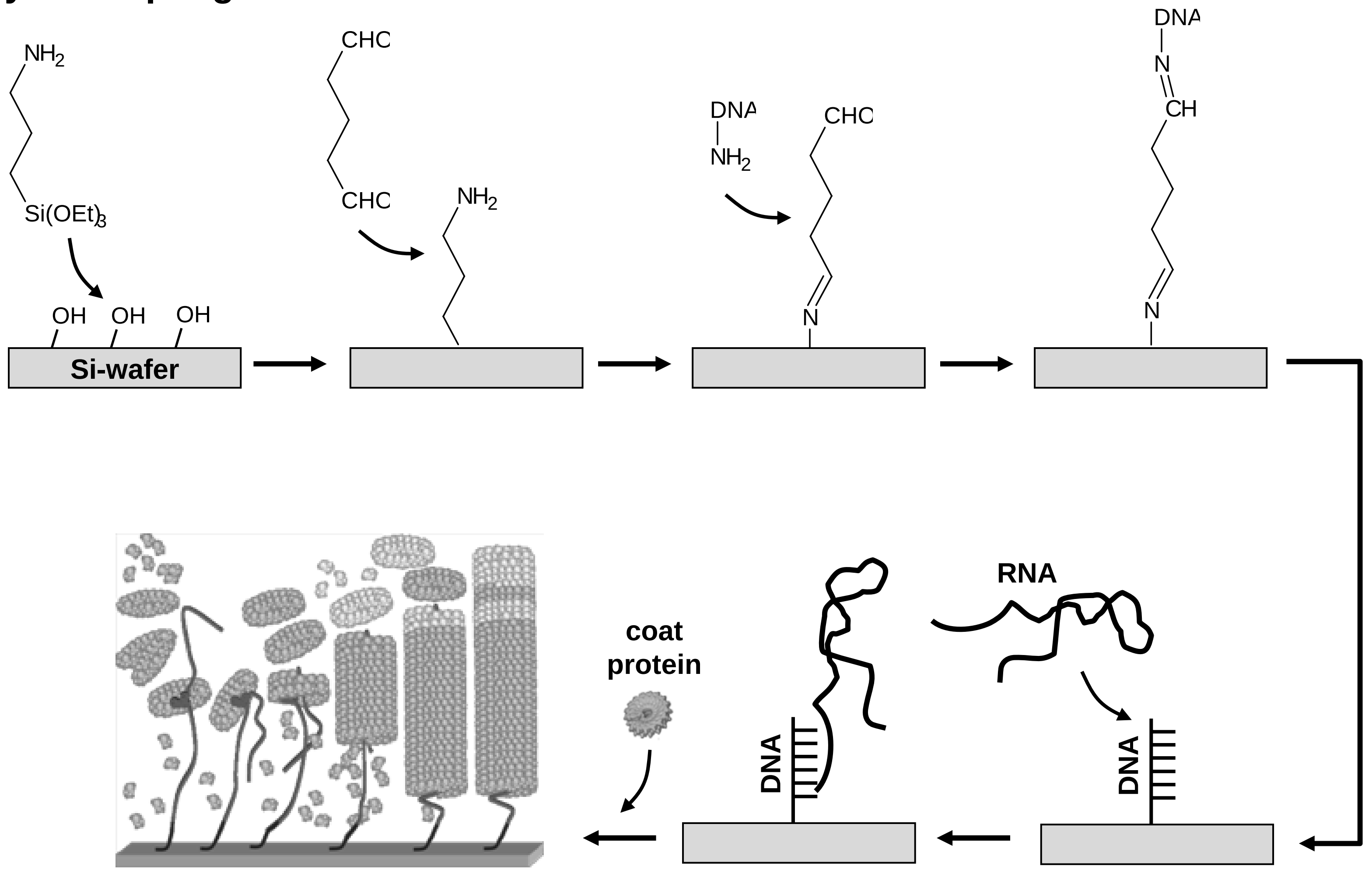




- **Kontrolliert selbst-assemblierende** TMV-Coatprotein-Typen:
  genetisch modifizierte Varianten → funktionale Enden
- **Synthetische Gerüst-RNA für *Sticks* und Bäumchen:**
  einfache und komplexe Architekturen → Länge und Form
- Wachstum auf **chemisch definierten Oberflächenarealen:**
  ortsselektive RNA-Bindung → lokale Assemblierung
- **Mikro-/ nanostrukturierte Substrate** für geordnete Muster:
  → kombinatorische Arrays, Integration in Technik-Umgebung
- ***" Finishing":*** → aufrechte, bioaktive Nanogerüste:
  metallorganische Stützschichten, Aktivierung der Funktion

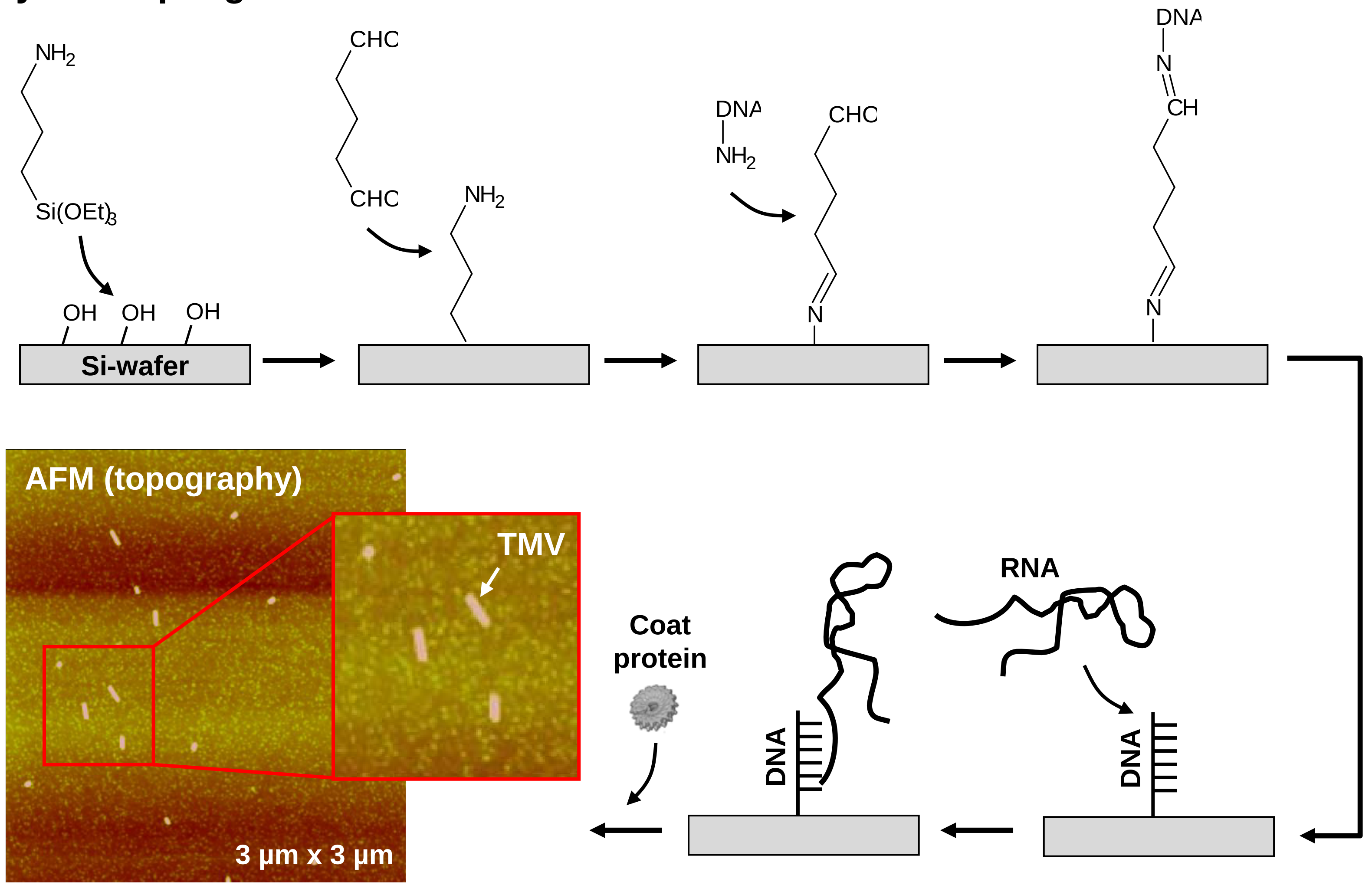
RNA Coupling and TMV Assembly

Aldehyde coupling



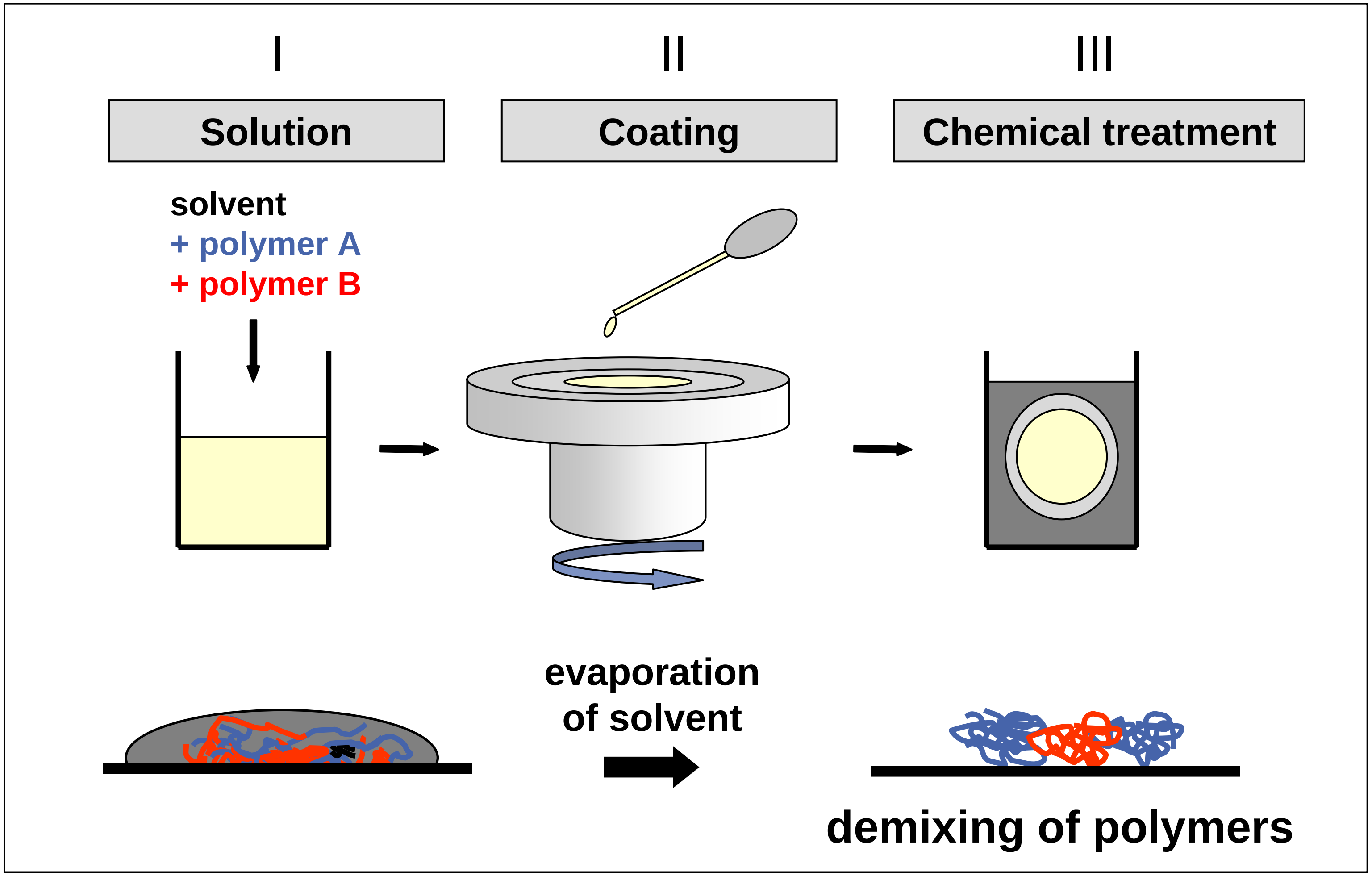
RNA Coupling and TMV Assembly

Aldehyde-coupling

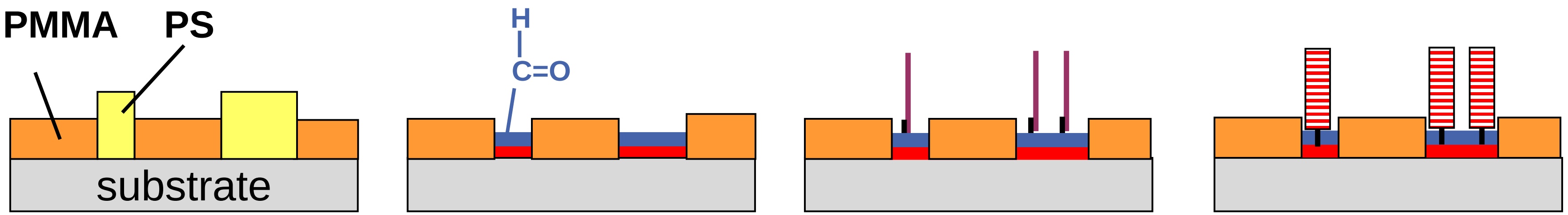


Site Selective RNA Coupling and TMV Assembly

Surface structures by polymer blend lithography



Site Selective RNA Coupling and TMV Assembly

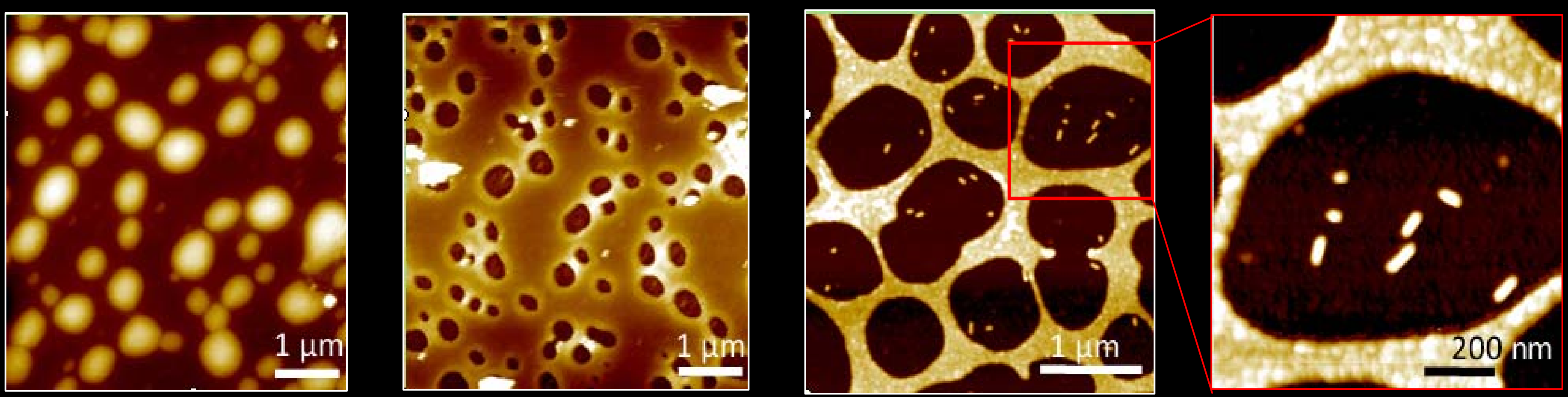


polmer blend formation

- selective resolving of one polymer
- functionalization with amine/ aldehyd

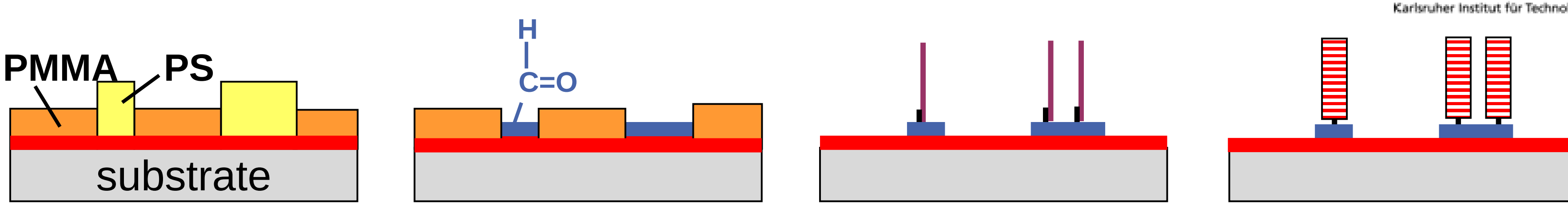
- coupling of linker-DNA
- coupling of virus-RNA

self assembly of TMV



AFM topography images of different states of self assembly of TMV on surface structures

Site Selective RNA Coupling and TMV Assembly



polymer blend on **aminated** substrate

- selective solving of one polymer
- functionalization with **aldehyd**
- removement of second polymer

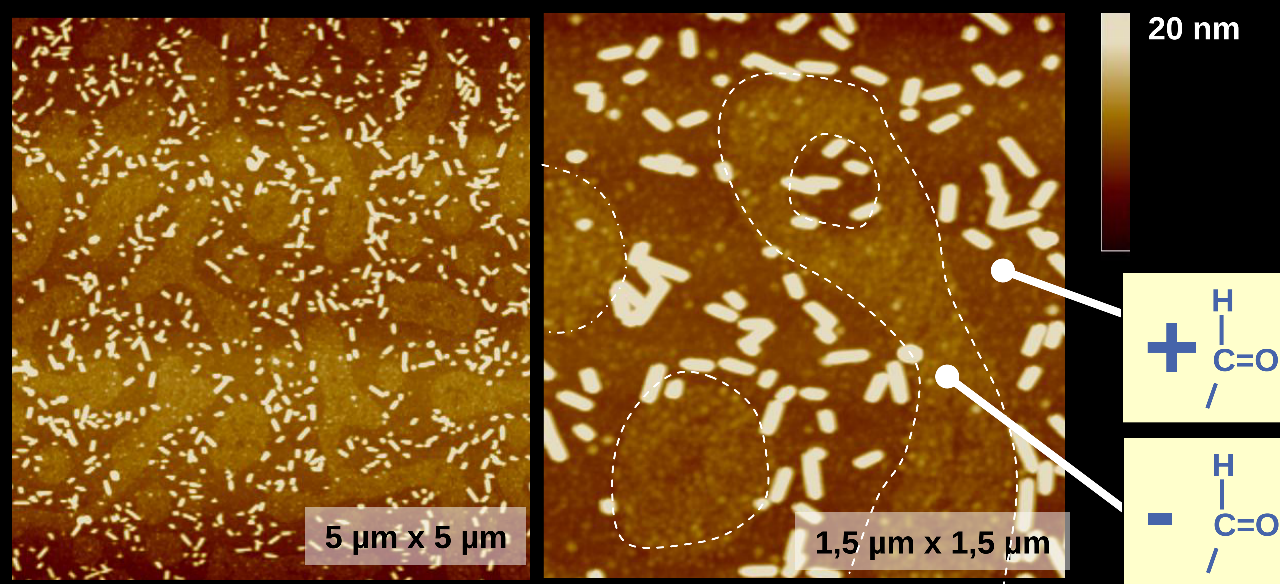
- coupling of linker-DNA
- coupling of **virus-RNA**

self assembly of TMV

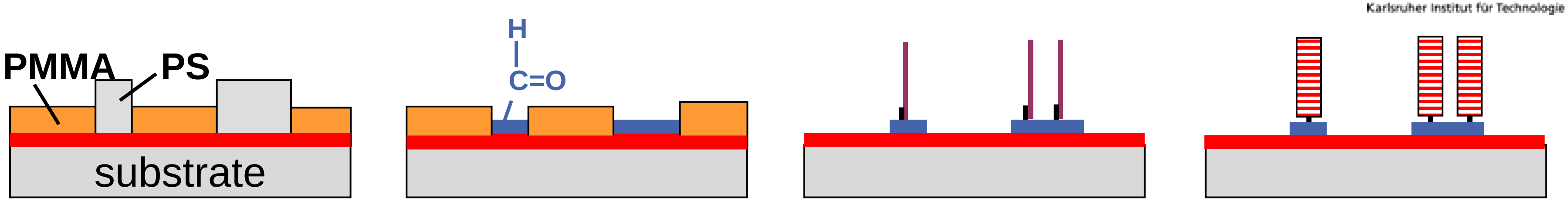
AFM-topography images of TMVs after site selective self assembly

⇩

high surface density



Site Selective RNA Coupling and TMV Assembly



polymer blend on aminated substrate

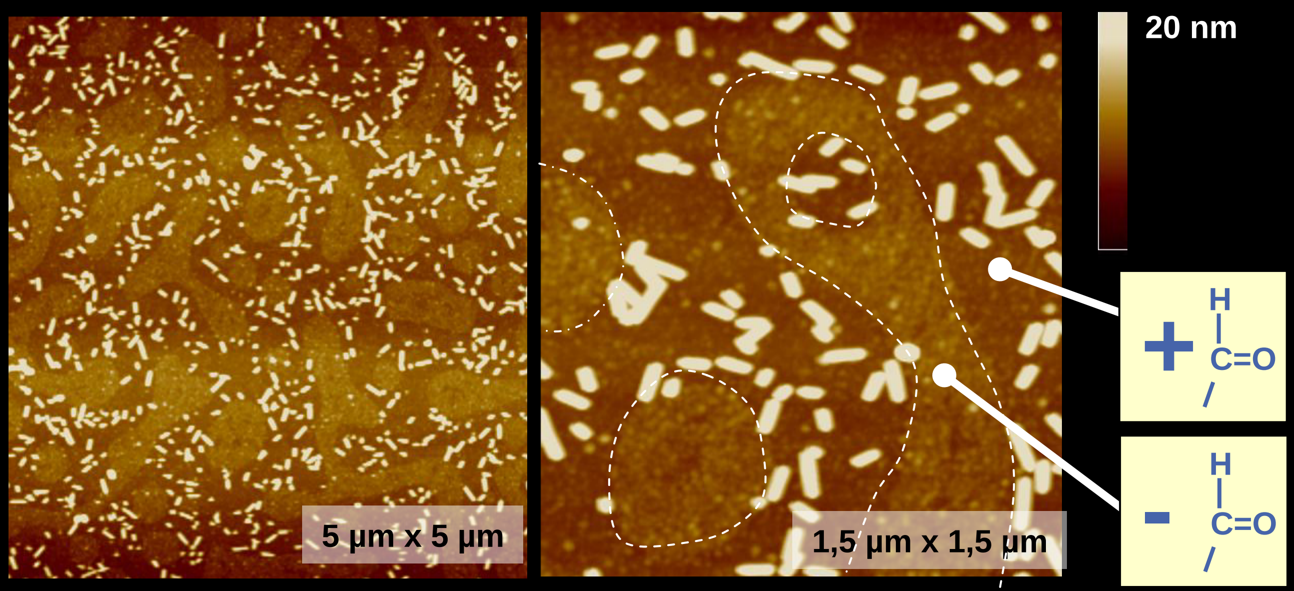
- selective solving of one polymer
- functionalization with aldehyd
- removement of second polymer

- coupling of linker-DNA
- coupling of virus-RNA

self assembly of TMV

Challanges:

- upright standing TMV
- nanostructured substrates



Acknowledgements and Cooperation

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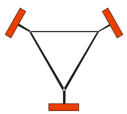
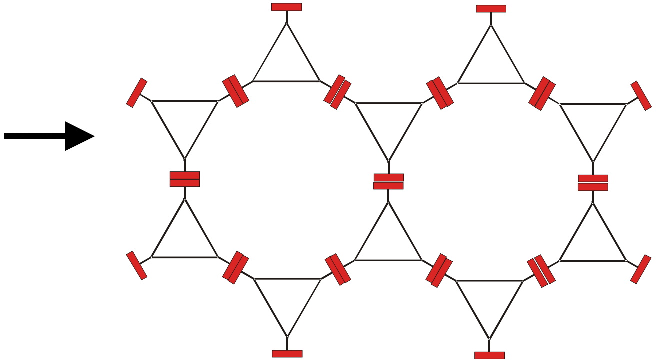
- Baden-Württemberg Stiftung
- DFG
- CFN

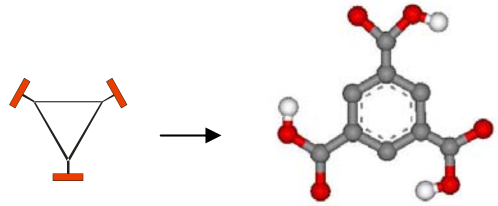
1. **Structured Surfaces for Specific Cell Adhesion**
   - Fibroblast adhesion on microstructured glass substrates
2. **Selfassembling of Biological Nanotemplates on Structured Surfaces**
   - Site selective assembling of tabacco mosaic viruses (TMV)
3. **Substrate Supported Metal Organic Frameworks (SURMOF)**
4. **Electron Transport in Graphene-Based Organic Monolayers**

Two Dimensional Porous Networks on Surfaces



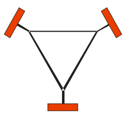
Organic ligand





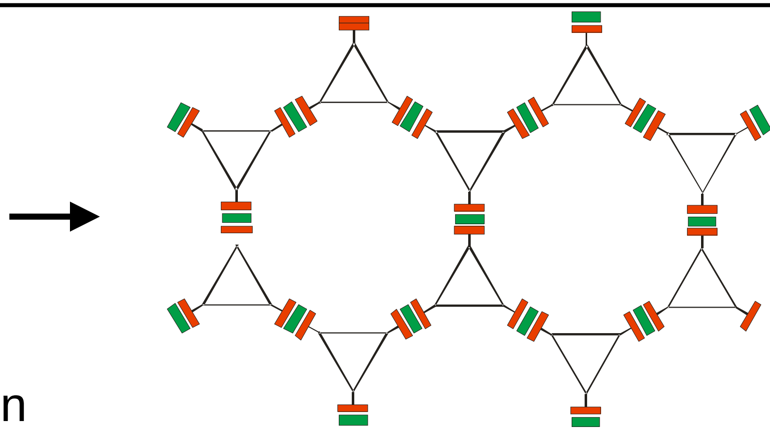
BTC

1,3,5-Benzenetricarboxylic acid



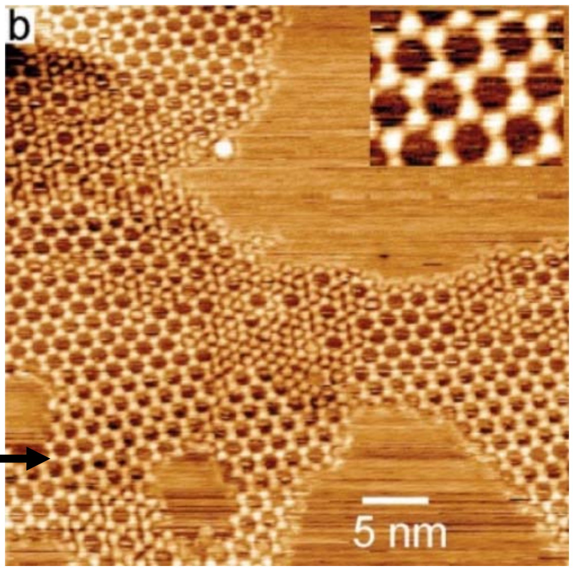
Organic ligand

\+ connector



Cu ion

STM image of BTS on Ag (111)



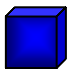
Self-assembled growth of 2d-networks on metal surfaces

J.V.Barth, *Molecular Architectonic on Metal Surfaces*, *Ann. Rev.Phys.Chem.* ***58***, 375 (2007)

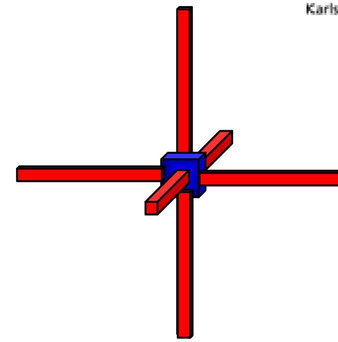
N.Lin, D.Payer, A.Dmitriev, T.Strunskus, Ch.Wöll, J.V.Barth, K.Kern, *Angew. Chemie Intern. Ed.* **44** ,1488 (2005)

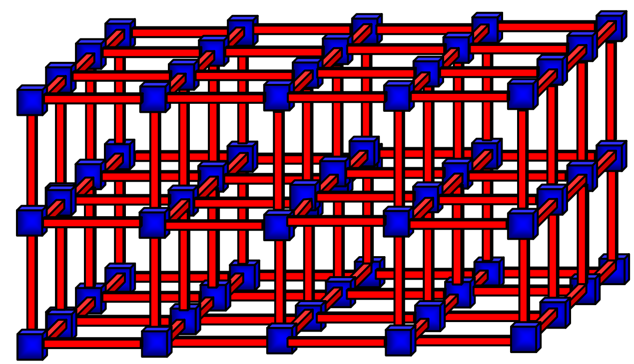
Nature Chemistry **2**, 374, (2010)

Going From Two to Three Dimensional Porous Networks



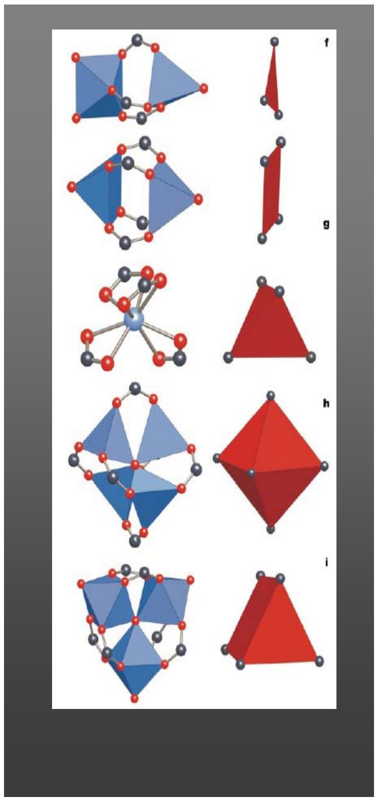
+

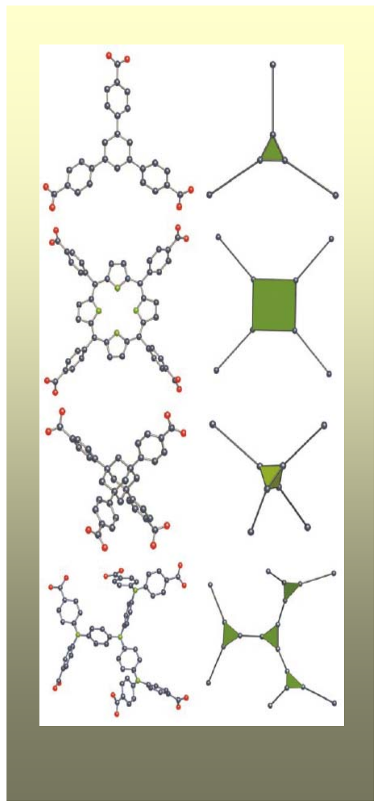




Inorganic Units

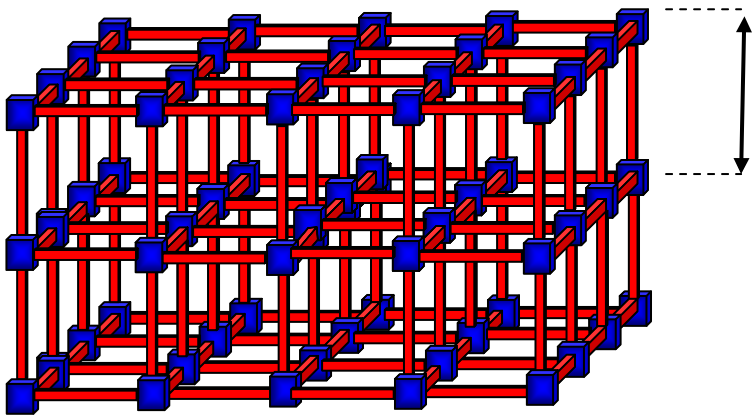
Organic Linkers



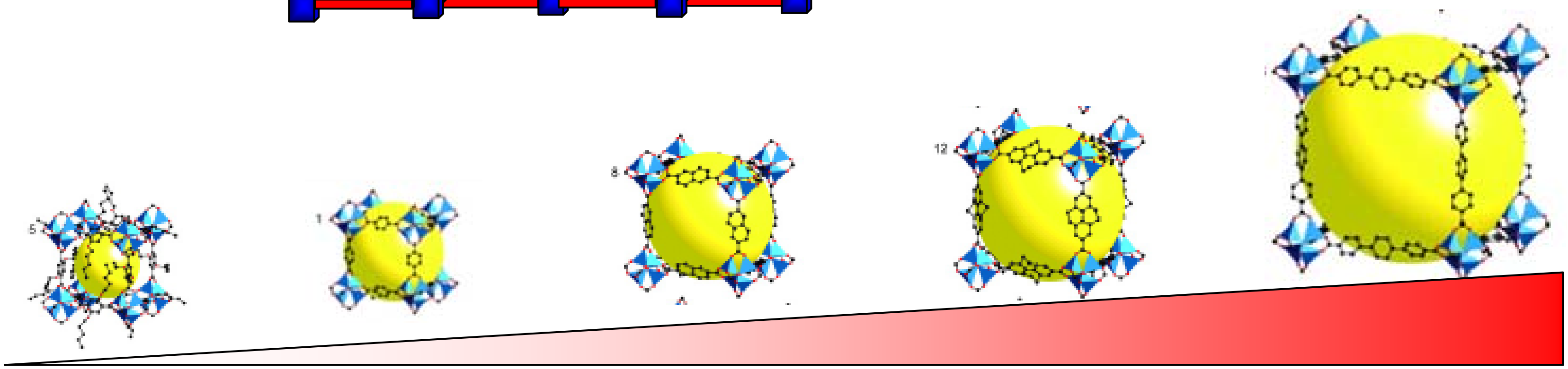


Well devoloped field in coordination chemistry
Several hundred structures known

Adjustable Metal Organic Framework (MOF)
Pore Size



0.5 nm - 10 nm



O. Yaghi et al., Micro- and Mesoporous Materials (2004)

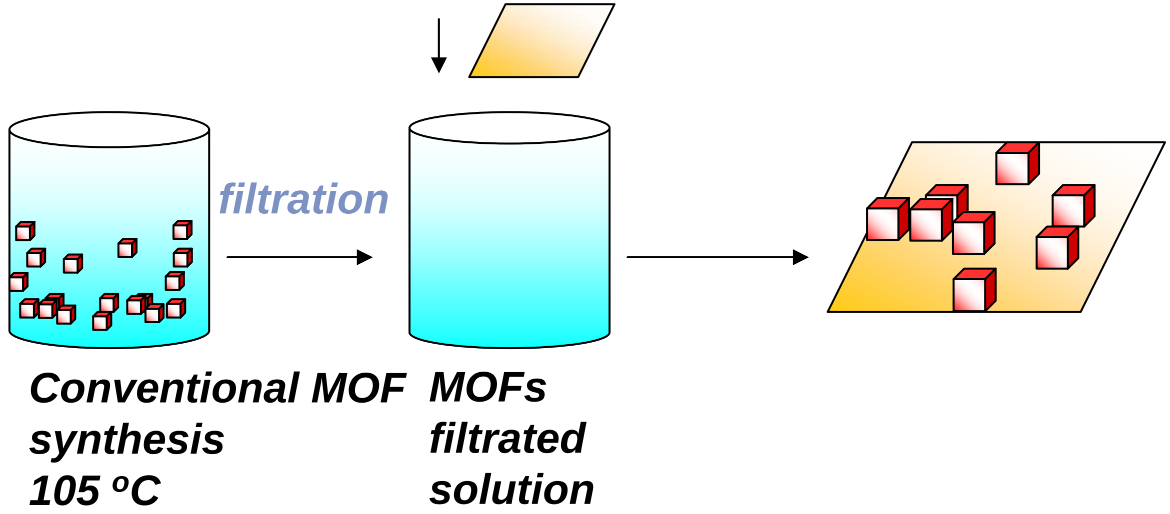
Surface area > 2000 m²/g

Temperature stability > 250°C

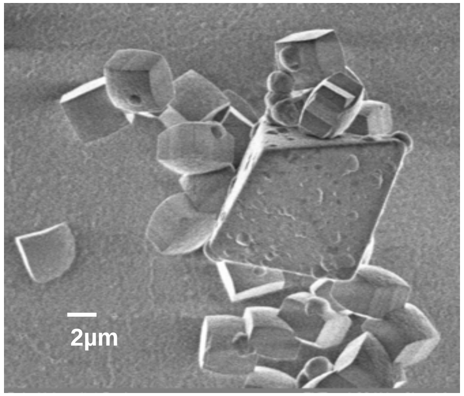
Physical and chemical properties adjustable (e.g. molecular magnets, dyes,…)

Deposition of MOFs on Surfaces: The Straightforward Approach

Grafting of preformed MOF crystallites on surface



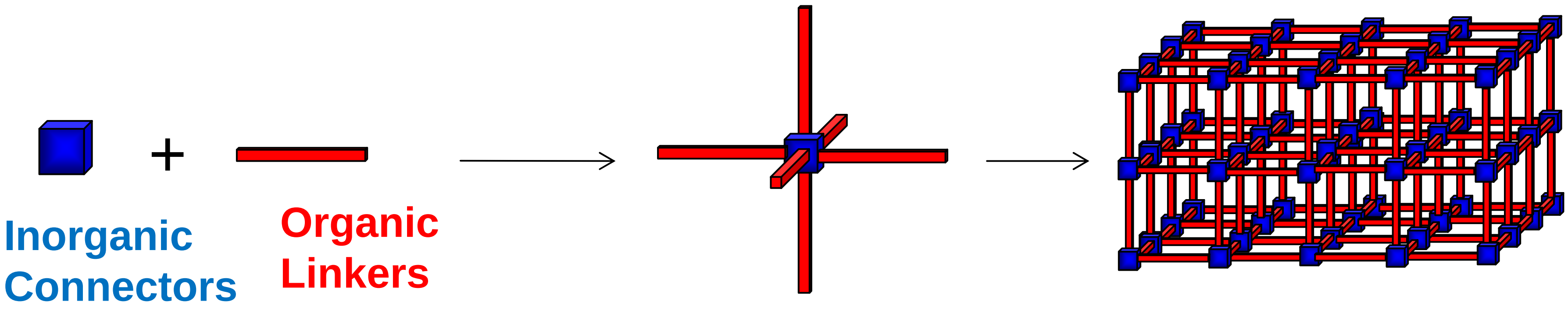
Robust method, but….
polycrystalline
disordered
no homogenous thickness

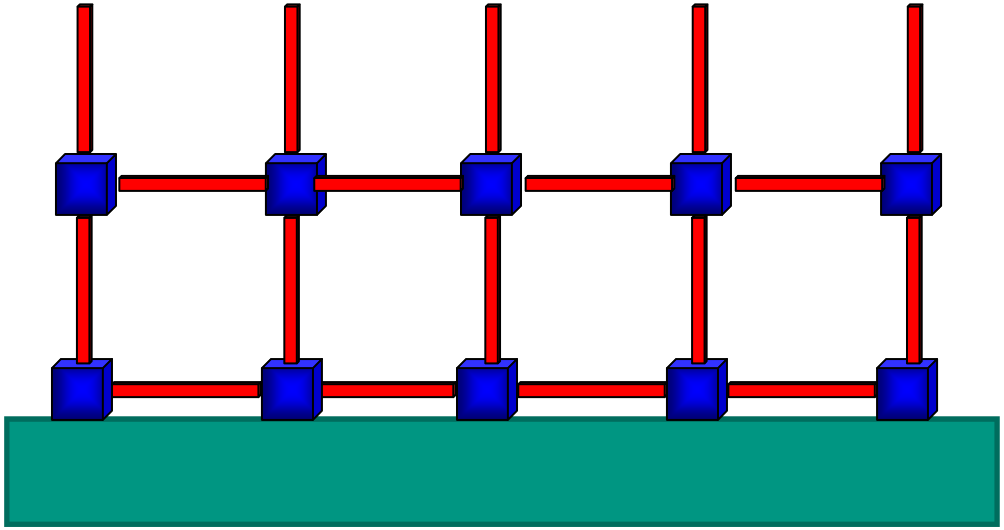


S.Hermes, F.Schröder, R.Chelmowski, Ch.Wöll, R.A.Fischer, J.Am.Chem.Soc. ***127***,13744 (2005)

Deposition of MOFs on Surfaces:
How to Define Thickness, Orientation and Order?

Karlsruher Institut für Technologie

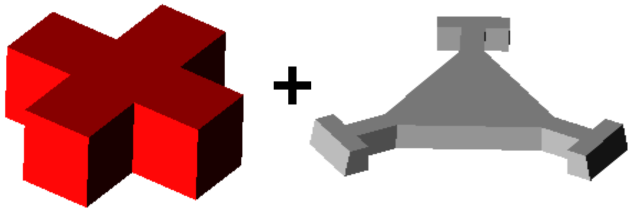




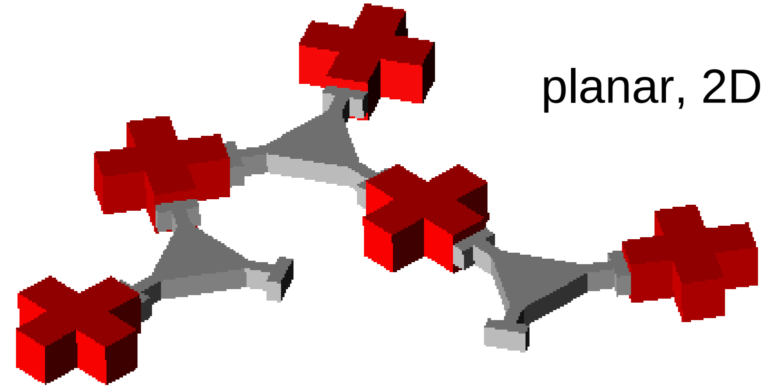
Connectivity of Framework Building Units: 2D vs. 3D

4-fold docking

3-fold docking



Cu_2^{2+} + BTC



Questions: Other ligands needed?
Other connectors needed?

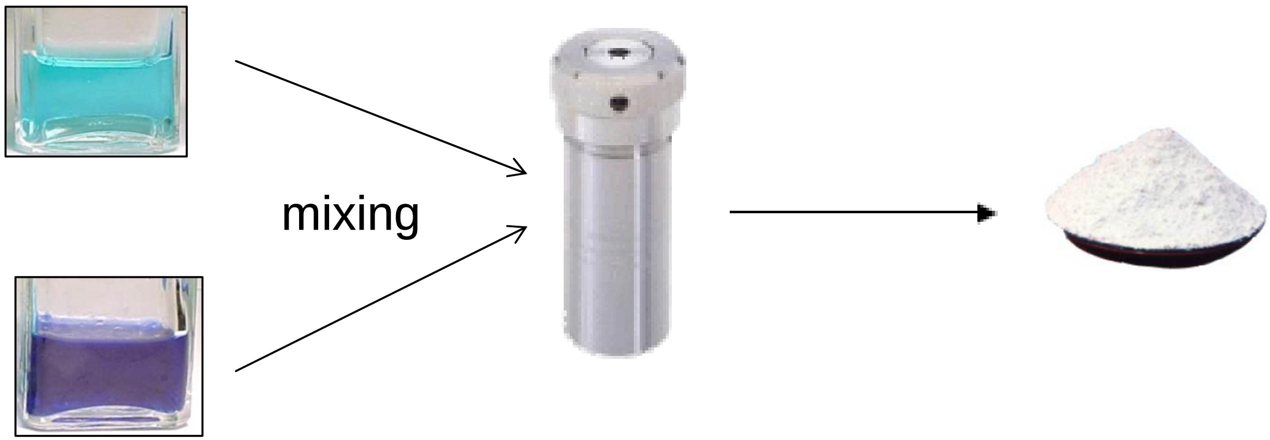
Epitaxial Growth of a Prototype MOF, HKUST-1

Conventional solvothermal synthesis of HKUST-I (Cu-BTC)

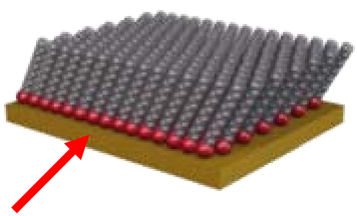
$Cu(NO_3)_2$

+

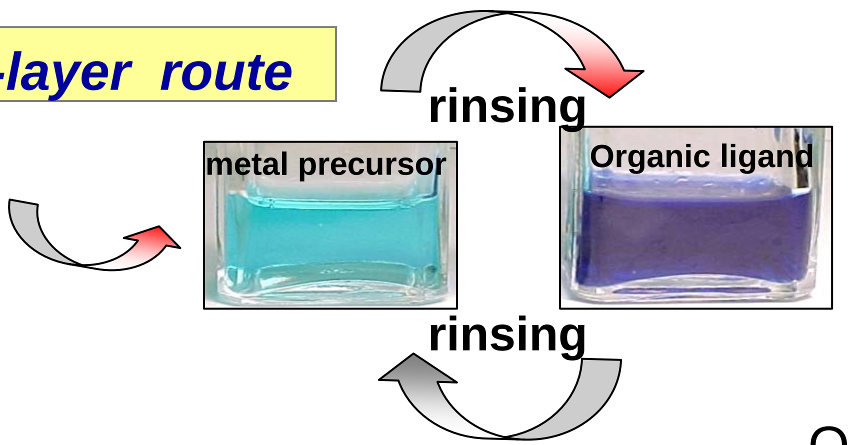
H_3BTC

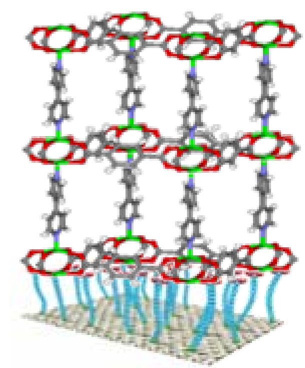


Novel Layer-by-layer route



self assembled monolayer (SAM)

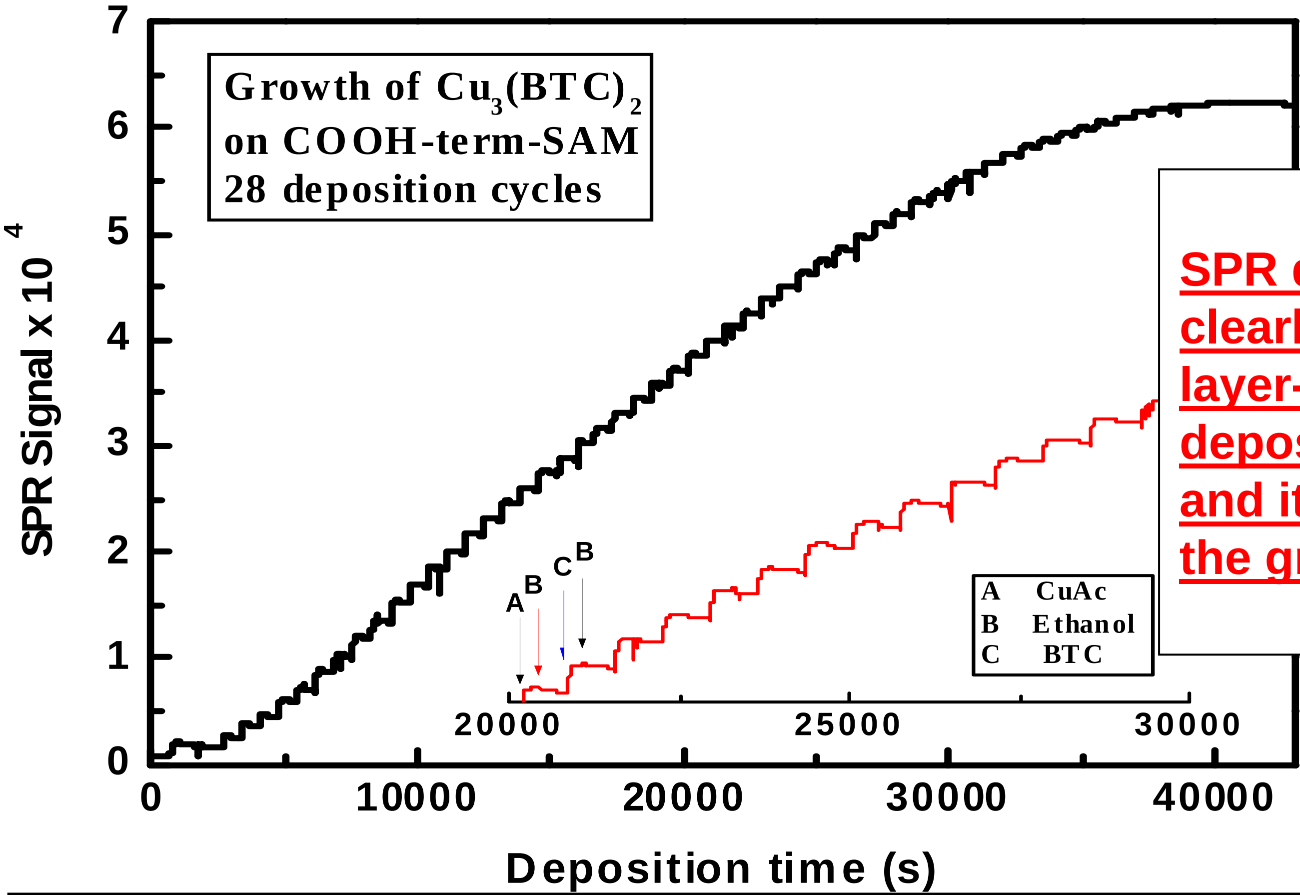


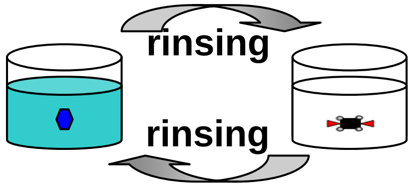


Quasi-Epitaxial growth

In-situ Monitoring of SURMOF Deposition with SPR

Surface Plasmon Resonance (SPR)

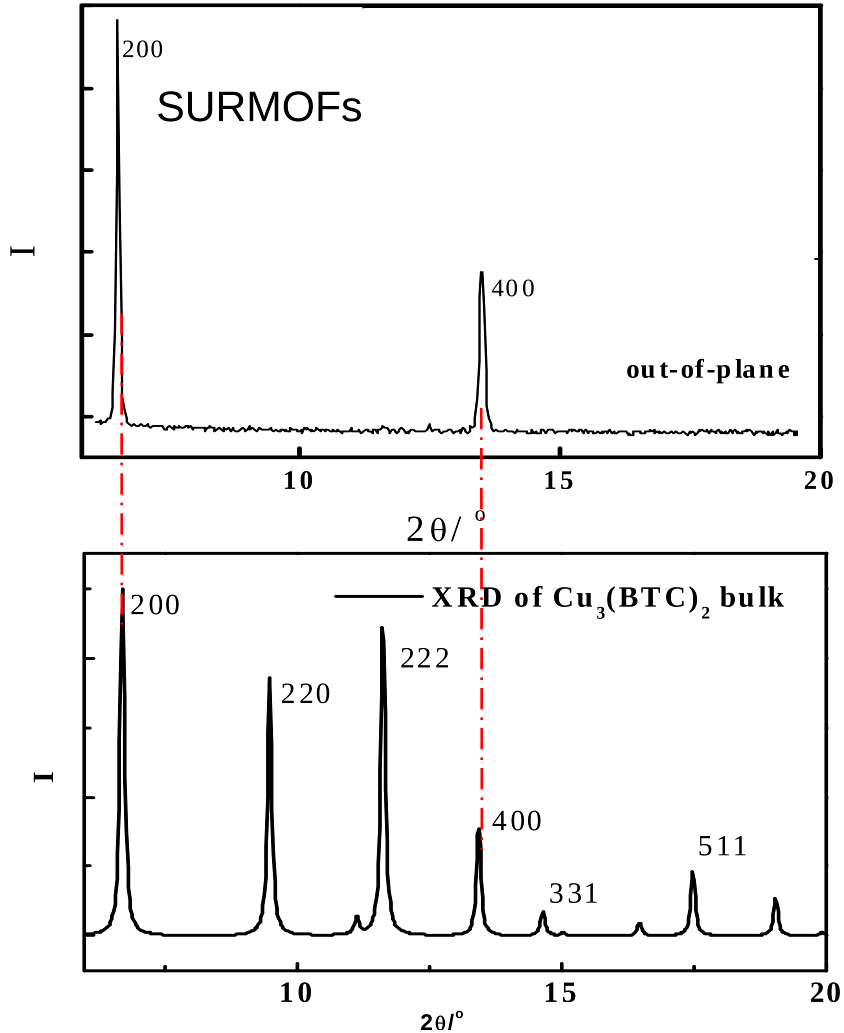




SPR demonstrates clearly that a layer-by-layer deposition is possible and it also allows to follow the growth in-situ.

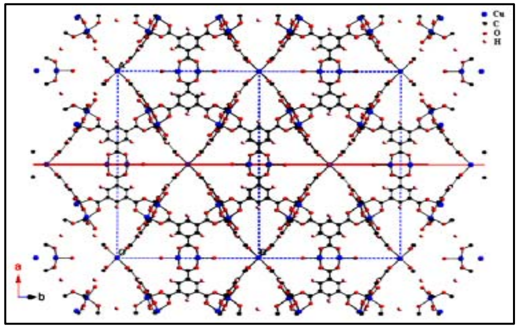
O.Shekhah, H.Wang, T.Strunskus, P.Cyganik, D.Zacher, R.A.Fischer,Ch.Wöll, Langmuir **23**,7440 (2007)

Characterization of SURMOFs: XRD



Out-of-plane XRD data for a Cu_3BTC_2 MOF sample (40 cycles) grown on a COOH terminated SAM.

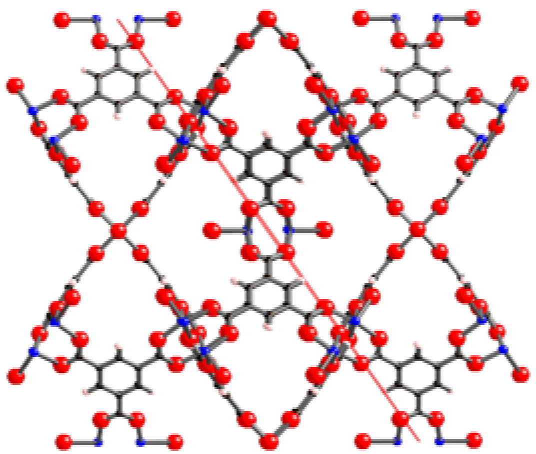
Oriented growth



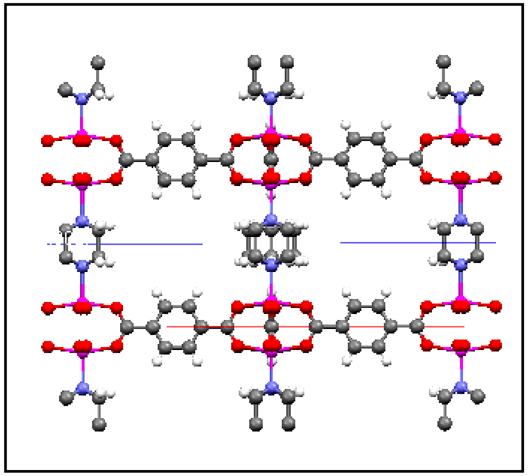
Shekhah,Wang,Kowarik,Schreiber,Paulus,Tolan,Sternemann,Evers,Zacher,Fischer,Wöll, JACS **129**, 15118, (**2007)**

MOFs which are suited for the LPE-method

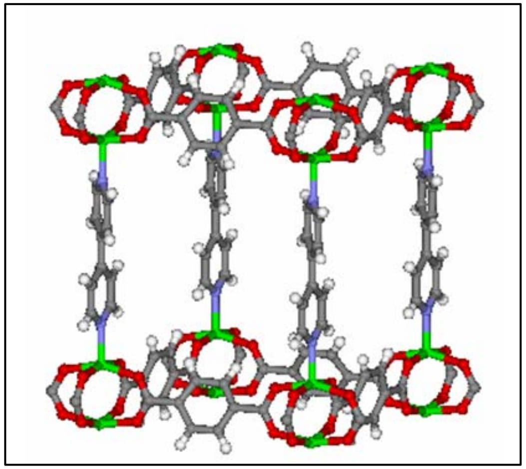
Karlsruher Institut für Technologie



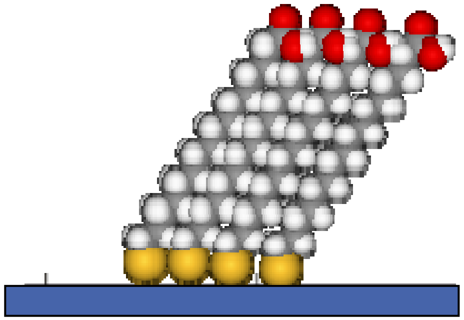
$Cu_3(BTC)_2$ MOF



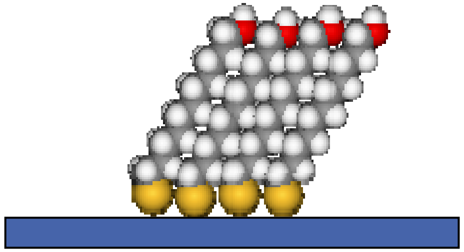
Zn(bdc)(dabco) MOF



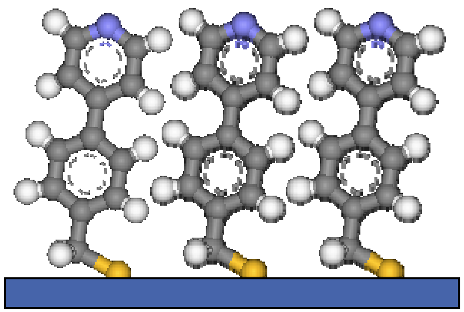
Zn(bdc)(bipy) MOF



HS $(CH_2)_{15}COOH$



HS $(CH_2)_{11}OH$



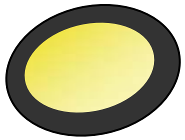
$HSCH_2(C_6H_4)(C_5H_4N)$

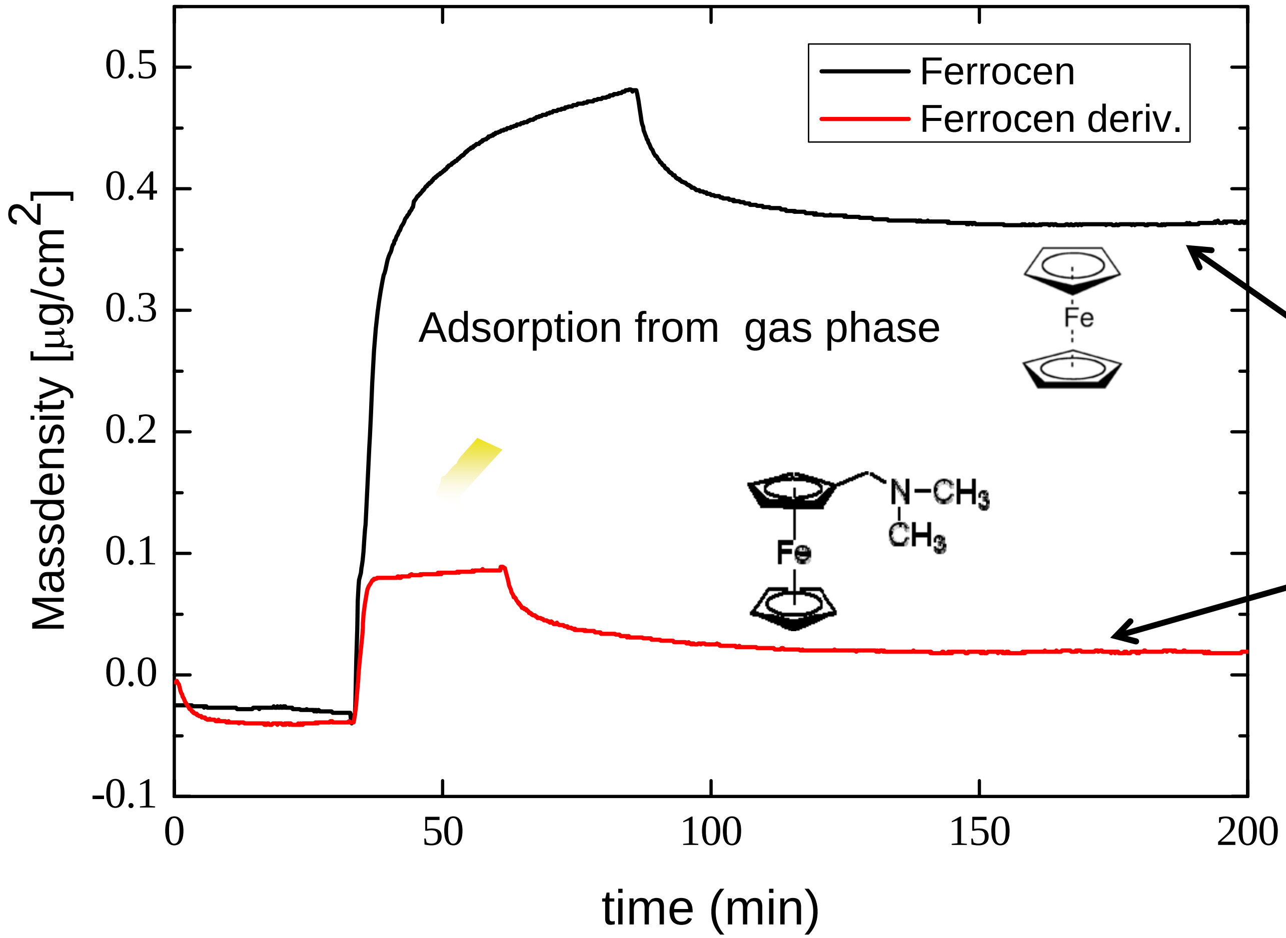
Shekhah, Wang, Zacher, Fischer, Wöll, J. Am. Chem. Soc., **129** (2007)15118

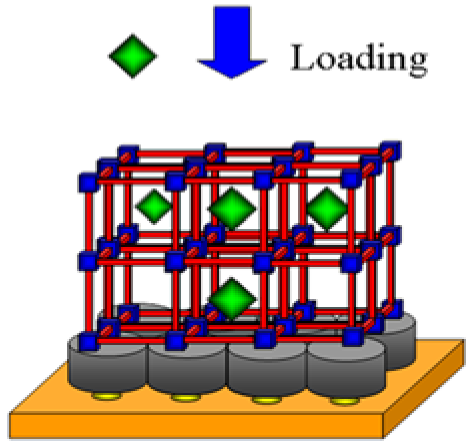
Shekhah, Wang, Paradinas, Ocal, Schüpbach, Terfort, Zacher, Fischer, Wöll, Nature Materials **8** (2009) 481

Loading of SURMOFs with Ferrocene derivatives: QCM results for Cu-ndc-dabco

QCM electrode





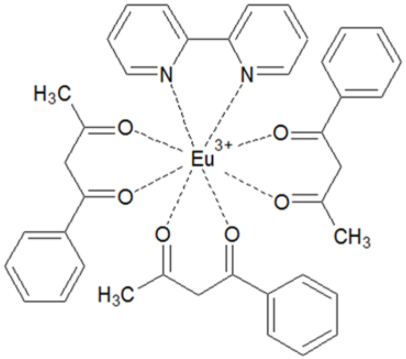


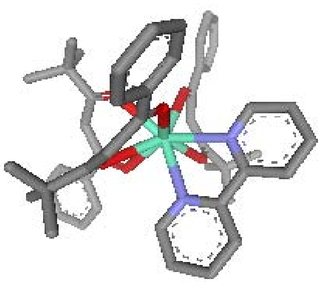
Cu-NDC-DABCO

Diffusion into SURMOF,
1 molecule/ pore

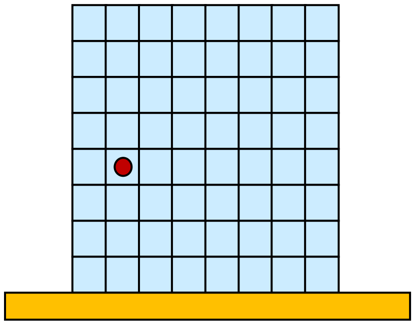
No diffusion into SURMOF,
surface decoration,
channels too small

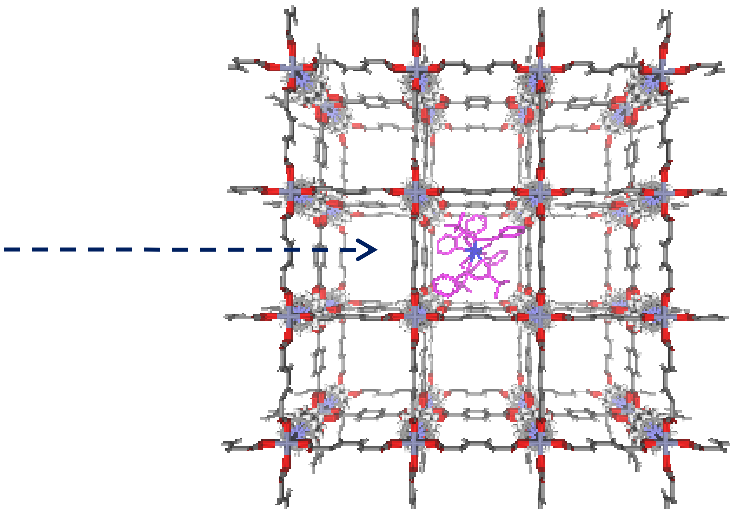
Loading of the $Cu_2(bdc)_2(dabco)$ MOF with a luminiscent molecule, $Eu(bzac)_3{\cdot}bipy$

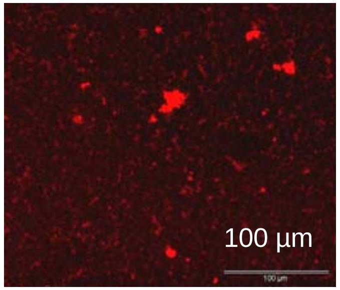


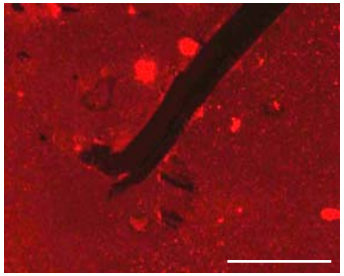


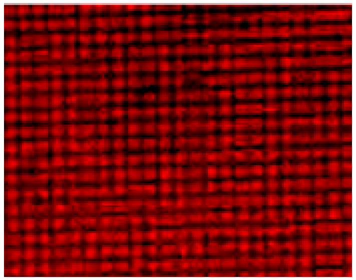
Eu(bzac)$_3$·bipy







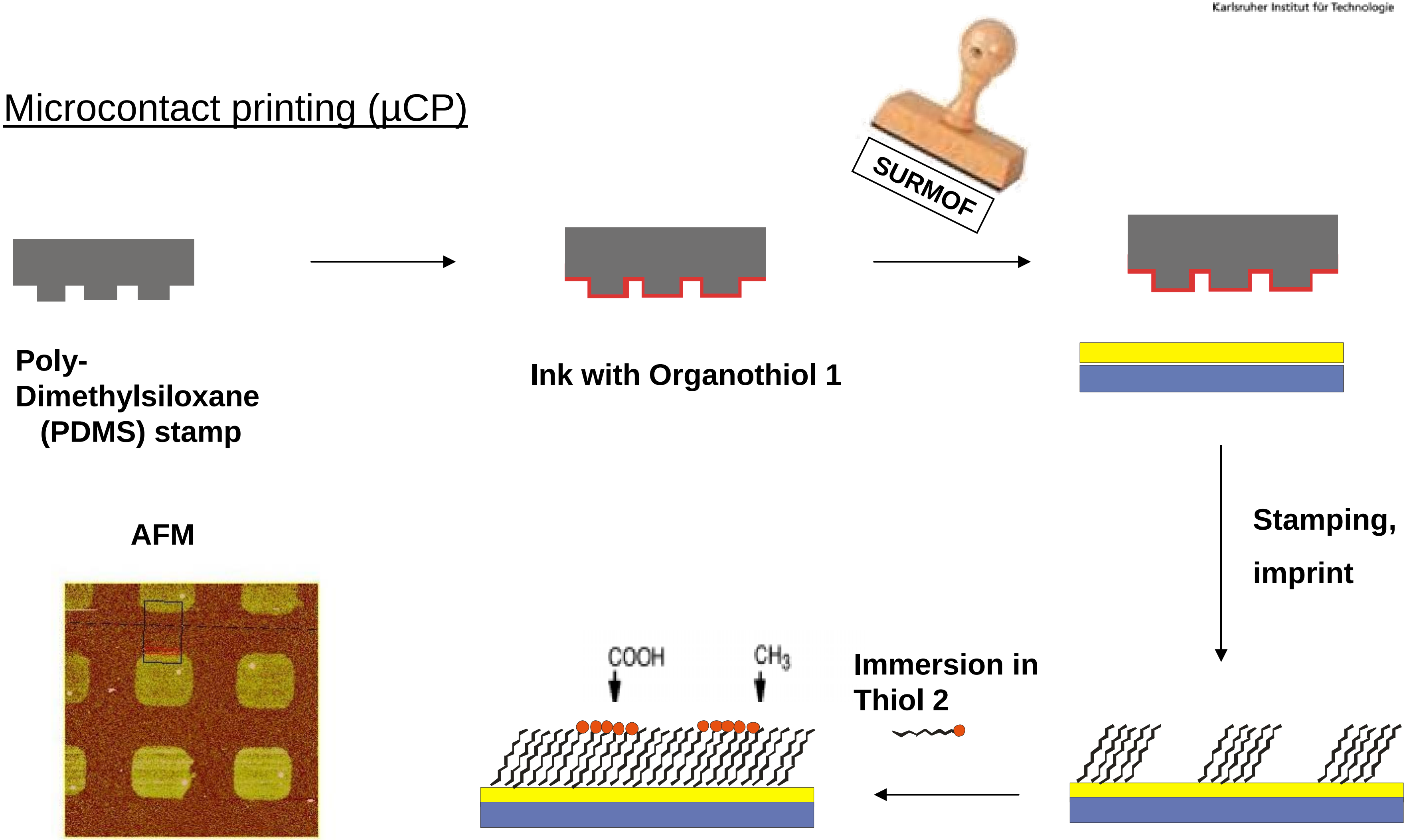




In collaboration with Prof. Claudia Wickleder, Univ. Siegen

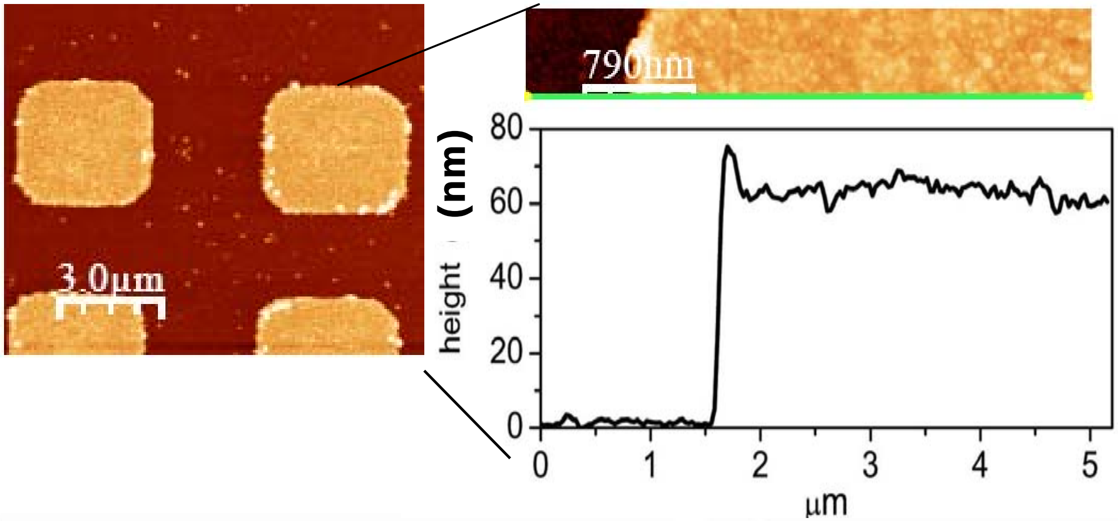
Fabricating Lateral Structures

Microcontact printing (µCP)

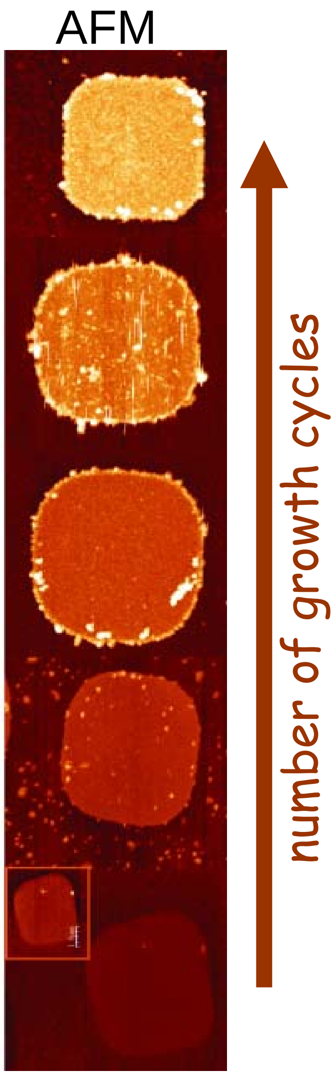


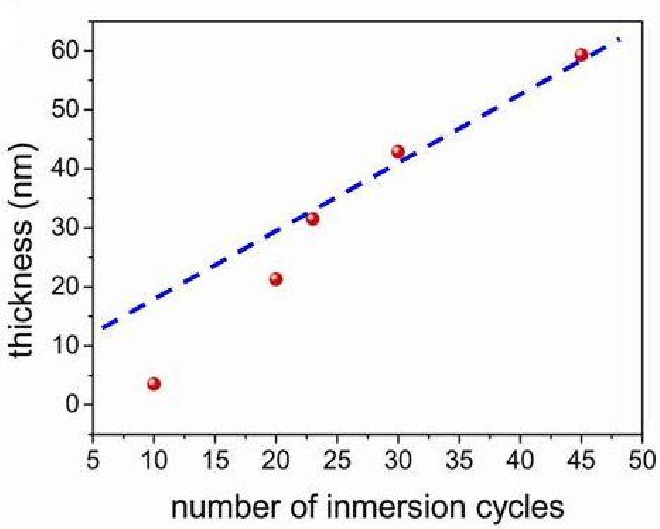
µCP: Xia, Whitesides, *Annu. Rev. Mater. Sci.*, ***28***, 84 (**1998)**

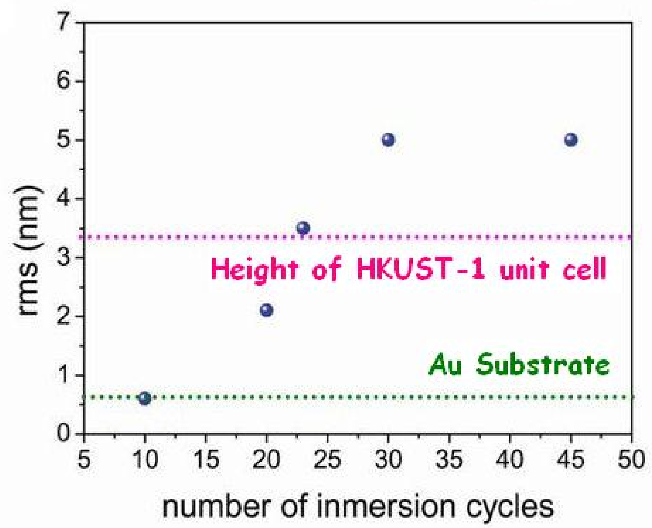
Characterization of SURMOFs with SEM & AFM



Cu_3BTC_2







C. Munuera, O. Shekhah, H. Wang, Ch. Wöll and C. Ocal; *PCCP* **10**, 7257 (2008)

Acknowledgements and Cooperation

Topics

Fabrication of highly ordered molecular adlayers (SAMs) using organothiols

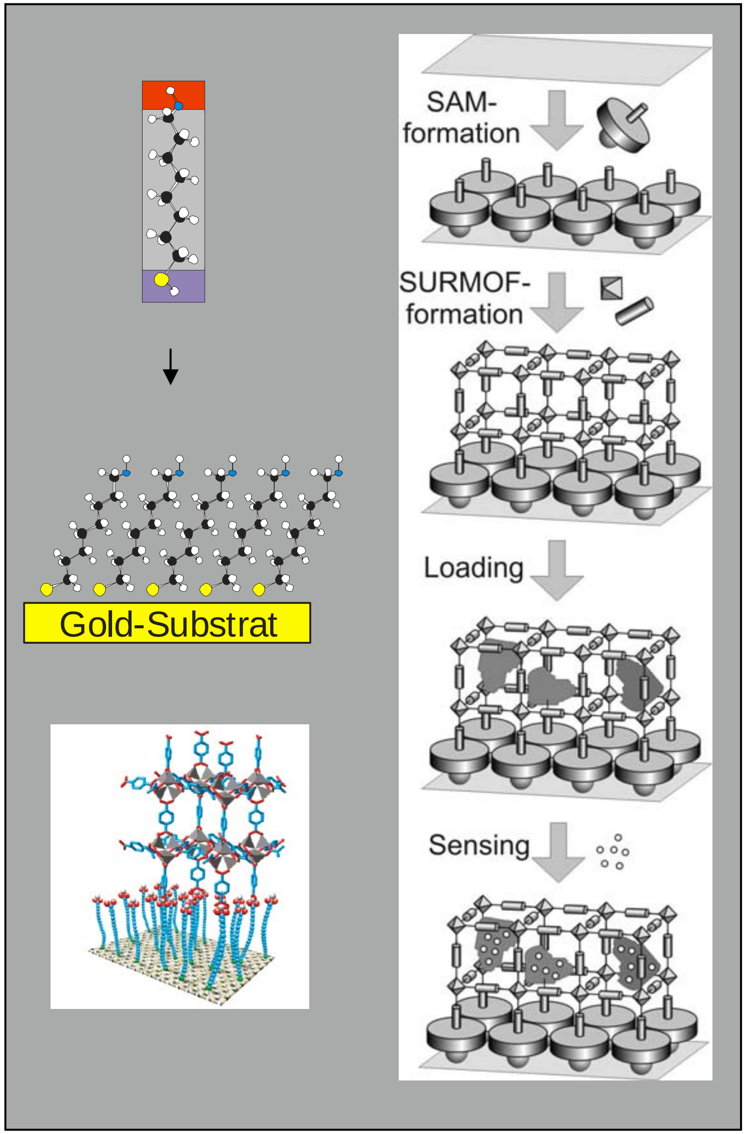
Metal-Organic Frameworks (MOFs)

Layer-by-Layer growth of MOFs on SAMs

Some applications SPR

Institute of Functional Interfaces (IFG), KIT

www.ifg.kit.edu



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Tatjana Ladnorg
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Prof. C. Wickleder (Siegen)
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Prof. C. Ocal, Barcelona (ES)
Prof. J. Veciana, Barcelona (ES)

Thank you for your attention