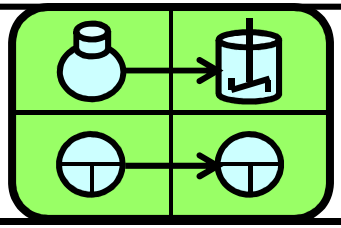
R&D Project Management in the Chemical Industry



The following collection of PowerPoint® Charts is intended to further clarify and supplement the relevant specialist publications on the subject matters dealt with. This collection in no way is used for any commercial purposes, but as learning material for students.

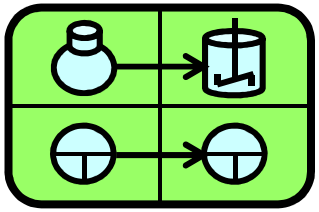
Selected sources for in-depth studies of the respective subject matters are given in some lists of references.

The chemical-technical target components, formulas, deadlines, data, project structures and action plans shown in project examples P1-P3 are widely with a practical orientation, but yet purely fictitious. They are solely used for a clear illustration of the particular topic and for learning purposes.

The names of all persons with project functions are solely fictional. Matches with the names of other people would be purely coincidental.

Rainer Buerstinghaus

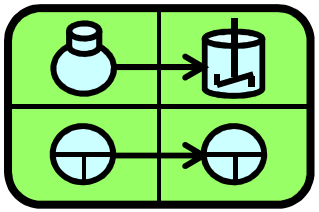
R&D Project Management in the Chemical Industry



The Subject Matter

- Innovations: Characteristics, Measures for its Promotion, Process Variants.
- **Three Examples for Innovation Projects (Chemistry and Technology):**
  1. Highly Elastic Clear Coats for the OEM Automotive Sector.
  2. Nitrilase Catalyzed Synthesis of a Chiral Hydroxy-Carboxylic Acid.
  3. New Metal-Organic Frameworks for the Adsorptive Storage of Gases.
- Projects, Target Systems, Project Management in R&D.
- Appropriate Organization and Effective Structure Planning of R&D Projects.
- Project Flow Planning, Milestones, the Stage-Gate®-Process, Network Diagrams.
- Effective Implementation and Control of R&D Projects, Trend Analyses.
- Success Risks: Identification, Classification and Treatment.
- Recruitment and Lead of Project Staff:
  Chemists (m/f/d) – Team Players, Pacemakers and Executives in Projects.
- Project Manager (m/f/d): Tasks, Leadership Functions and Personality Profile.
- The Systematic Evaluation of Individual R&D Projects.
- R&D Strategy: The Planning of a Project Portfolio.

R&D Project Management in the Chemical Industry



Subject Matter →

P1: Highly Elastic Clear Coats for the OEM Automotive Sector.

(Chemistry and Technology)

Example P1

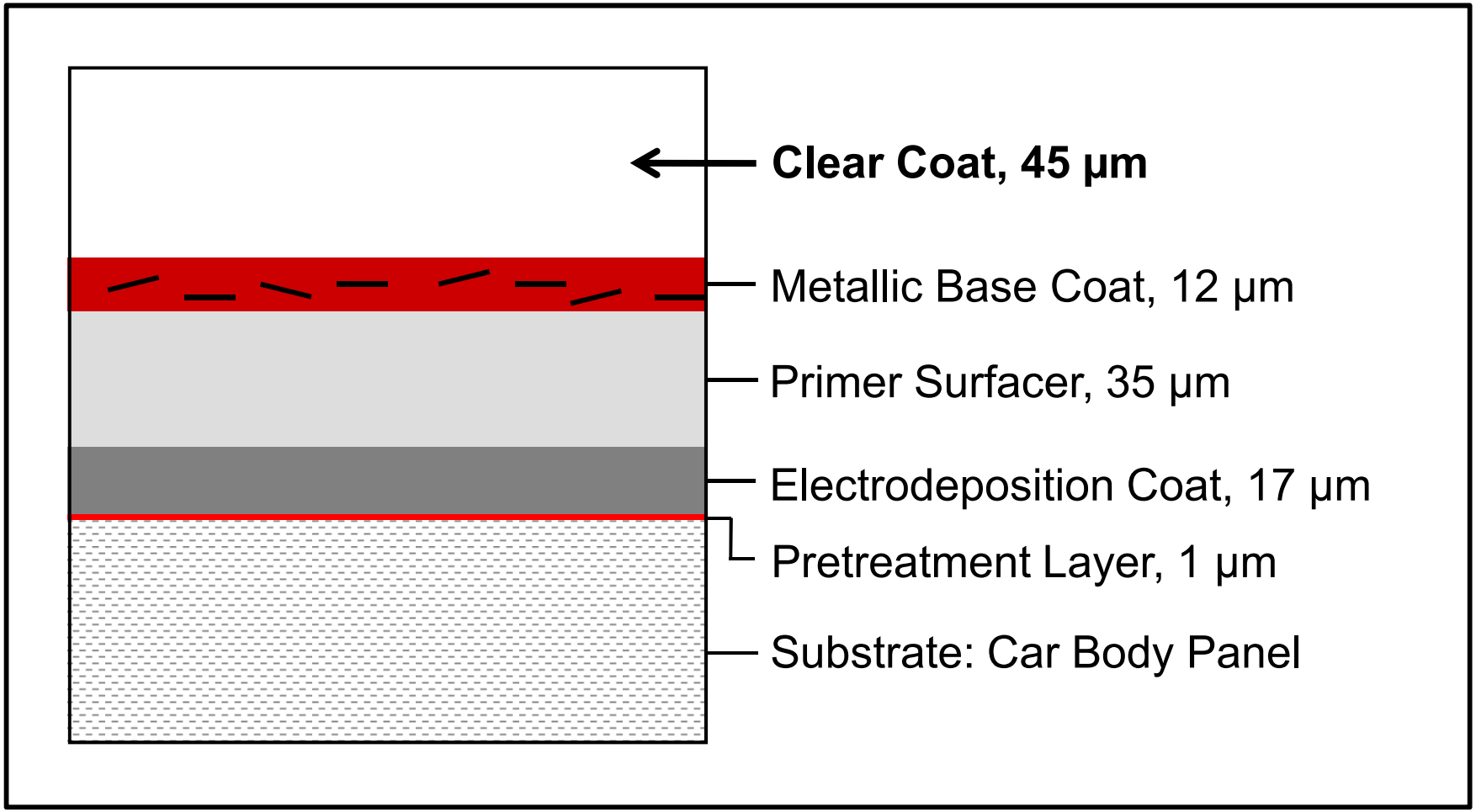
Innovation Project P1: →

"Highly Elastic Clear Coats for the OEM Automotive Sector".

(Chemistry and Technology)

Highly Elastic Clear Coats for the OEM Automotive Sector

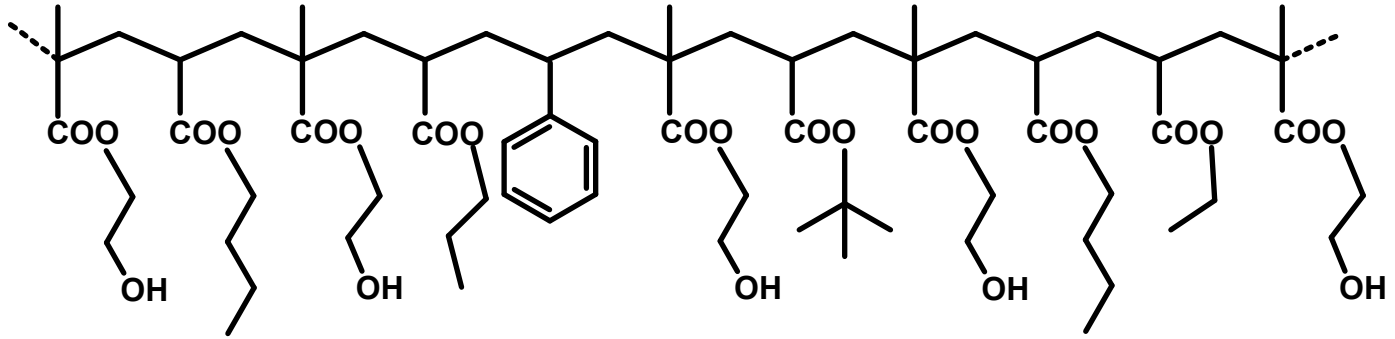
Clear Coat-Function: "Wet look", UV-Light-/Chemical-Protection, Resistance to Mechanical Stresses.



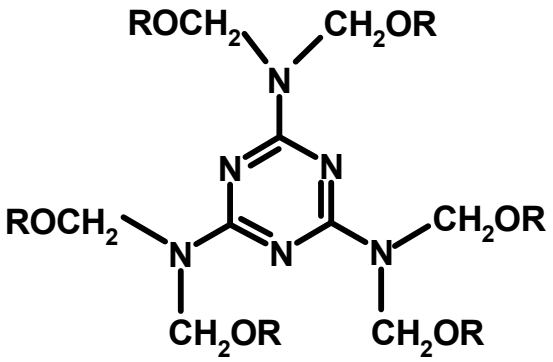
Rainer Buerstinghaus

Highly Elastic Clear Coats for the OEM Automotive Sector

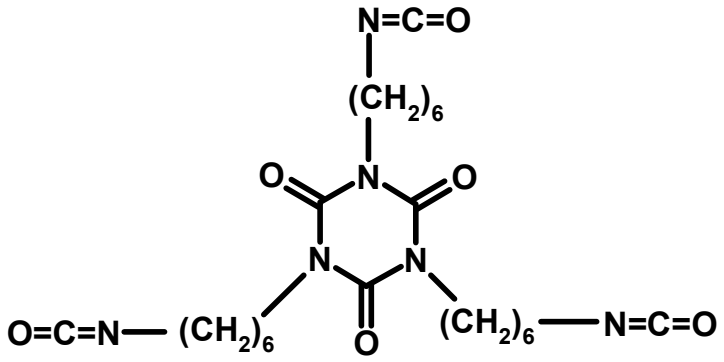
Coating Resins for 1- und 2-Component Systems:



OH-Functional Polyacrylate-Resin, "Polyacrylatol" (Detail from the Chain)



Crosslinker for 1C-Clear Coats
(R = H, CH_3, n-C_4H_9)

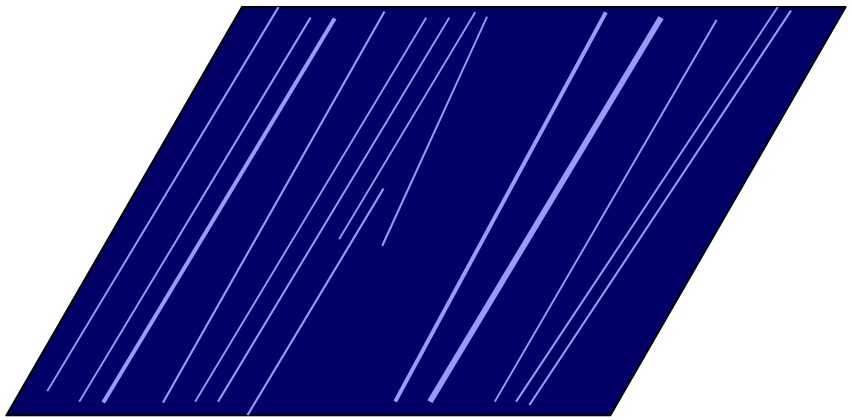


Crosslinker for 2C-Clear Coats
(Trimeric Diisocyanate)

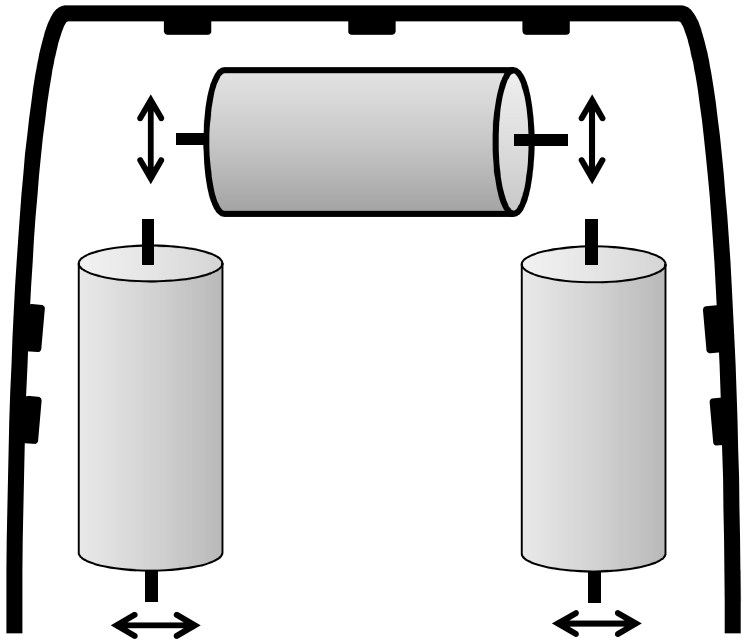
Rainer Buerstinghaus

Highly Elastic Clear Coats for the OEM Automotive Sector

Scratches due to Multiple Utilization of Car Washes:



Scratches on a clear coat finish with a dark blue underground.



Gantry car wash: brushes, spray nozzles (scheme).

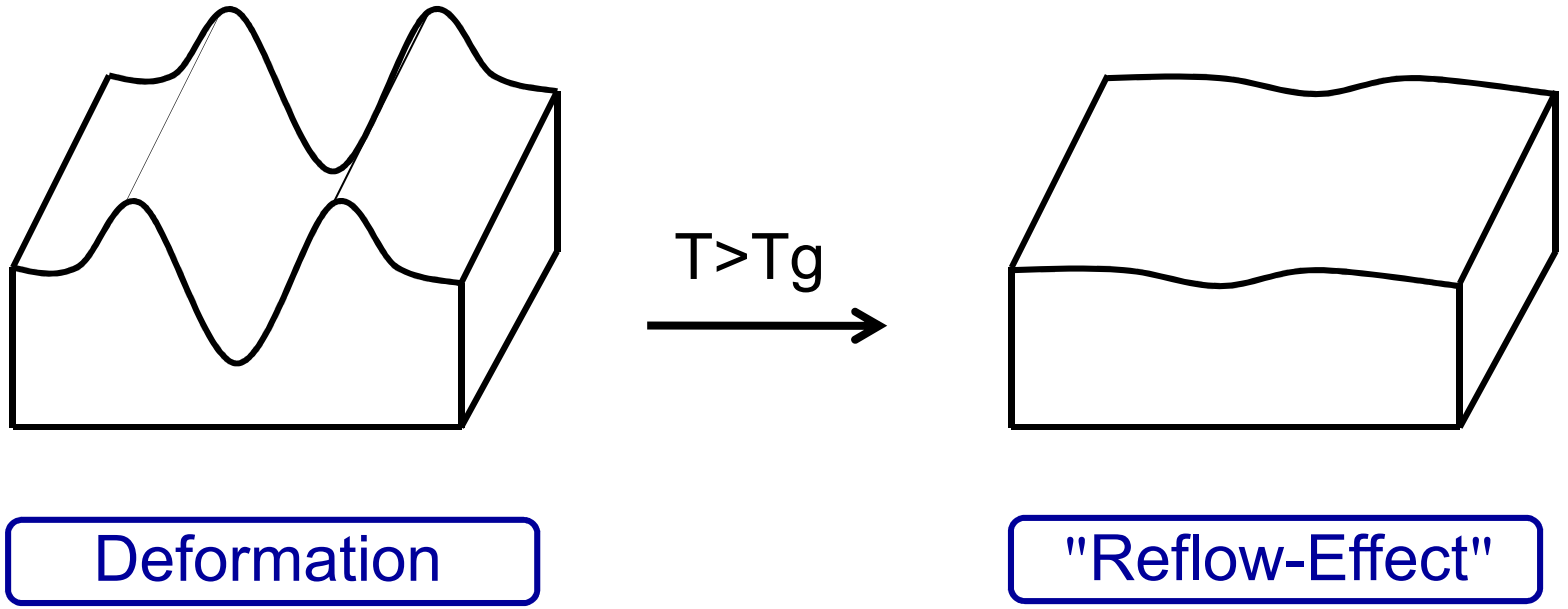
Dimensions of car wash scratches:
Depth: 0,1…0,3 µm (<< 1µm !)
Width: 1,0… 4,0 µm

Abrasive scratches are particularly problematic: they are *deeper, wider, rougher* than deformation scratches!

Rainer Buerstinghaus

Highly Elastic Clear Coats for the OEM Automotive Sector

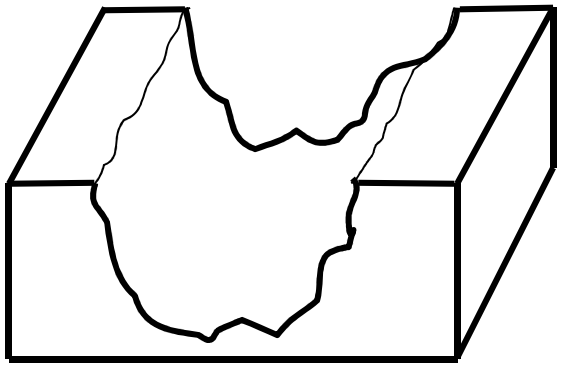
Scratches, "Reflow Effect" after Plastic Deformation:



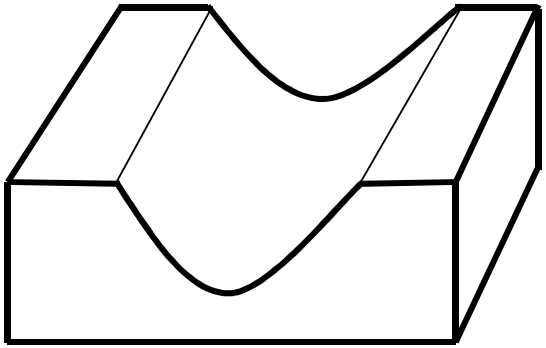
Tg: Glass Transition Temperature.

Highly Elastic Clear Coats for the OEM Automotive Sector

Scratches, "Reflow Effect" after Plastic Deformation:



T>Tg



Abrasion of Duromer

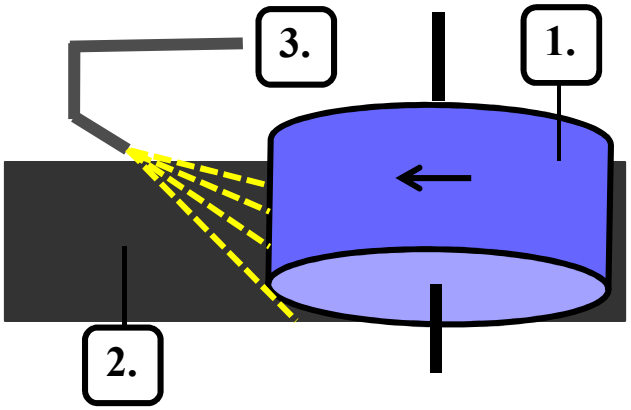
Remanent Material Removal

Tg: Glass Transition Temperature.

Rainer Buerstinghaus

Highly Elastic Clear Coats for the OEM Automotive Sector

TSC (AWETA), Scratch Resistance Test for Clear Coats:



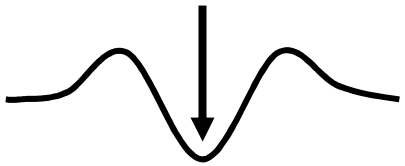
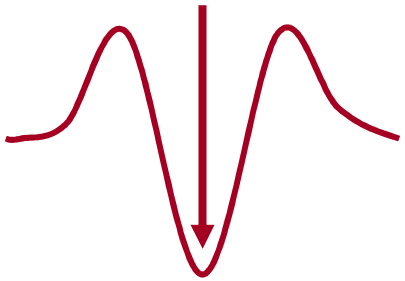
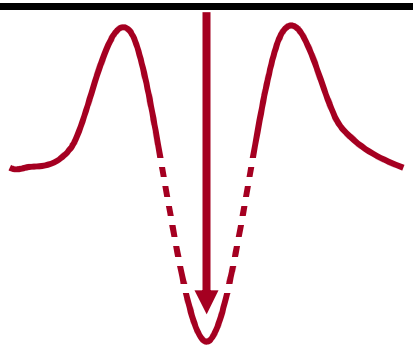
1. **Rotating nylon brush with contact to the panel.**
2. **Black panel with a clear coat finish.**
3. **Supply of sand slurry by means of an injector.**

Practical Test after AMTEC-Kistler according to DIN ISO 20566.
Sand Quantity: 1,5g/l H_2O; ø−Particle Size of the Sand: ≈ 24µm.

- Good correlation with the typical, practice relevant scratch damages.
- Possibility for differentiation between highly scratch resistant coatings.

Highly Elastic Clear Coats for the OEM Automotive Sector

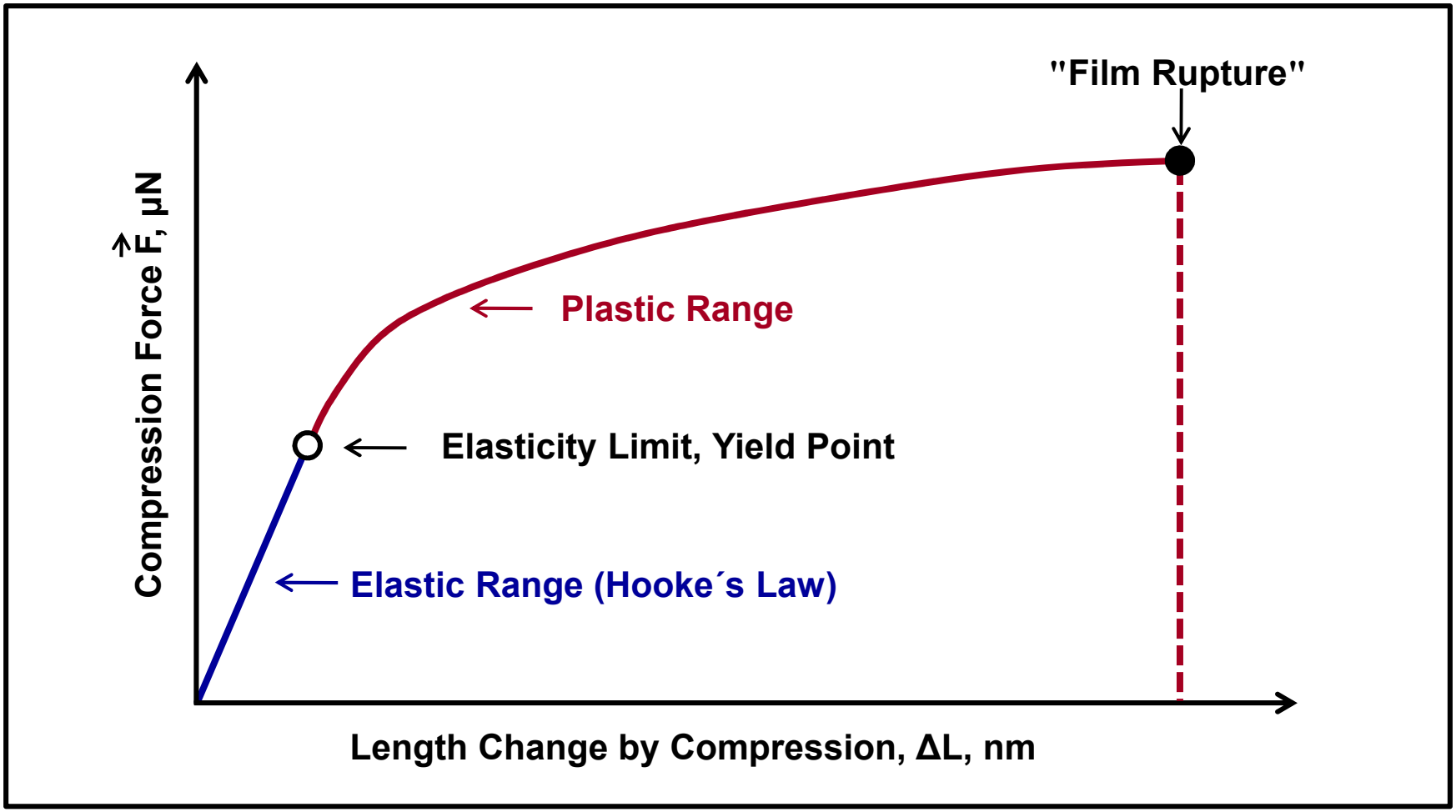
Mechanical Film Behavior at Local Micro-Compression:

	→	No Change *Solely Elasticity*
	→	 Permanent Deformation *Plastic Shares*
	→	 Film Break *Brittle Shares*

Rainer Buerstinghaus

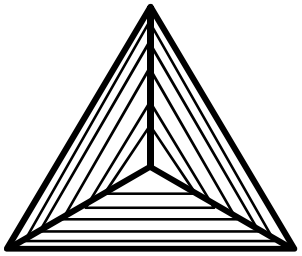
Highly Elastic Clear Coats for the OEM Automotive Sector

Mechanical Behavior of the Film during Compression by the Tip of an Atomic Force Microscope (AFM):



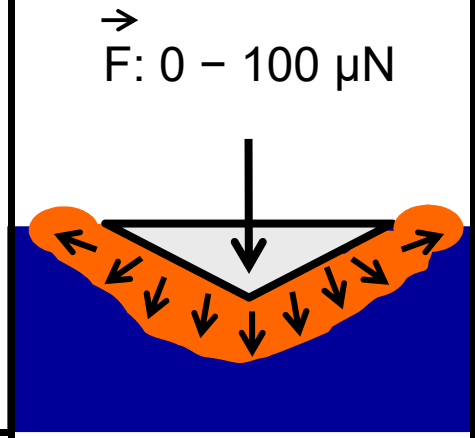
Atomic Force Microscope (AFM) as Nanoindention-Setup

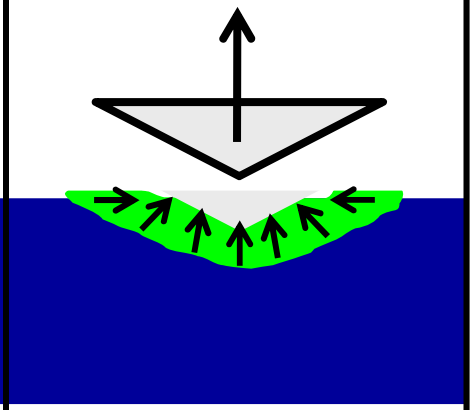
Measurement of Elastic Restoring Forces on Clear Coats:



The angle between an edge and its "counter-face": 142,3º.

$\vec{F}$ ~ Penetration Depth

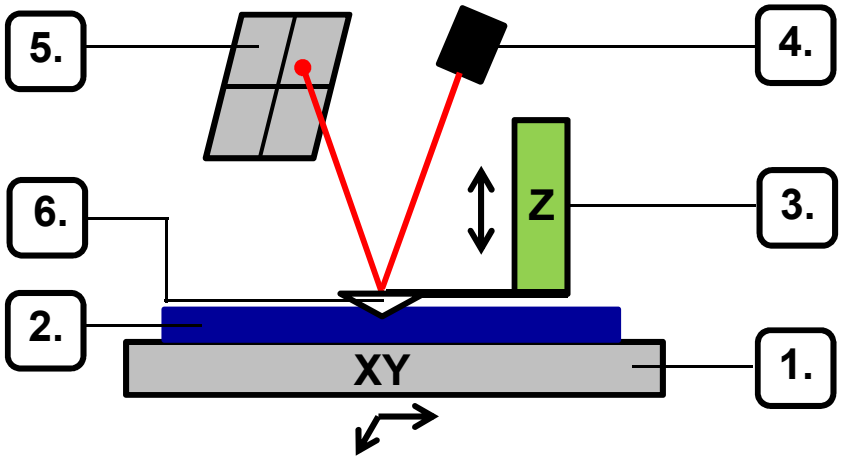




Berkovich-Pyramid; Basiskante: 50 nm.
Material: Diamond or Sapphire.

Plastic flow under pressure.

Recovery by elastic portions.

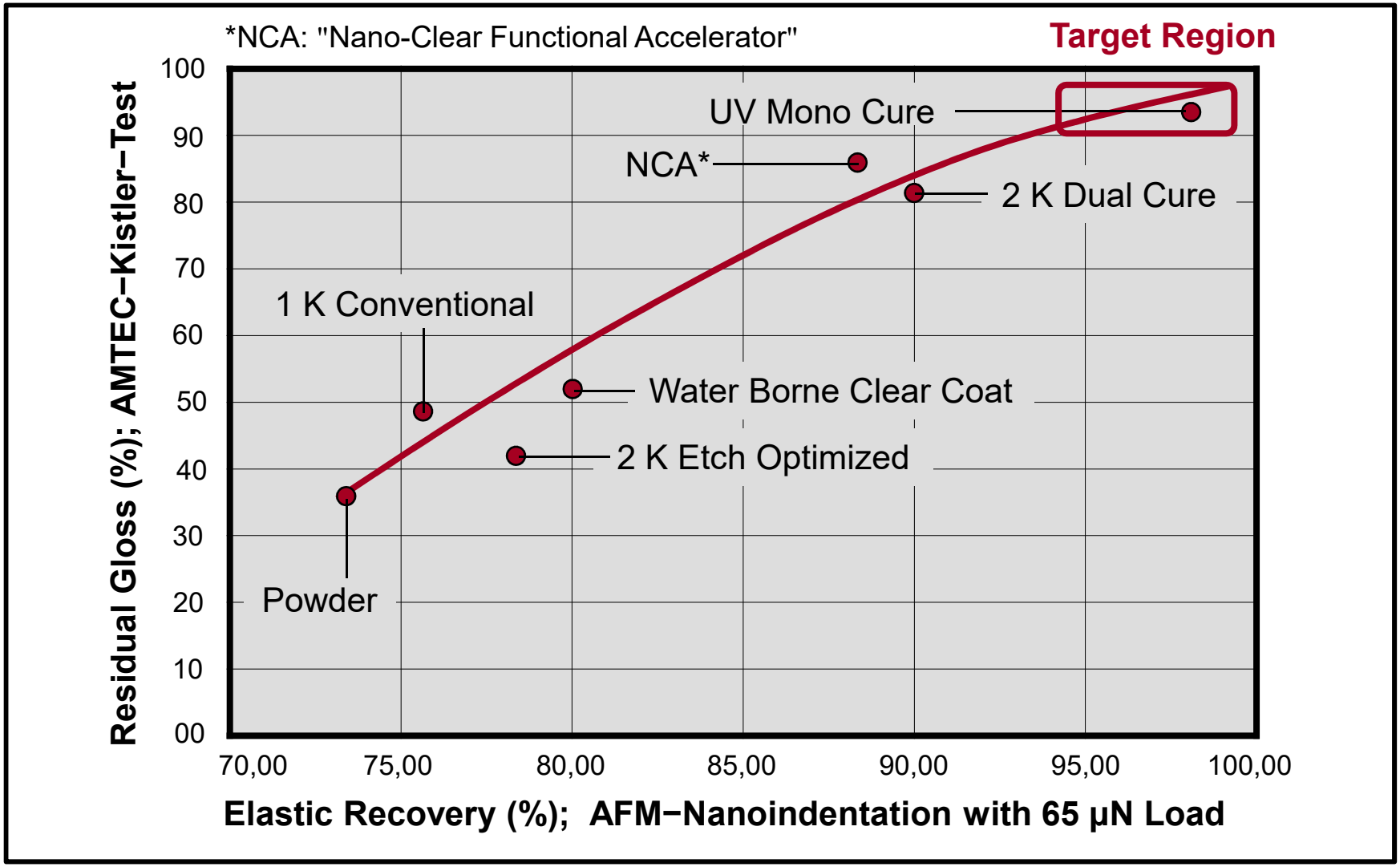


1. **XY-Scanner**
2. **Coat of Varnish, Surface**
3. **Piezoelectric Z-Scanner**
4. **Laser Diode**
5. **Position Detector**
6. **Berkovich Pyramid**

Rainer Buerstinghaus

Highly Elastic Clear Coats for the OEM Automotive Sector

AFM-Indentation, Correlation with the AMTEC-Kistler-Test:

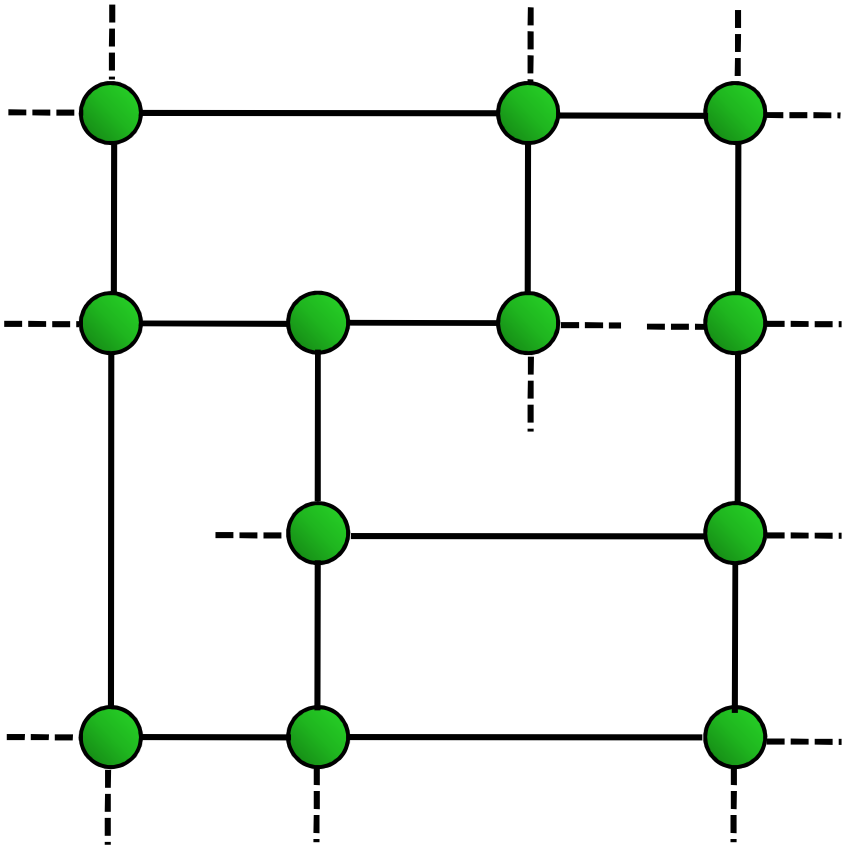


Rainer Buerstinghaus

Highly Elastic Clear Coats for the OEM Automotive Sector

Polymeric Network Types in Automotive Coatings.

→ **Standard Coating, Structural Scheme:**



Thermoset-Network

↓

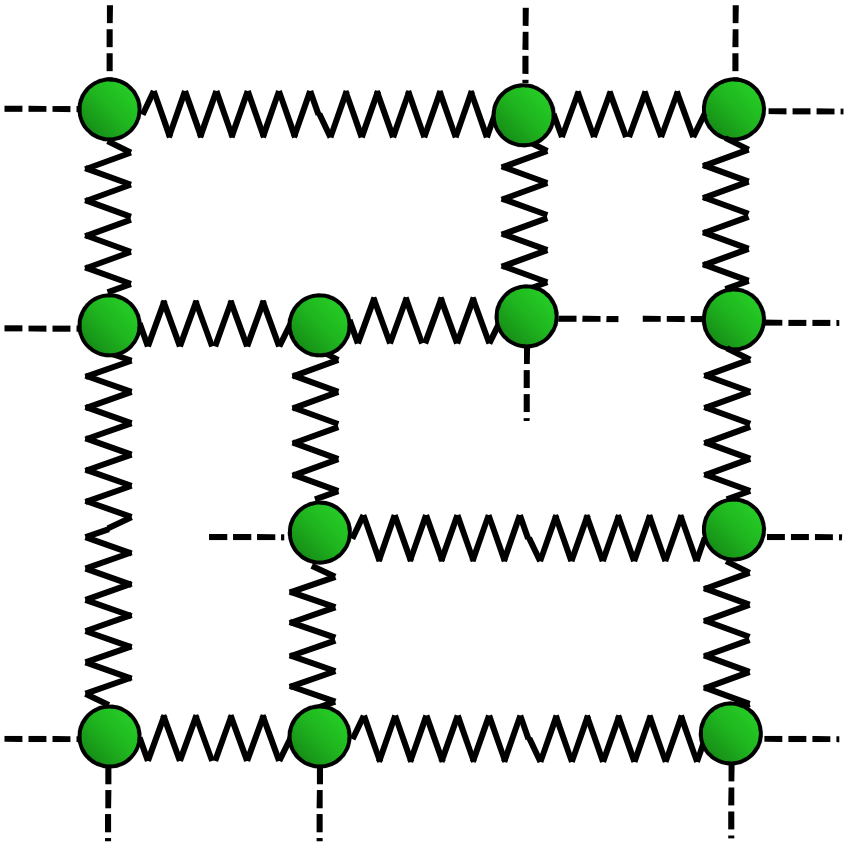
- Low Crosslinking Density.
- Rigid Molecular Chains.
- High T_g-Values.
- Medium Hardness.
- High Chemical Resistance.

Rainer Buerstinghaus

Highly Elastic Clear Coats for the OEM Automotive Sector

Polymeric Network Types in Automotive Coatings.

⟶ Plastic Coating, Structural Scheme:



Thermoset-Network

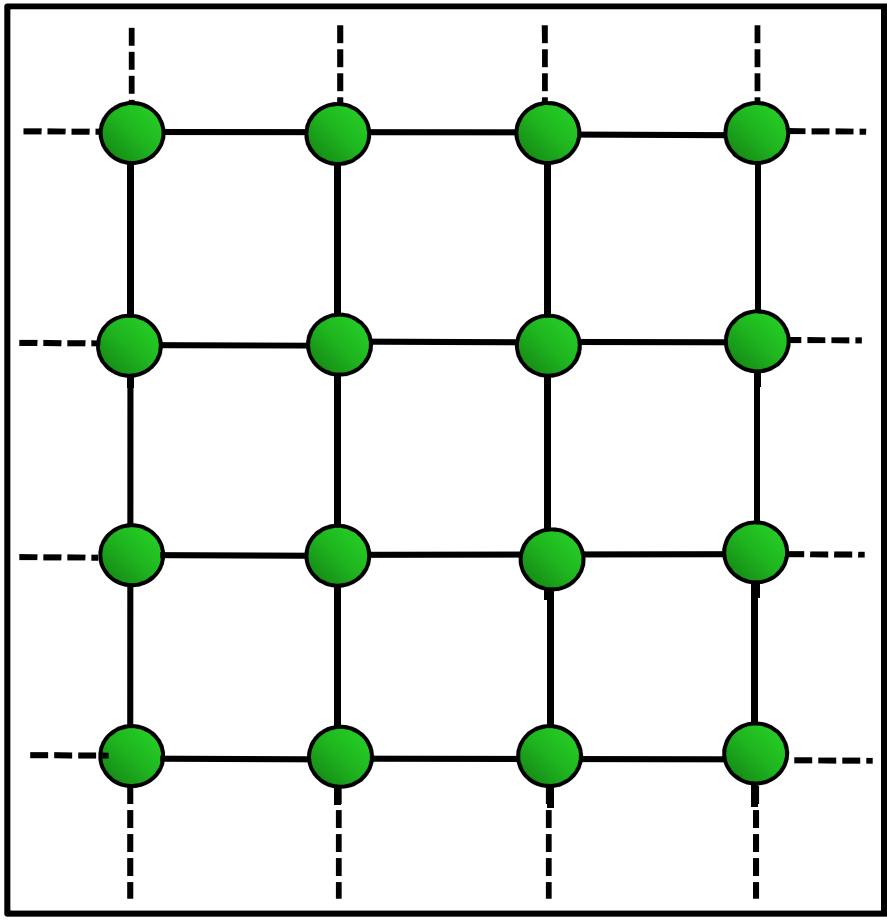
↓

- Low Crosslinking Density.
- Flexible Molecular Chains.
- Low T_g-Values.
- Poor Hardness.
- Use as Plastic Coating.

Highly Elastic Clear Coats for the OEM Automotive Sector

Polymeric Network Types in Automotive Coatings.

→ **Hard Coating, Structural Scheme:**



Thermoset-Network

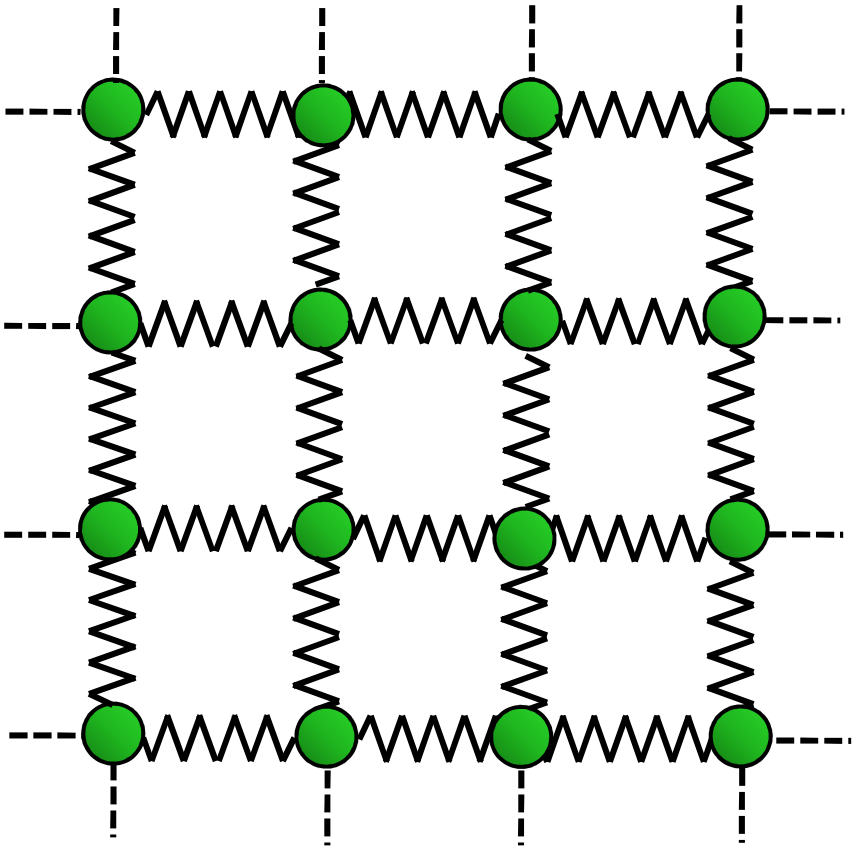
↓

- High Crosslinking Density.
- Rigid Molecular Chains.
- High T_g-Values.
- Extreme Hardness.
- Very Brittle ("Glaze").

Highly Elastic Clear Coats for the OEM Automotive Sector

Polymeric Network Types in Automotive Coatings.

Scratch-Resistant Coating, Impact Resistant Structure:



Thermoset-Network

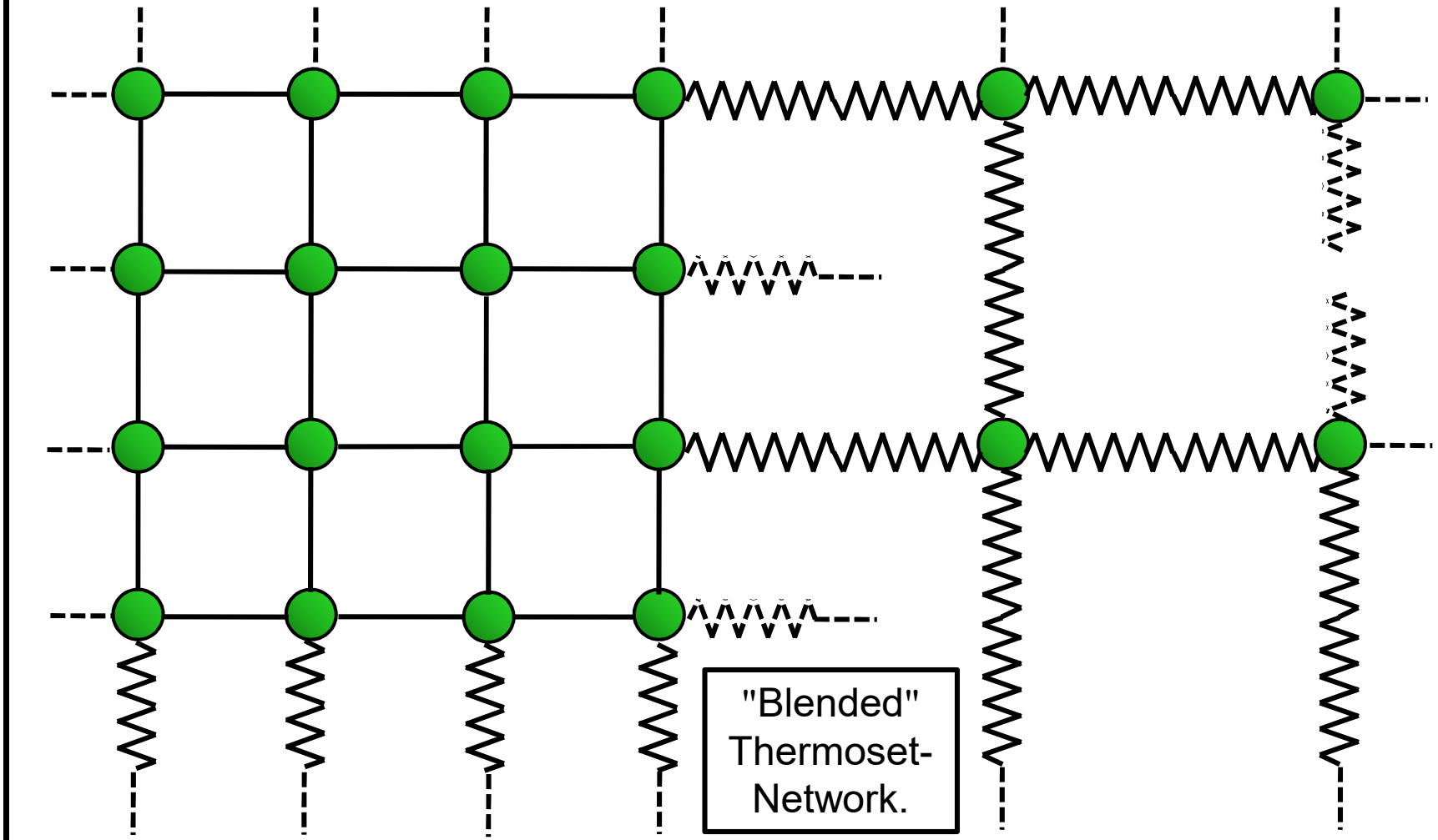
↓

- High Crosslinking Density.
- Flexible Molecular Chains.
- Medium T_g-Values.
- Medium − High Hardness.
- Low Brittleness.

Highly Elastic Clear Coats for the OEM Automotive Sector

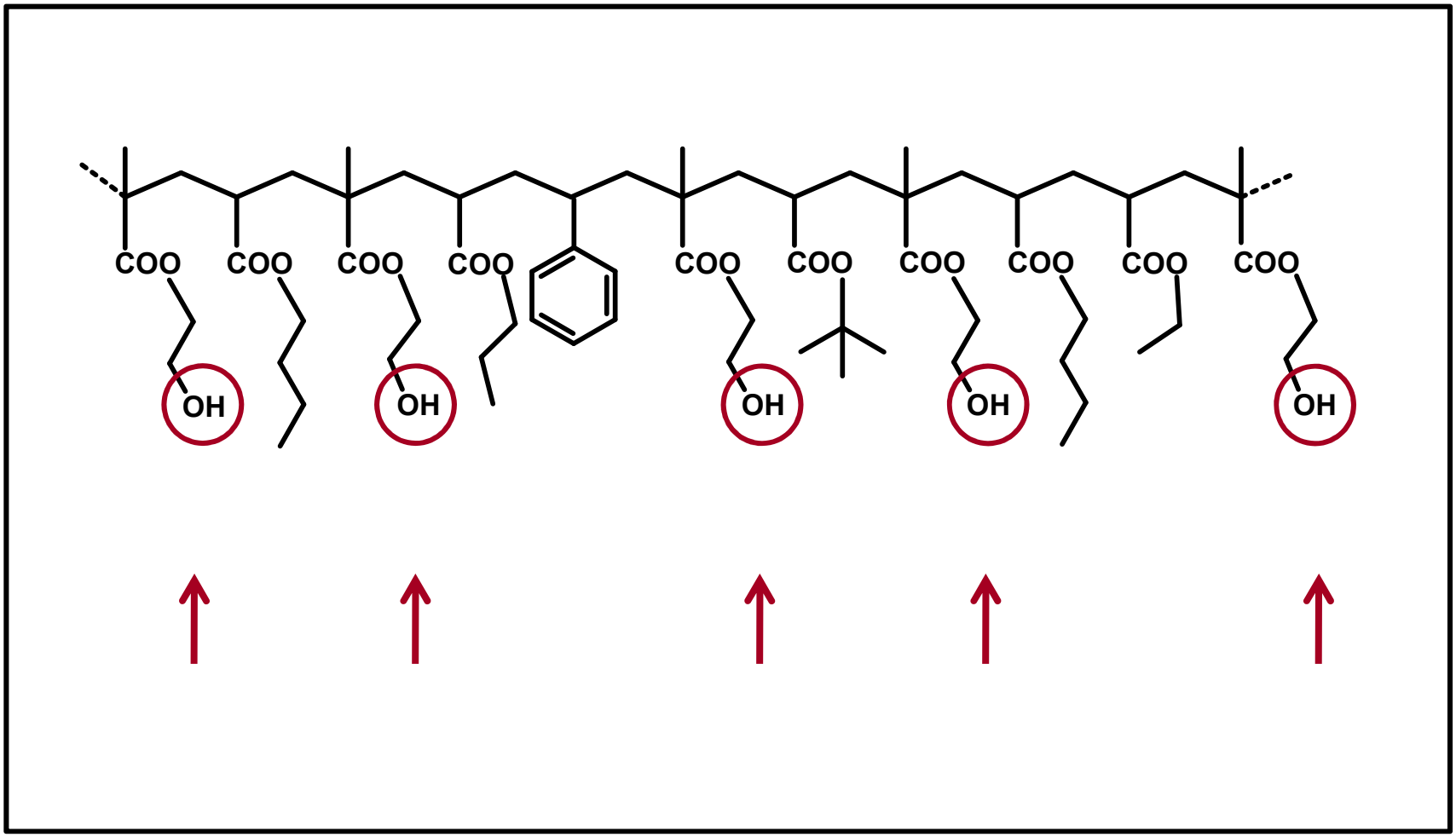
Polymeric Network Types in Automotive Coatings.

Srcatch-Resistant Coating, Impact Resistant Structure:



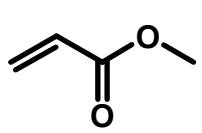
Highly Elastic Clear Coats for the OEM Automotive Sector

Clear Coat, Soluble OH-Functional Polyacrylate-Resin:

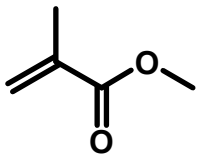


Rainer Buerstinghaus

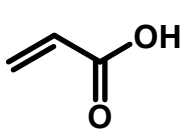
Polyacrylate-Building Blocks for Coating Resin Syntheses:



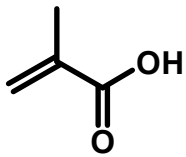
MA



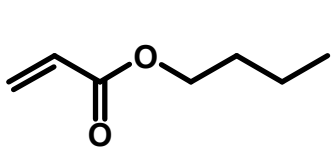
MMA



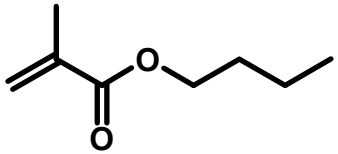
AA



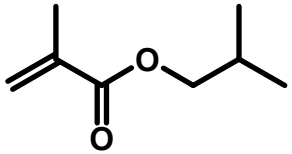
MAA



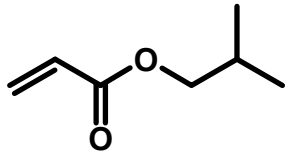
BA



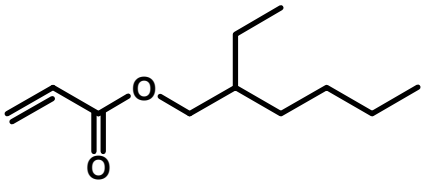
BMA



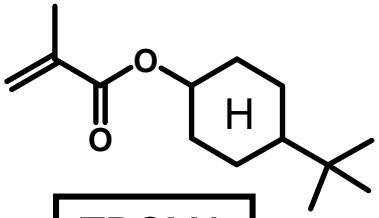
IBMA



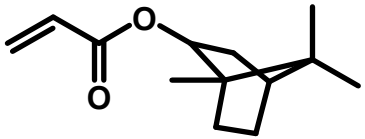
IBA



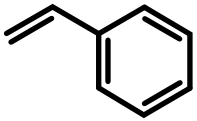
EHA



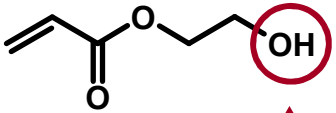
TBCMA



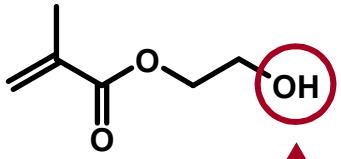
TMNA



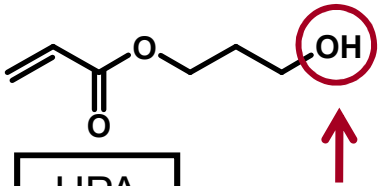
Styrene



HEA



HEMA



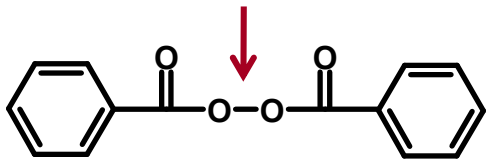
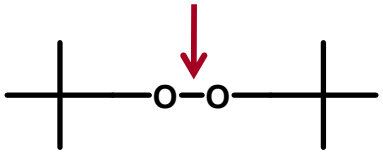
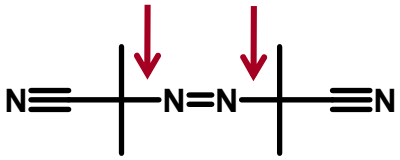
HPA

Rainer Buerstinghaus

Highly Elastic Clear Coats for the OEM Automotive Sector

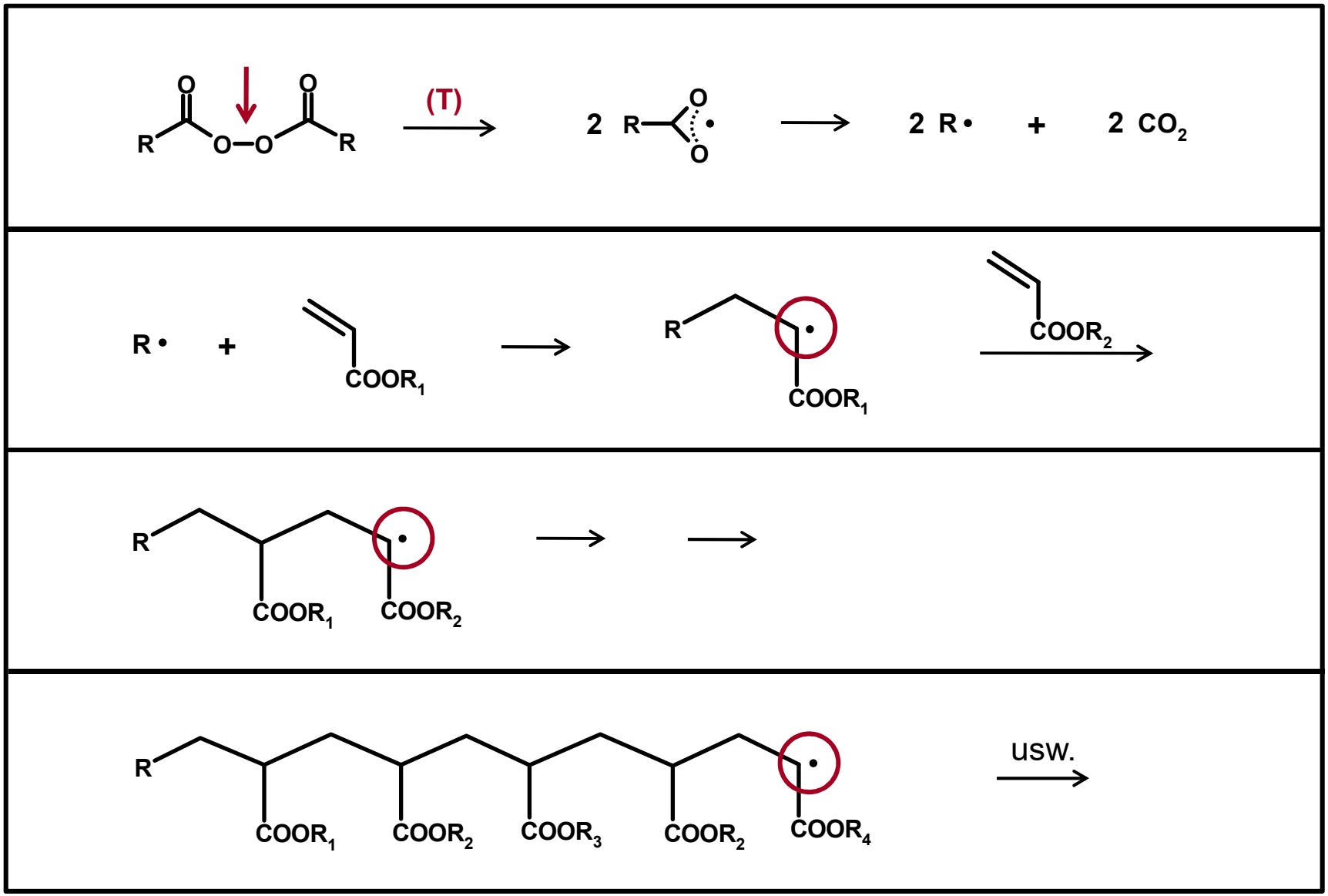
Radical-Forming Initiators for Syntheses of Polyacrylates.

Thermolabile Organic Peroxides and Azocompounds:

	Dibenzoylperoxide
	Di-tert.-Butylperoxide
	Azobisisobutyronitrile

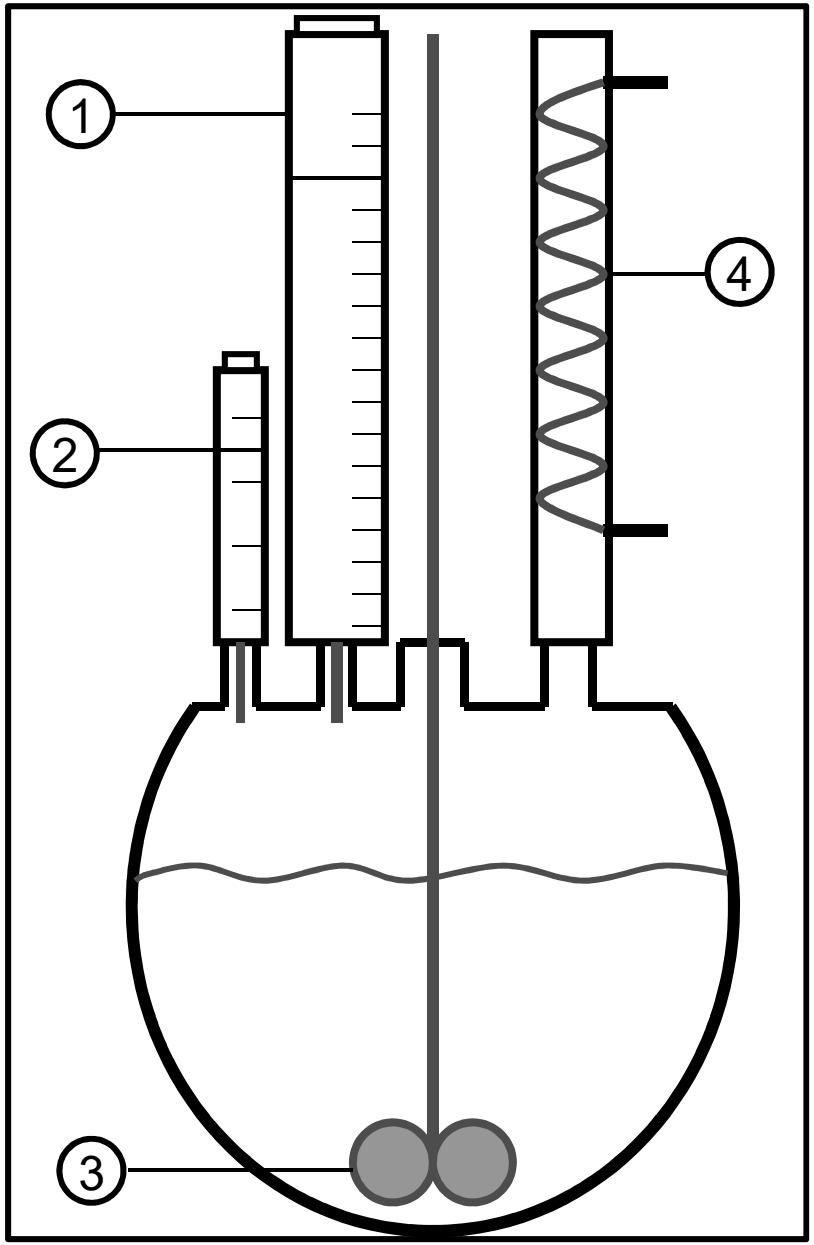
Rainer Buerstinghaus

Mechanism of the Radical Acrylate-Polymerization:



Rainer Buerstinghaus

Polyacrylate Resin, Lab.-Synthesis, Work Prescription:



1. Monomer Feed
2. Initiator Feed
3. Stirrer
4. Reflux Condenser

Three-necked flask, Solvent: Shellsol

Solution of the initiator is added drop by drop at 142ºC within 4,75h.

In Parallel: The mixture of monomers is added within 4,00h at 142ºC.

This all should react 3,00h at 142ºC.

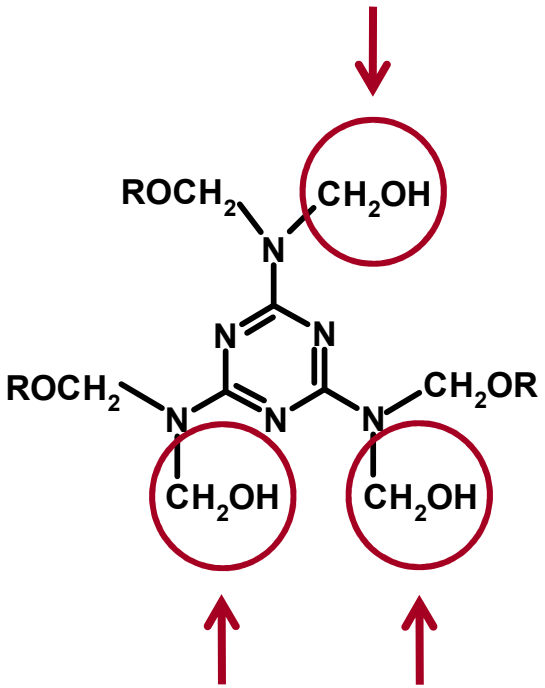
Dilute with suitable solvent mixture.

Rainer Buerstinghaus

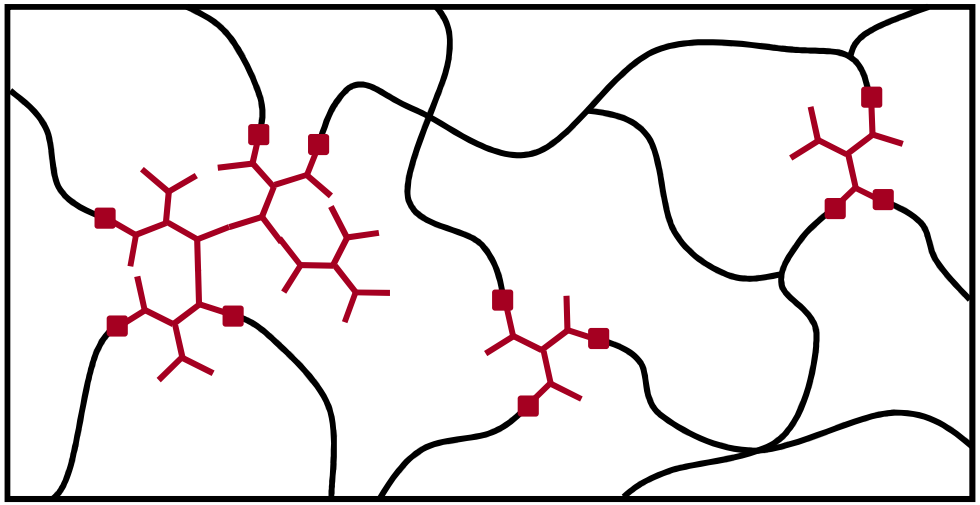
Highly Elastic Clear Coats for the OEM Automotive Sector

One-Component (1K) Clear Coat;

⟶ Polyacrylatol + Melamine Formaldehyde Resin:



(R = H, CH_3, n-C_4H_9)



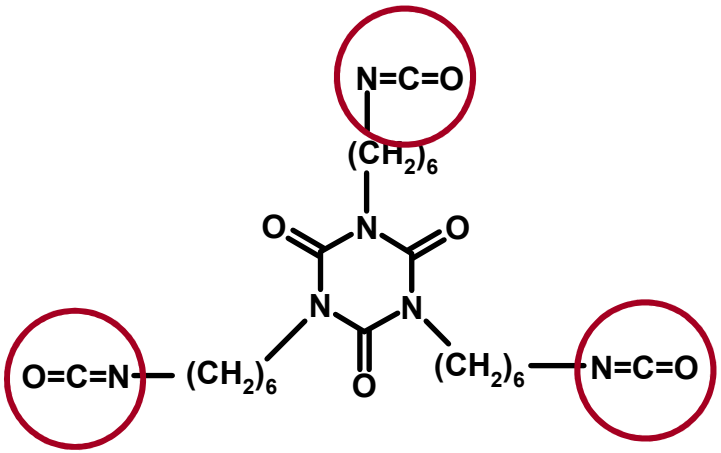
Relatively inhomogeneous network.

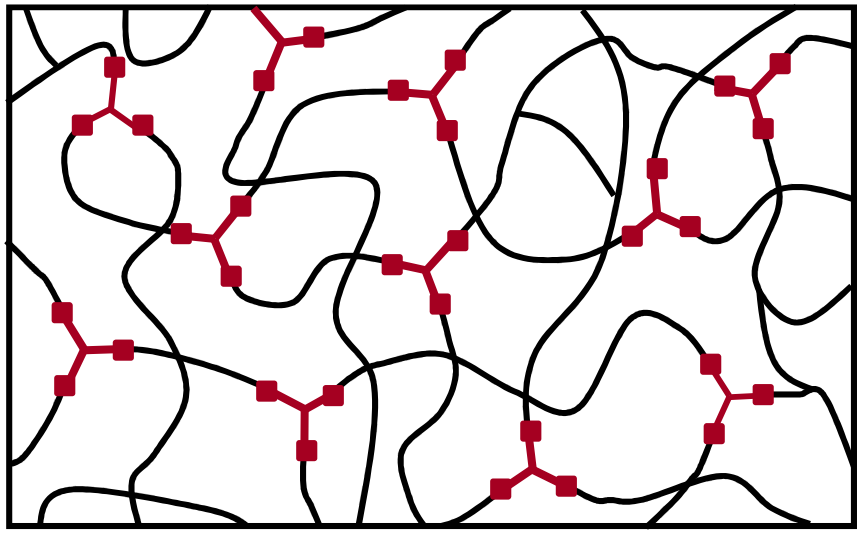
Rainer Buerstinghaus

Highly Elastic Clear Coats for the OEM Automotive Sector

Two-Component (2K) Clear Coat;

⟶ Polyacrylatol + Trimeric Diisocyanate (HDI):



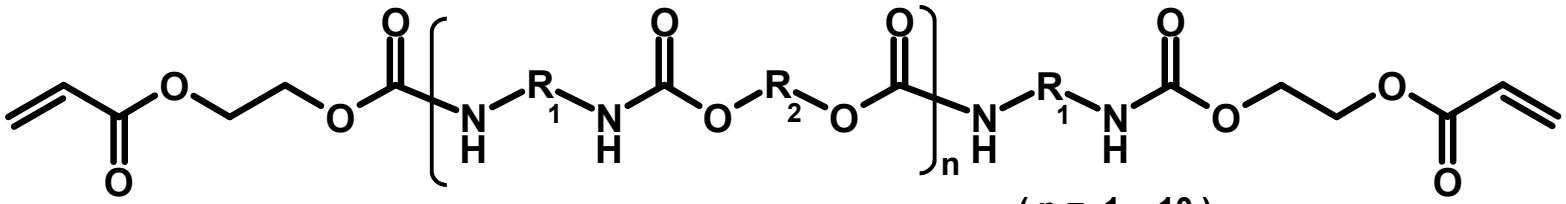


Relatively "homogeneous" network.

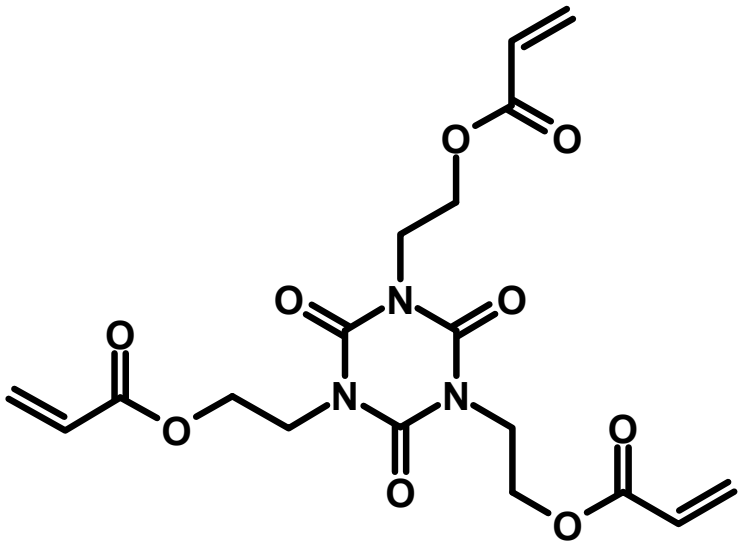
Rainer Buerstinghaus

Highly Elastic Clear Coats for the OEM Automotive Sector

UV-Curable Polyurethane Acrylate, UV-Reactive Diluent:

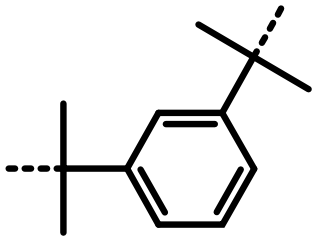


(n = 1 – 10)



Tris-(2-hydroxiethyl)isocyanurate-triacrylate

R_1 =

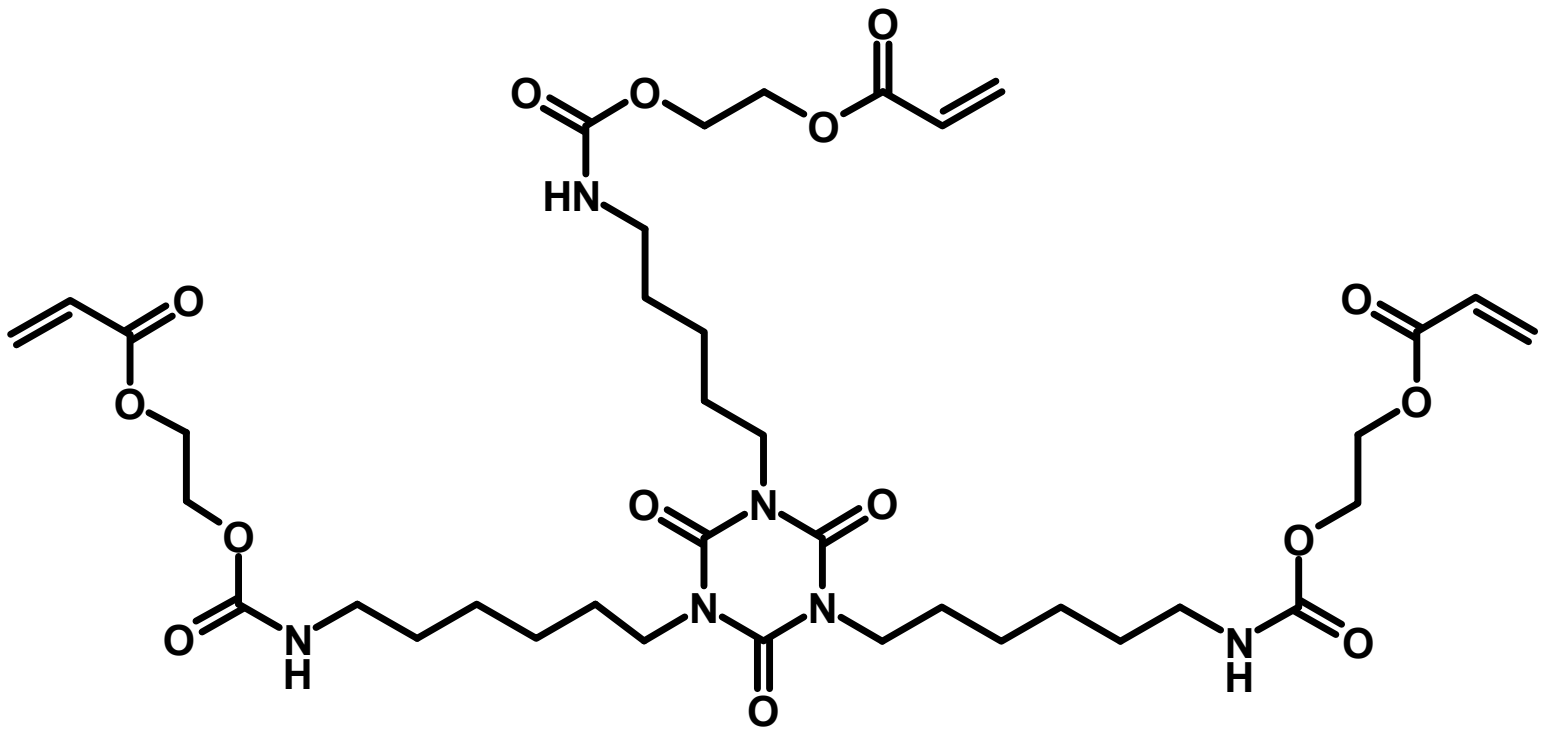


R_2 =

Rainer Buerstinghaus

Highly Elastic Clear Coats for the OEM Automotive Sector

UV-Reactive Diluent (OEM), Analogous to HDI-Trimer:

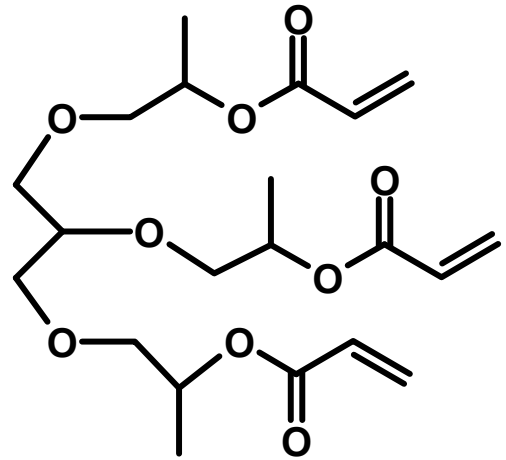


Adduct of HDI-trimer and 2-hydroxyethyl acrylate.

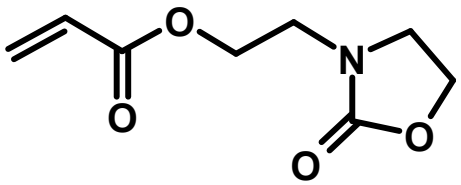
Rainer Buerstinghaus

Highly Elastic Clear Coats for the OEM Automotive Sector

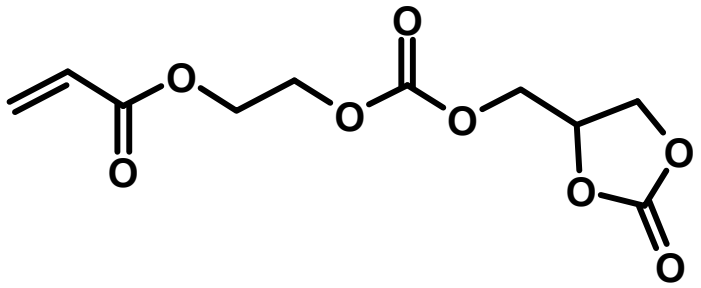
Further UV-Reactive Diluents for Clear Coats (OEM):



Propoxylated Glycerinetriacrylate.



Acrylic acid-modified oxazolidone.

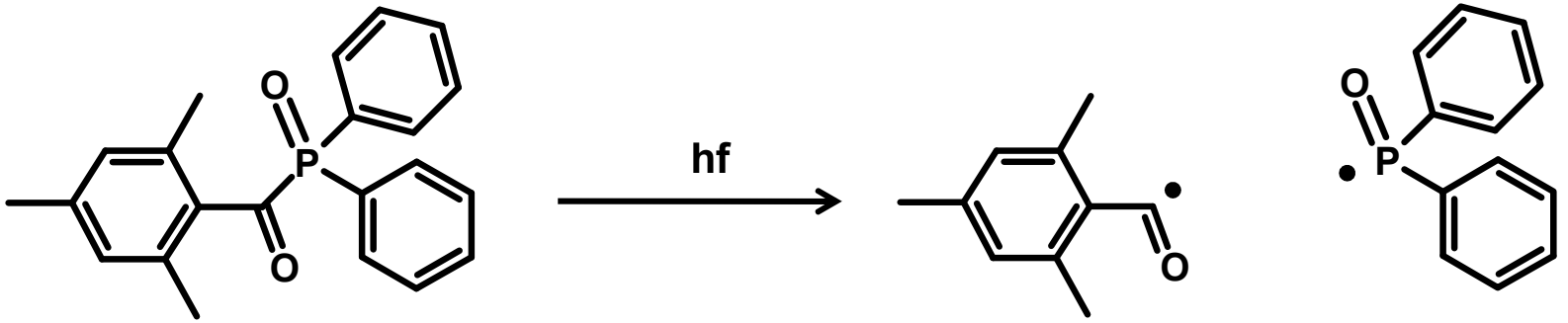


Acrylic acid-modified carbonic acid ester.

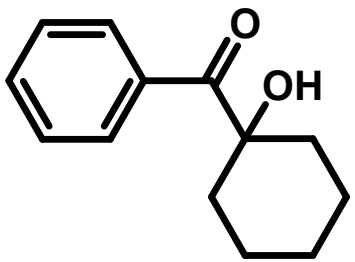
Rainer Buerstinghaus

Highly Elastic Clear Coats for the OEM Automotive Sector

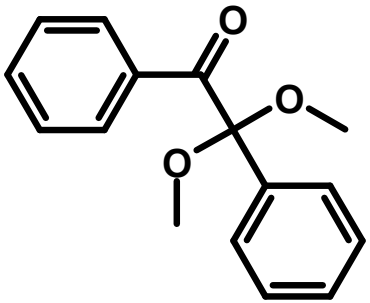
Photoinitiators for the Activation of UV Curing:



Trimethylbenzoyl-phosphinoxide (TPO)



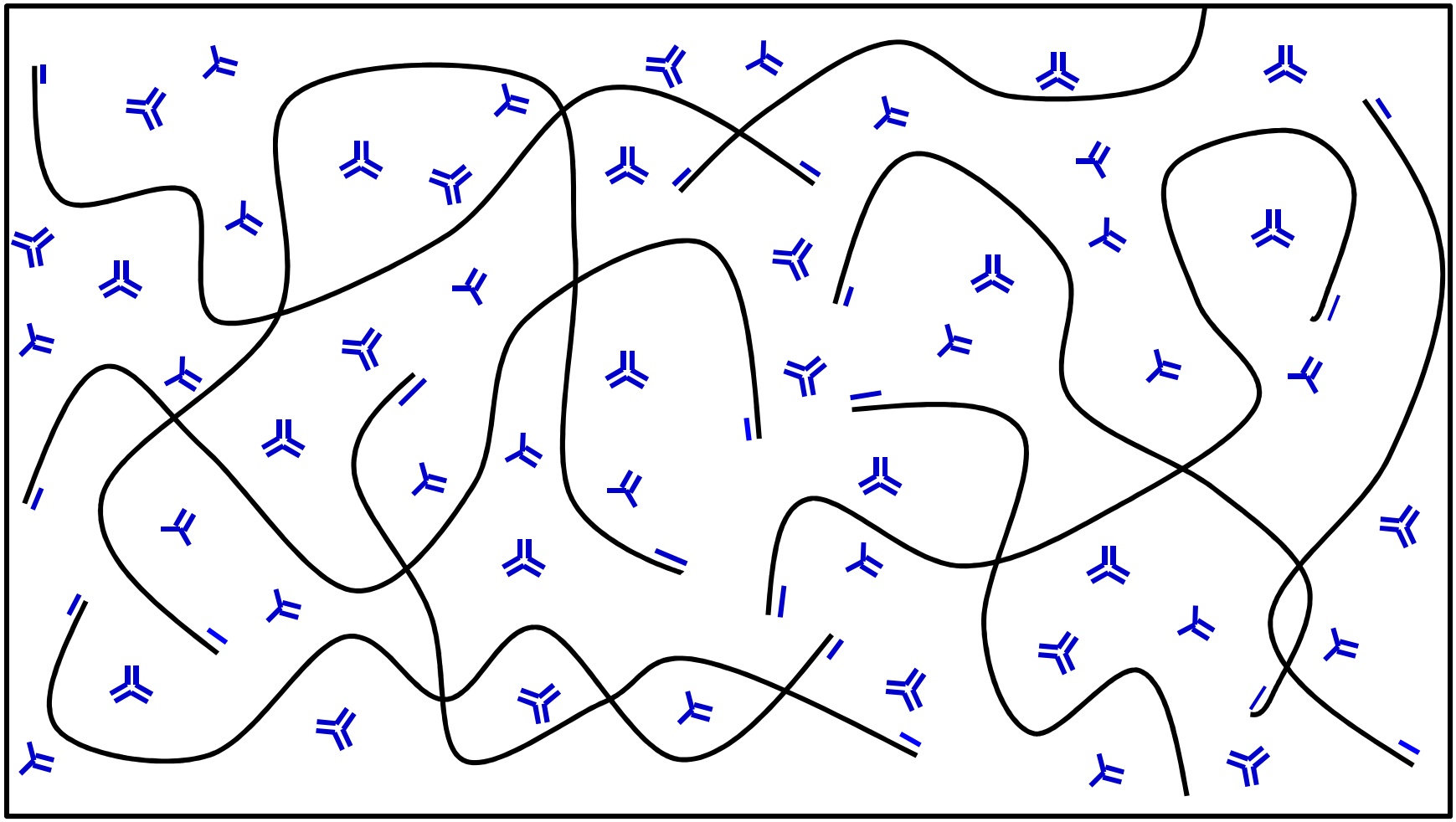
1-Hydroxy-Cyclohexylphenylketone



Benzildimethylketale

Highly Elastic Clear Coats for the OEM Automotive Sector

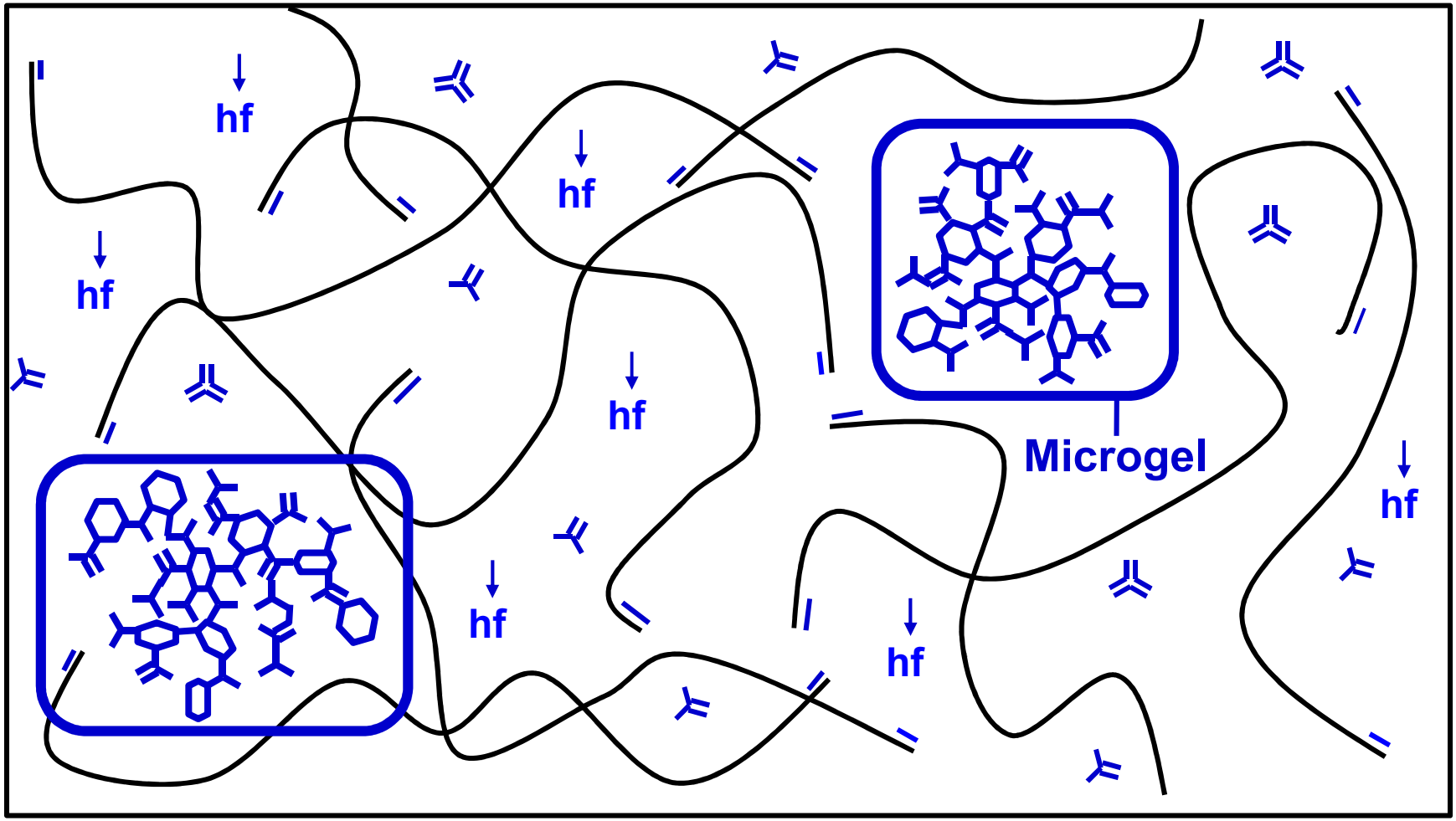
Liquid Coating, PUR-Acrylate + Reactive Diluents (/):



Rainer Buerstinghaus

Highly Elastic Clear Coats for the OEM Automotive Sector

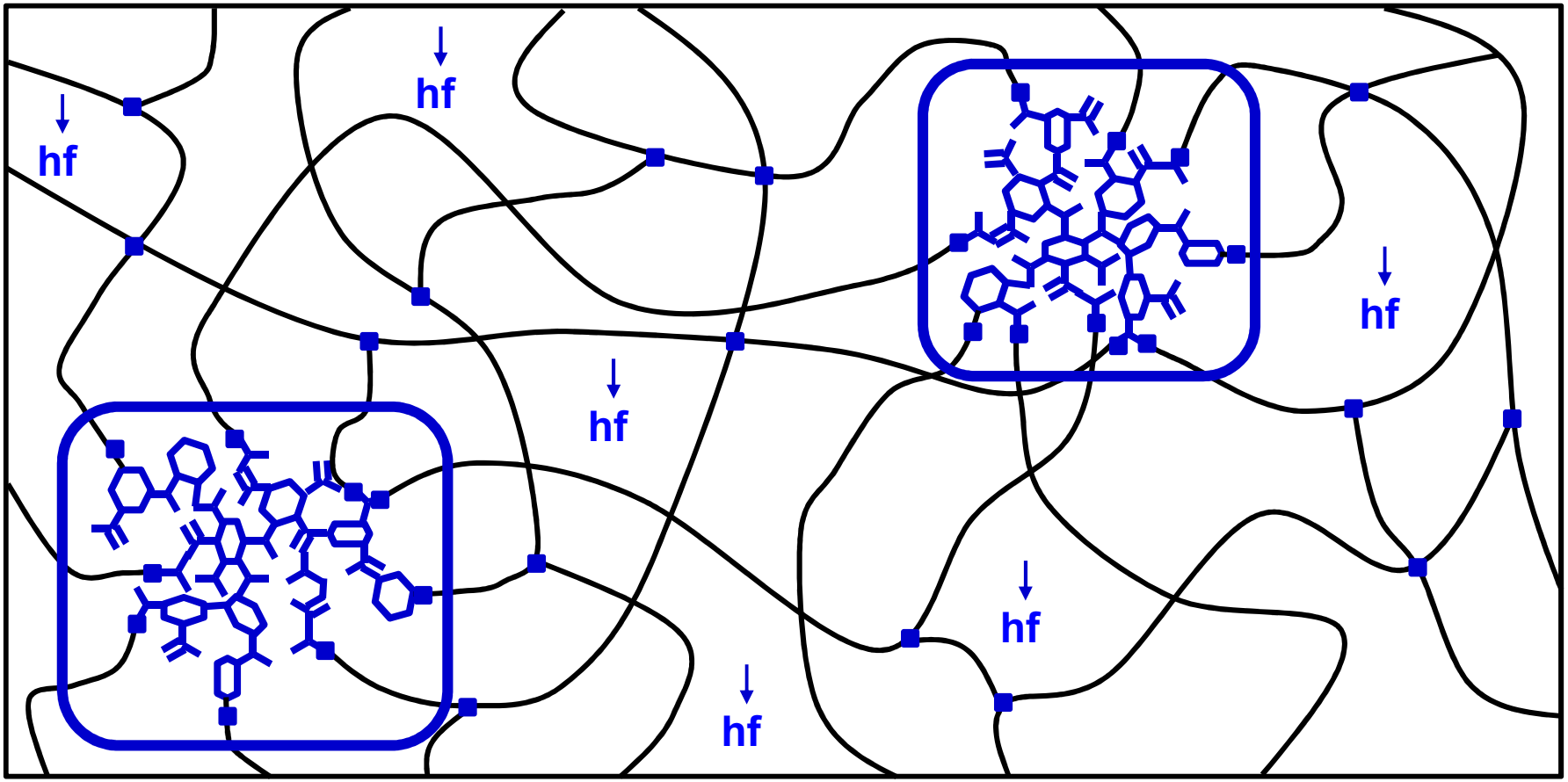
Partial Curing, Polyurethane-Acrylate + Reactive Diluents:



Rainer Buerstinghaus

Highly Elastic Clear Coats for the OEM Automotive Sector

Curing of the UV Varnish by Complete Crosslinking;
Compact Domains With Relatively High Crosslink Density:



Rainer Buerstinghaus

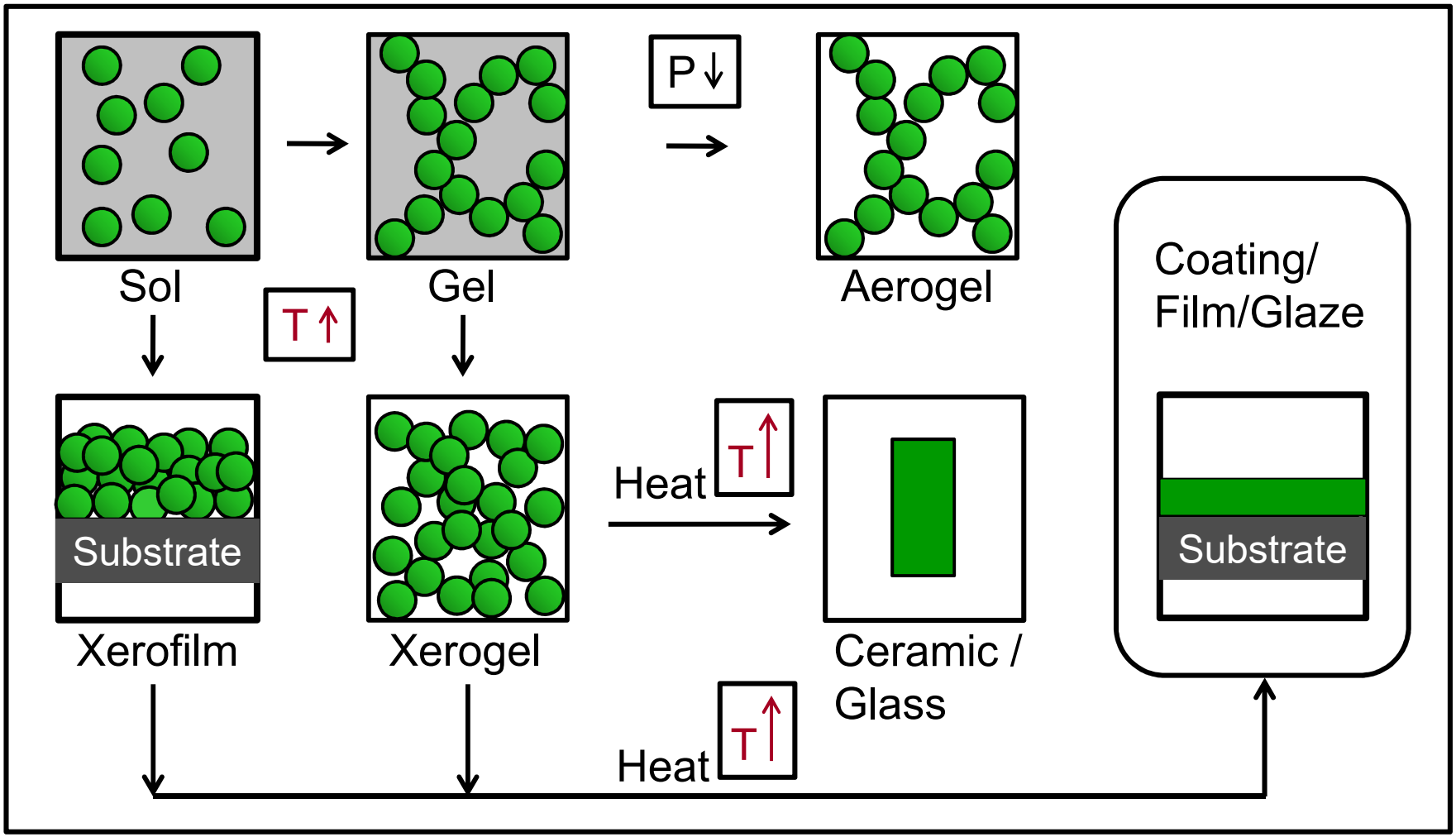
Highly Elastic Clear Coats for the OEM Automotive Sector

Disadvantages in the Application of UV-Curable Coatings:

- The coating of three-dimensional surfaces requires special robot-controlled lighting installations.
- Unwanted emission of the reactive diluent by infrared portions from the Hg-high-pressure lamp. Cumbersome fume cupboard systems on the paint line.
- Intense cooling of the UV lamps required during continuous operation, because of their heating.
- Oxygen-induced inhibition of radical chain reactions prevent complete curing of the paint film.

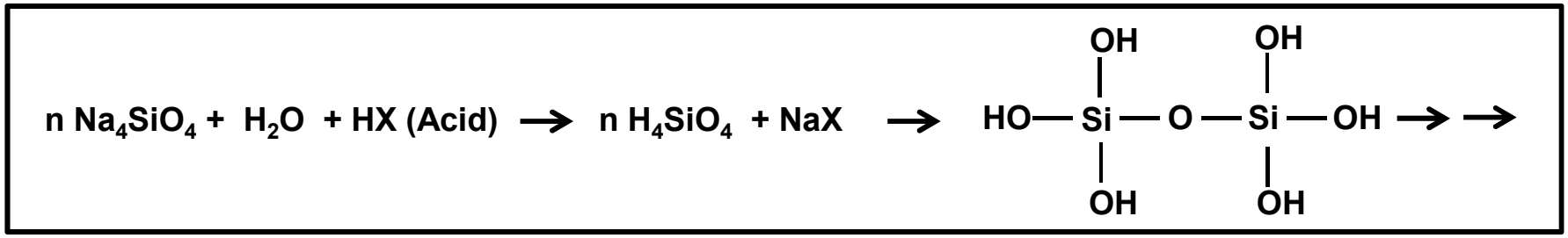
Highly Elastic Clear Coats for the OEM Automotive Sector

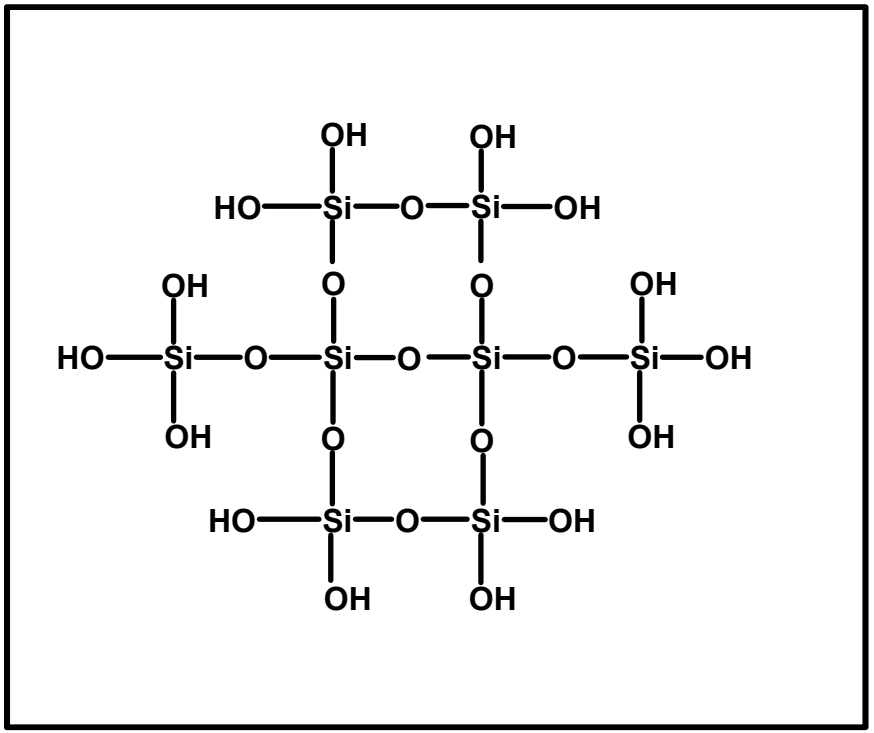
Sol-Gel Technique for the Production of Ceramics and Coatings; Principle and Technical Variants:

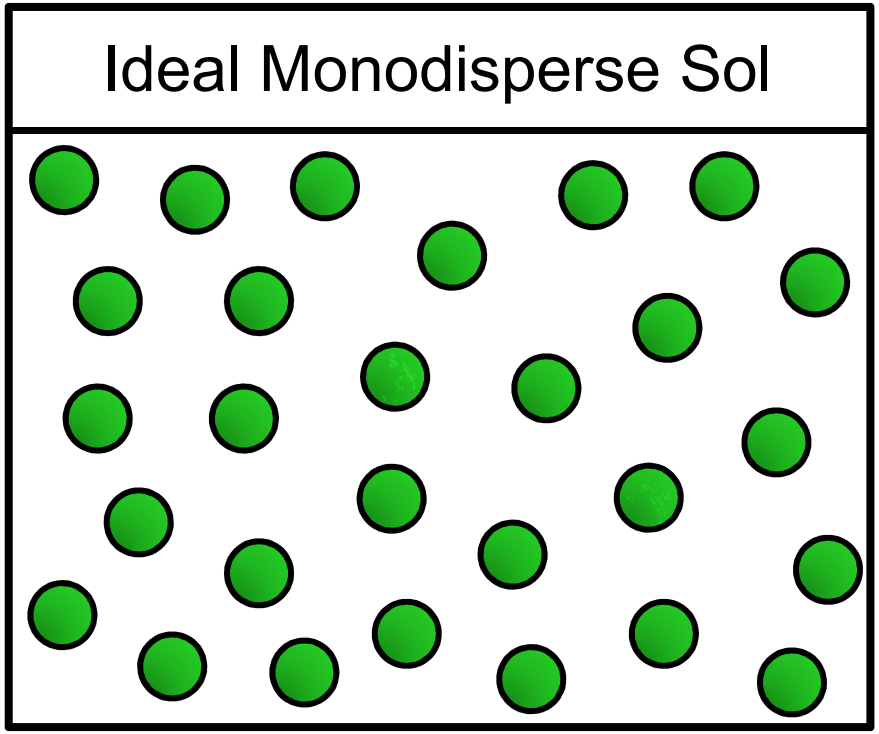


Highly Elastic Clear Coats for the OEM Automotive Sector

Glaze, Formation of Silica-Sol, Growth of the Particles:



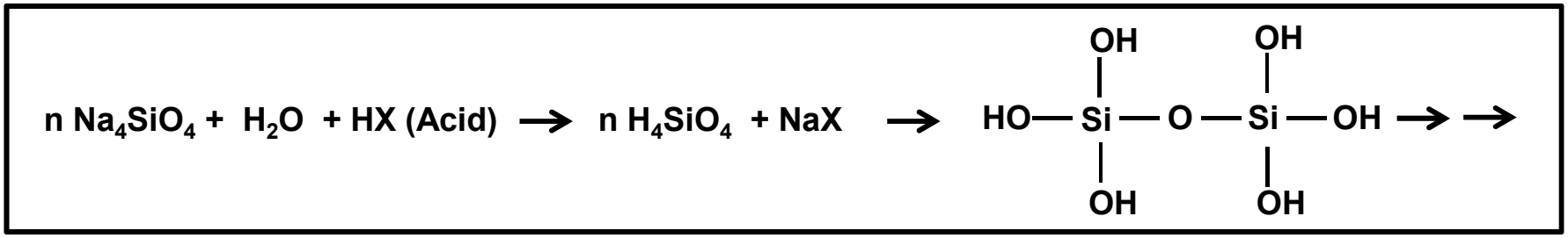


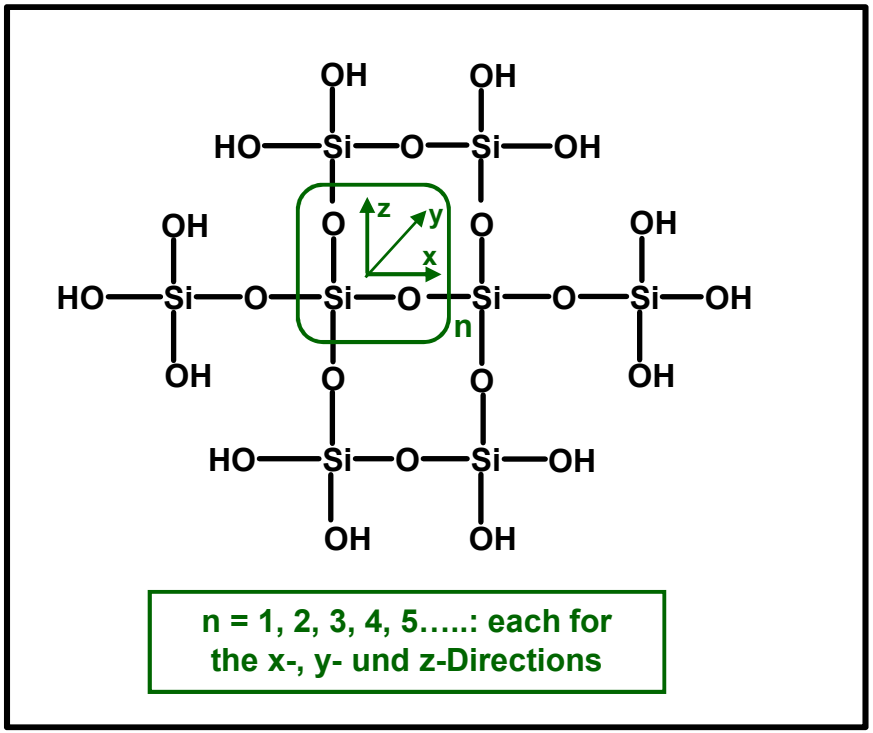


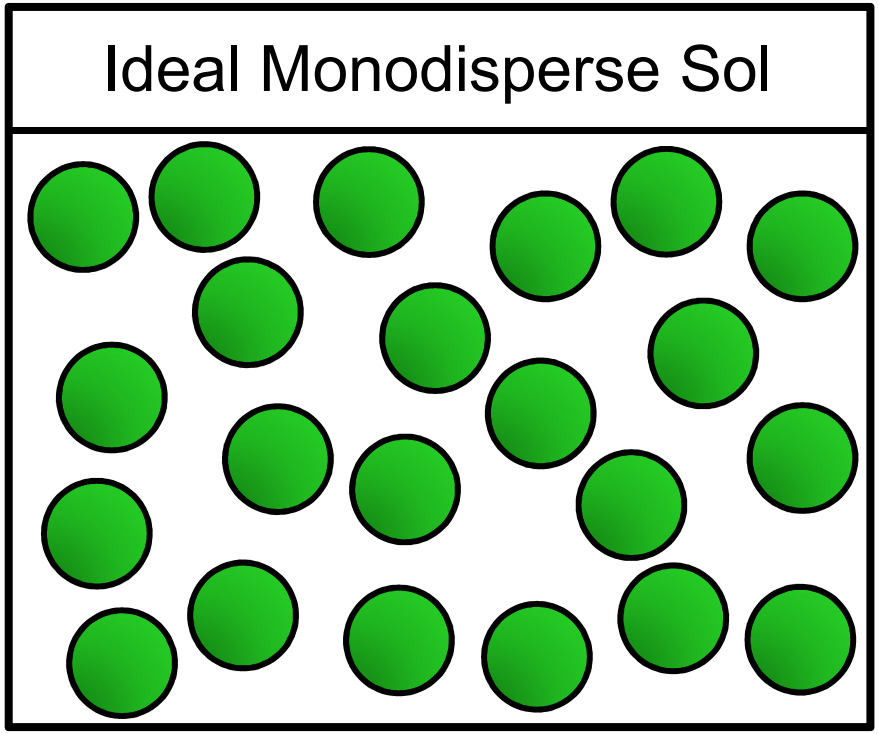
Rainer Buerstinghaus

Highly Elastic Clear Coats for the OEM Automotive Sector

Glaze, Formation of Silica-Sol, Growth of the Particles:



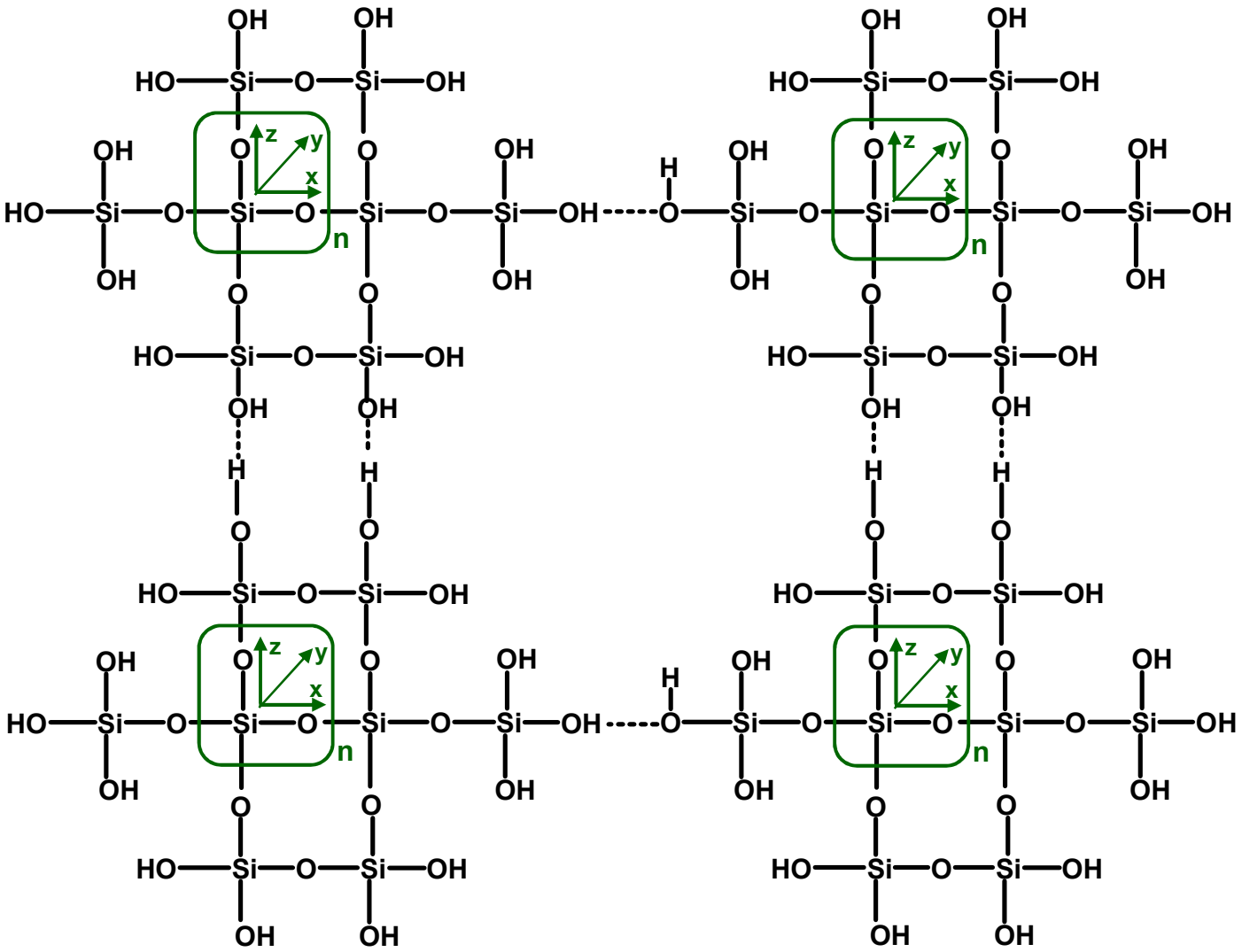




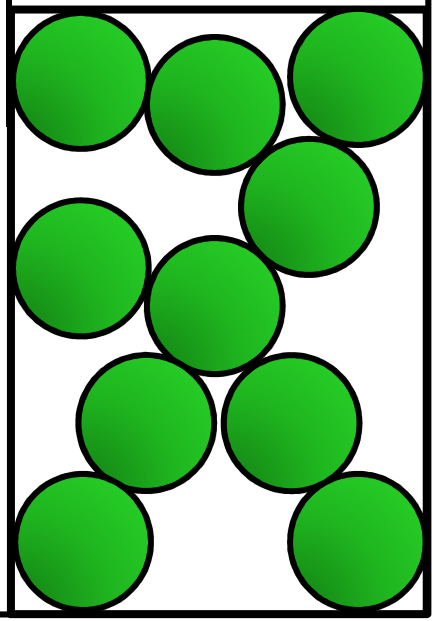
Rainer Buerstinghaus

Highly Elastic Clear Coats for the OEM Automotive Sector

Glaze, Formation of Silica-Gel by Hydrogen Bonds:



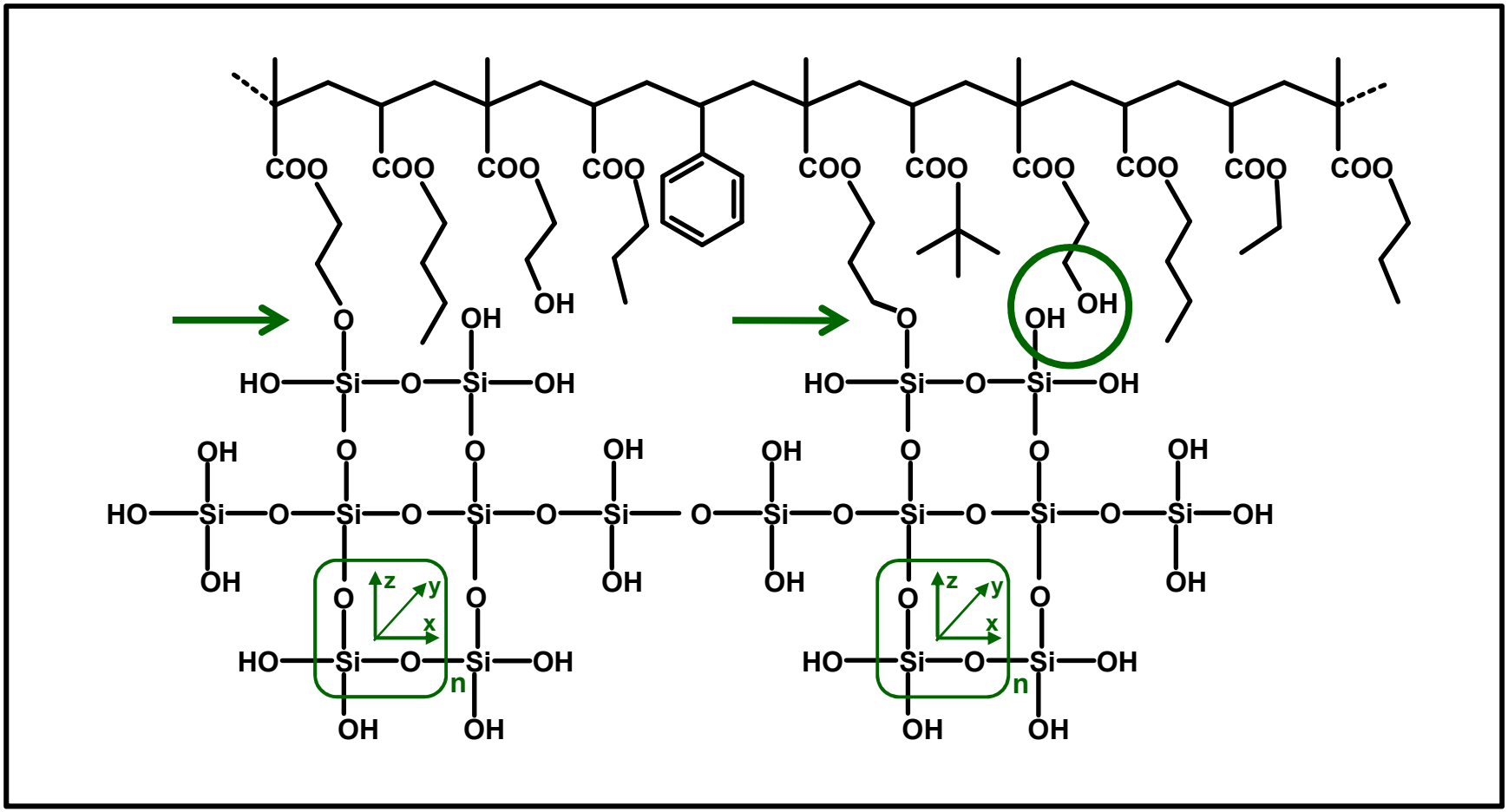
Silica-Gel



Rainer Buerstinghaus

Highly Elastic Clear Coats for the OEM Automotive Sector

"Organic Modified Ceramics" ; Sol-Gel-Process: Gelation before the Desired Formation of the Xerofilms.

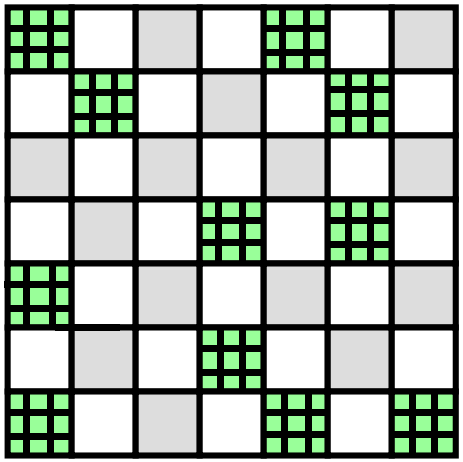


Highly Elastic Clear Coats for the OEM Automotive Sector

Cured Coating Film After the Addition of "Silica Sol", Nanometer Domains with Very High Network Density (⟶ Structural Scheme):

"Hard", SiO_2−crosslinked structural elements (≈10 nm)

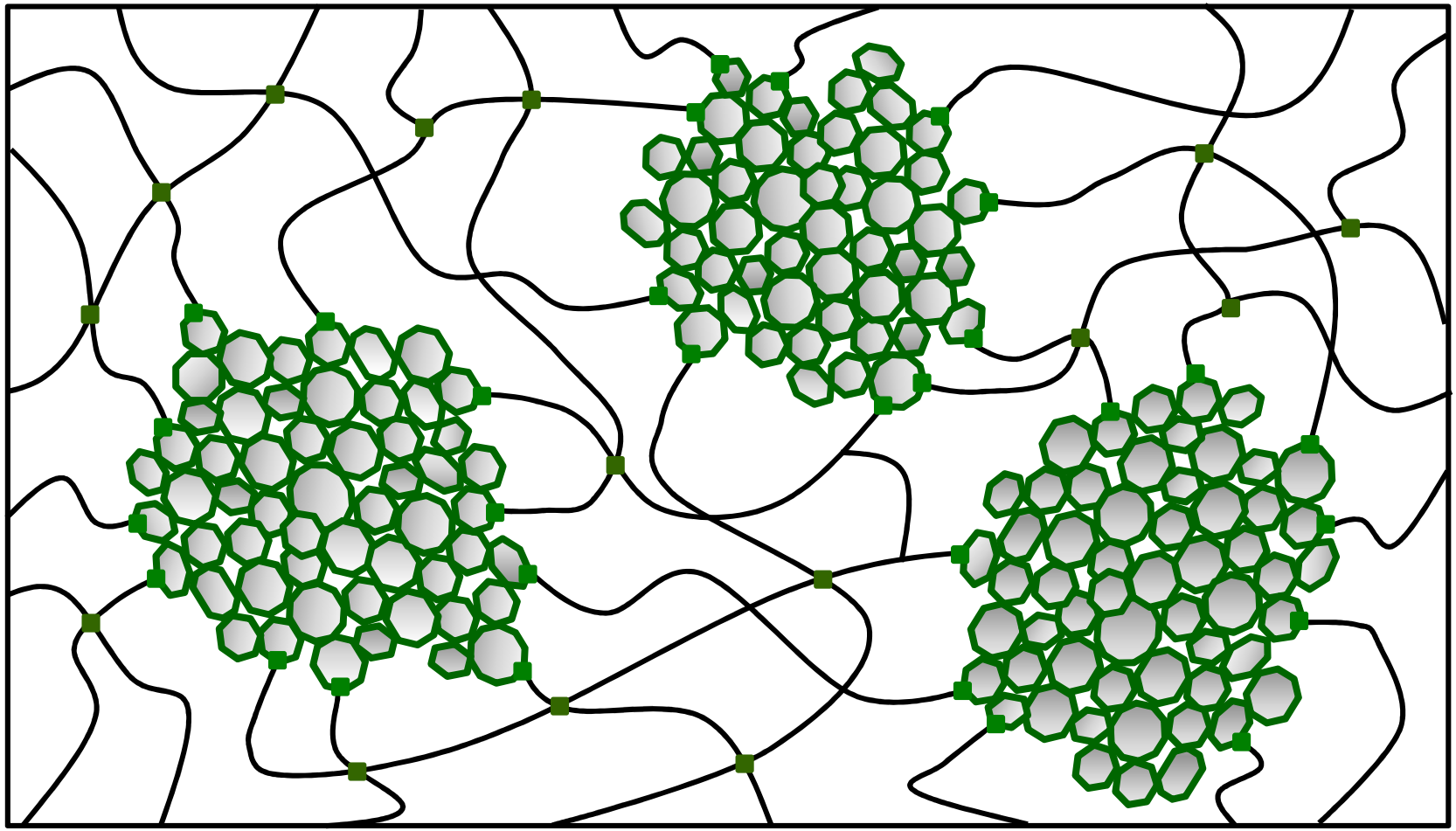
"Soft", less strong crosslinked structural elements



Rainer Buerstinghaus

Highly Elastic Clear Coats for the OEM Automotive Sector

Cured Coating Film After Addition of "Silica Sol", Nanometer Domains with Very High Network Density:



Rainer Buerstinghaus

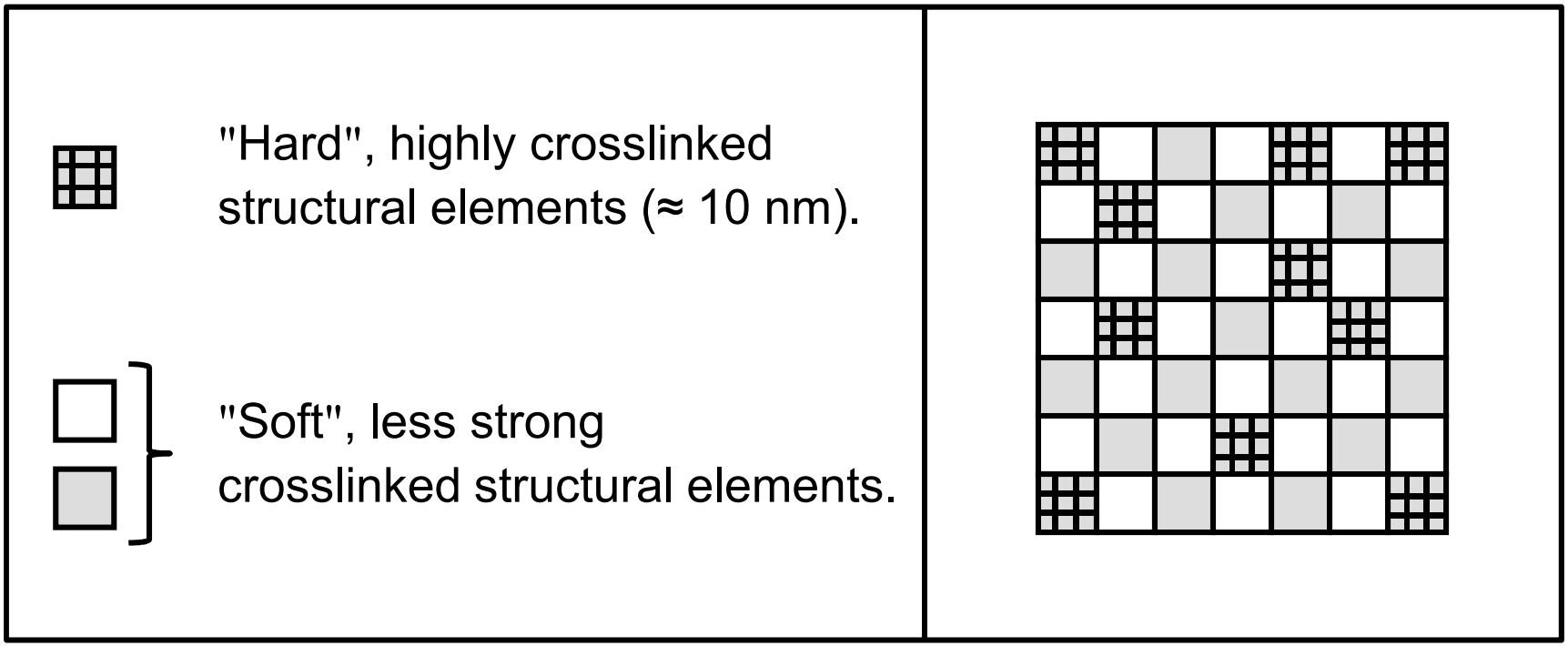
Highly Elastic Clear Coats for the OEM Automotive Sector

Limitations of Sol-Gel-Applications for Automobiles:

- Sol-gel-varnishes must be stored refrigerated.
- Lifetime <6 months.
- Mostly, solvent-based paint formulations are used.
- Critical application conditions regarding particular parameters like humidity and temperature.
- The compatibility of the silicate network with the organic polymer is not always given.

Highly Elastic Clear Coats for the OEM Automotive Sector

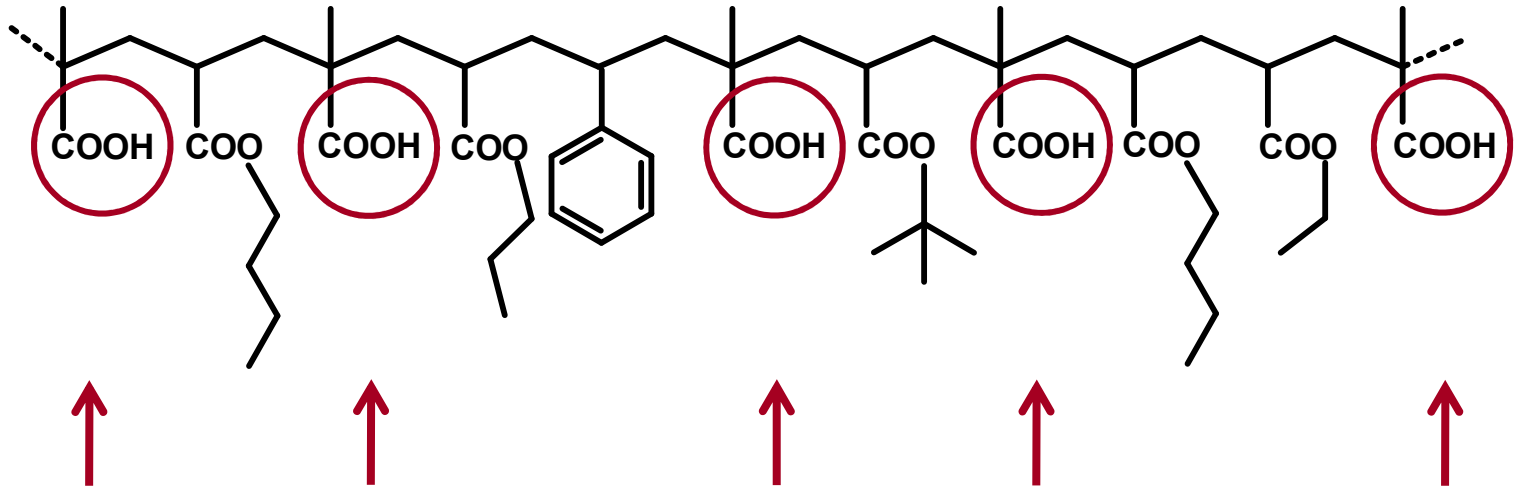
Alternative to Glaze: Polyacrylates with High OH-Number, or High COOH-Number, Crosslinked with Dendrimeric or Highly Branched Oligomers (⟶ Structural Scheme):



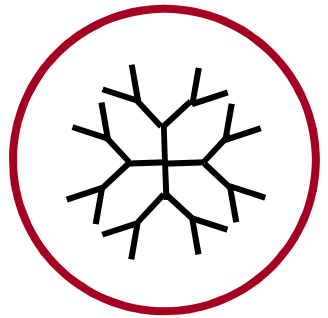
Rainer Buerstinghaus

Highly Elastic Clear Coats for the OEM Automotive Sector

COOH-Functional Polyacrylate with High Acid Number:



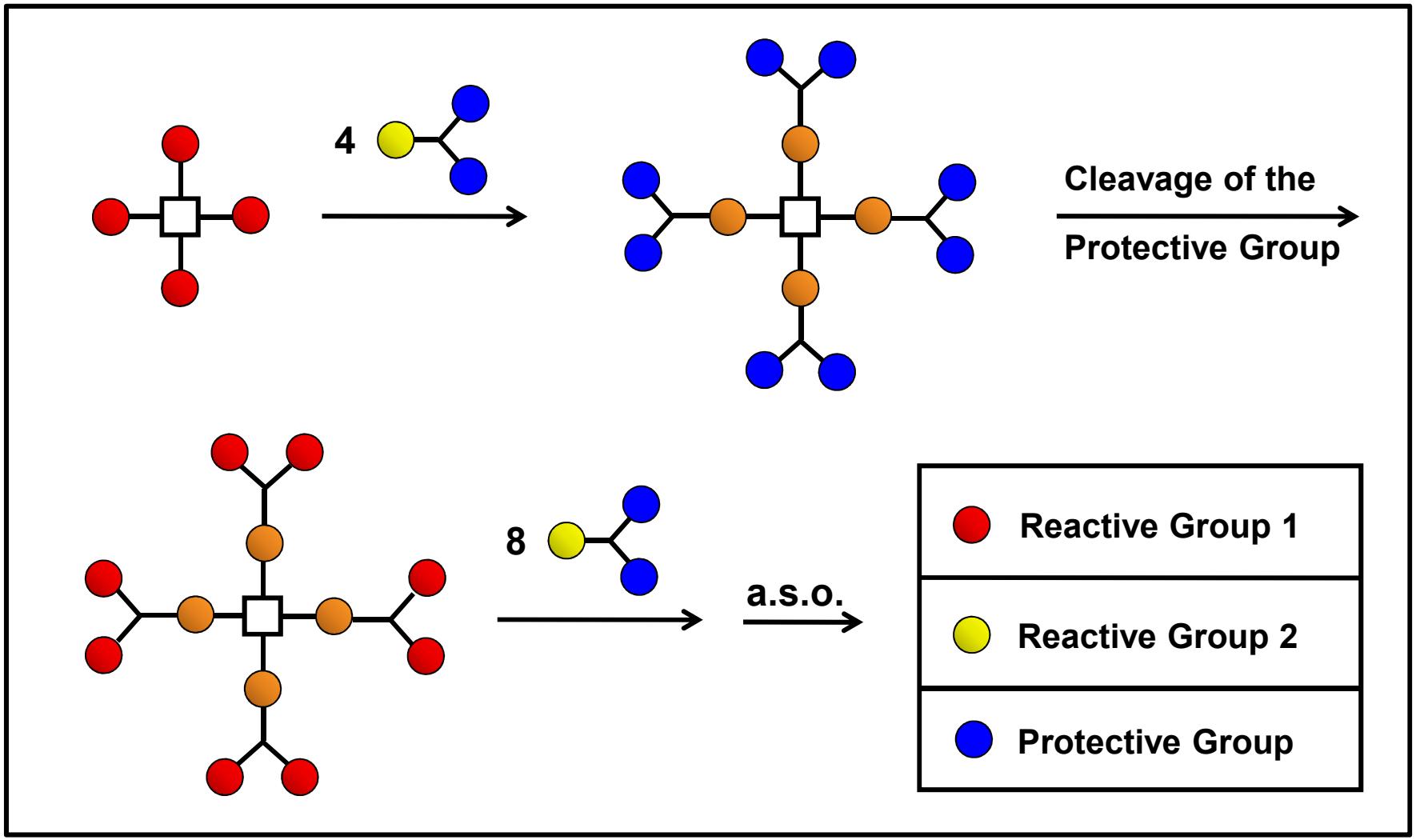
OH-functional, dendrimeric crosslinker:



Rainer Buerstinghaus

Highly Elastic Clear Coats for the OEM Automotive Sector

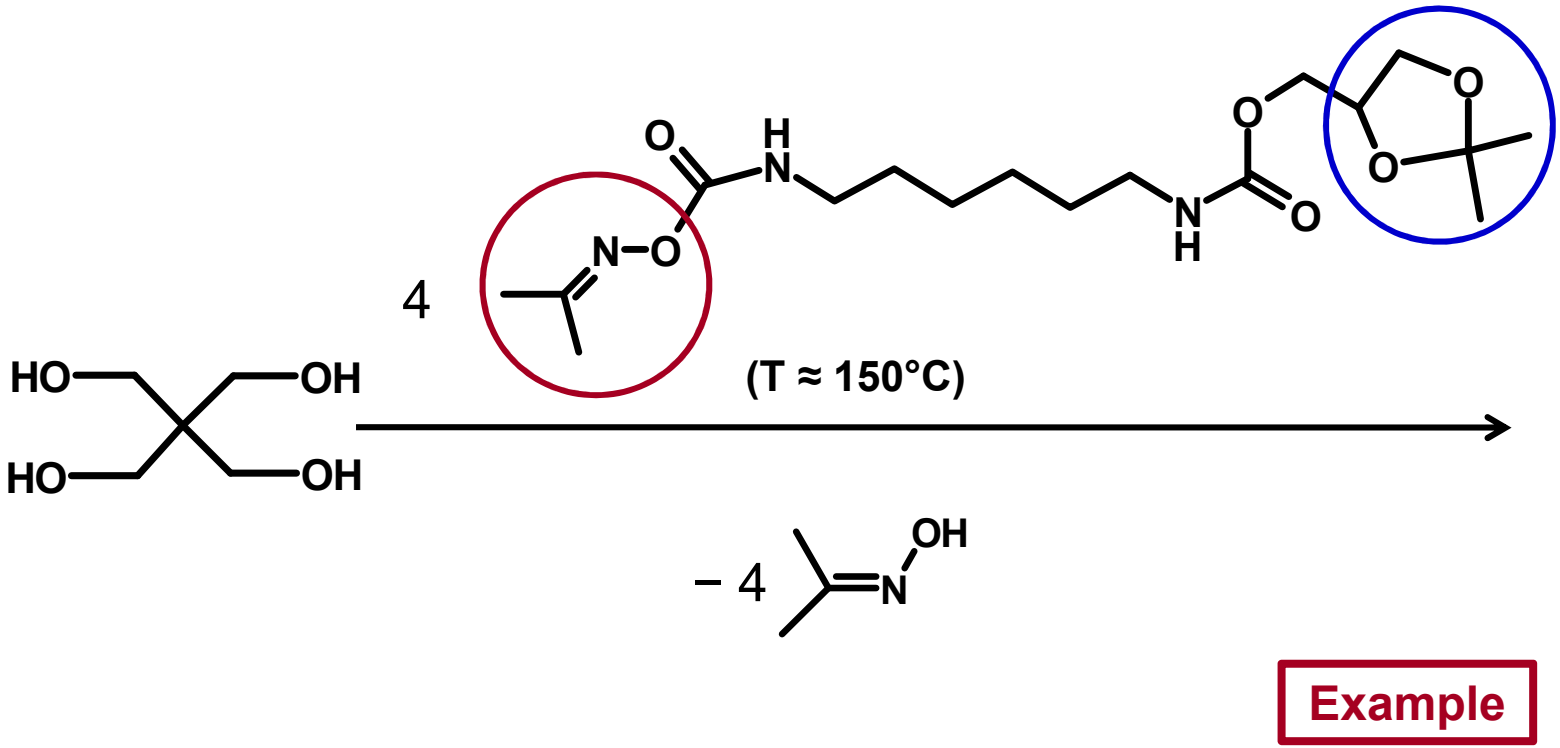
"Dendrimeric" Crosslinker, Divergent Multistep-Access:



Rainer Buerstinghaus

Highly Elastic Clear Coats for the OEM Automotive Sector

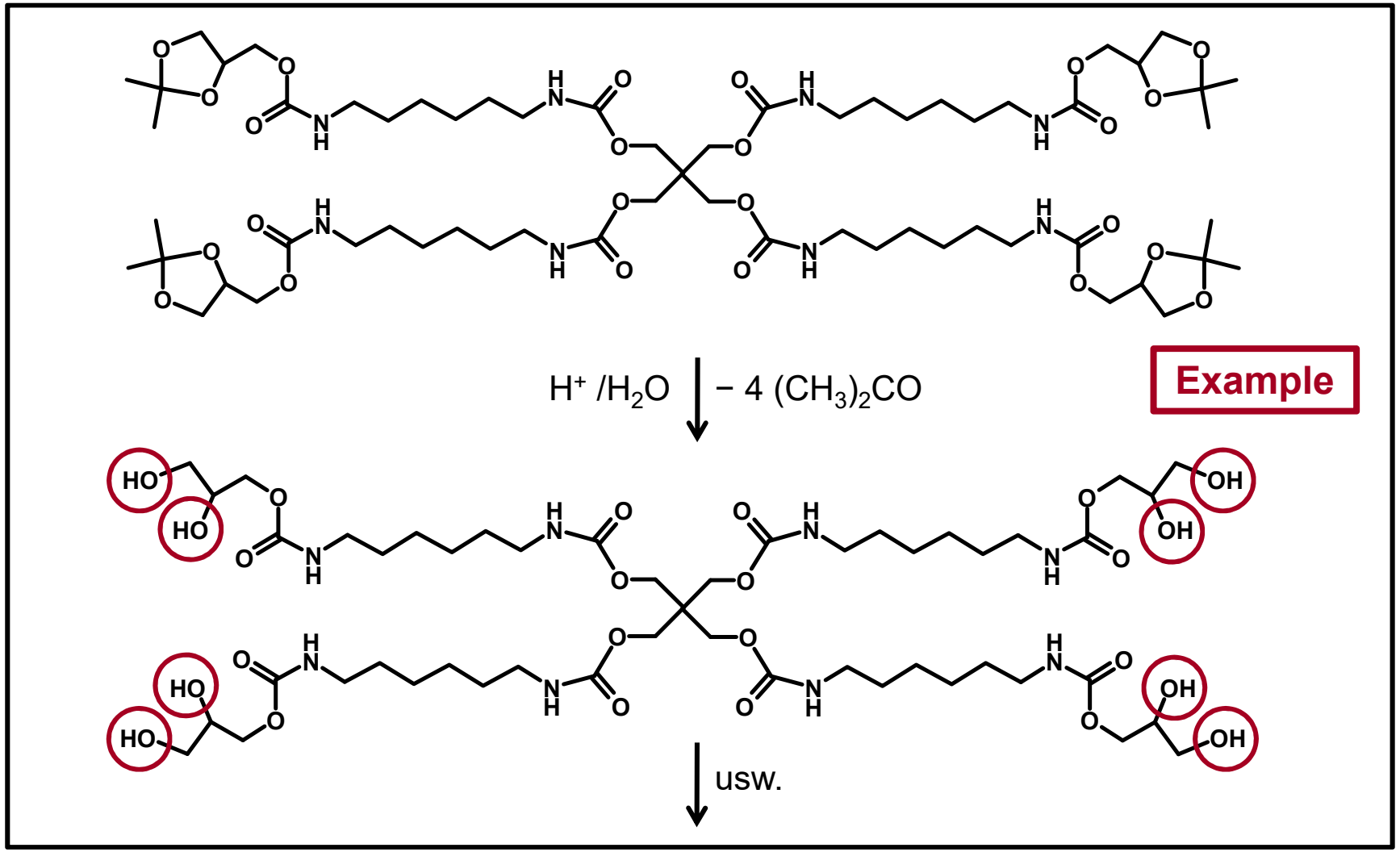
Divergent Synthesis of a Crosslinker-Oligool:



Rainer Buerstinghaus

Highly Elastic Clear Coats for the OEM Automotive Sector

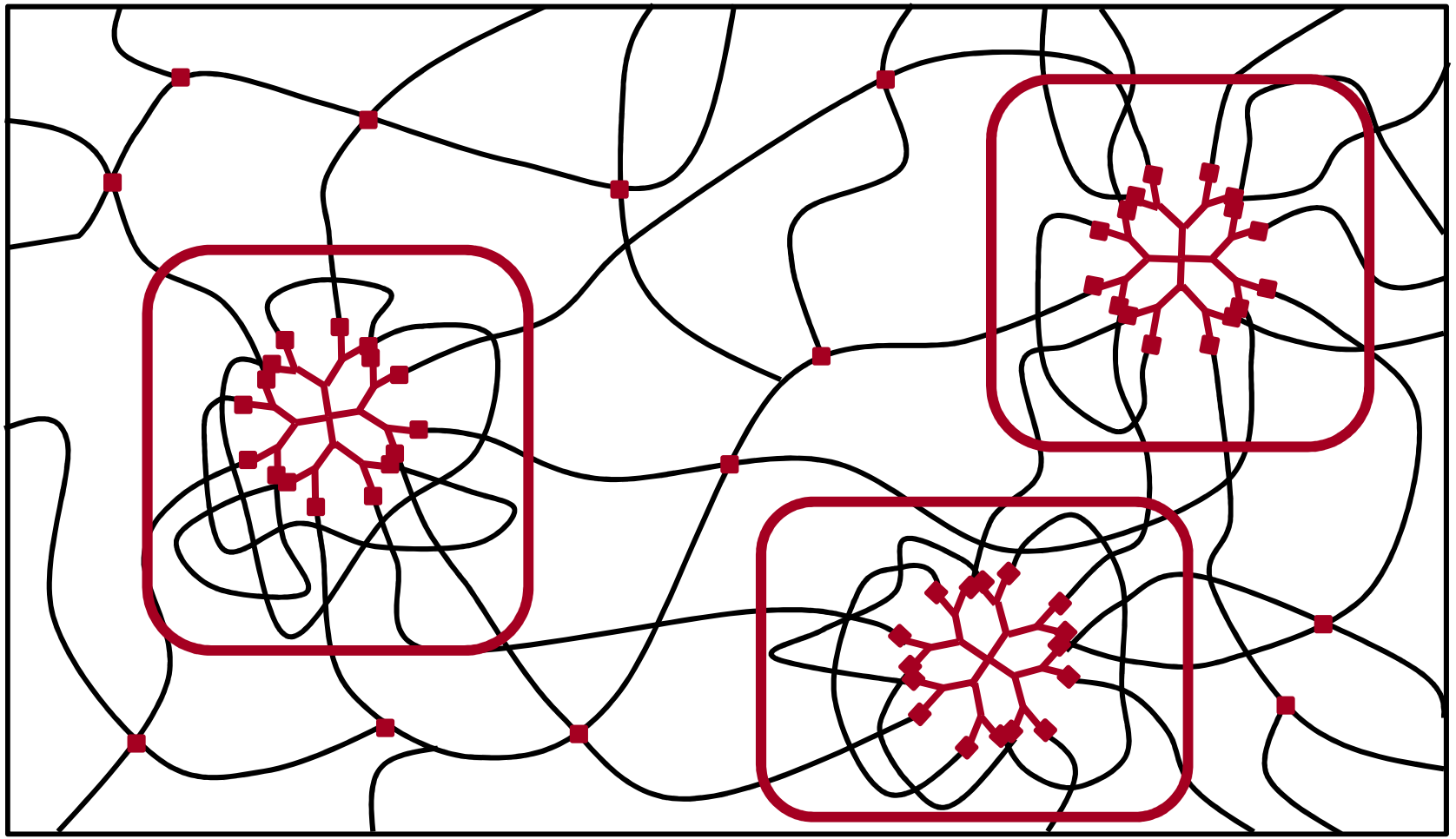
Divergent Synthesis of a Crosslinker-Oligool:



Rainer Buerstinghaus

Highly Elastic Clear Coats for the OEM Automotive Sector

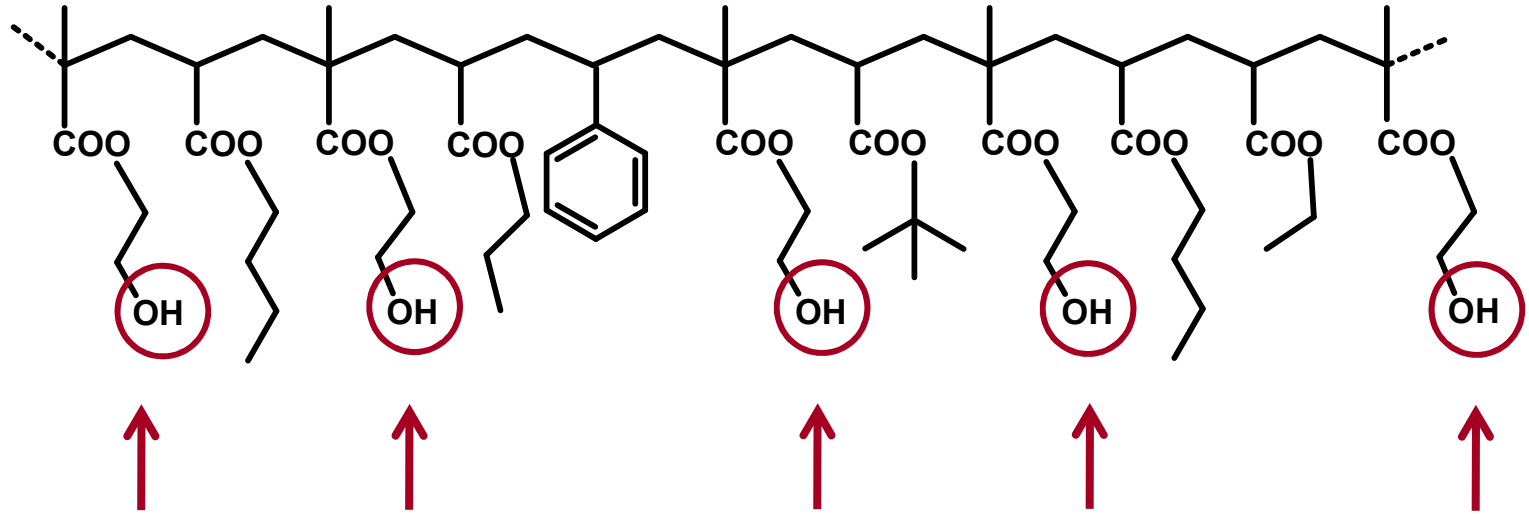
Cured Coating Film with a "Dendrimeric Crosslinker", Nanometer Domains of High Network Density:



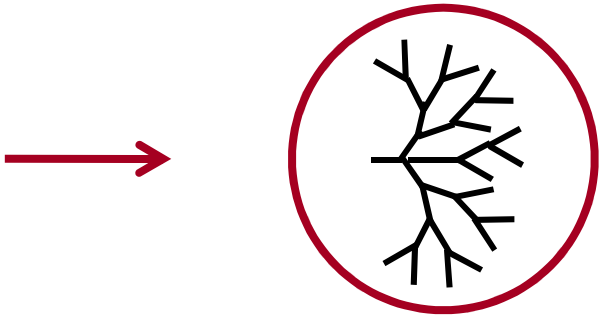
Rainer Buerstinghaus

Highly Elastic Clear Coats for the OEM Automotive Sector

OH-Functional Polyacrylate With High OH-Number:



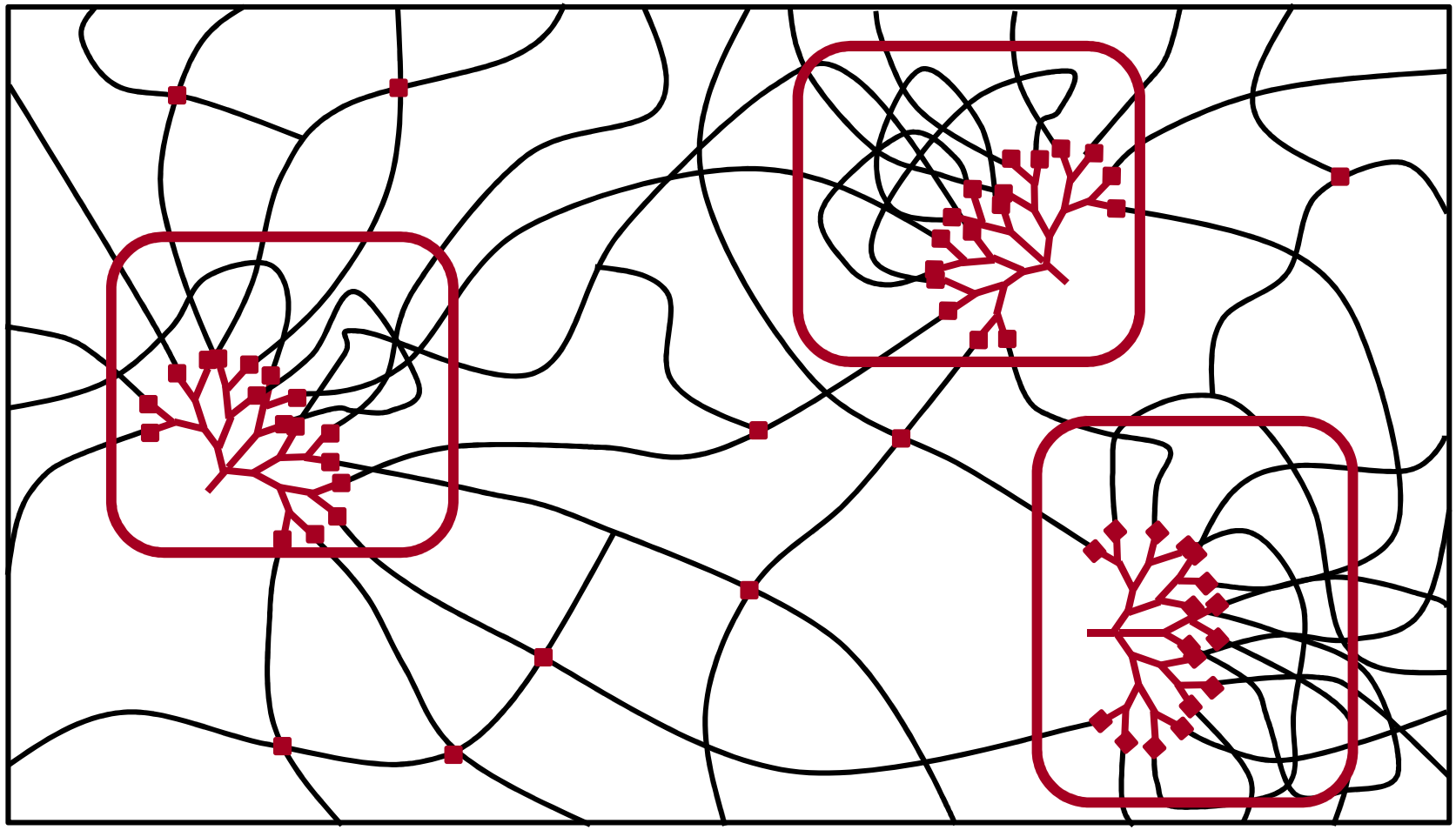
Multi-N=C=O-functional,
highly branched crosslinker.



Rainer Buerstinghaus

Highly Elastic Clear Coats for the OEM Automotive Sector

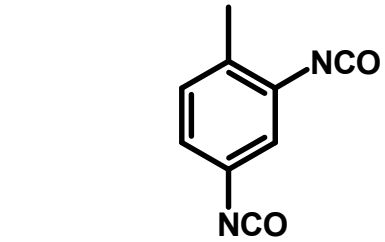
Cured Coating Film with "Hyperbranched Crosslinker", Nanometer Domains of High Network Density:



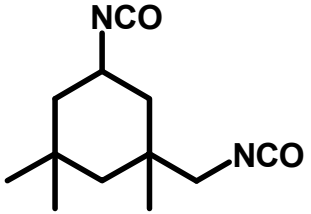
Rainer Buerstinghaus

Highly Elastic Clear Coats for the OEM Automotive Sector

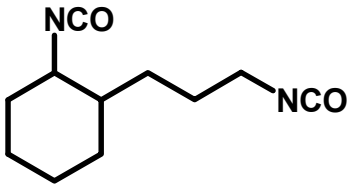
Highly Branched Crosslinkers, Technical Diisocyanates:



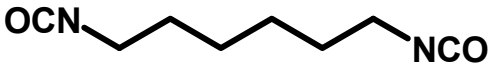
TDI



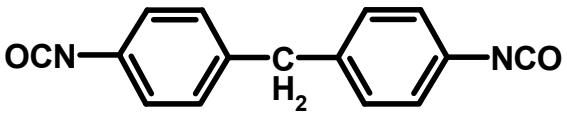
IPDI



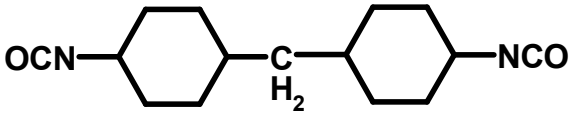
IPCI



HDI



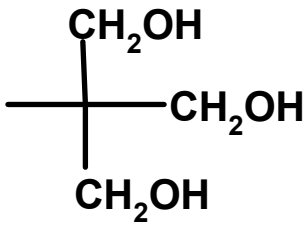
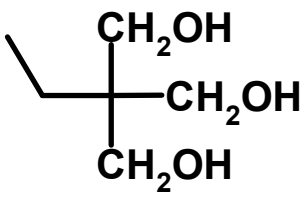
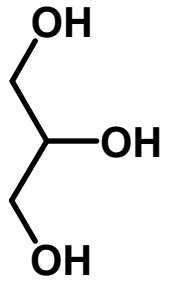
MDI



HMDI

Highly Elastic Clear Coats for the OEM Automotive Sector

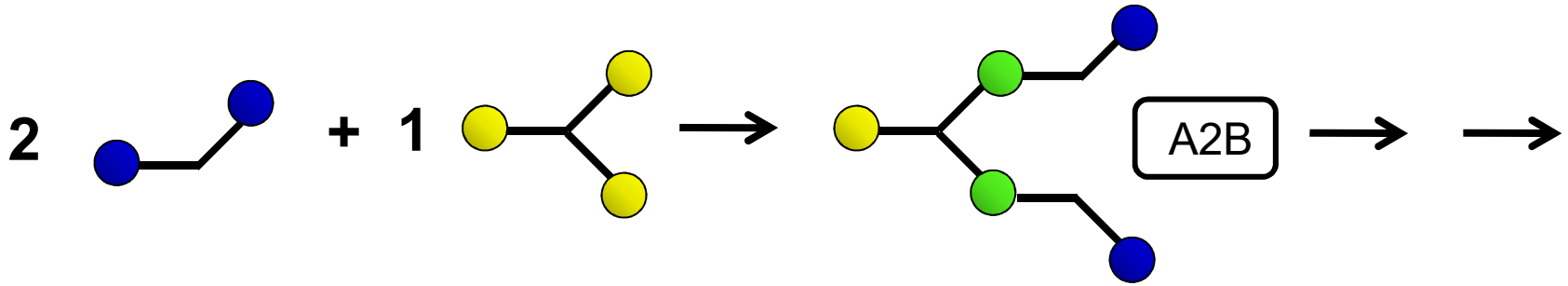
Highly Branched Crosslinkers, Technical Tri-Alcohols:

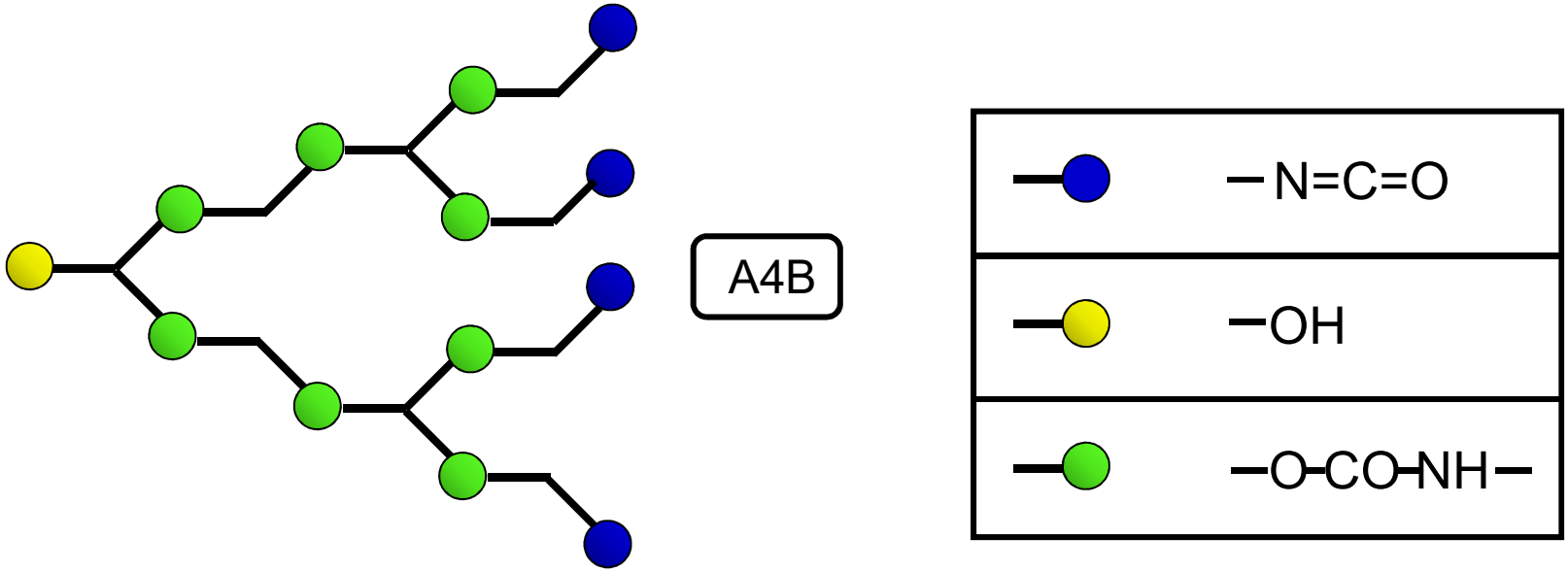
		
1,1,1-Trimethylol-ethane **(TME)**	1,1,1-Trimethylol-propane **(TMP)**	Glycerol

Rainer Buerstinghaus

Highly Elastic Clear Coats for the OEM Automotive Sector

Highly Branched Isocyanate-Crosslinkers; One-Pot-Synthesis of an Oligoisocyanate. First Steps (Idealized):





Rainer Buerstinghaus

Highly Elastic Clear Coats for the OEM Automotive Sector

Highly Branched Crosslinker; "One-Pot Synthesis" of Lacquer-Curing Oligo-Isocyanates:

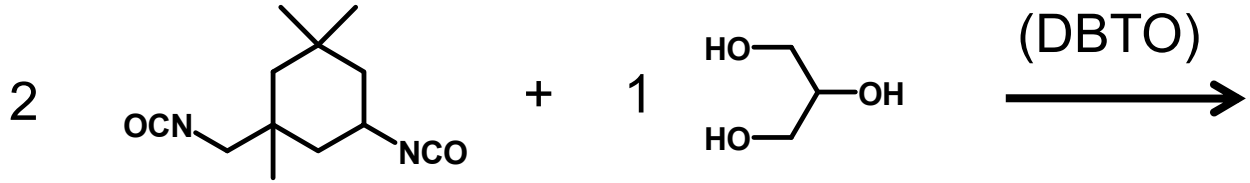
1. 2,0 Mol diisocyanate is dissolved in 500 ml THF.
2. Dry nitrogen is bubbled through the liquid, the solution is cooled down to 0ºC.
3. 1,0 Mol Triol in 250 ml THF is added below 5ºC.
4. 30 Minutes stirred at 0-5ºC, then 0,1 g dibutyltindilaurate in 10 ml THF is added and temperature elevated to 60ºC.
5. 0,08 Mol diisocyanate in 20 ml THF is added and the mixture stirred at 60ºC. THF is removed at 80ºC in an rotary evaporator.

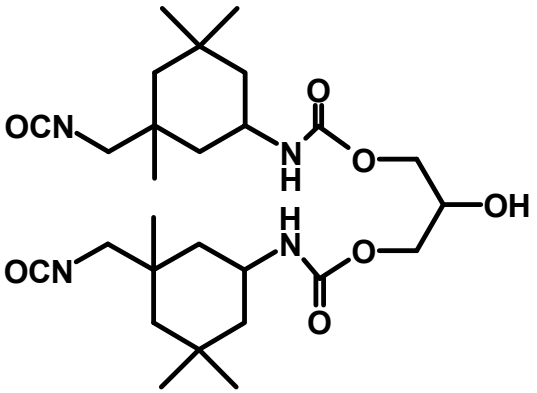
Rainer Buerstinghaus

Highly Elastic Clear Coats for the OEM Automotive Sector

Highly Branched Crosslinker: IPDI + Glycerol (2 : 1),
One-Pot-Synthesis of an Oligo-Isocyanate;
First Steps (Idealized):

Example





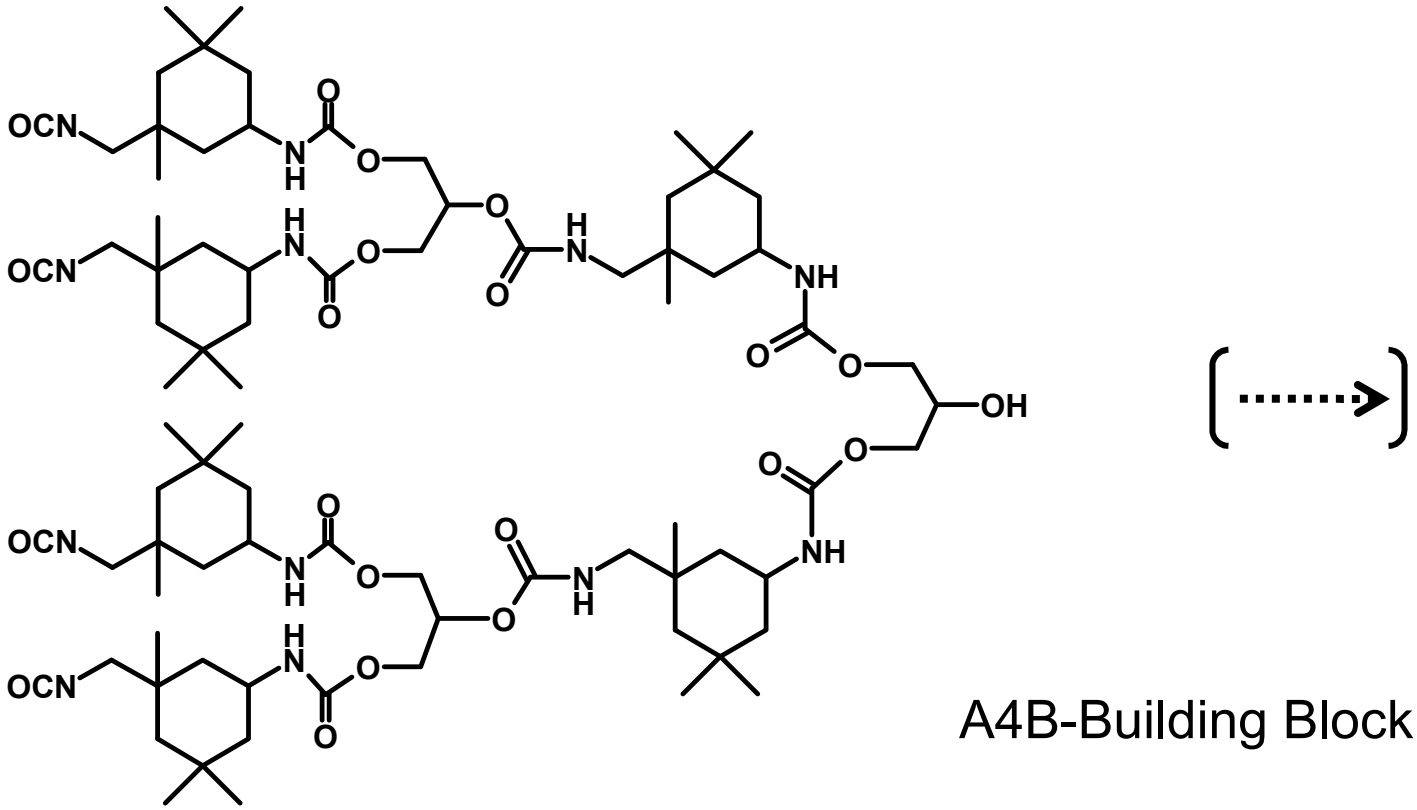
A2B-Building Block

(DBTO: Dibutylzinnoxid)

Highly Elastic Clear Coats for the OEM Automotive Sector

Highly Branched Crosslinker: IPDI + Glycerol (2 : 1),
One-Pot-Synthesis of an Oligo-Isocyanate;
First Steps (Idealized):

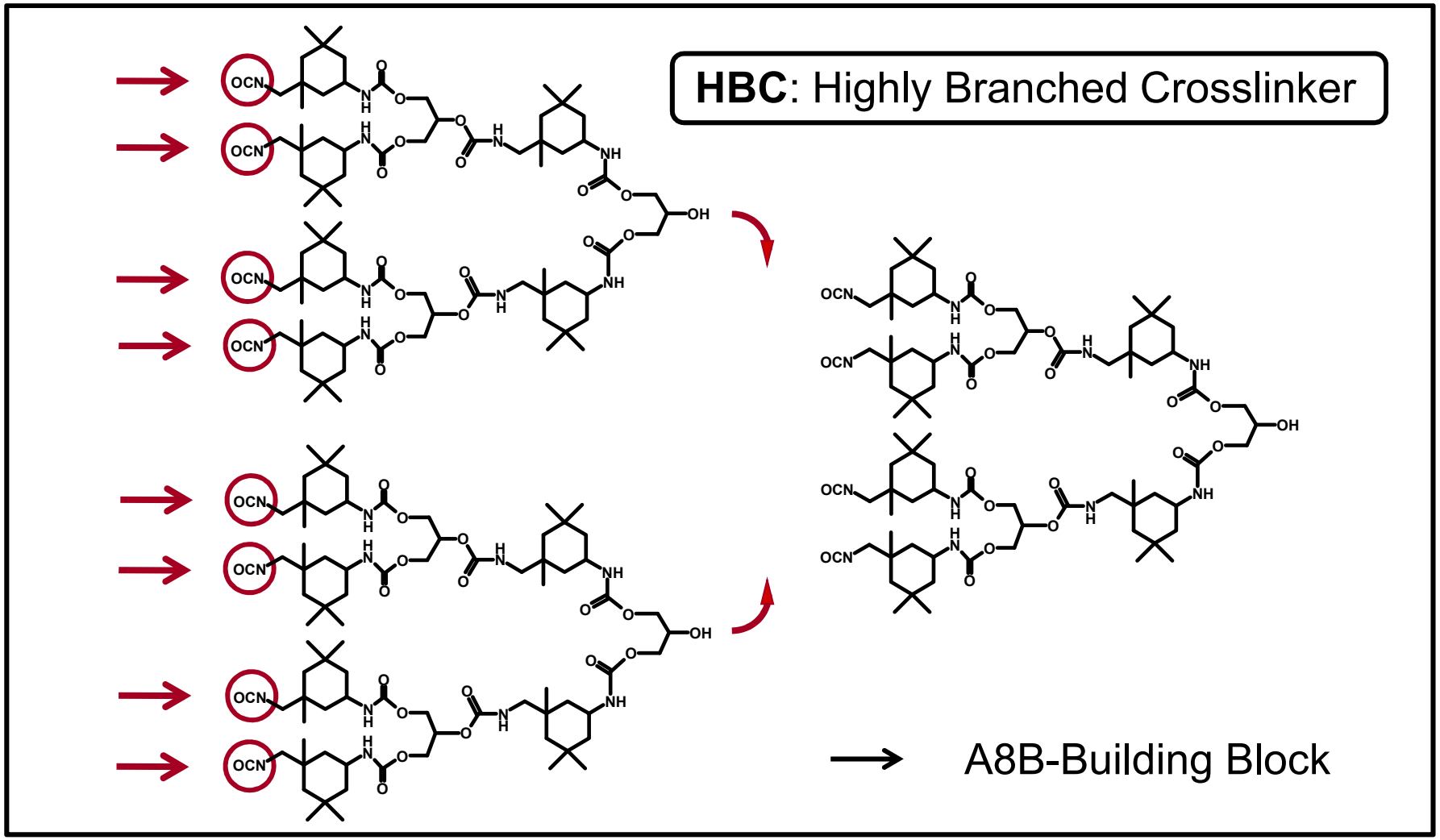
Example



A4B-Building Block

Highly Elastic Clear Coats for the OEM Automotive Sector

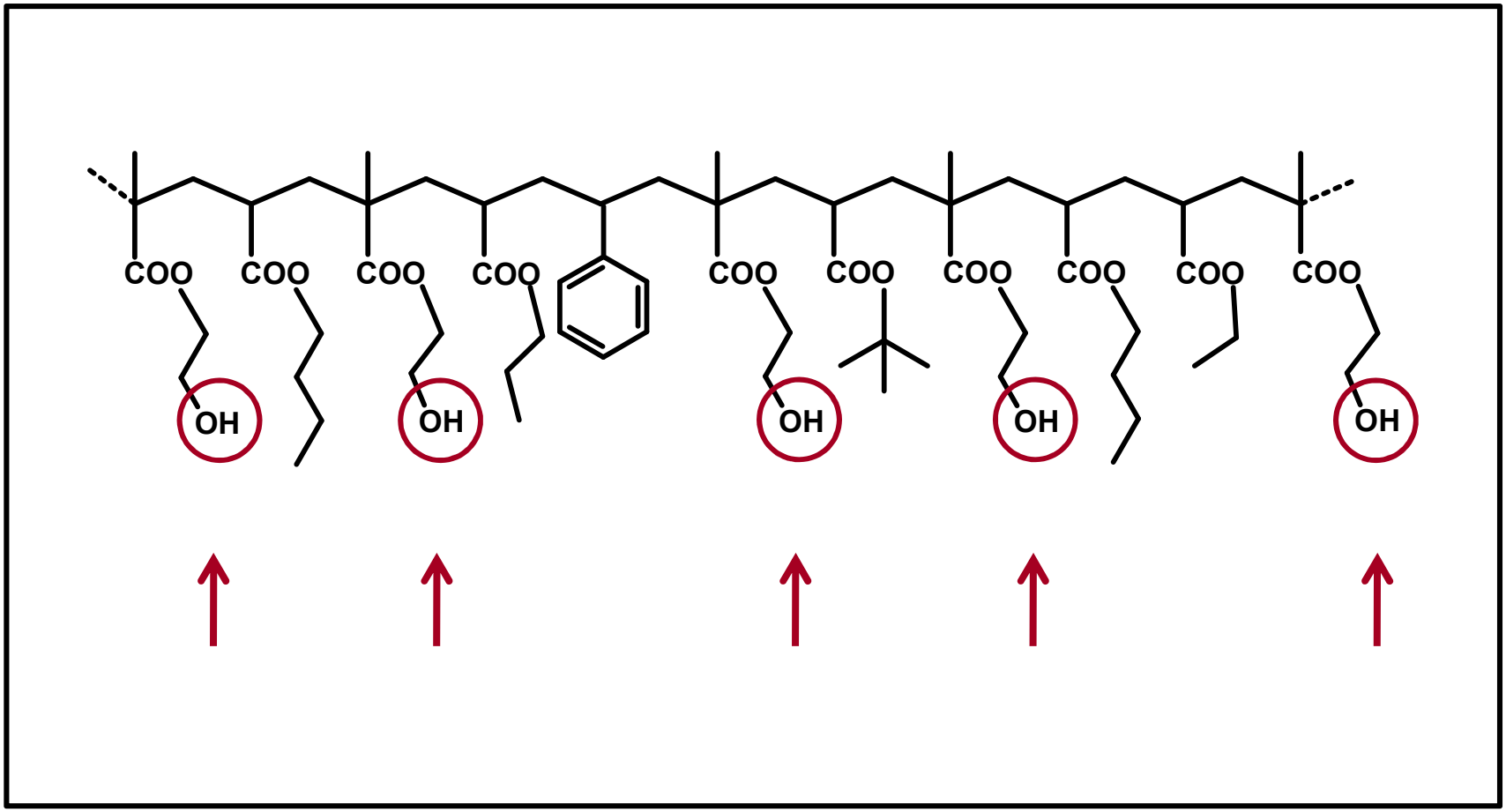
Branched Oligoisocyanate-Crosslinker via One-Pot-Synthesis (Idealized Reaction Cascade: IPDI:Glycerol = 2:1):



Rainer Buerstinghaus

Highly Elastic Clear Coats for the OEM Automotive Sector

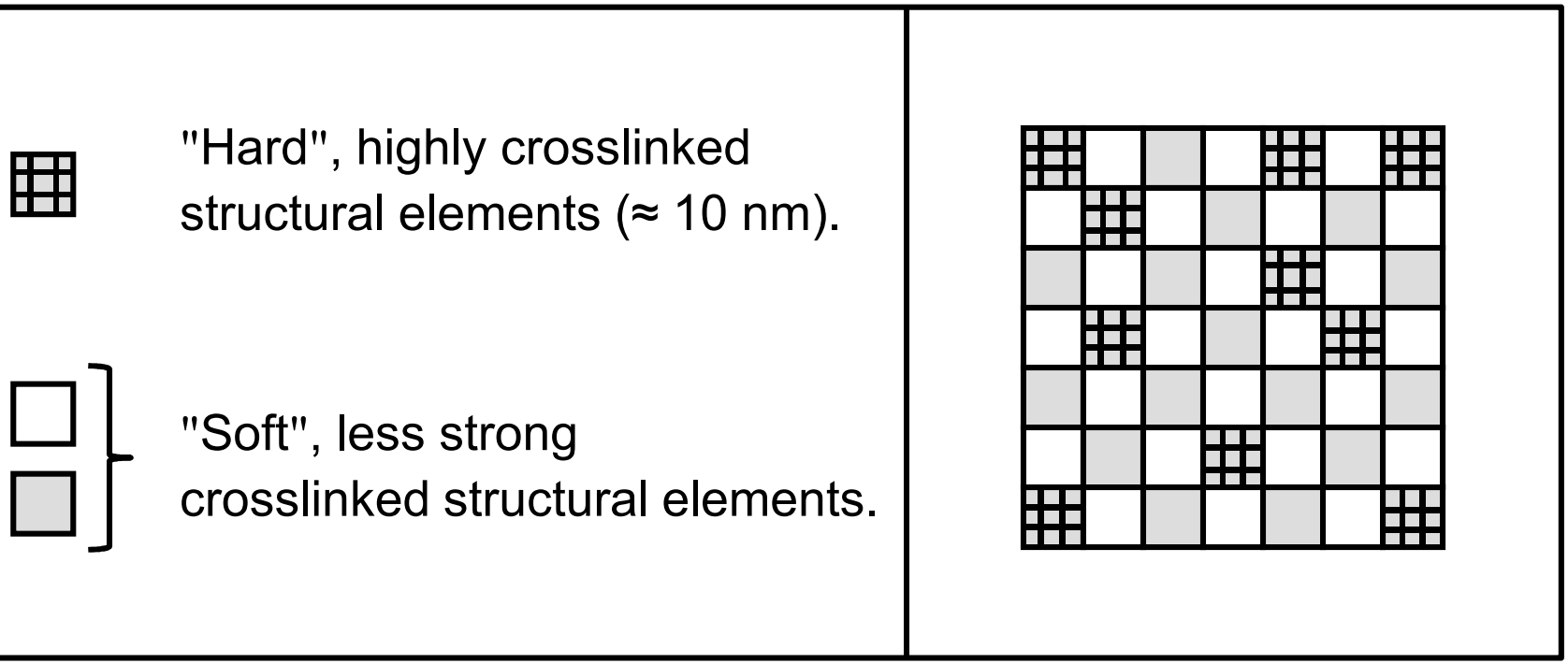
OH-Functionalized Polyacrylate with High OH-Number:



Rainer Buerstinghaus

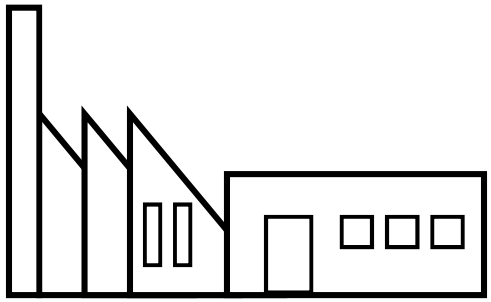
Highly Elastic Clear Coats for the OEM Automotive Sector

Cured Paint Film after Addition of "Hyperbranched Crosslinker"; Nanometer Domains with High Network Density (⟶ Structural Scheme):



The firm in which the lacquer development is to take place.

R&D Project “Highly Elastic Clear Coats for the OEM…“



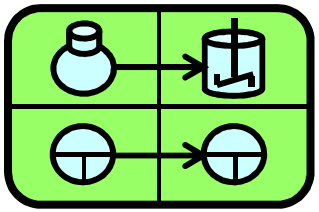
The Coatings and Chemical Company "[…GmbH 1]":

Larger, medium-sized company: 1270 employees worldwide, including 25 chemists, 37 engineers (FH), 19 engineers (TU).

Own research and development, own production facilities for synthetic polyacrylates and paints made from these. Active for 15 years in the field of "clear coats for the OEM finishing of automobiles".

Chemical specialty: Production of "tailor-made" OH-polyacrylates.

R&D Project Management in the Chemical Industry



Subject Matter →

P2: Nitrilase-Catalyzed Synthesis of a Chiral α-Hydroxycarboxylic Acid.

("White" Biotechnology)

Example P2

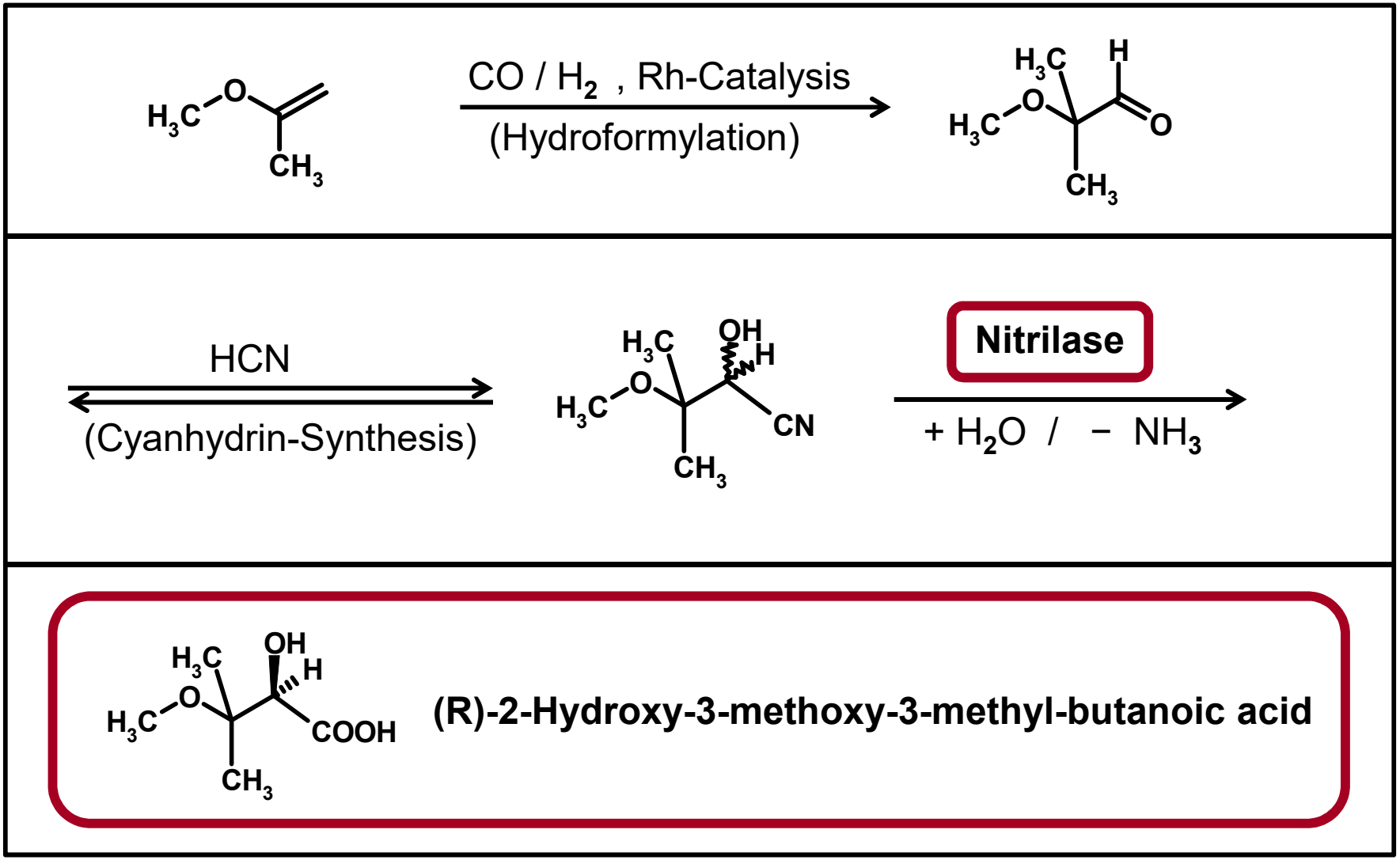
Innovation Project P2: →

"Nitrilase-Catalyzed Synthesis of an Enantiomerically Pure α-OH-Carboxylic Acid".

(Chemistry and Microbiology)

(R)-2-Hydroxy-3-Methoxy-3-Methyl-Butanoic Acid

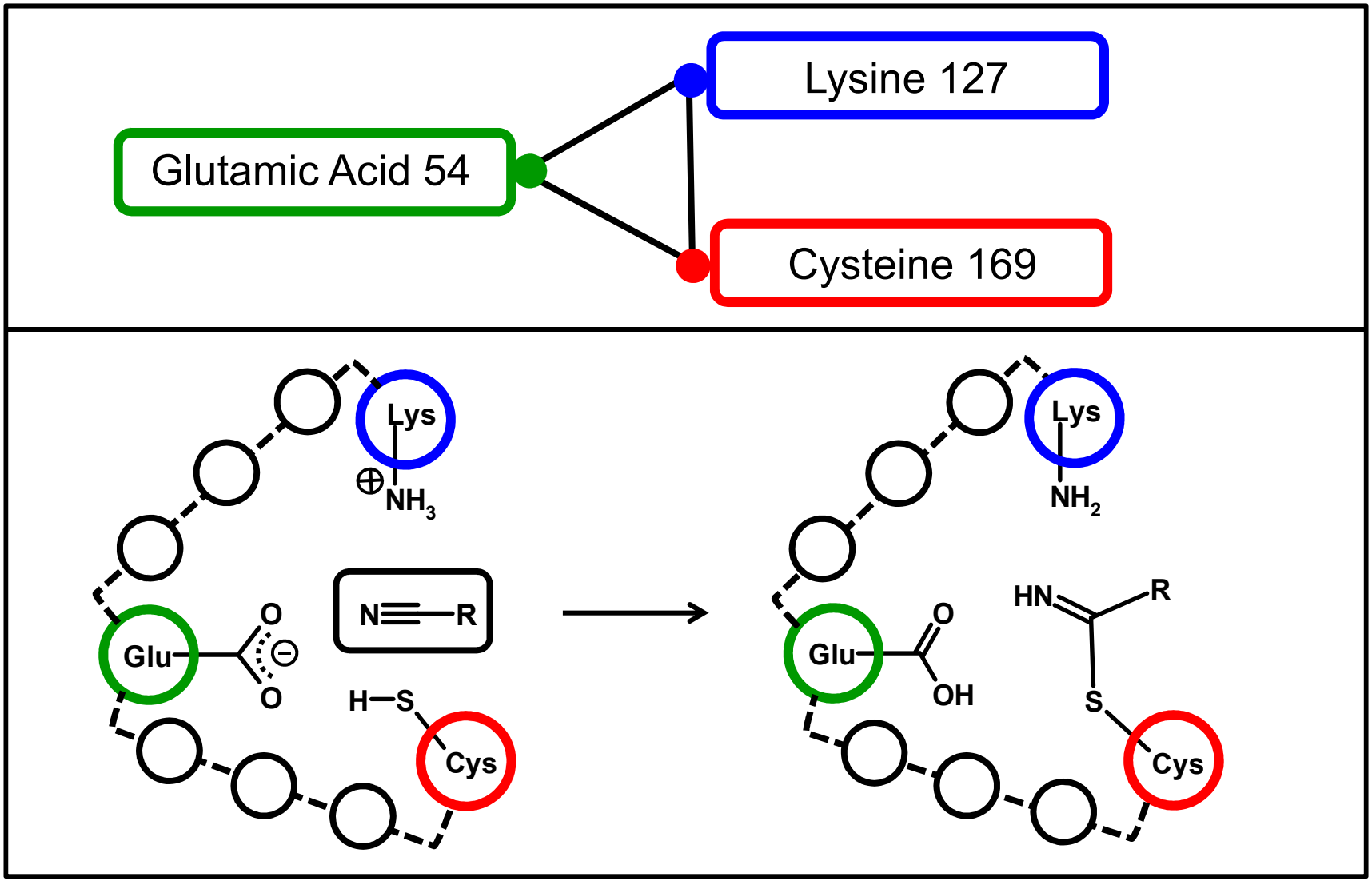
Stereospecific Synthesis of the Target Molecule, 3 Steps:



Rainer Buerstinghaus

Nitrilase A, Catalysis-Mechanism: Nitrile → Carboxylic Acid

"Conserved" Amino Acids of the "Catalytic Triad":

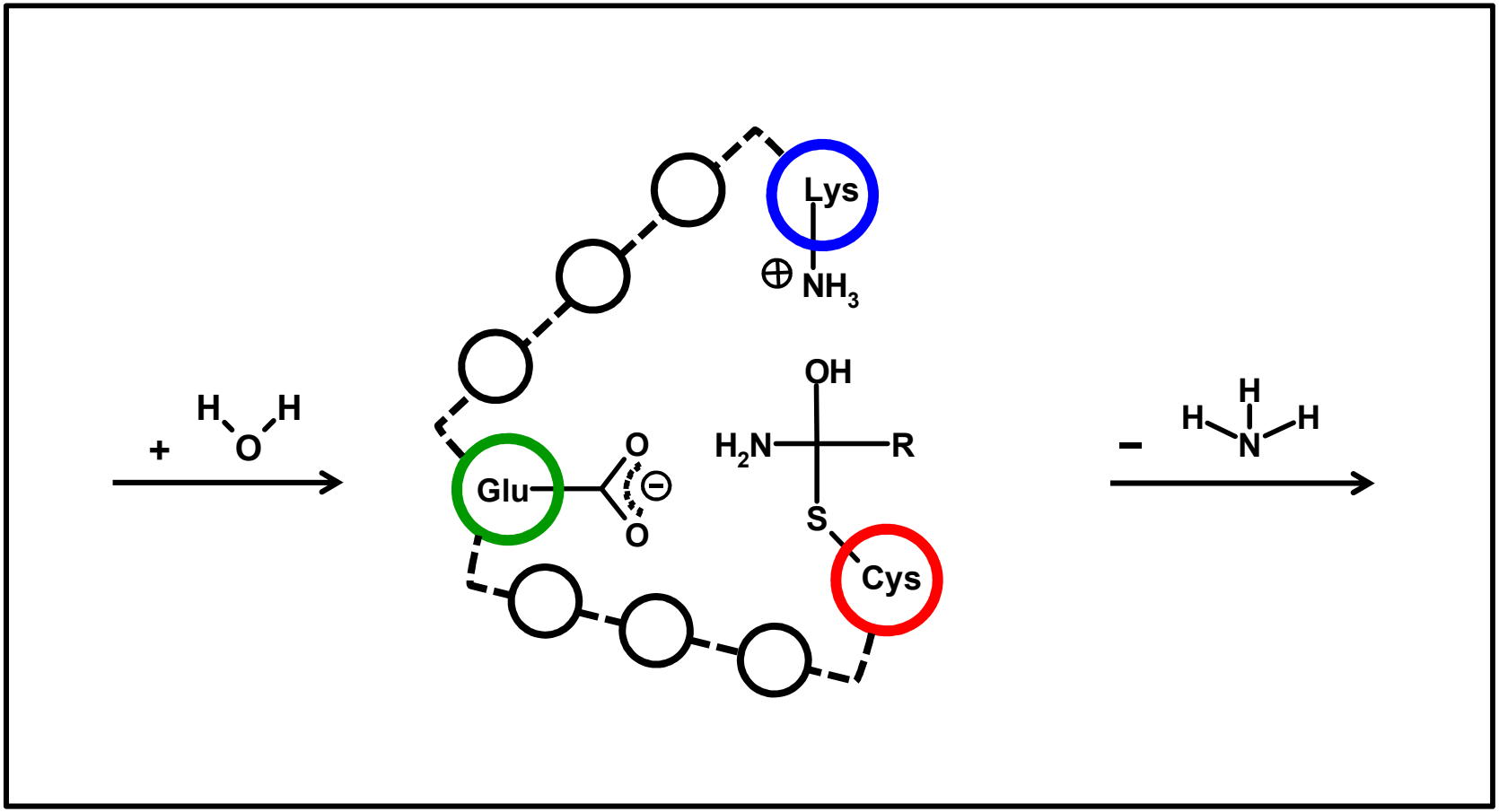


Rainer Buerstinghaus

(R)-2-Hydroxy-3-Methoxy-3-Methyl-Butanoic Acid

Nitrilase A, Catalytic Mechanism: Nitrile ⟶ Carboxylic Acid

Nitrilase A: 320-340 Amino Acids, α-Helixes, β-Sheets.

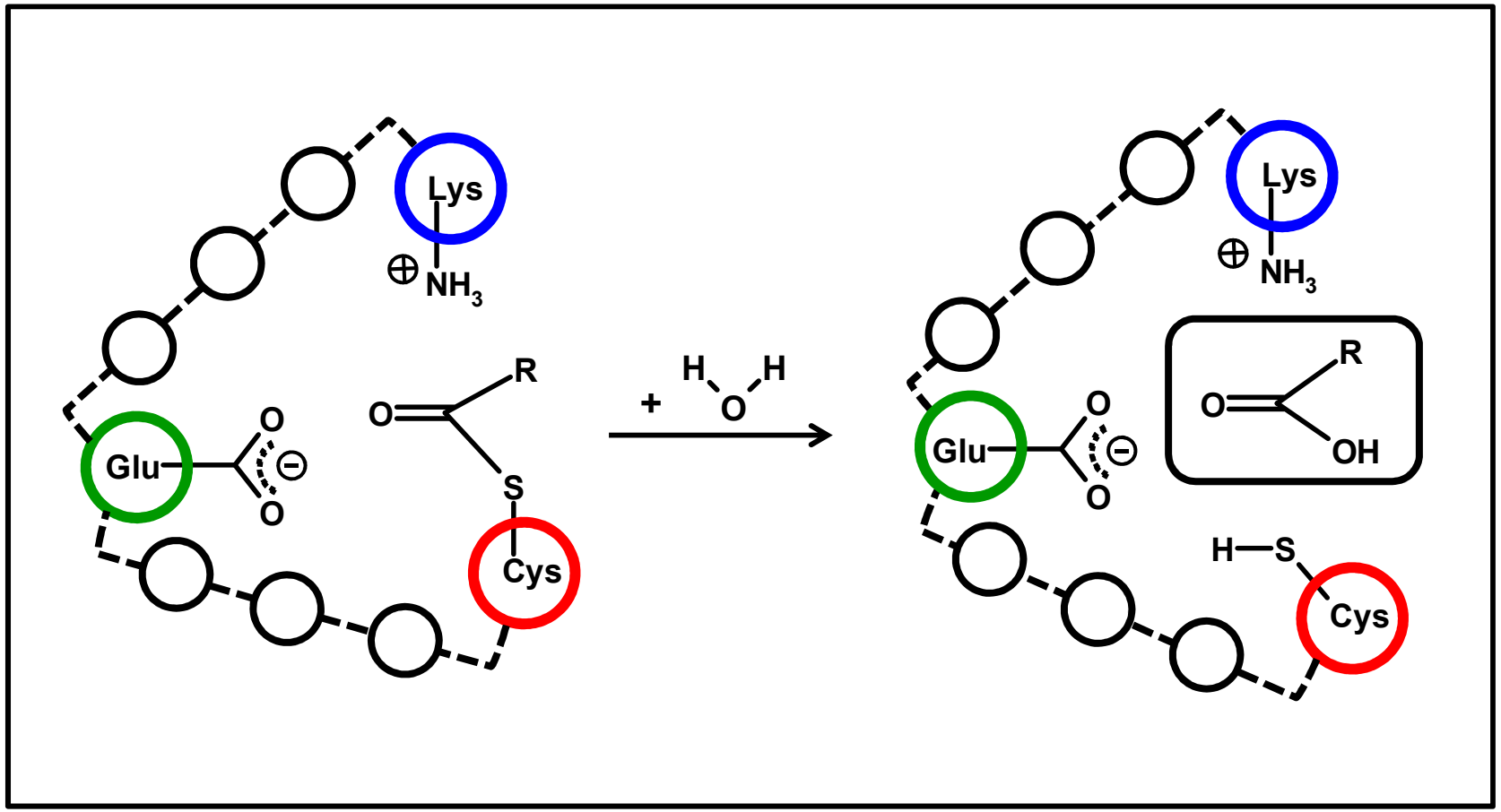


Rainer Buerstinghaus

(R)-2-Hydroxy-3-Methoxy-3-Methyl-Butanoic Acid

Nitrilase A, Catalytic Mechanism: Nitrile ⟶ Carboxylic Acid

Nitrilase A: 320-340 Amino Acids, α-Helixes, β-Sheets.

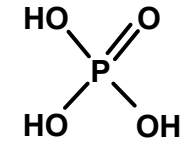


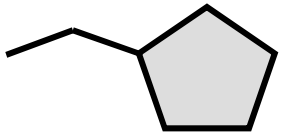
Rainer Buerstinghaus

(R)-2-Hydroxy-3-Methoxy-3-Methyl-Butanoic Acid

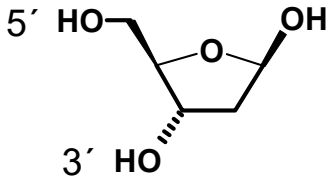
Nitrilase-Coding DNA-Sections; Building Blocks, Formulas:

P Phosphoric Acid →

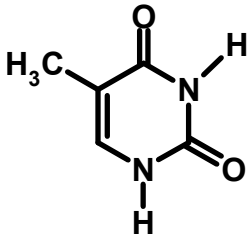




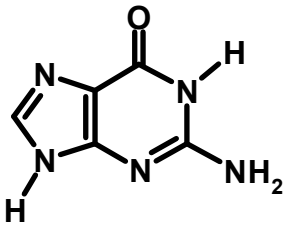
Desoxyribose →



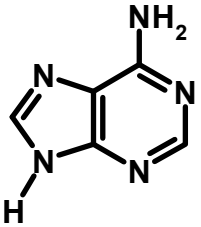
Thymine



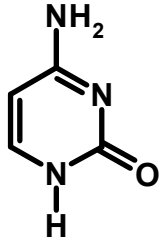
Guanine



Adenine



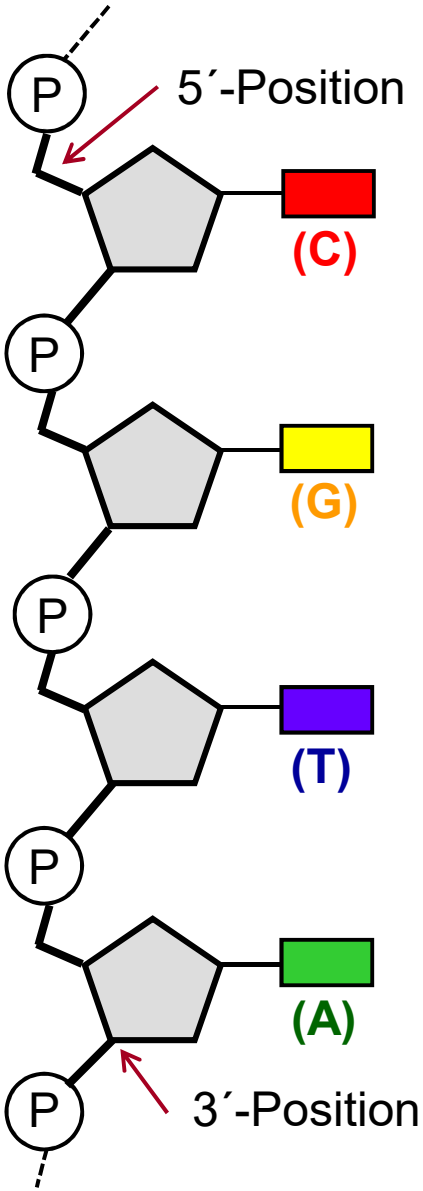
Cytosine



Rainer Buerstinghaus

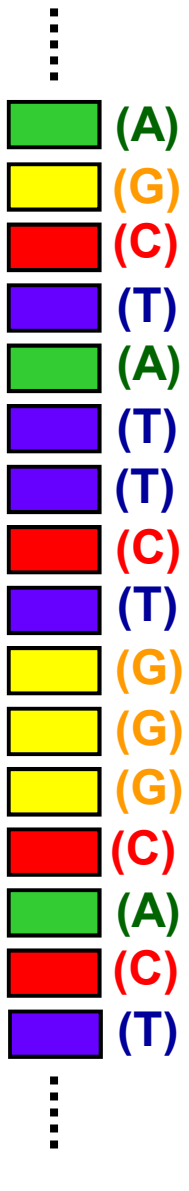
(R)-2-Hydroxy-3-Methoxy-3-Methyl-Butanoic Acid

Oligonucleotide Structure (Detail) from a DNA Single-Strand:



The oligonucleotide single strand serves as **information store** by its set **sequence of the bases** adenine (A), cytosine (C), thymine (T) and guanine (G).

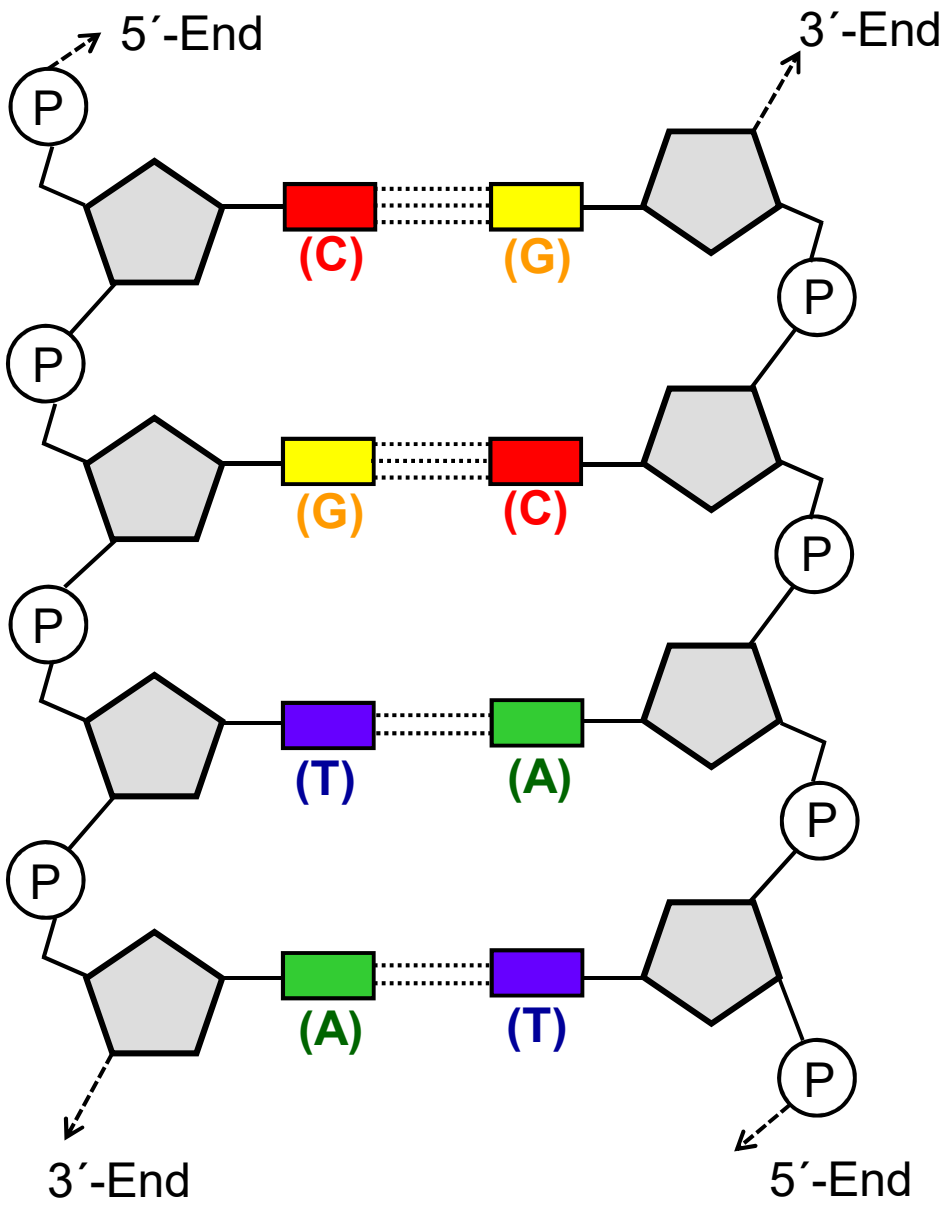
This sequence is the basis for an universal programming language (Genetic code, including the code for the protein "nitrilase"). **The fixed "backbone"** of the single strand, consisting of alternating phospha-te and sugar residues, **ensures the stability of the information** through its covalent bonds.

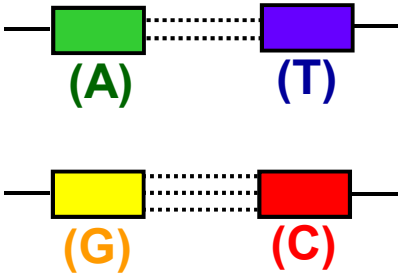


Rainer Buerstinghaus

(R)-2-Hydroxy-3-Methoxy-3-Methyl-Butanoic Acid

Oligonucleotide-Double Strand, General Structure (Detail):



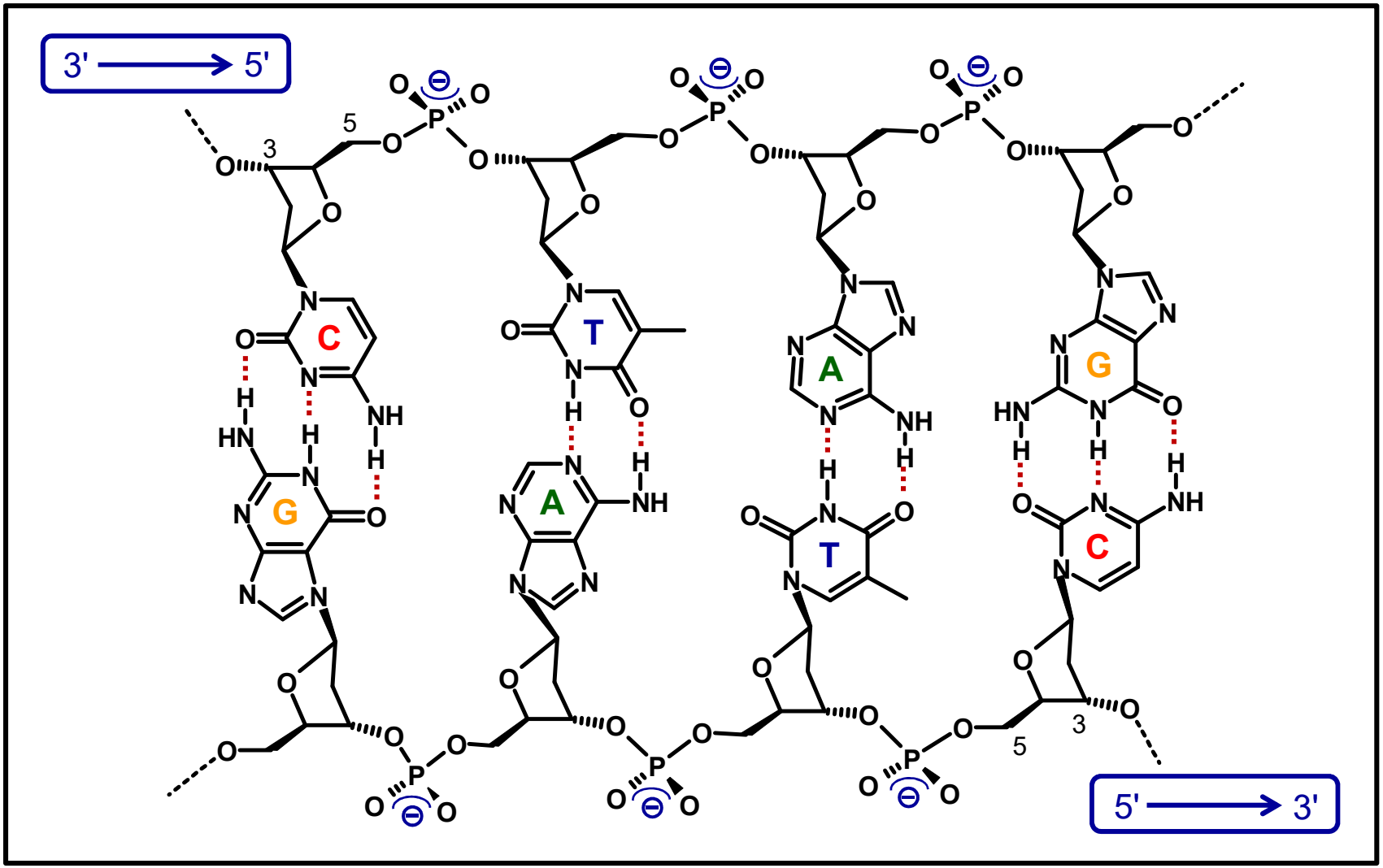


Complementary base pairs whose pairwise arrangements are stabilized via 2 or 3 intermolecular hydrogen bonds. .....

Rainer Buerstinghaus

(R)-2-Hydroxy-3-Methoxy-3-Methyl-Butanoic Acid

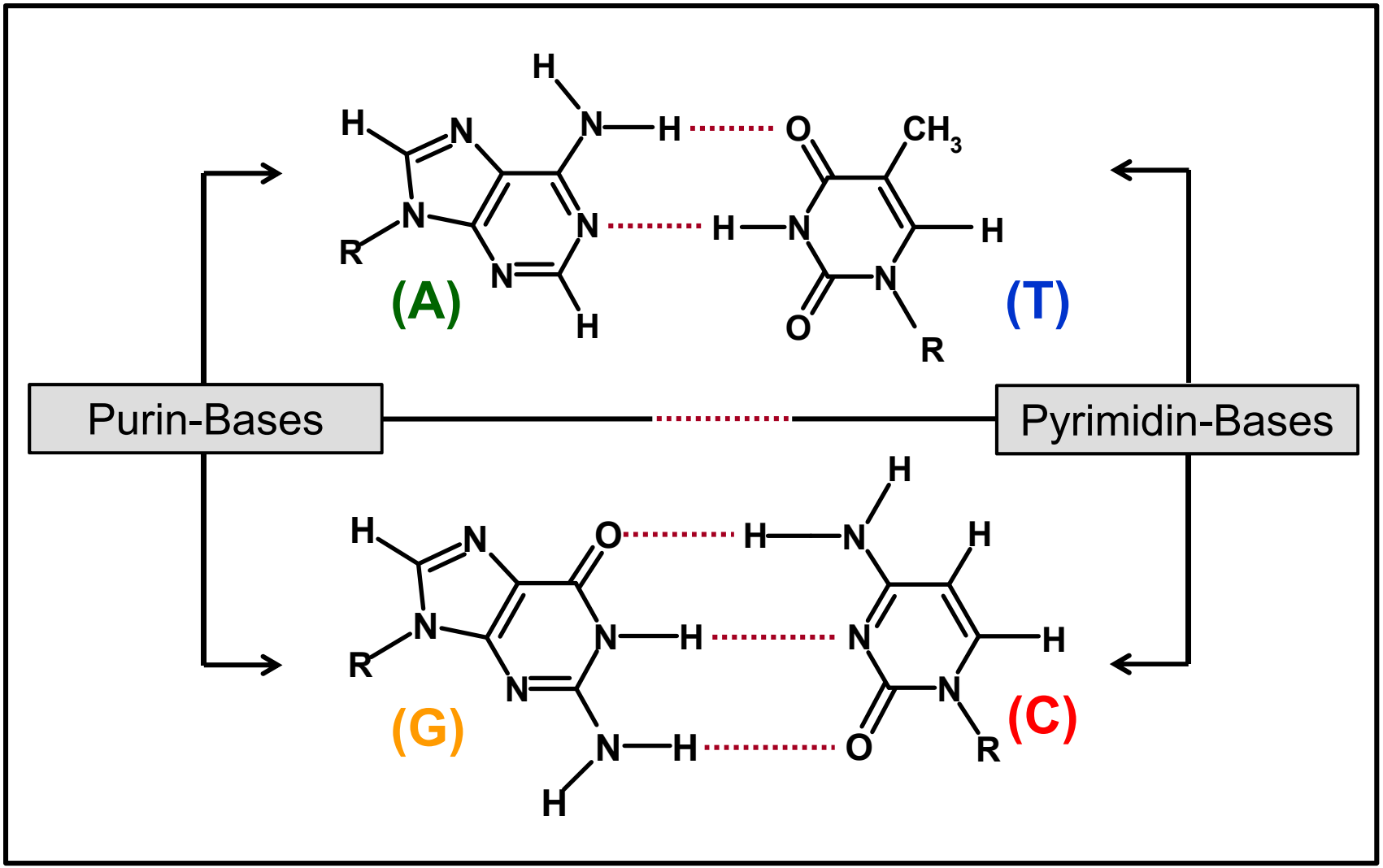
DNA-Molecule (Detail), Simplified Representation:



Rainer Buerstinghaus

(R)-2-Hydroxy-3-Methoxy-3-Methyl-Butanoic Acid

H^+-Bridges Between the Complementary DNA-Bases:



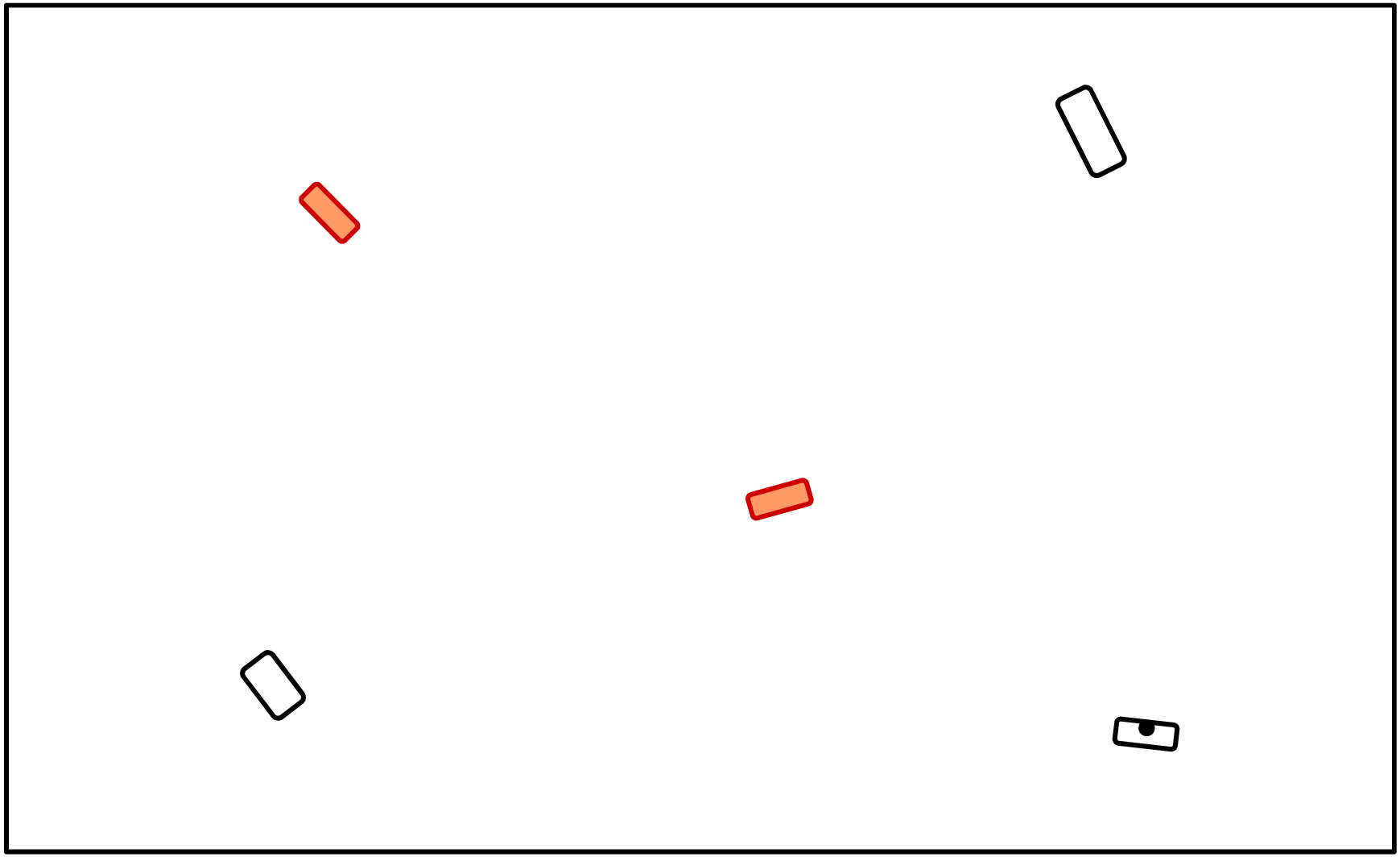
Rainer Buerstinghaus

(R)-2-Hydroxy-3-Methoxy-3-Methyl-Butanoic Acid

Biodiversity, Microbes From a Soil Sample:

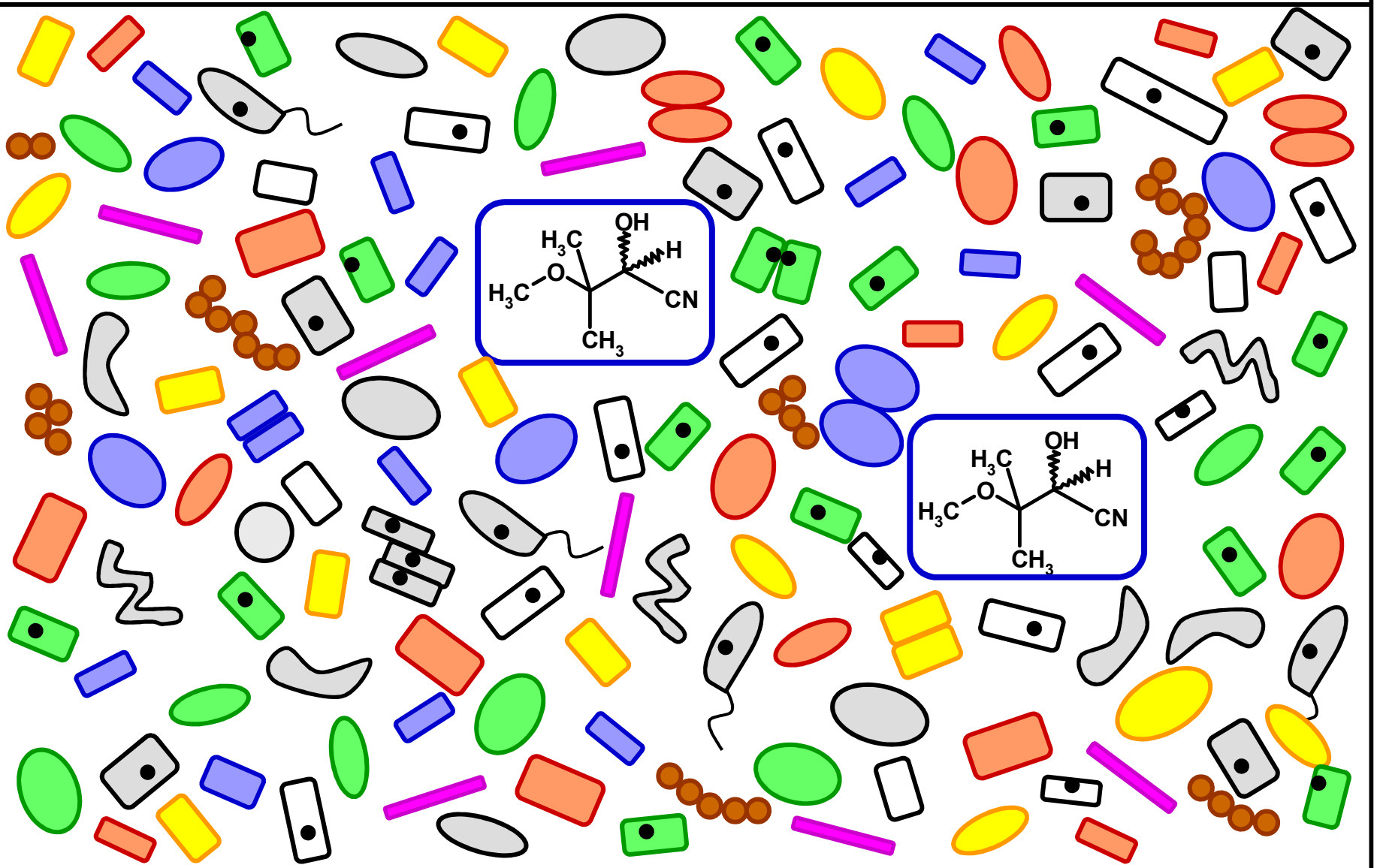
Rainer Buerstinghaus

Disadvantage: A maximum of 3% of these can be successfully cultivated and multiplied in the laboratory or in the pilot plant!



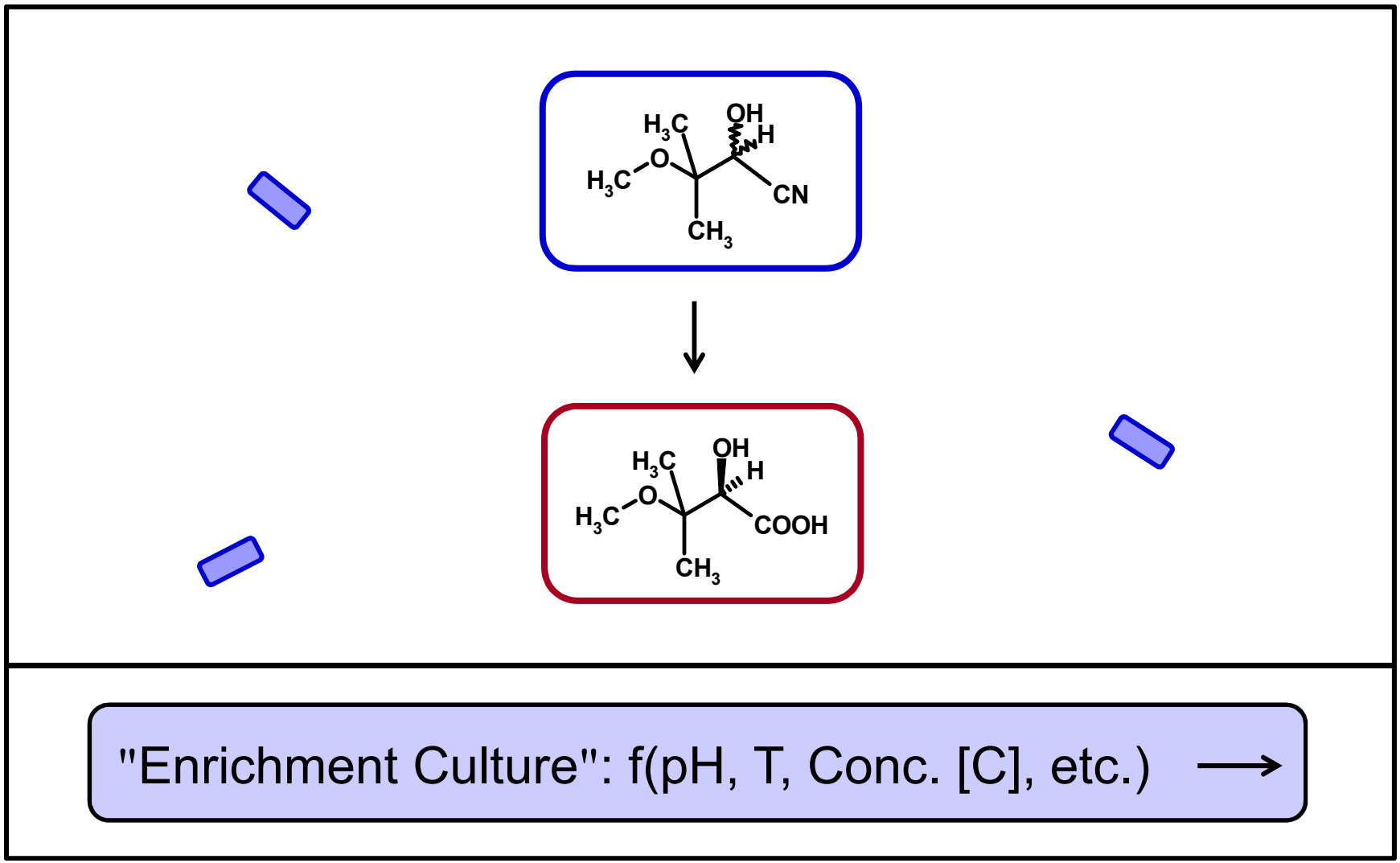
Rainer Buerstinghaus

"Feeding" with 2-hydroxy-3-methoxy-3-methyl-butyronitrile as the sole source of nitrogen and carbon.



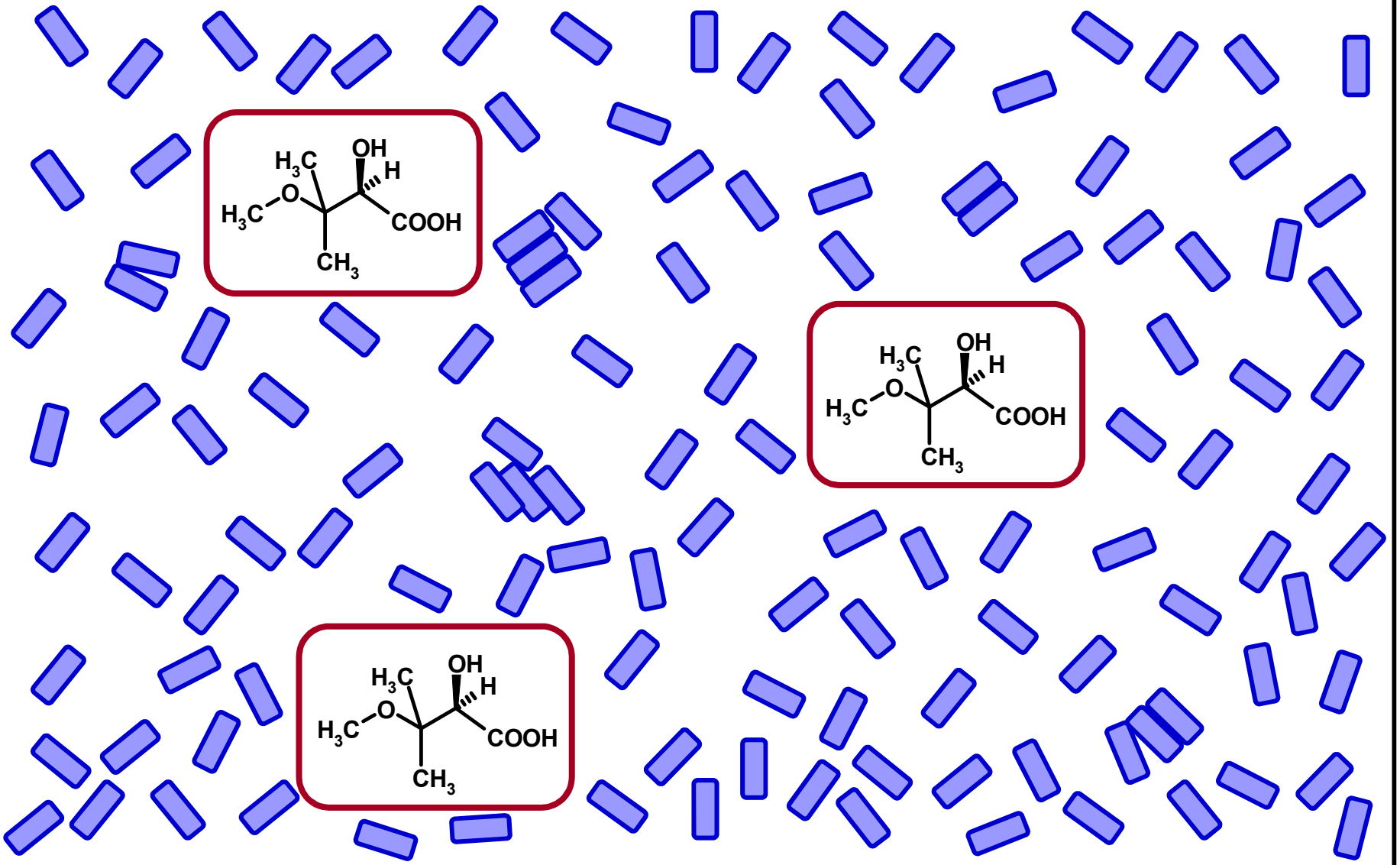
Rainer Buerstinghaus

"Survival of the Fittest": These could produce (R)-2-hydroxy-3-methoxy-3-methyl-butanoic acid, e. g. by means of nitrilase.



Rainer Buerstinghaus

"Survival of the Fittest": These could produce (R)-2-hydroxy-3-methoxy-3-methyl-butanoic acid, e. g. by means of nitrilase.

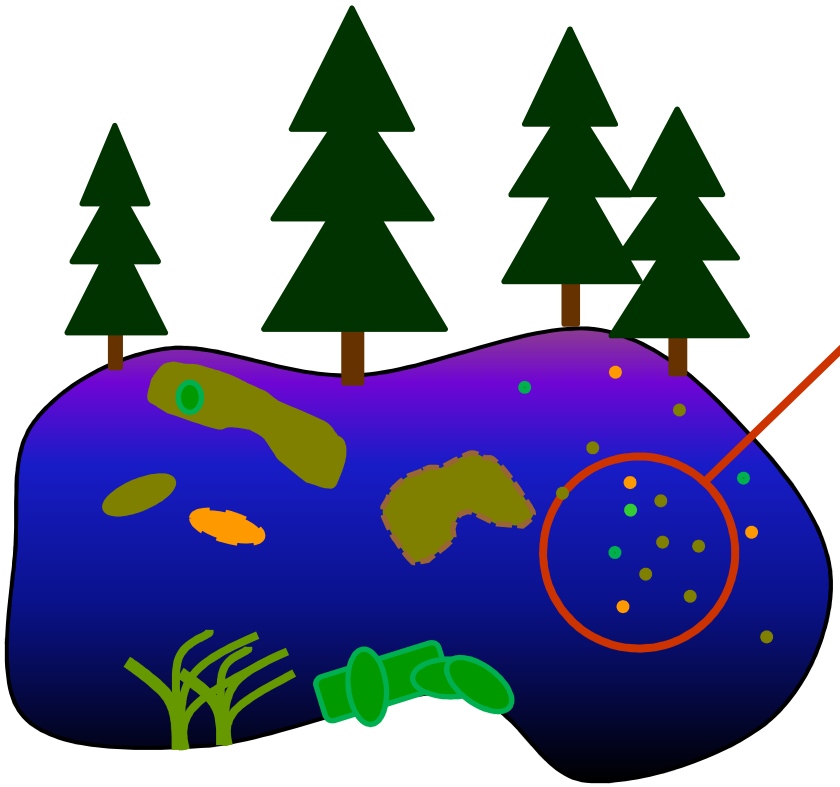


Rainer Buerstinghaus

(R)-2-Hydroxy-3-Methoxy-3-Methyl-Butanoic Acid

Microbes in a Biotope, Access to the Metagenome, Steps:

1) **Sampling / Preparation** of all microbes of a biotope (Water samples / Soil samples).



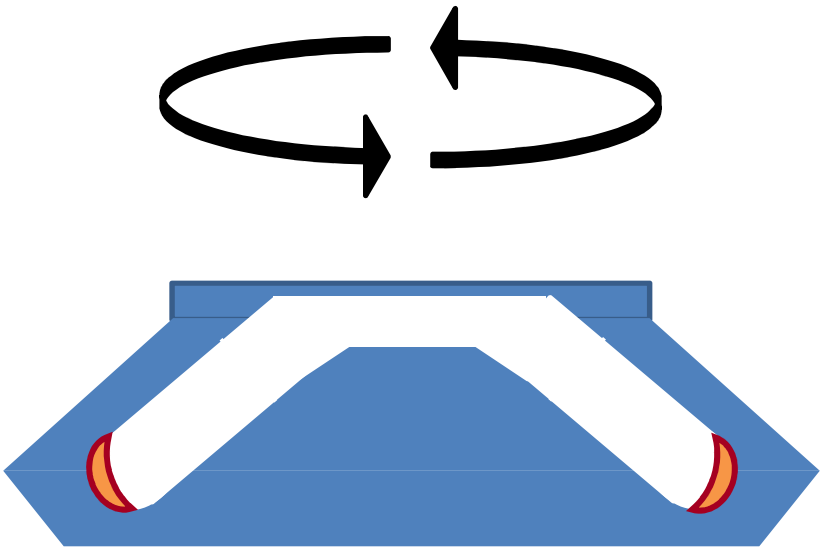
Rainer Buerstinghaus

(R)-2-Hydroxy-3-Methoxy-3-Methyl-Butanoic Acid

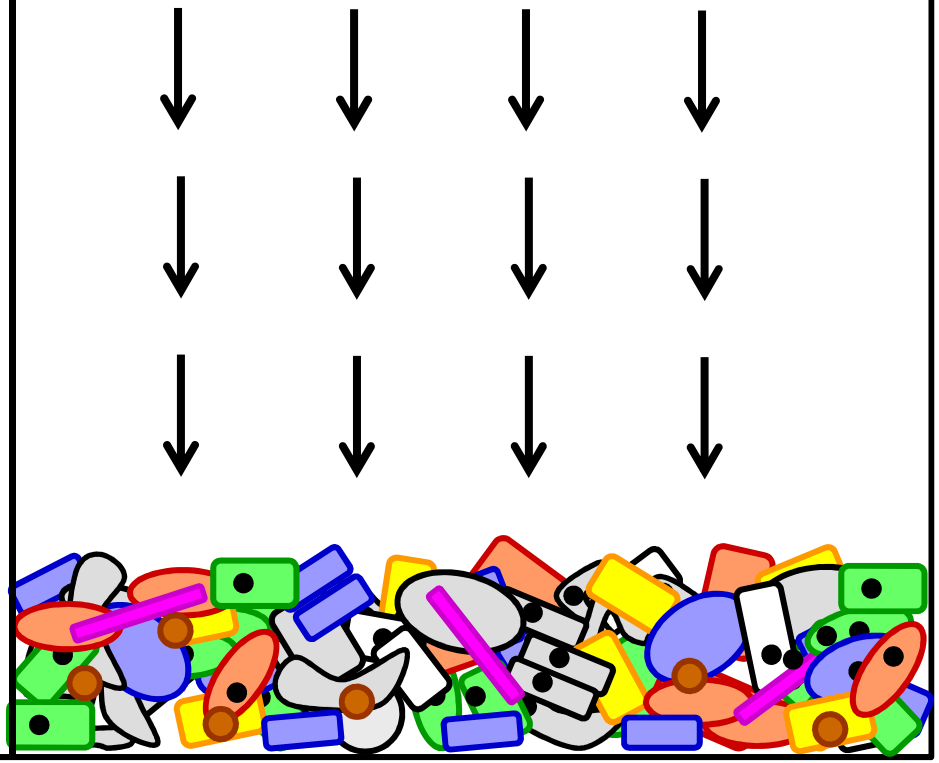
Microbes in a Biotope, Access to the Metagenome, Steps:

2) **Centrifugation:**
Ten minutes at 8000 revolutions per minute.

Sedimentation of all microbes from the sample of the biotope.



Centrifuge-Rotor

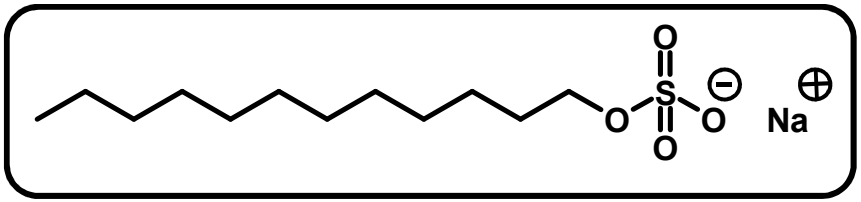


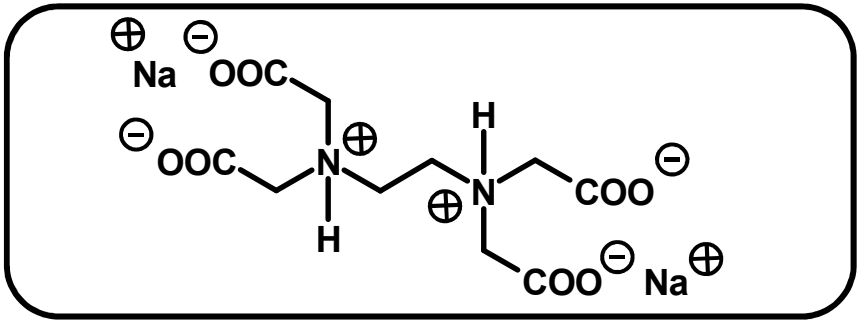
Rainer Buerstinghaus

(R)-2-Hydroxy-3-Methoxy-3-Methyl-Butanoic Acid

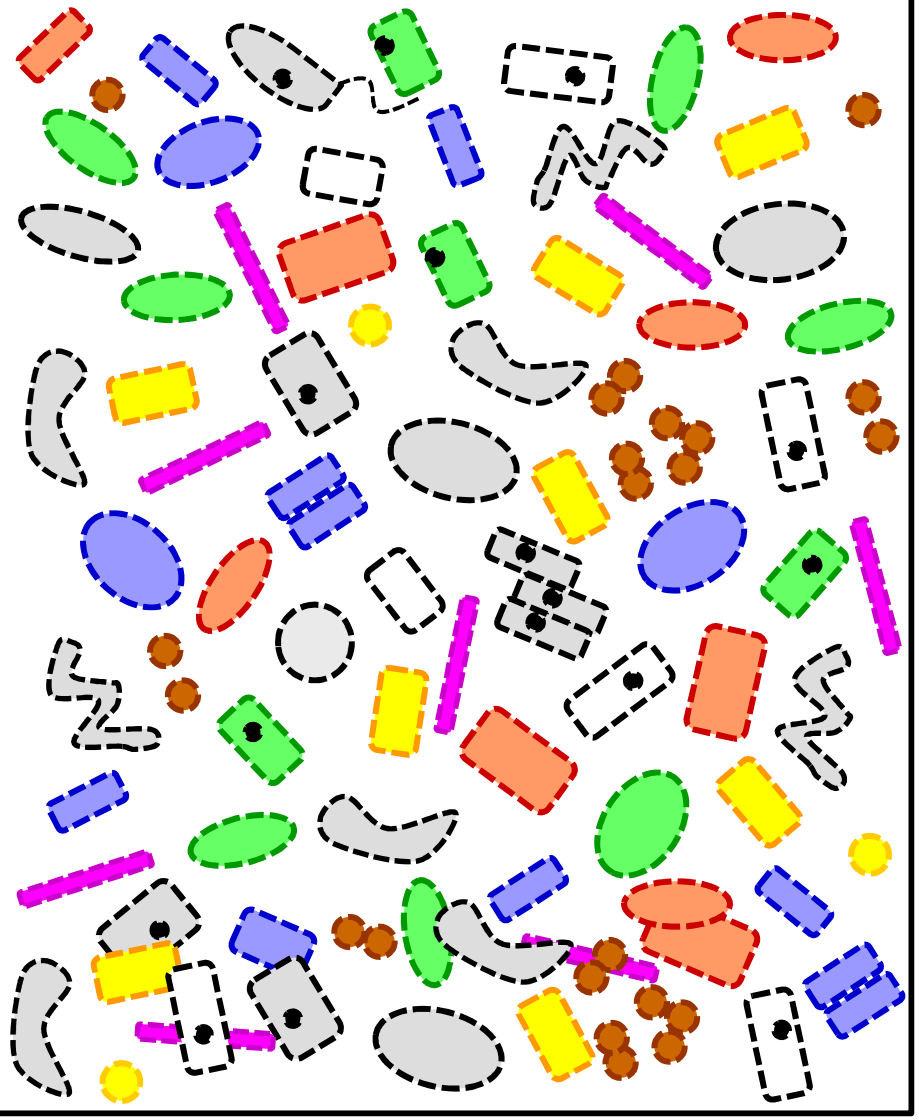
Microbes in a Biotope, Access to the Metagenome, Steps:

3a) **(Chemical) Lysis** of all in water suspended cells.





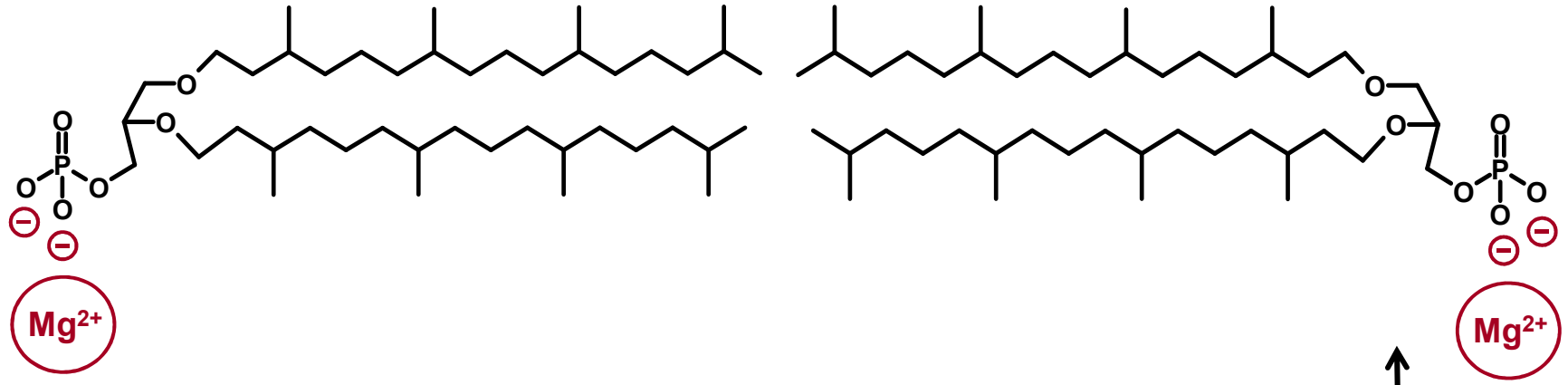
Lysozyme: Hydrolytic degradation of the crosslinked peptidoglycanes (Mureins for stabilization of cellwalls).



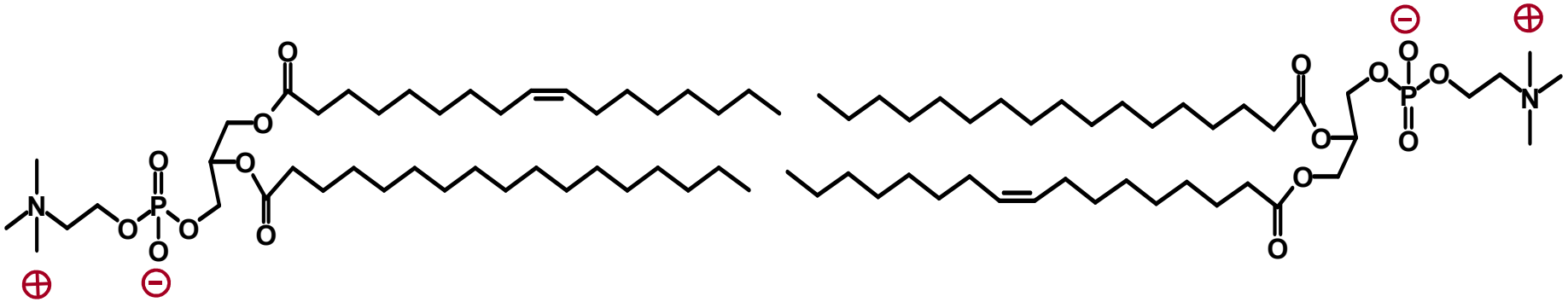
Rainer Buerstinghaus

(R)-2-Hydroxy-3-Methoxy-3-Methyl-Butanoic Acid

Bacterial Cell Membrane: Glycerol Diether / Glycerol Triester:



Double layer from two glycerol phytanyl diethers:

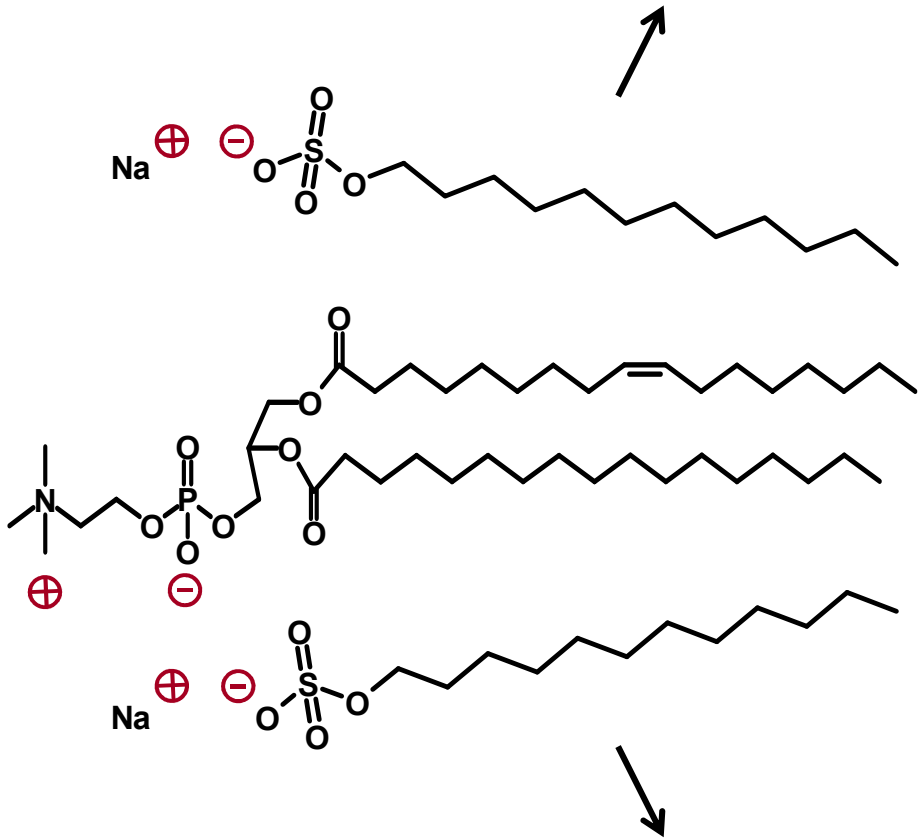


Zwitterionic glycerol-triesters:

Rainer Buerstinghaus

(R)-2-Hydroxy-3-Methoxy-3-Methyl-Butanoic Acid

Microbes from a Biotope: Lysis of the Cell Membrane (SDS):

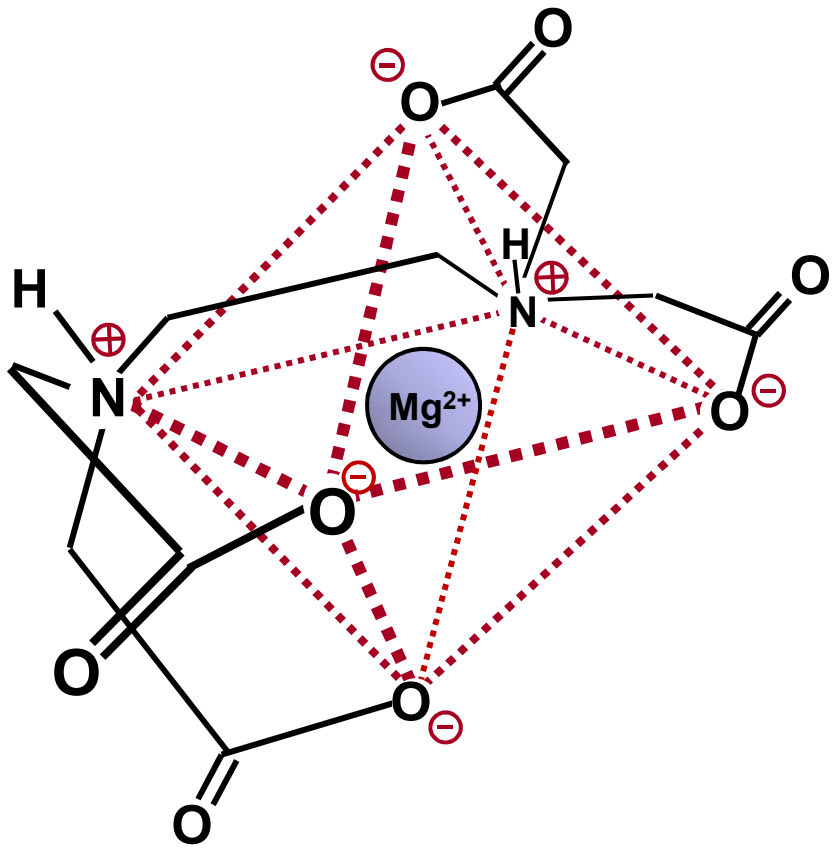


Formation of micelles by the invasion of sodium dodecyl sulfate (SDS) into the membrane.

Rainer Buerstinghaus

(R)-2-Hydroxy-3-Methoxy-3-Methyl-Butanoic Acid

Microbes from a Biotop, Lysis of the Cell Membrane (EDTA):



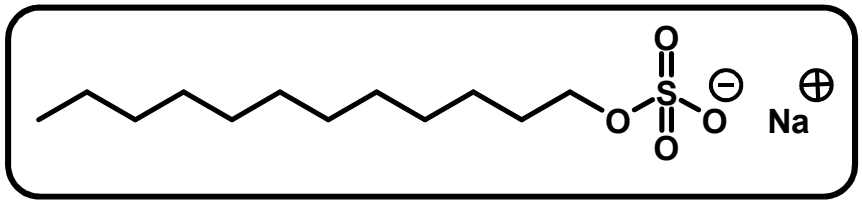
Formation of octahedrally coordinated magnesium complexes with ethylene-diaminotetra-acetic acid (EDTA).

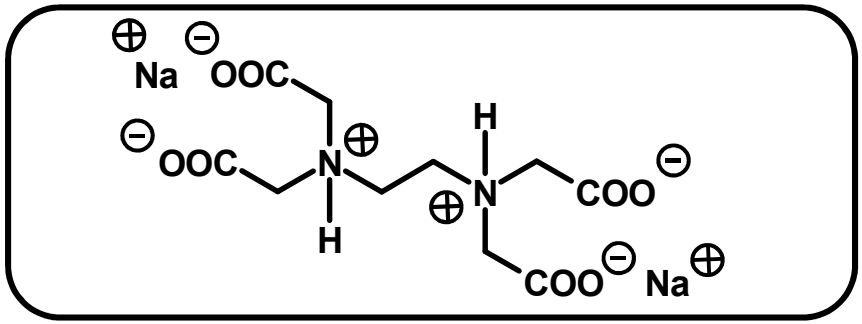
Rainer Buerstinghaus

(R)-2-Hydroxy-3-Methoxy-3-Methyl-Butanoic Acid

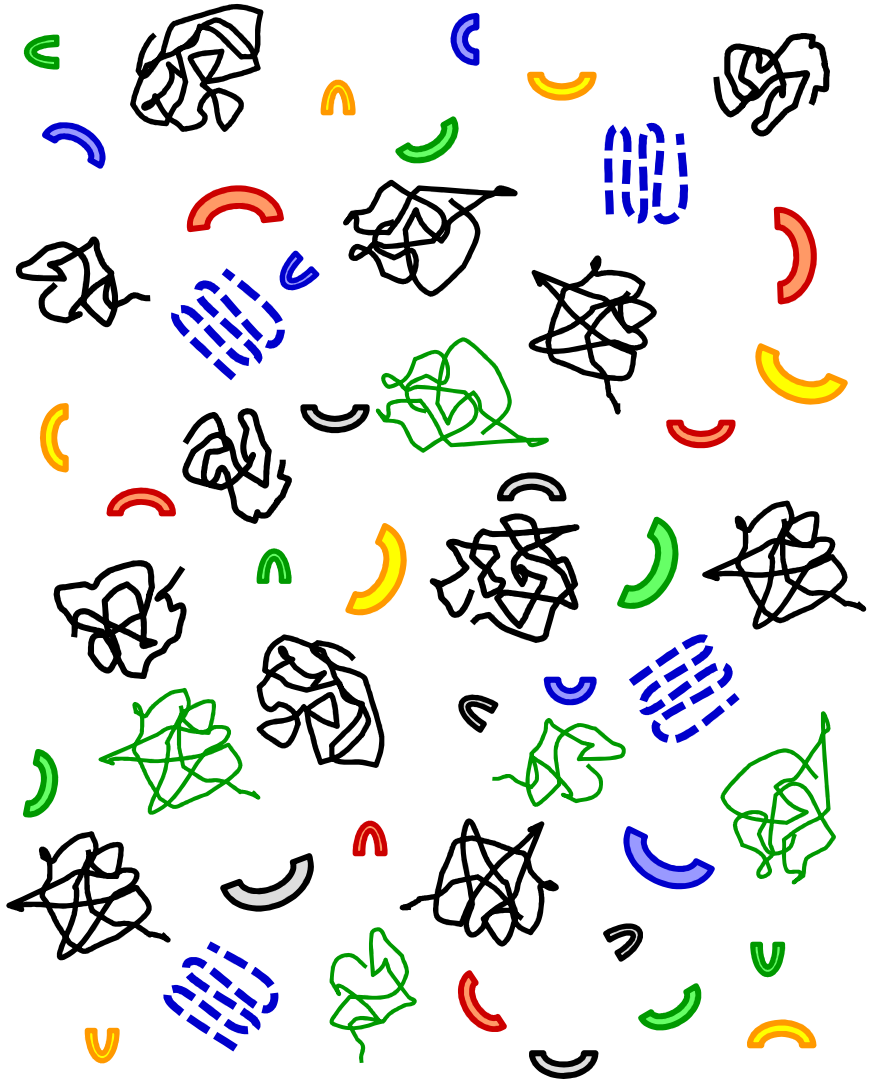
Microbes from a Biotope, Access to the Metagenome, Steps:

3b) **(Chemical) Lysis** of all in water suspended cells.





Lysozyme: Hydrolytic degradation of the crosslinked peptidoglycanes (Mureines for stabilization of cellwalls).

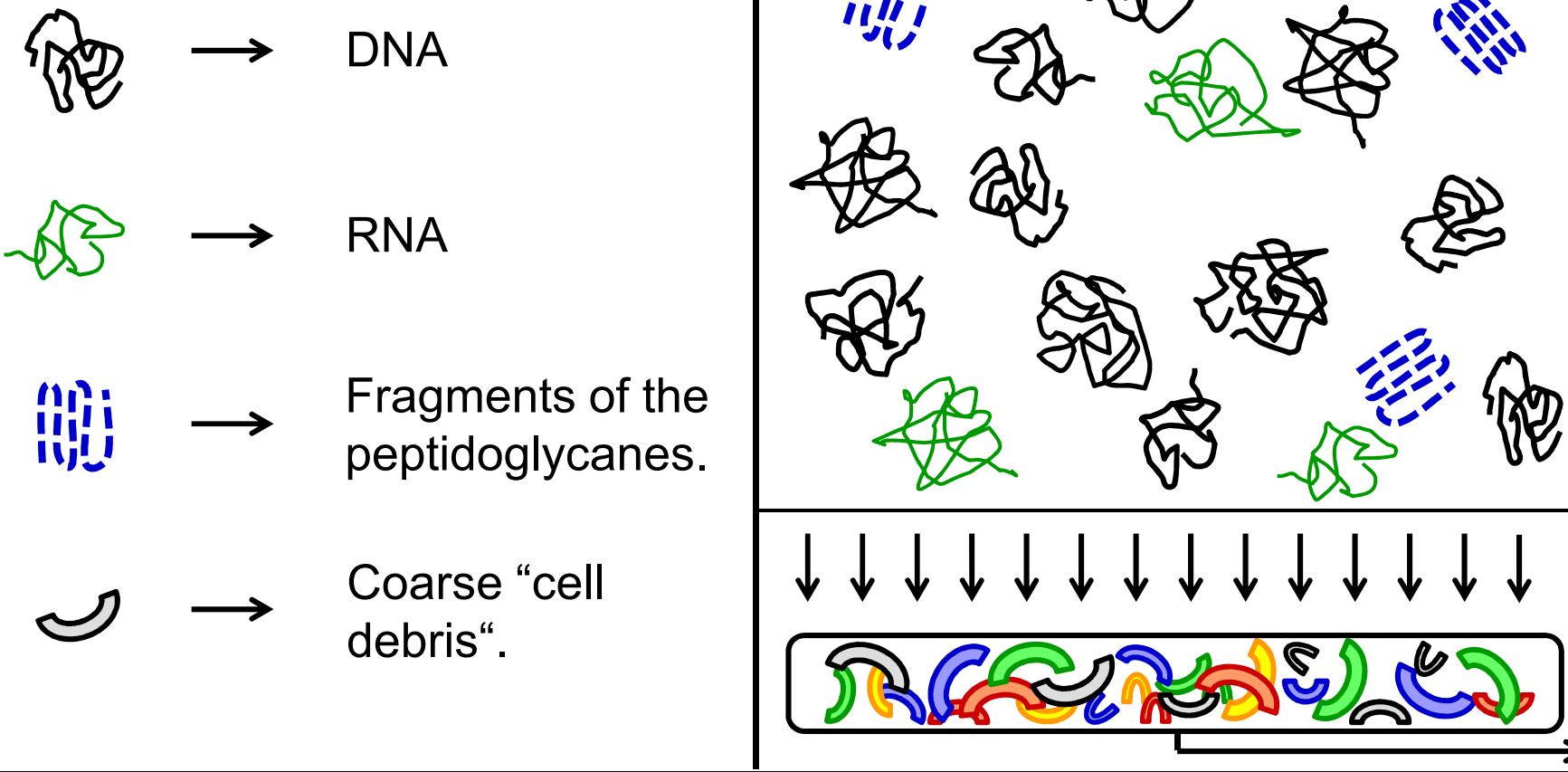


Rainer Buerstinghaus

(R)-2-Hydroxy-3-Methoxy-3-Methyl-Butanoic Acid

Microbes from a Biotope, Access to the Metagenome, Steps:

3c) Centrifugation and **separation** of the **coarse "cell debris".**



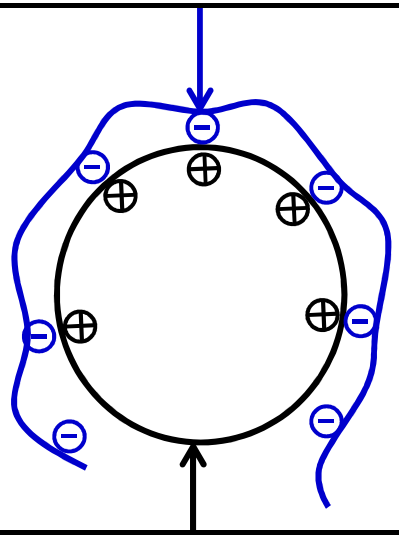
Rainer Buerstinghaus

(R)-2-Hydroxy-3-Methoxy-3-Methyl-Butanoic Acid

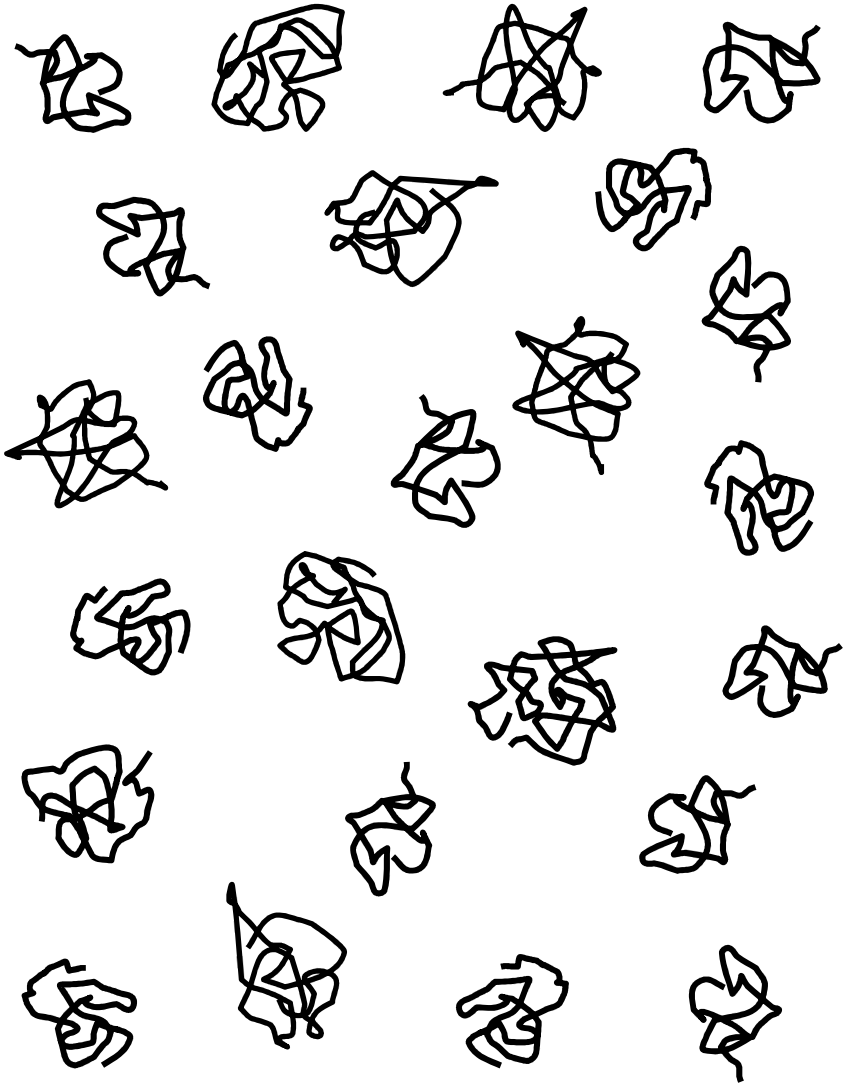
Microbes from a Biotope, Access to the Metagenome, Steps:

3d) **Purification** of DNA by ion exchange chromatography: "Metagenome". →

DNA/RNA/Protein



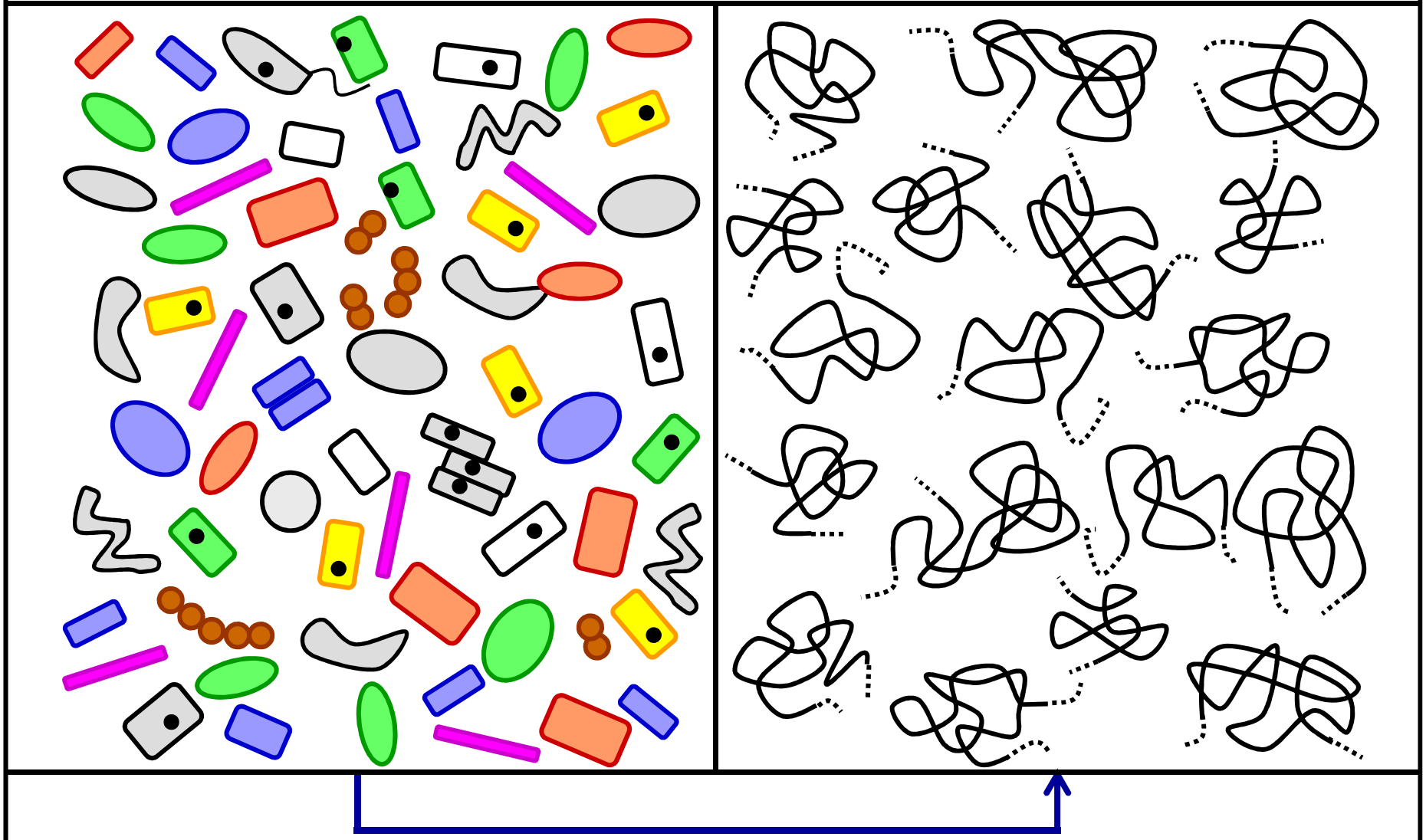
Positively charged resin particle.
Elution with NaCl solutions:
The DNA elutes at the very end.



Rainer Buerstinghaus

(R)-2-Hydroxy-3-Methoxy-3-Methyl-Butanoic Acid

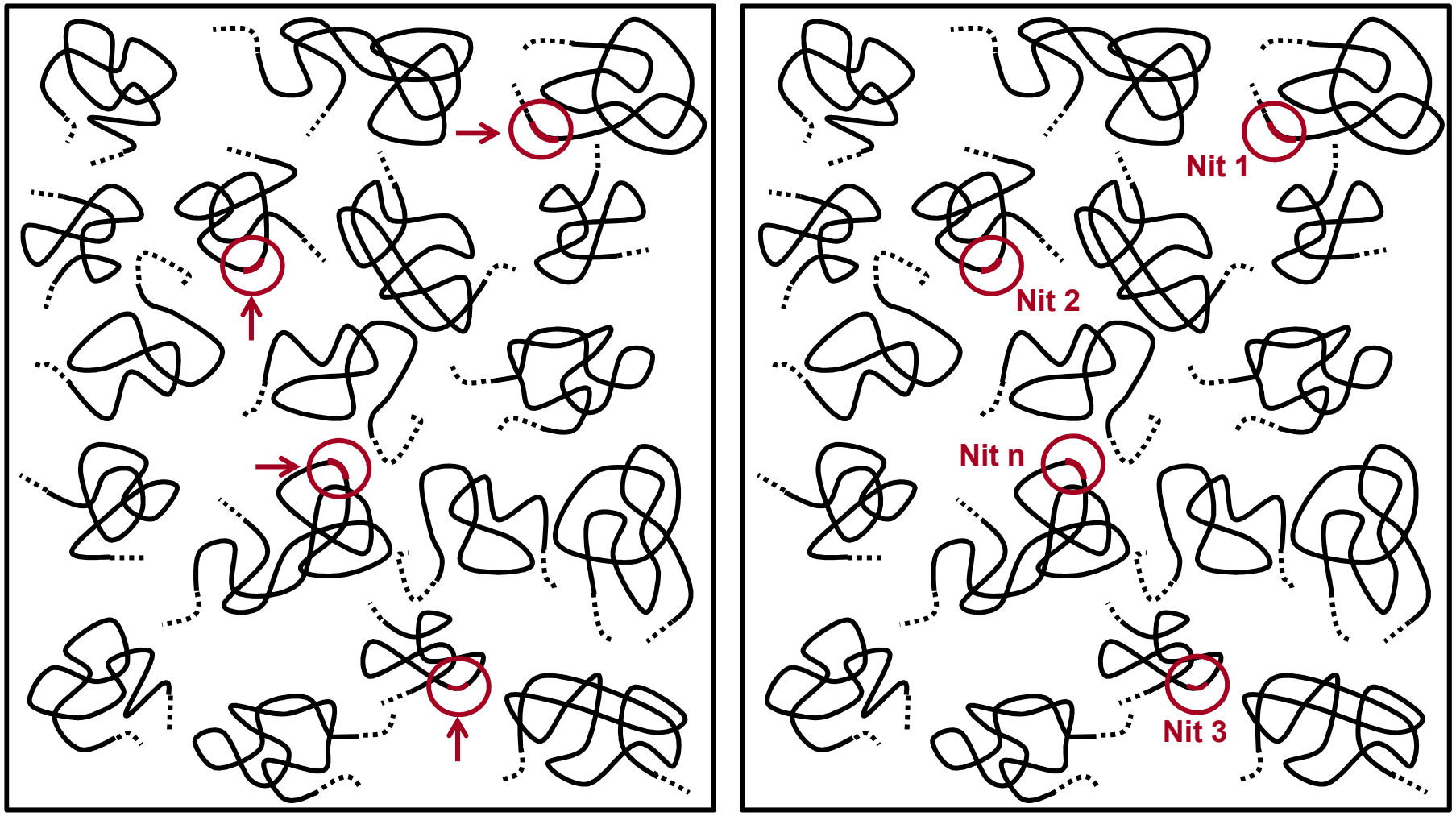
Microbes from a Soil Sample were Lysed, Metagenome:



Rainer Buerstinghaus

(R)-2-Hydroxy-3-Methoxy-3-Methyl-Butanoic Acid

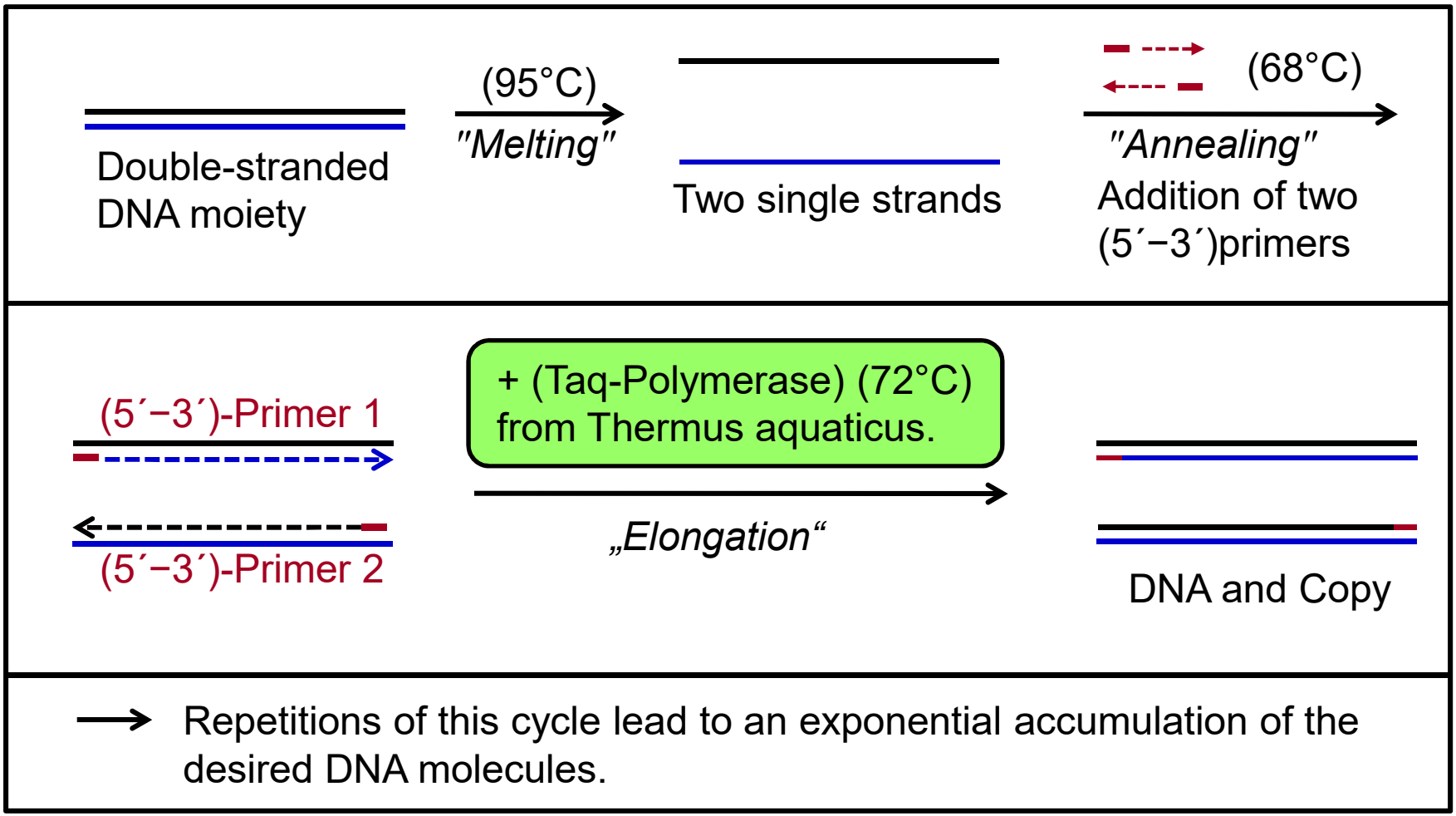
Metagenome, Nitrilase-Encoding DNA Regions — (Nit n):



Rainer Buerstinghaus

(R)-2-Hydroxy-3-Methoxy-3-Methyl-Butanoic Acid

PCR Method According to K. Mullis; Amplification of the Nitrilase-Encoding DNA Fragments, General Scheme:



→ Repetitions of this cycle lead to an exponential accumulation of the desired DNA molecules.

Rainer Buerstinghaus

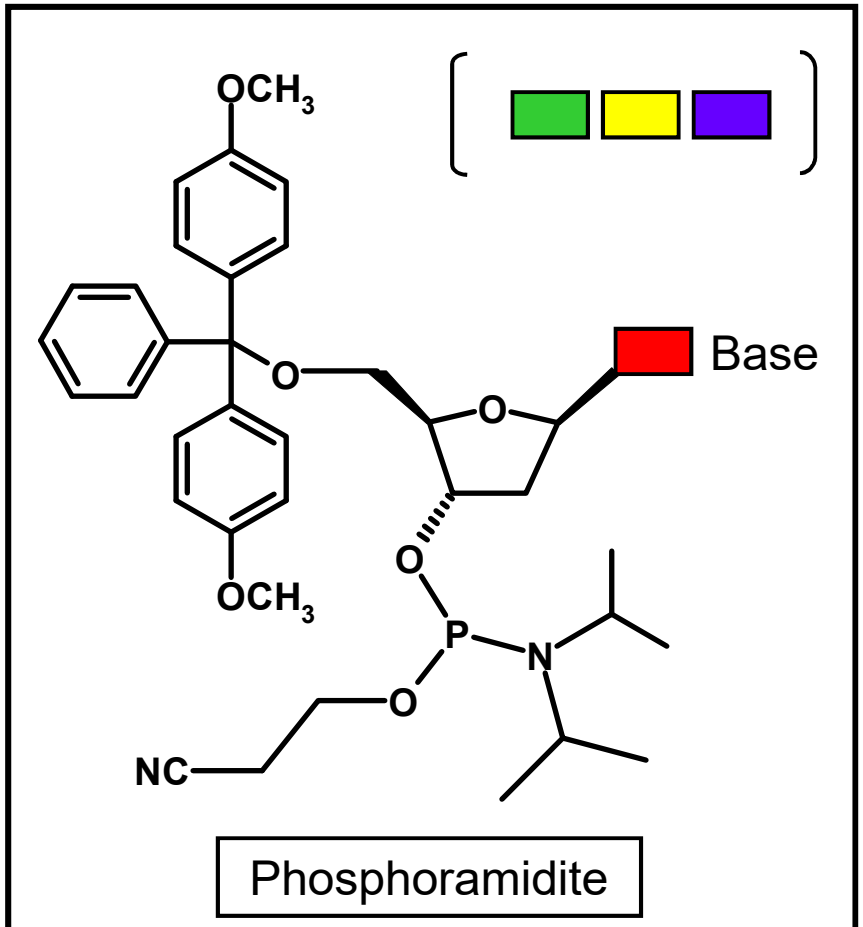
(R)-2-Hydroxy-3-Methoxy-3-Methyl-Butanoic Acid

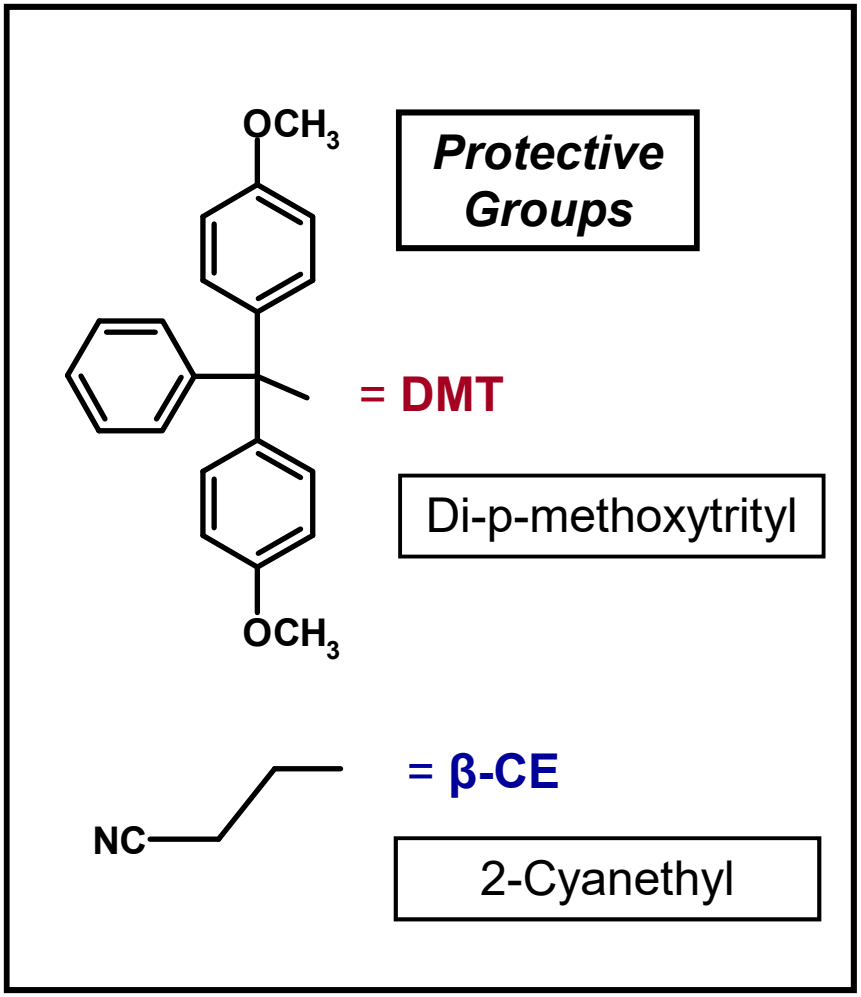
Nitrilase Primers (5'−3') for Gene Isolation by Means of PCR:

N	0	1	C	T	A	T	T	T	G	T	T	T	G	A	G	T	C	A	T	C	C	T	C	A										
N	0	2	C	A	C	C	A	T	G	T	C	T	A	G	T	A	C	T	A	A	A	G	A	T	A	T	G	T	C	A	A	C	T	
N	0	3	C	A	C	C	A	T	G	T	C	A	A	C	T	T	C	A	G	A	A	A	A	C	A	C	T	C	C	G	T			
N	0	4	C	T	A	C	T	T	G	T	T	T	G	A	G	T	C	A	T	C	T	T	C	C										
N	0	5	C	A	C	C	A	T	G	T	C	T	A	G	T	A	C	T	G	A	A	G	A	A	A	T	G	T	C	A	T	C	A	
N	0	6	C	T	A	T	T	T	G	T	T	T	G	A	T	T	C	A	T	C	C	T	C	T										
N	0	7	C	A	T	A	T	G	T	C	T	A	G	T	A	C	T	A	A	A	G	A	T	A	T	G	T	C	A	A	C	T		
N	0	8	C	A	T	A	T	G	G	C	T	A	T	G	G	T	C	C	C	C	T	C	G	G	G	C	T	C						
N	0	9	T	T	A	G	T	A	G	G	G	C	T	T	T	G	C	A	G	T	G	C	T	G	T	C	A	C						
N	1	0	G	A	T	C	C	A	T	A	T	G	A	C	A	A	C	A	C	A	T	C	G	A	A	T	C	G	C	C	G	T		
N	1	1	G	A	T	C	A	A	G	C	T	T	C	A	T	C	T	A	G	G	G	T	T	T	G	A	G	C	G	T	G	G	T	
N	1	2	G	A	T	C	C	C	A	T	G	G	G	G	T	T	C	T	G	G	A	A	A	G	T	T	G	C	A	G	C	A	G	
N	1	3	G	A	T	C	A	A	G	C	T	T	C	T	A	G	C	G	T	A	A	T	G	G	A	A	T	G	A	T	A	T	C	G	C
N	1	4	G	A	T	C	C	C	A	T	G	G	G	T	G	T	C	G	C	A	C	T	A	G	C	A	C	A	A	C	T	T	A	
N	1	5	G	A	T	C	A	A	G	C	T	T	C	C	C	C	A	A	T	T	T	A	C	G	C	T	T	C	A	G				
N	1	6	G	A	T	C	C	C	A	T	G	G	G	T	A	A	G	T	T	G	A	A	A	G	T	C	G	C	G	G	C	A	G	T	
N	1	7	G	A	T	C	A	A	G	C	T	T	G	C	G	C	C	G	C	G	C	T	T	A	G	T	T	C							
																																Rainer Buerstinghaus	
N	X	X	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33

Oligonucleotide Syntheses for the Nitrilase Primers

Solid-Phase-Method (Merrifield Principle, after R.L. Letsinger):

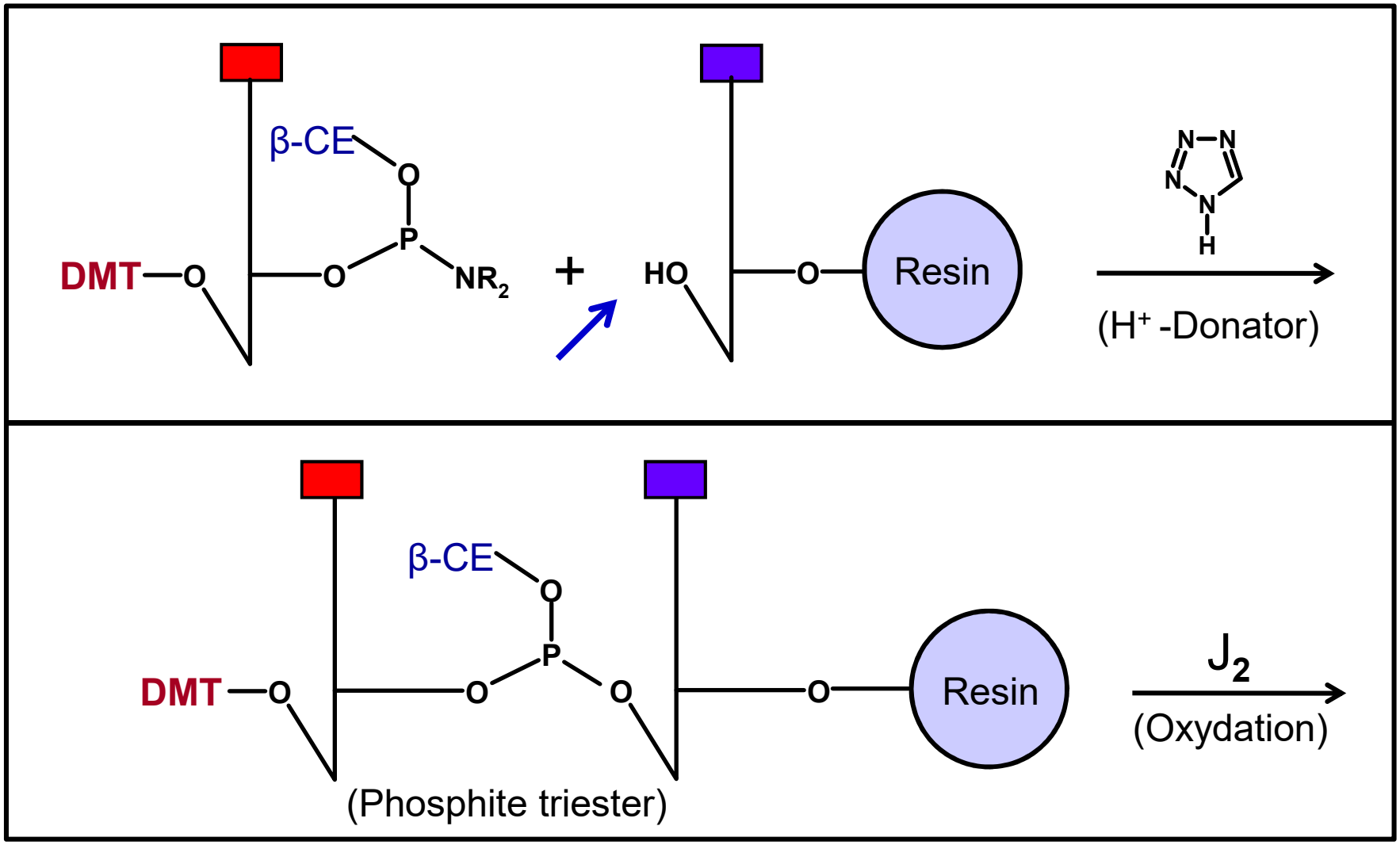




Rainer Buerstinghaus

Oligonucleotide Syntheses for the Nitrilase Primers

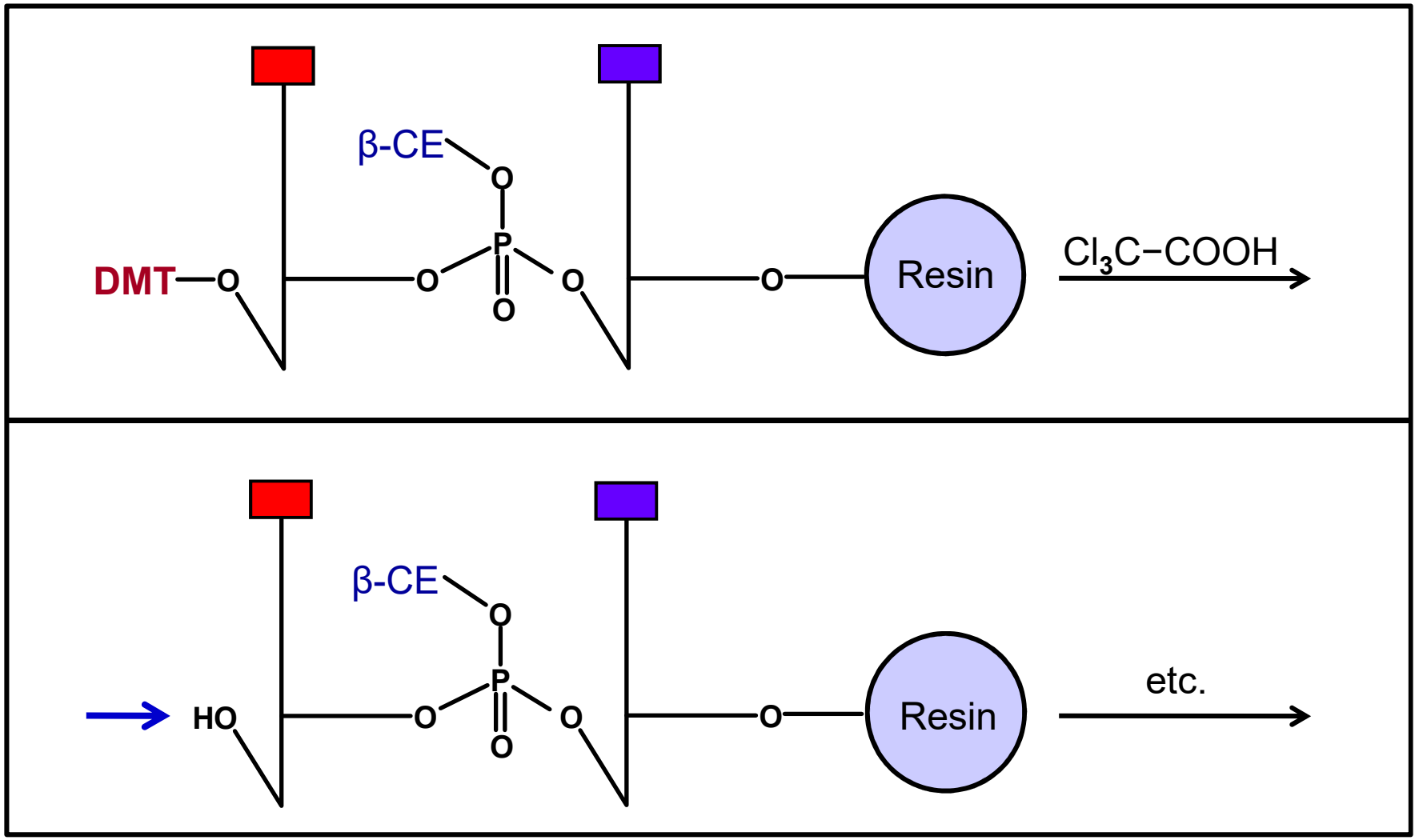
Solid-Phase-Method (Merrifield Principle, after R.L. Letsinger):



Rainer Buerstinghaus

Oligonucleotide Syntheses for the Nitrilase Primers

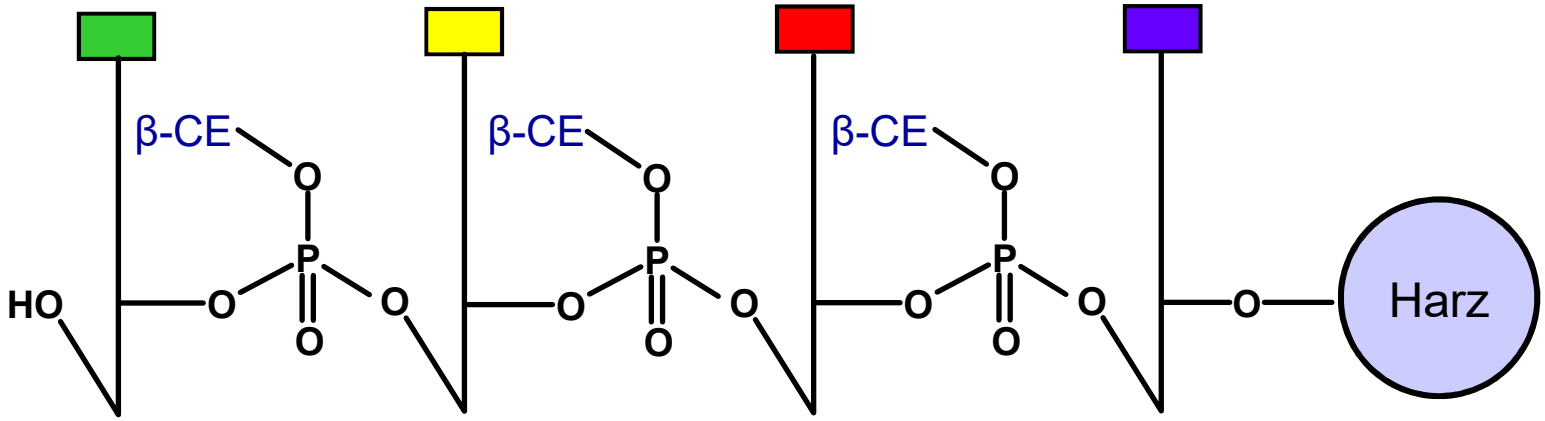
Solid-Phase-Method (Merrifield Principle, after R.L. Letsinger):



Rainer Buerstinghaus

Oligonucleotide Syntheses for the Nitrilase Primers

Solid-Phase-Method (Merrifield Principle, after R.L. Letsinger):

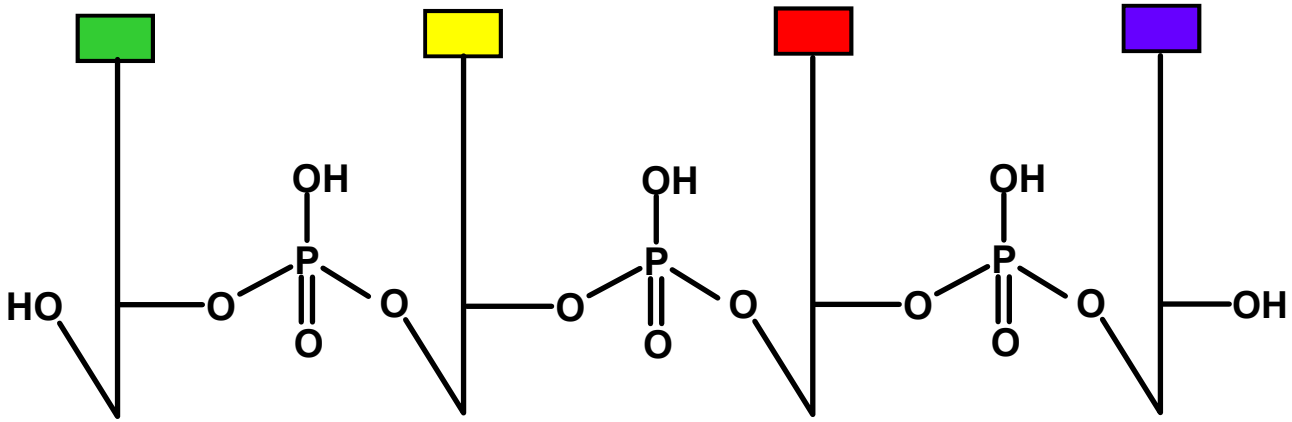


At the end of the reaction sequence, NH_3 is added to the mixture (Removal of all β-CE groups and removal of the oligonucleotide from the resin).

Rainer Buerstinghaus

Oligonucleotide Syntheses for the Nitrilase Primers

Solid-Phase-Method (Merrifield Principle, after R.L. Letsinger):

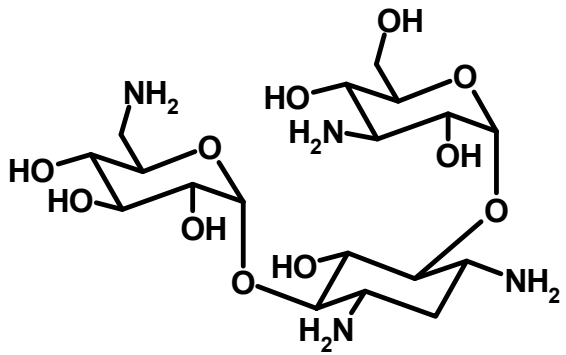


The resulting polynucleotide is purified by HPLC or by electrophoresis on polyacrylamide gels.

Rainer Buerstinghaus

Commercially available plasmids for the incorporation into nitrilase genes, each with a resistance gene against Kanamycin A:
pNit 01 (Source: Invitrogen)
pNit 02 (Source: Novagen)
pNit 03 (Source: Invitrogen)
pNit 04 (Source: Invitrogen)
pNit 05 (Source: Novagen)
pNit 06 (Source: Novagen)
pNit 07 (Source: Invitrogen)
pNit 08 (Source: Novagen)
pNit 09 (Source: Novagen)
pNit 10 (Source: Invitrogen)
pNit 11 (Source: Novagen)
pNit 12 (Source: Invitrogen)

Organisms with activatable nitrilase genes which can be cloned with PCR primers:
Arabidopsis thaliana (Thale Cress)
Brassica napus (Rape)
Zea mays (Corn)
Bordetella bronchiseptica (Whooping Cough Germ)
Escherichia coli (Intestinal Bacterium)
Lactobacillus plantarum (Fermented Foods)
Rhodopseudomonas palustris (Purple Bacterium)
Oryza sativa (Rice)

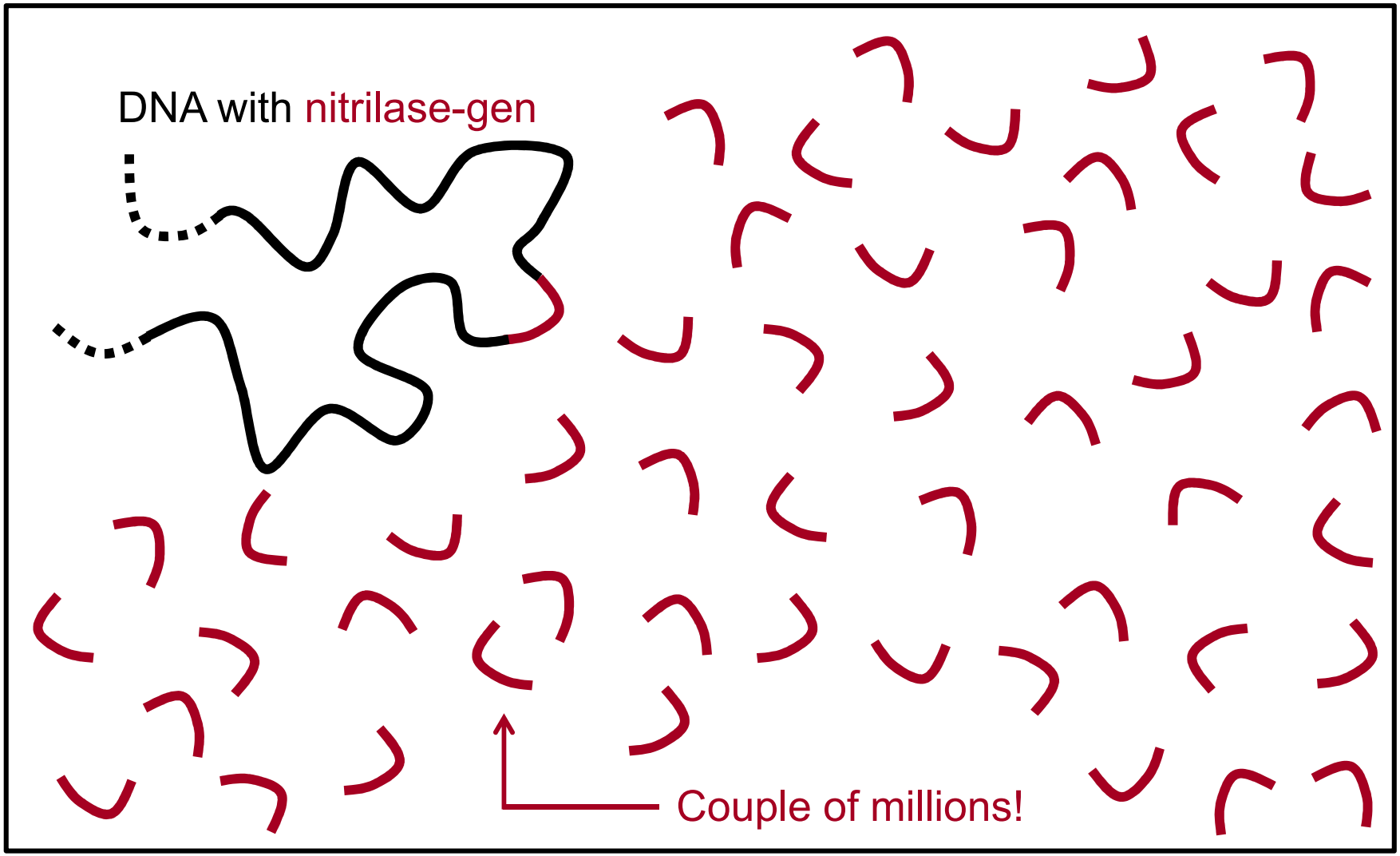


Kanamycin:
Aminoglycoside-antibiotic, inhibitor of the ribosomal protein synthesis.

Rainer Buerstinghaus

(R)-2-Hydroxy-3-Methoxy-3-Methyl-Butanoic Acid

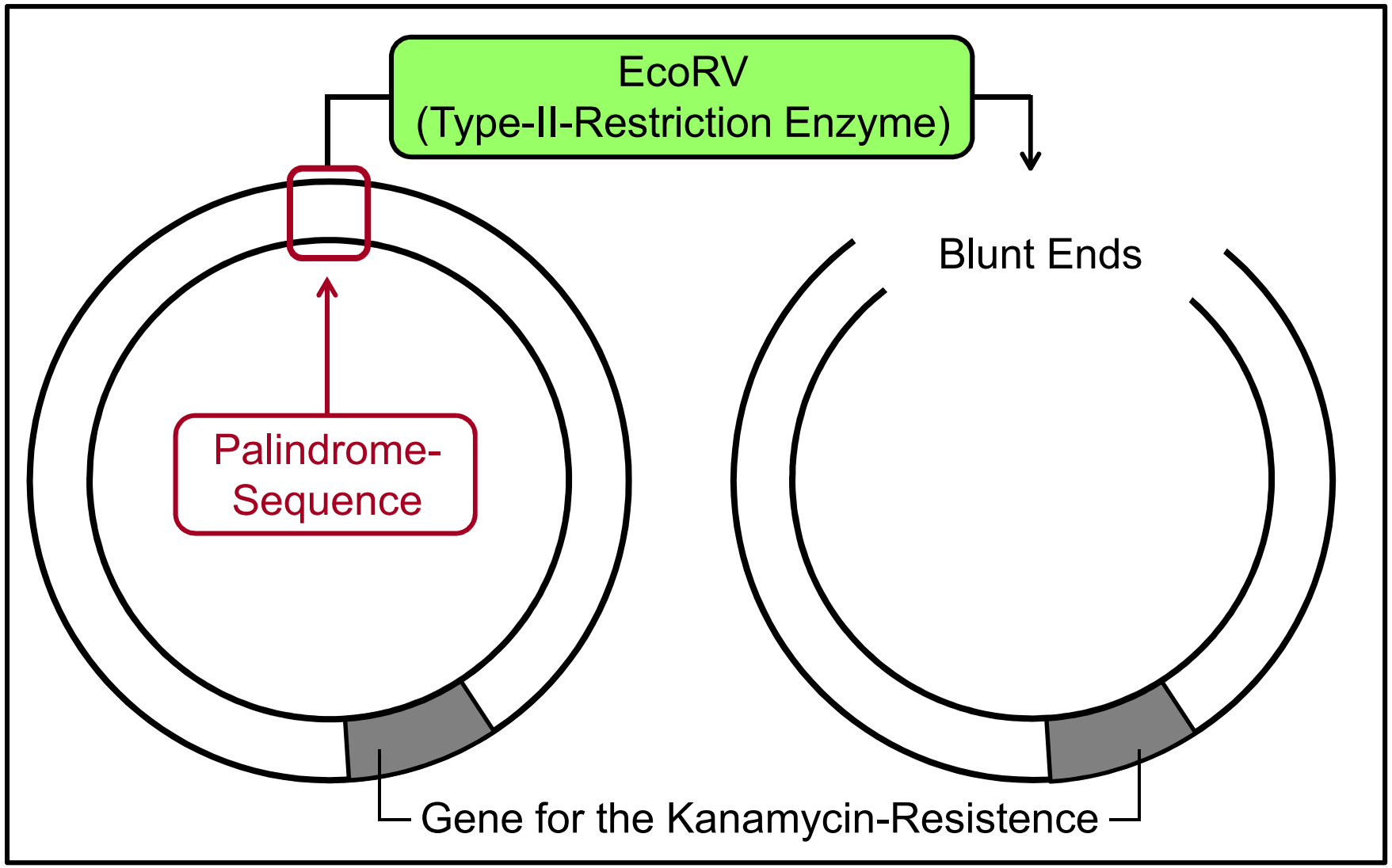
Gene Isolation by PCR Technique (Amplification):



Rainer Buerstinghaus

(R)-2-Hydroxy-3-Methoxy-3-Methyl-Butanoic Acid

Restriction Cleavage of a Plasmid ("Straight Cleavage"):

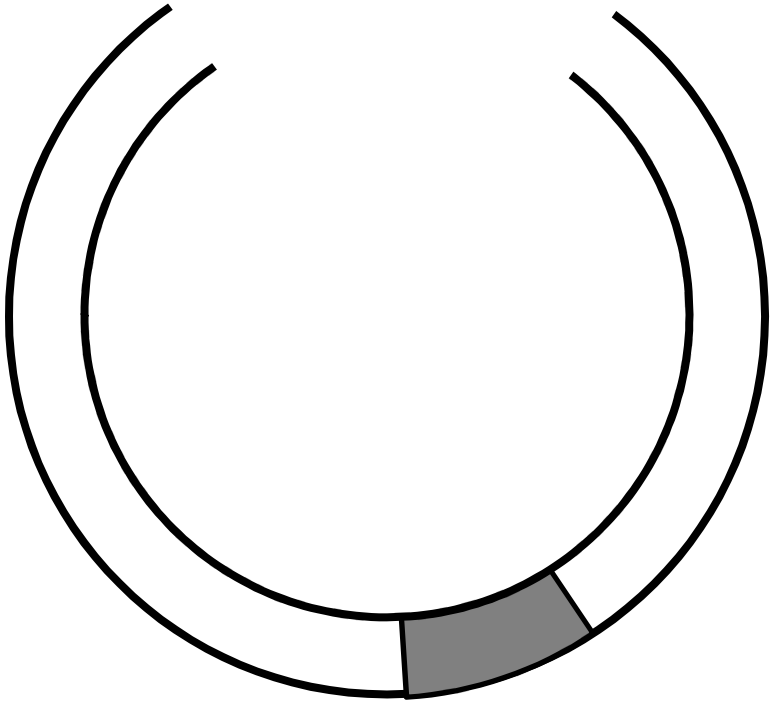


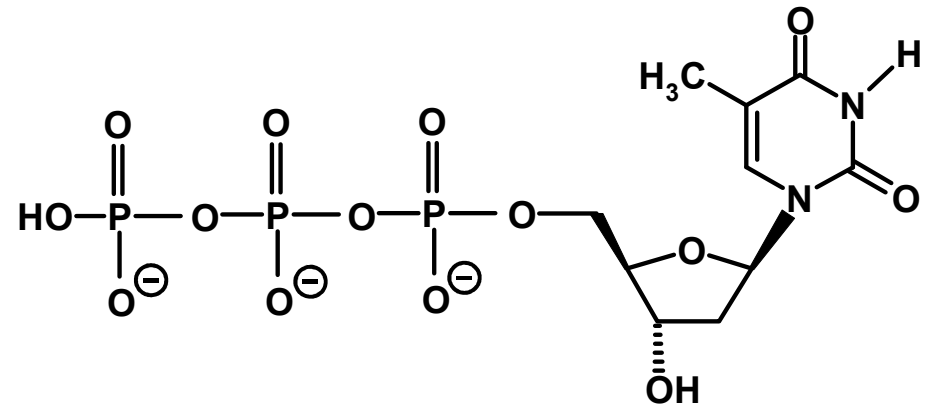
Rainer Buerstinghaus

(R)-2-Hydroxy-3-Methoxy-3-Methyl-Butanoic Acid

Synthesis of a Vector with an Overhanging Thymidine (T):

2´-Desoxythymidine-5´-triphosphate (dTTP)





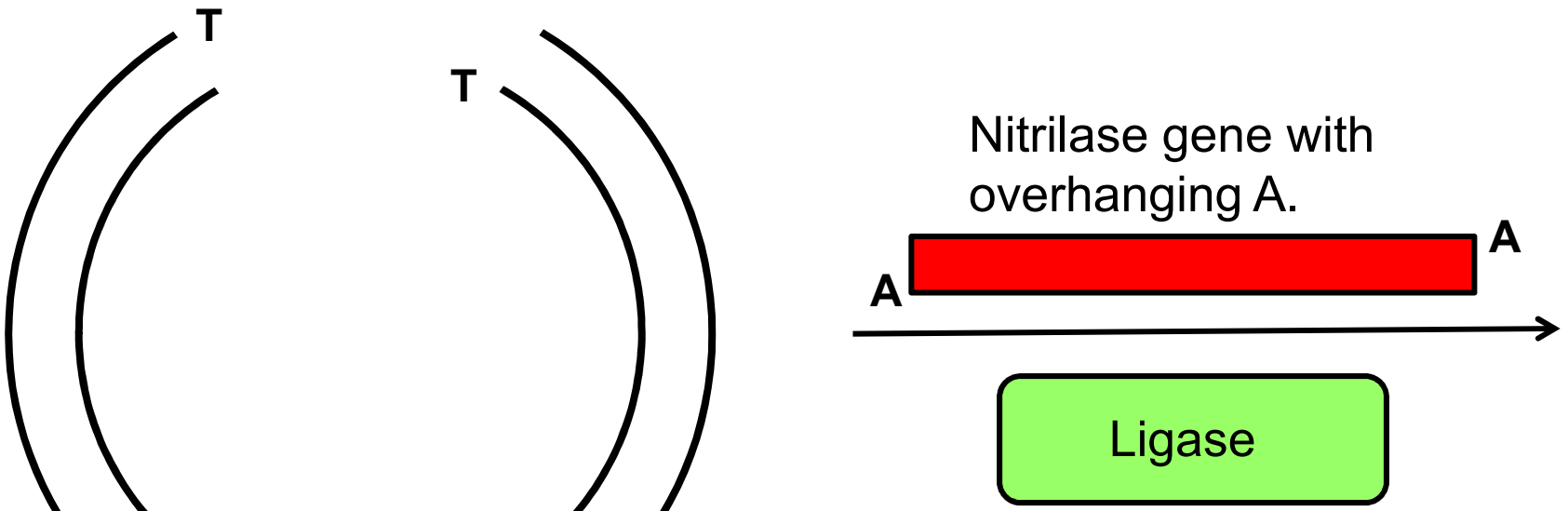
Taq-Polymerase

(Absence of Primers!)

Rainer Buerstinghaus

(R)-2-Hydroxy-3-Methoxy-3-Methyl-Butanoic Acid

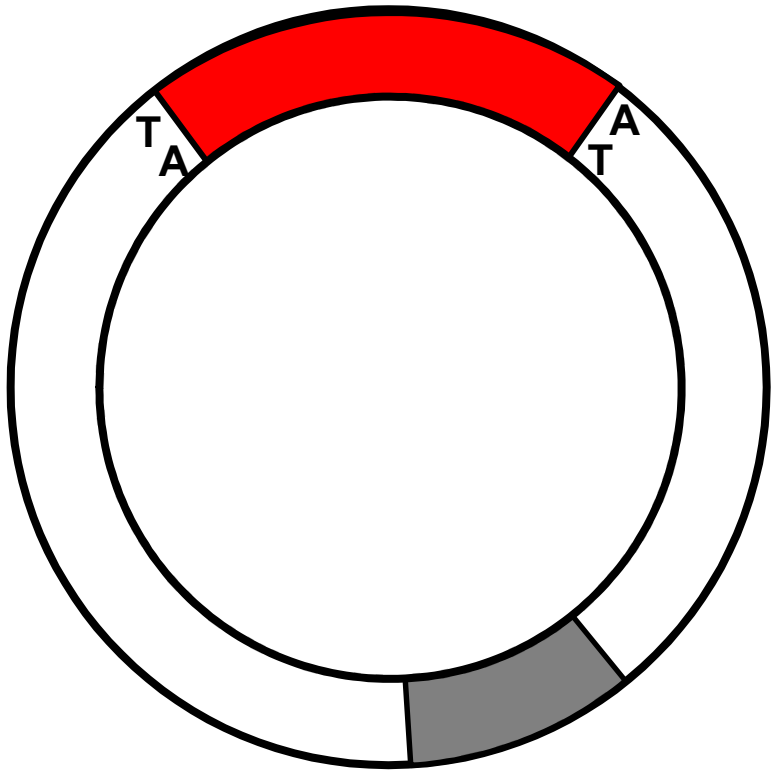
Ligation with the PCR-Amplified Nitrilase Gene:



Rainer Buerstinghaus

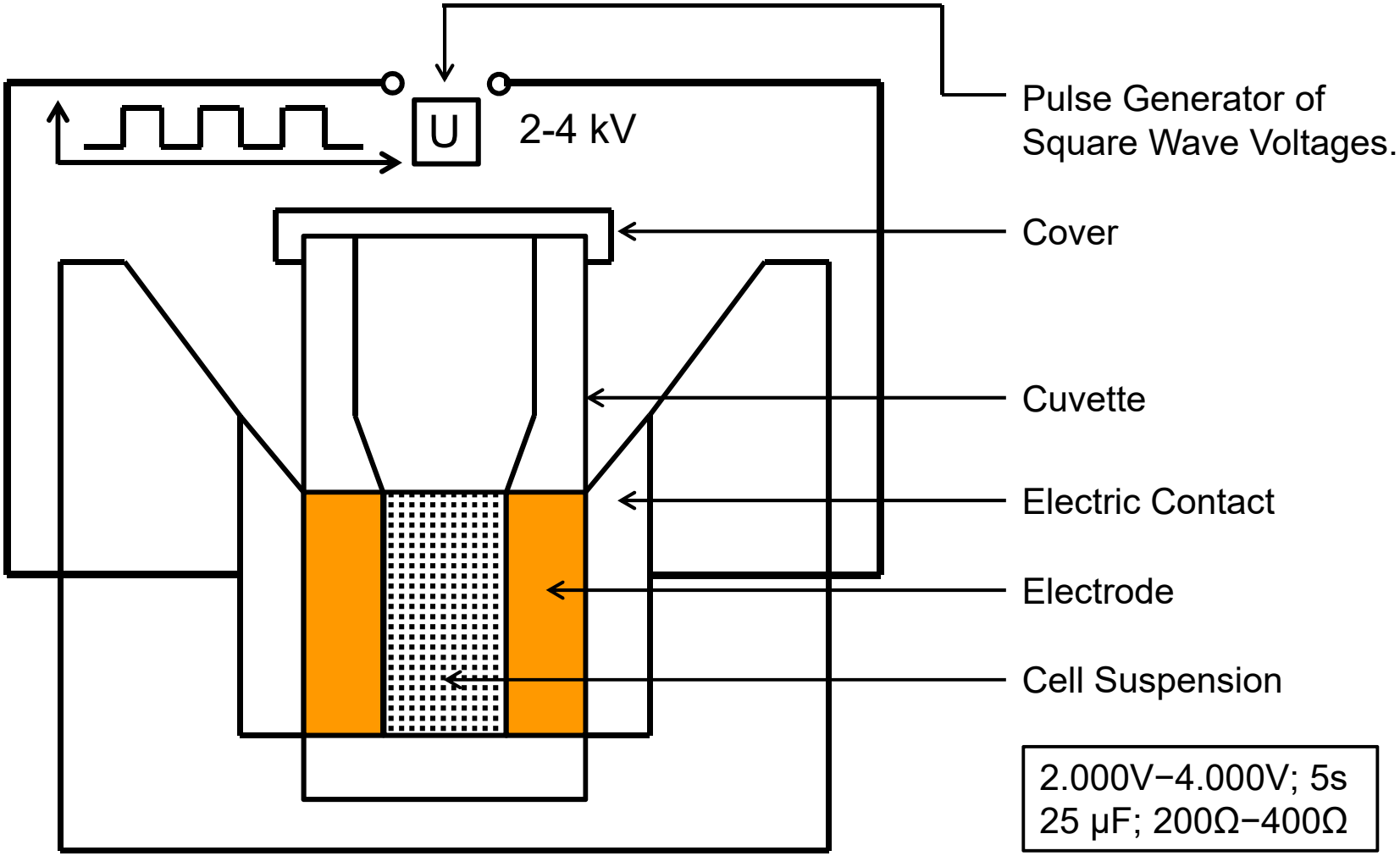
(R)-2-Hydroxy-3-Methoxy-3-Methyl-Butanoic Acid

Plasmid Vector with the Implemented Nitrilase Gene:



Rainer Buerstinghaus

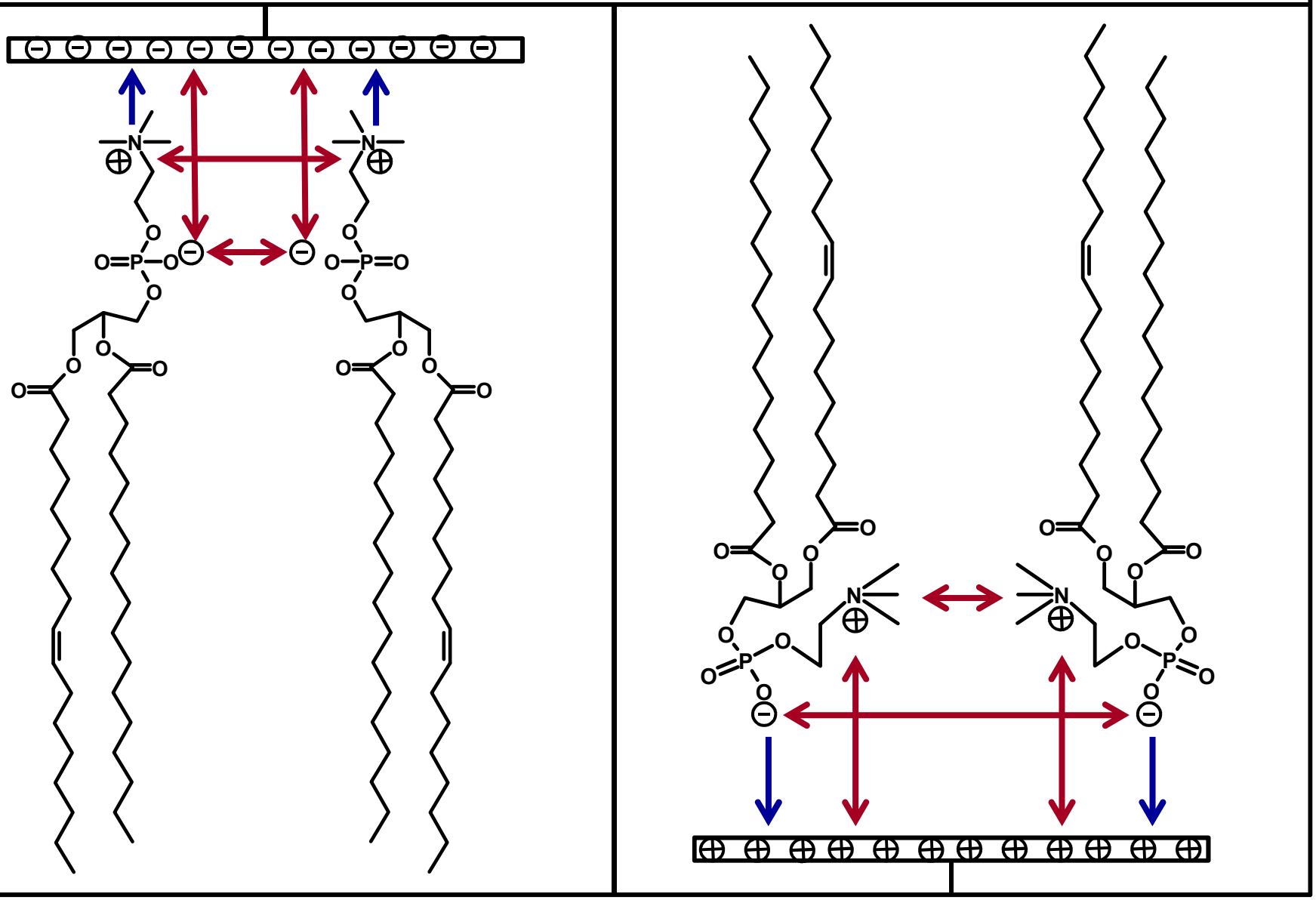
Electroporator for introducing plasmids into host cells through the porous phospholipid membrane (Transfection):



Rainer Buerstinghaus

Plasmid-Transfektion by **Electroporation,** U = 3.000V, 5 s.

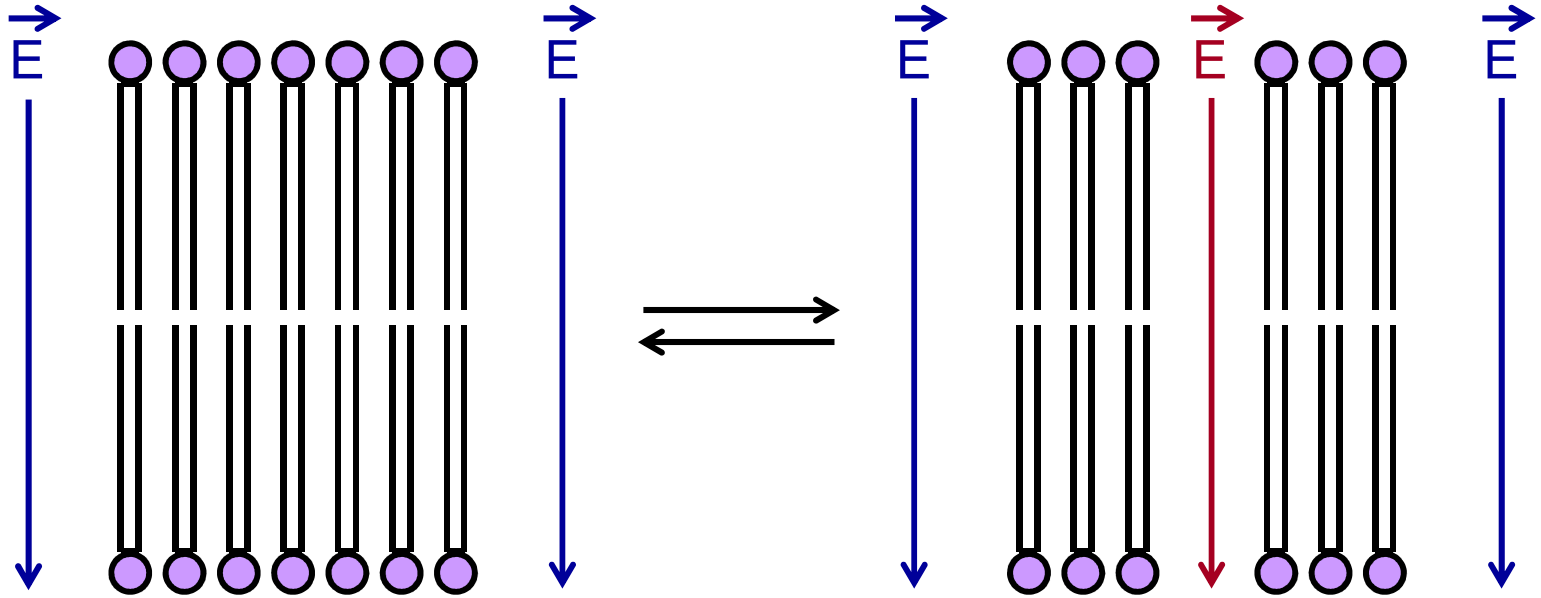
Effective Forces: **Attraction** → Repulsion ↔



Rainer Buerstinghaus

(R)-2-Hydroxy-3-Methoxy-3-Methyl-Butanoic Acid

Electroporation, Physical Mechanism (?):

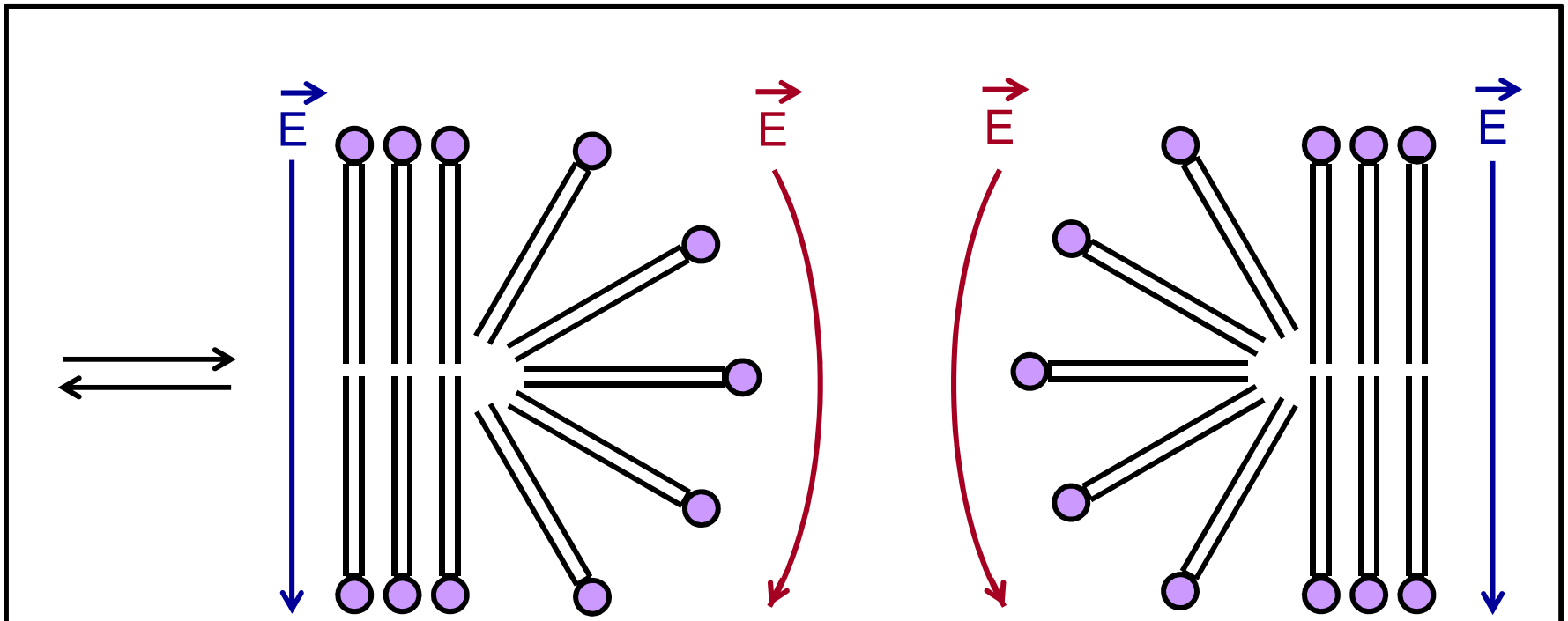


Intact double layer as a **two-dimensional liquid.**	Hydrophobic pore by **lateral tearing up** of the **double layer.**

Rainer Buerstinghaus

(R)-2-Hydroxy-3-Methoxy-3-Methyl-Butanoic Acid

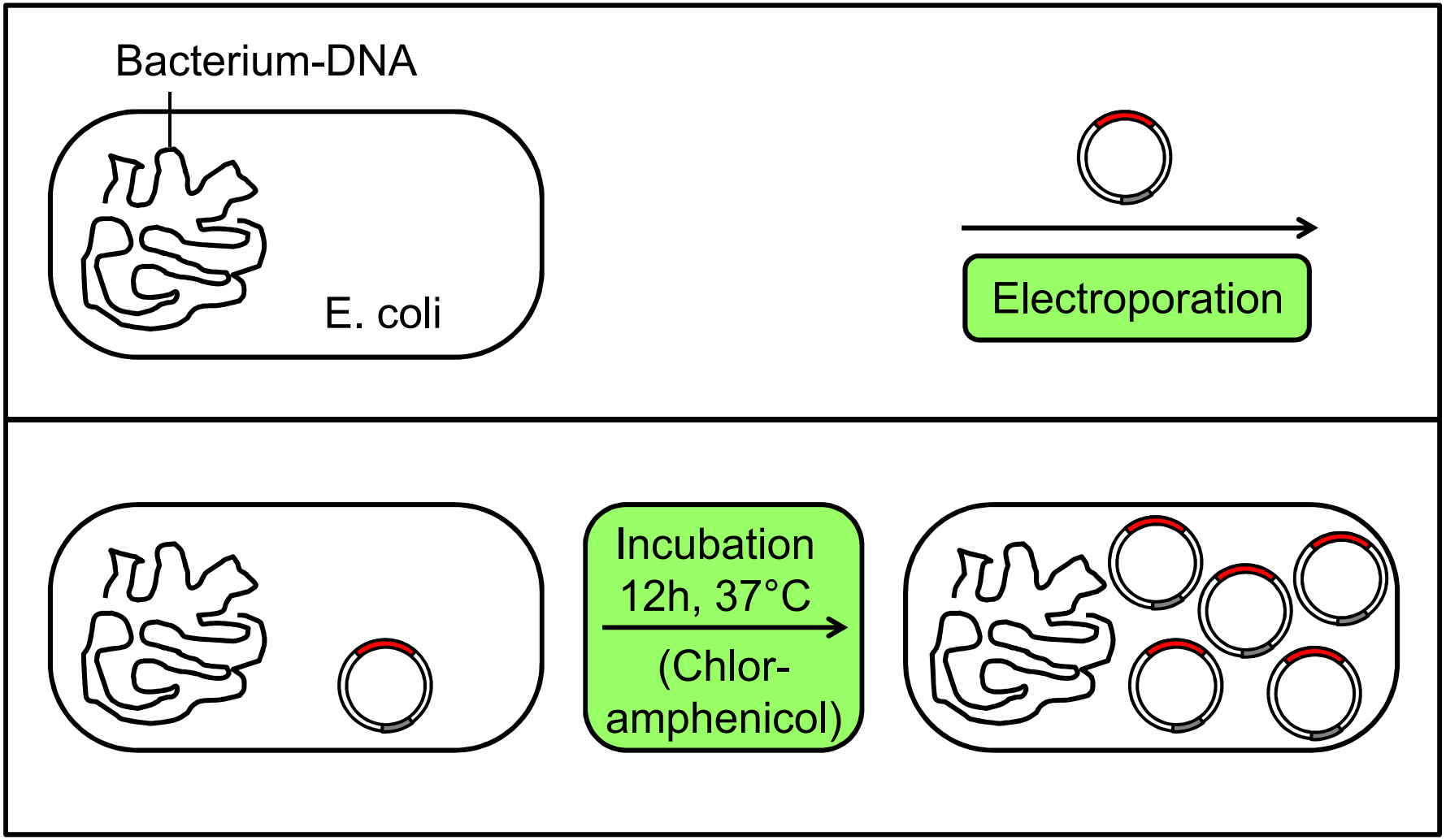
Electroporation, Physical Mechanism (?):



Hydrophilic pore: The induced membrane potential on the cell surface initiates a **"Dielectric Breakdown"**.

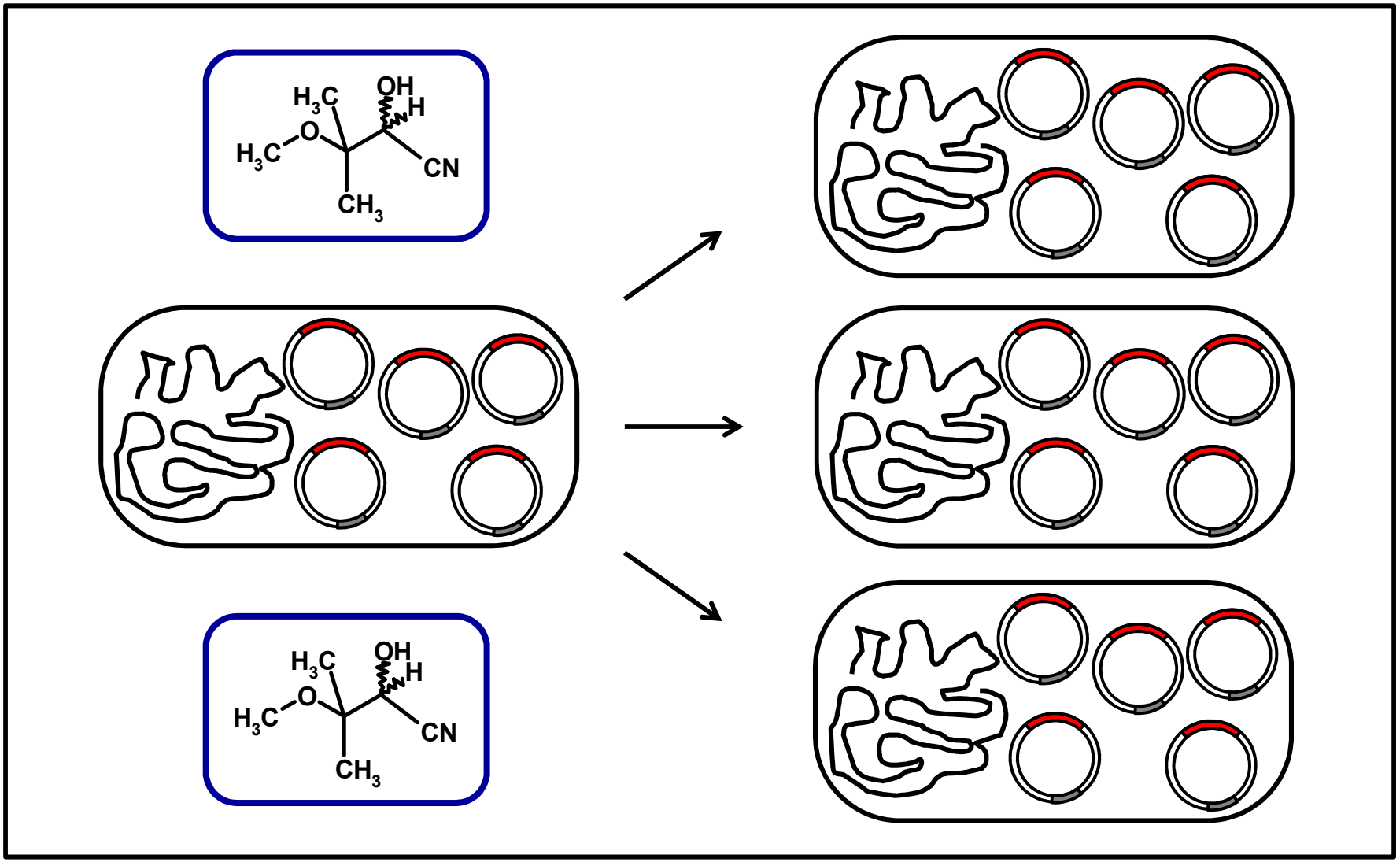
Rainer Buerstinghaus

Electroporation for Introducing the recombinant plasmid into the host cell; Selective multiplication of the new plasmid within the host cell in the presence of chloramphenicol.



Rainer Buerstinghaus

Multiplication of the host cell with the recombinant plasmid DNA. The nutrient medium contains Kanamycin.



Rainer Buerstinghaus

(R)-2-Hydroxy-3-Methoxy-3-Methyl-Butanoic Acid

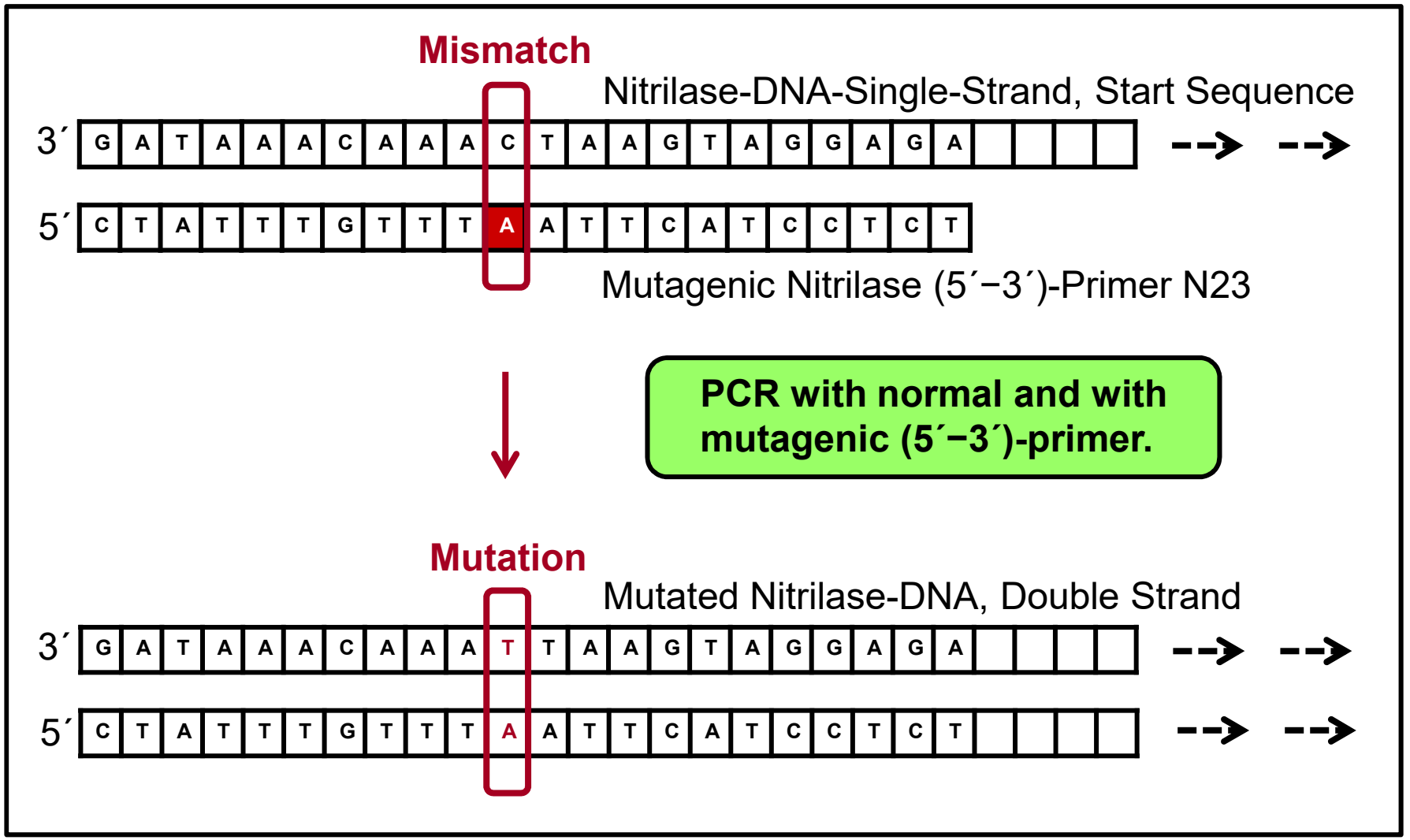
Mutagenic Nitrilase Primers (5'−3') for Gene Mutations by PCR:

N	1	8	C	T	A	T	T	T	G	T	T	T	A	A	G	T	C	A	T	C	C	T	C	A										
N	1	9	C	A	C	C	A	T	G	T	C	T	A	G	G	A	C	T	A	A	A	G	A	T	A	T	G	T	C	A	A	C	T		
N	2	0	C	A	C	C	A	T	G	T	G	A	A	C	T	T	C	A	G	A	A	A	A	C	A	C	T	C	C	G	T				
N	2	1	C	T	A	C	T	T	G	T	T	A	G	A	G	T	C	A	T	C	T	T	C	C											
N	2	2	C	A	C	C	A	T	G	T	C	T	A	G	T	T	C	T	G	A	A	G	A	A	A	T	G	T	C	A	T	C	A		
N	2	3	C	T	A	T	T	T	G	T	T	T	A	A	T	T	C	A	T	C	C	T	C	T											
N	2	4	C	A	T	A	T	G	T	C	T	A	G	T	G	C	T	A	A	A	G	A	T	A	T	G	T	C	A	A	C	T			
N	2	5	C	A	T	A	T	G	G	C	T	A	A	G	G	T	C	C	C	C	T	C	G	G	G	C	T	C							
N	2	6	T	T	A	G	T	A	G	G	G	A	T	T	T	G	C	A	G	T	G	C	T	G	T	C	A	C							
N	2	7	G	A	T	C	C	A	T	A	T	G	A	C	A	A	C	T	C	A	T	C	G	A	A	T	C	G	C	C	G	T			
N	2	8	G	A	T	C	A	A	G	C	T	T	C	A	T	G	T	A	G	G	G	T	T	T	G	A	G	C	G	T	G	G	T		
N	2	9	G	A	T	C	C	C	A	T	G	G	G	G	A	T	C	T	G	G	A	A	A	G	T	T	G	C	A	G	C	A	G		
N	3	0	G	A	T	C	A	A	G	C	T	T	A	T	A	G	C	G	T	G	A	T	G	G	A	A	T	G	A	T	A	T	C	G	C
N	3	1	G	A	T	C	C	C	A	T	G	G	G	T	G	T	C	T	C	A	C	T	A	G	C	A	C	A	A	A	C	T	T	A	
N	3	2	G	A	T	C	A	A	G	C	T	G	C	C	C	C	A	A	T	T	T	A	C	G	C	T	T	C	A	G					
N	3	3	G	A	T	C	C	C	A	T	G	G	G	T	A	A	T	T	T	G	A	A	A	G	T	C	G	C	G	G	C	A	G	T	
N	3	4	G	A	T	C	A	A	G	C	T	T	G	A	G	C	C	G	C	G	C	T	T	A	G	T	T	C							
N	X	X	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33

Rainer Buerstinghaus

(R)-2-Hydroxy-3-Methoxy-3-Methyl-Butanoic Acid

Point Mutated Nitrilase-DNA via (5´−3´)-Primer N23 and PCR:

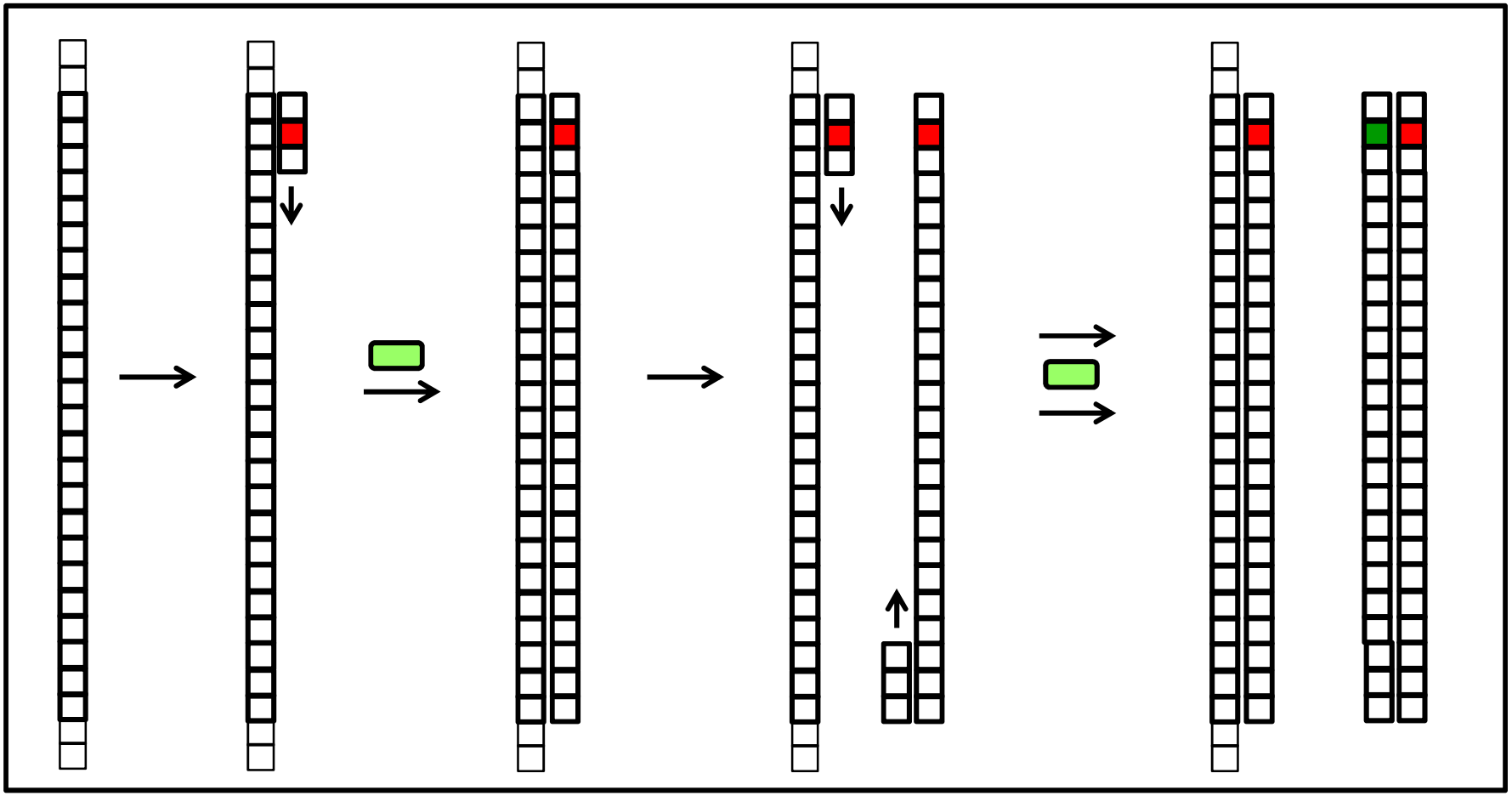


Rainer Buerstinghaus

(R)-2-Hydroxy-3-Methoxy-3-Methyl-Butanoic Acid

Point Mutated Nitrilase-DNA via (Mutated) Primer and PCR:

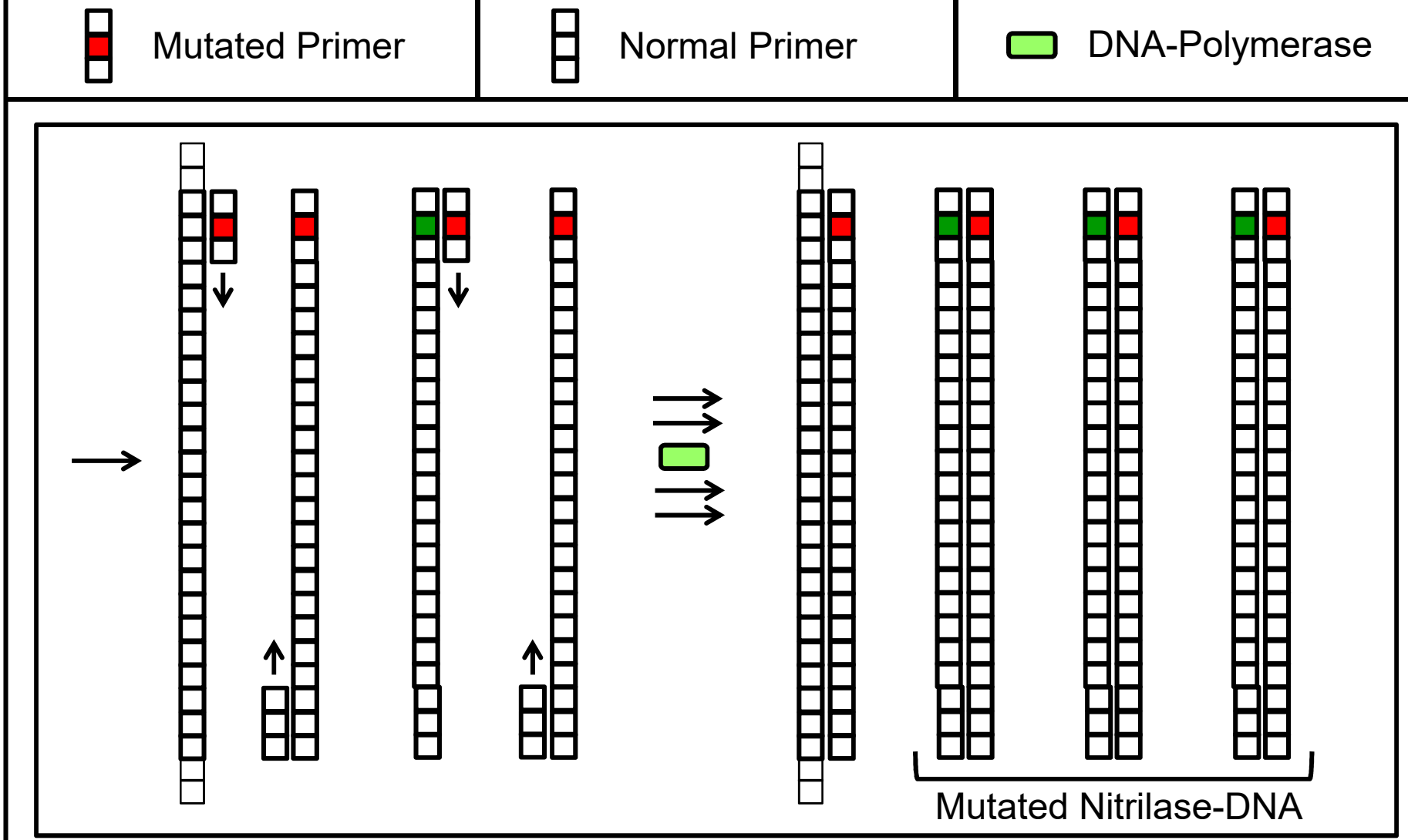
Mutated Primer | Normal Primer | DNA-Polymerase



Rainer Buerstinghaus

(R)-2-Hydroxy-3-Methoxy-3-Methyl-Butanoic Acid

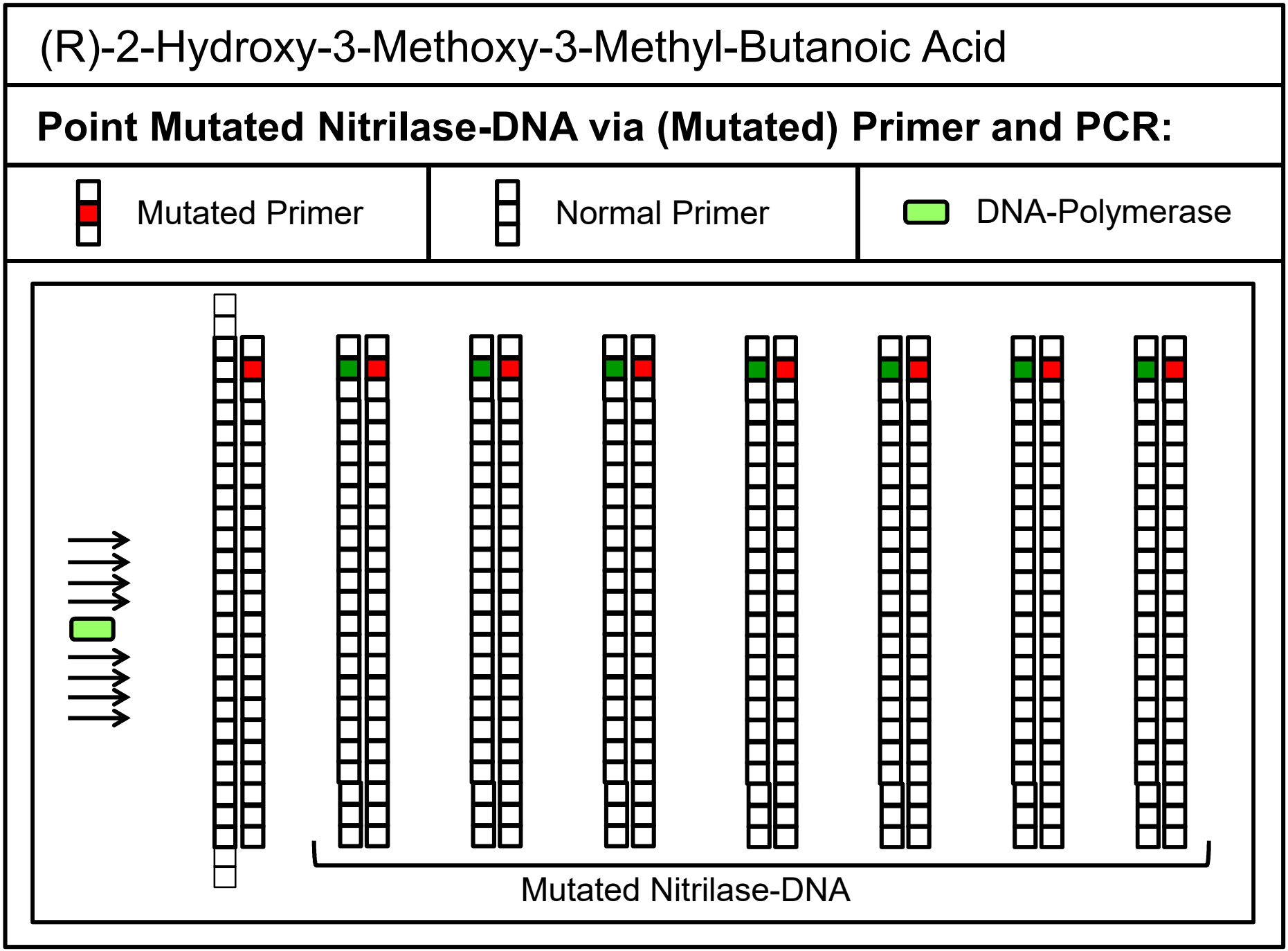
Point Mutated Nitrilase-DNA via (Mutated) Primer and PCR:



Rainer Buerstinghaus

(R)-2-Hydroxy-3-Methoxy-3-Methyl-Butanoic Acid

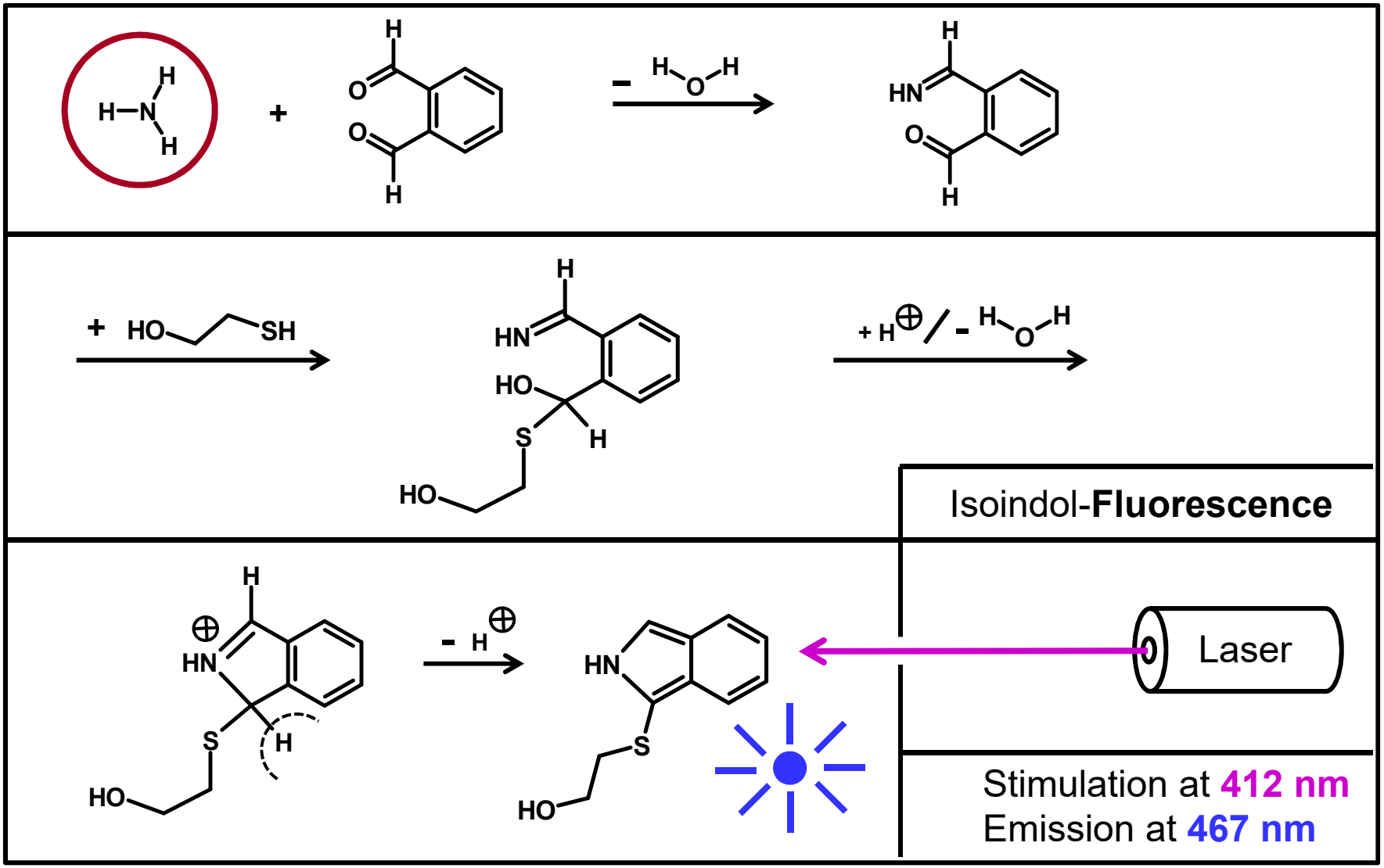
Point Mutated Nitrilase-DNA via (Mutated) Primer and PCR:



Rainer Buerstinghaus

(R)-2-Hydroxy-3-Methoxy-3-Methyl-Butanoic Acid

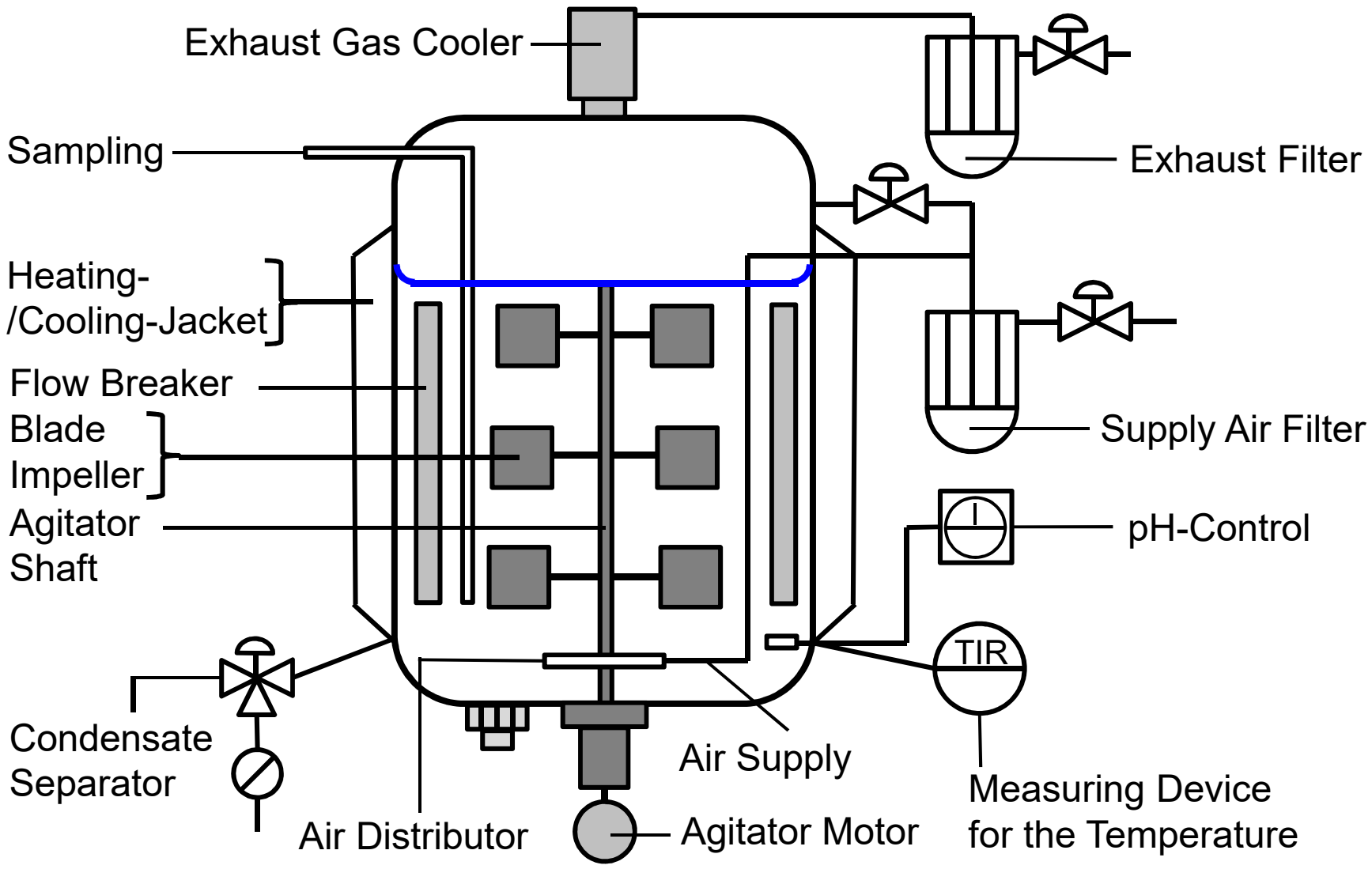
Measurement of Nitrilase Activities by Isoindole Fluorescence:



Rainer Buerstinghaus

(R)-2-Hydroxy-3-Methoxy-3-Methyl-Butanoic Acid

Scale-up, Stirring Tank Reactor after Sternad (STR, H/D ≈ 2-3):



Rainer Buerstinghaus

(R)-2-Hydroxy-3-Methoxy-3-Methyl-Butanoic Acid

Scale-up, Stirring Tank Reactor after Sternad (STR, H/D ≈ 2-3):

Capacity

- Laboratory reactors (< 50 l)
- Experimental reactors (50 – 5.000 l)
- Operating reactors (> 5.000 l up to 1.500.000 l)

Process Engineering

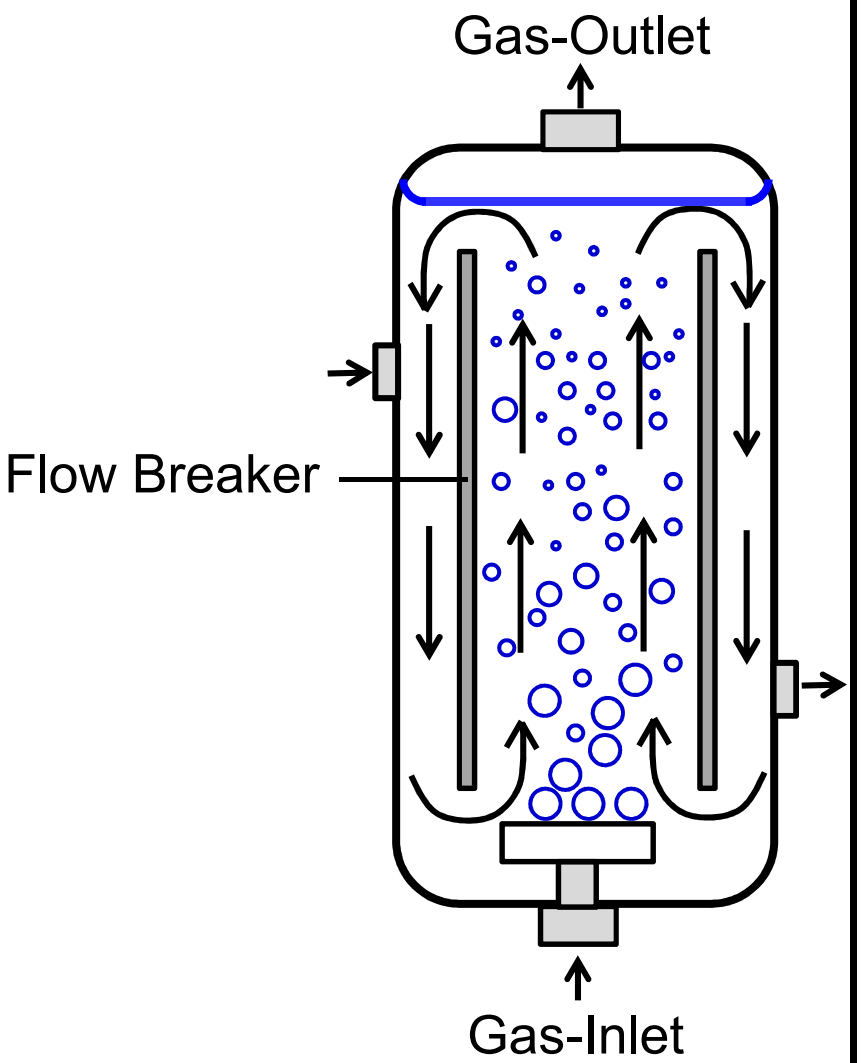
- Batch operation
- Continuous, with internally or externally integrated membrane.

Rainer Buerstinghaus

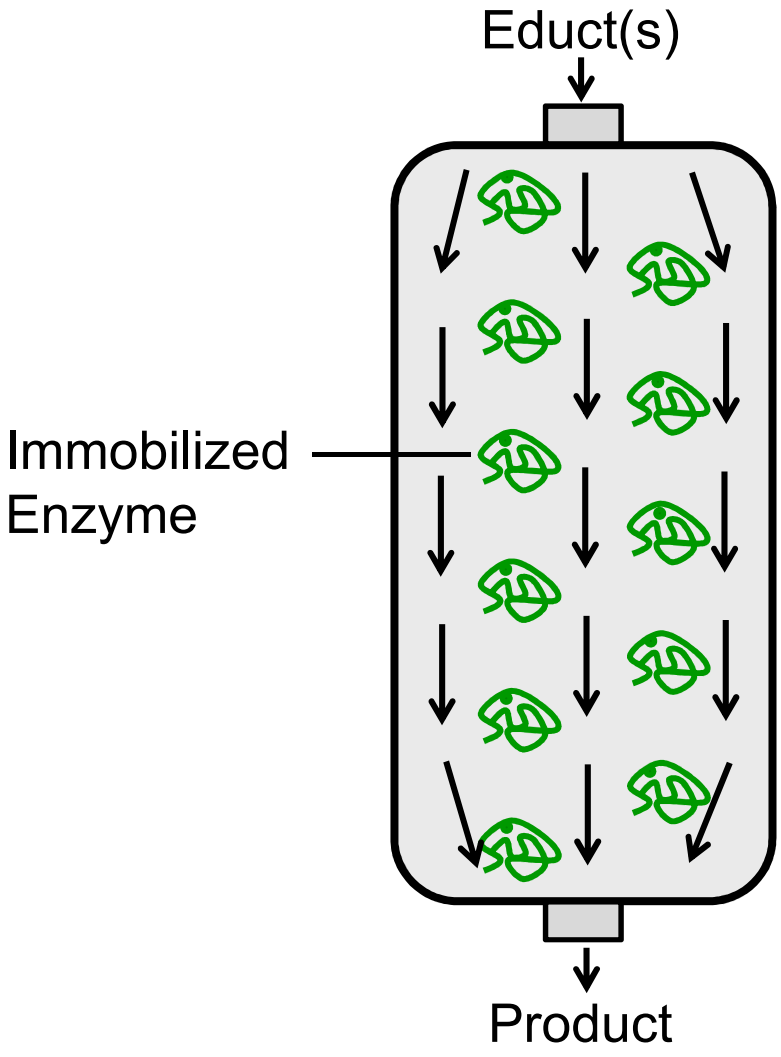
(R)-2-Hydroxy-3-Methoxy-3-Methyl-Butanoic Acid

Scale-up, Bioreactors, Types. General Functions:

Air-Lift-Bioreactor



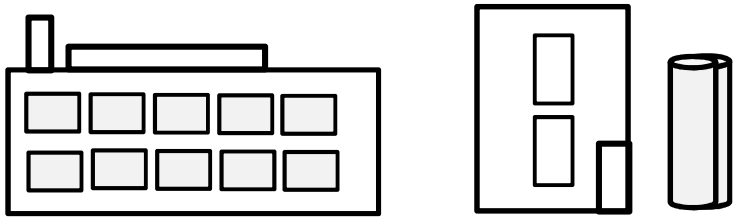
Fixed-Bed-Bioreactor



Rainer Buerstinghaus

The firm in which the new carboxylic acid synthesis is to take place.

R&D Project "Nitrilase-Catalyzed Synthesis…"



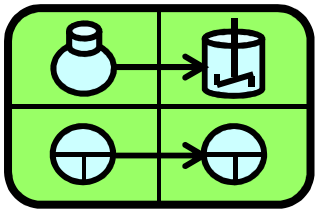
The Biotech-Company "[…GmbH 2]":

Start-up company with 77 employees throughout Europe, including 15 (bio) chemists, 7 microbiologists, 13 engineers (FH), 4 engineers (TU).

Own research and development with attached production and pilot plants. Active for 8 years in R&D, scale-up and the production of ChiPros using "White Biotechnology".

Special products: Enantiomeric pure, optically active carboxylic acids, carboxylic esters and amines as intermediates for new pharmaceutical agents and crop protection products.

R&D Project Management in the Chemical Industry



Subject Matter →

P3: New Metal-Organic Frameworks for the Adsorptive Storage of Gases.

(Chemistry and Technology)

Example P3

Innovation Project P3: →

"New Metal-Organic Frameworks for the Adsorptive Storage of Gases".

(Chemistry and Technology)

New MOFs for the Adsorptive Storage of Gases

→ **Porous Coordination Polymers.**

→ **Scaffolding for Nano-Architectures.**

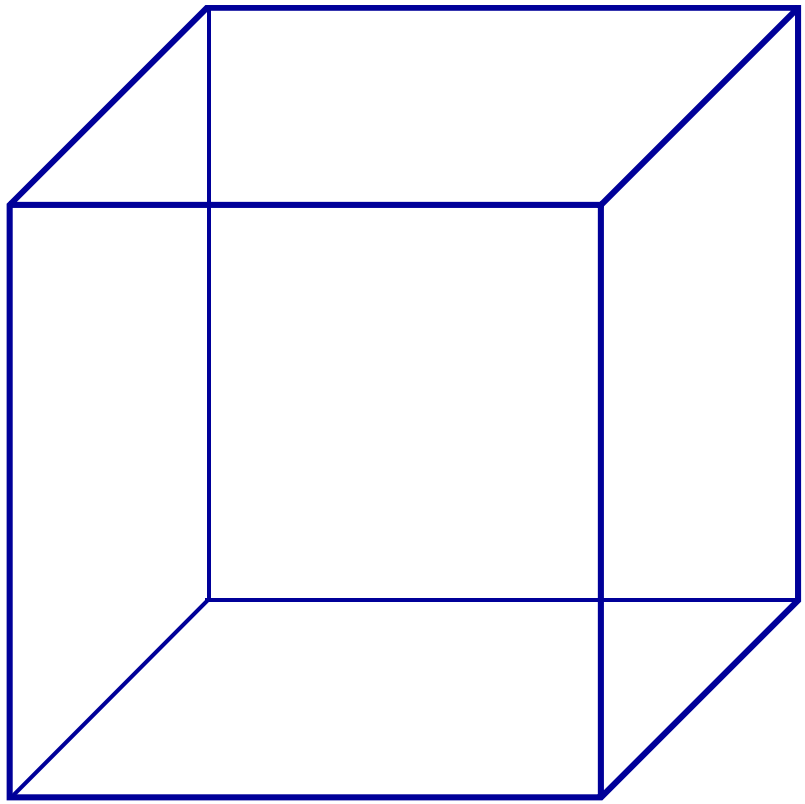
→ **Technical Characteristics.**

- Solids of highest porosity, hardly any "dead volumes“.
- Huge surfaces per gram of material.
- Flexible, "stretchy" grids.
- Stability against lattice twisting / lattice fractures.
- High mobility of guest molecules within the pores.
- Suitability as "atomic or molecular sieves“.
- Nanocontainers for separation, storage, catalysis.

Rainer Buerstinghaus

New MOFs for the Adsorptive Storage of Gases

Hexahedron, Perspective View:

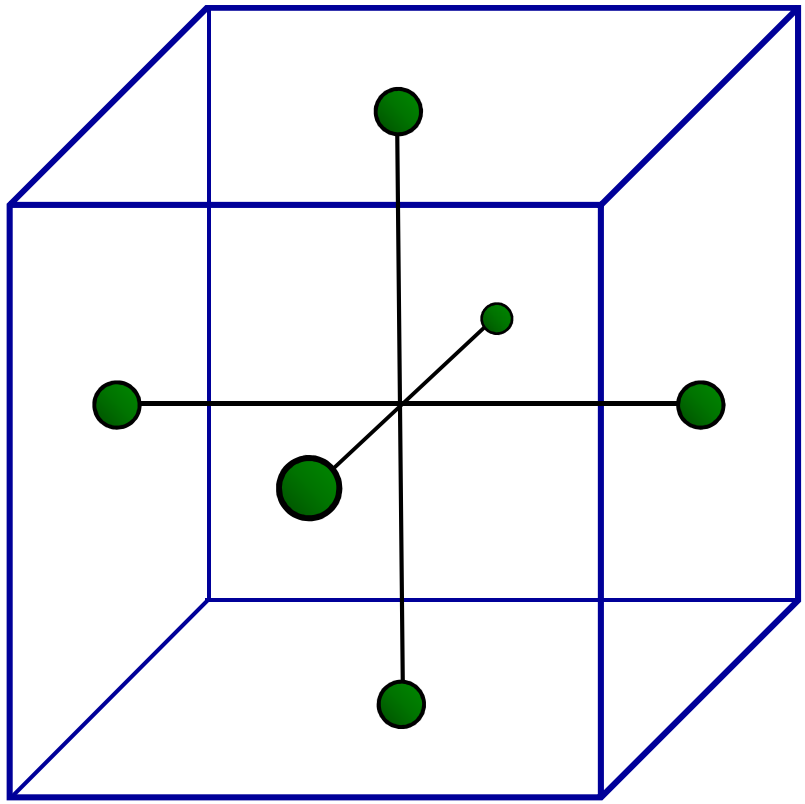


(Platonic Solids: Regular Polyhedra, Cube, 6 Squares)

Rainer Buerstinghaus

New MOFs for the Adsorptive Storage of Gases

Octahedron in a Hexahedron, Perspective View:

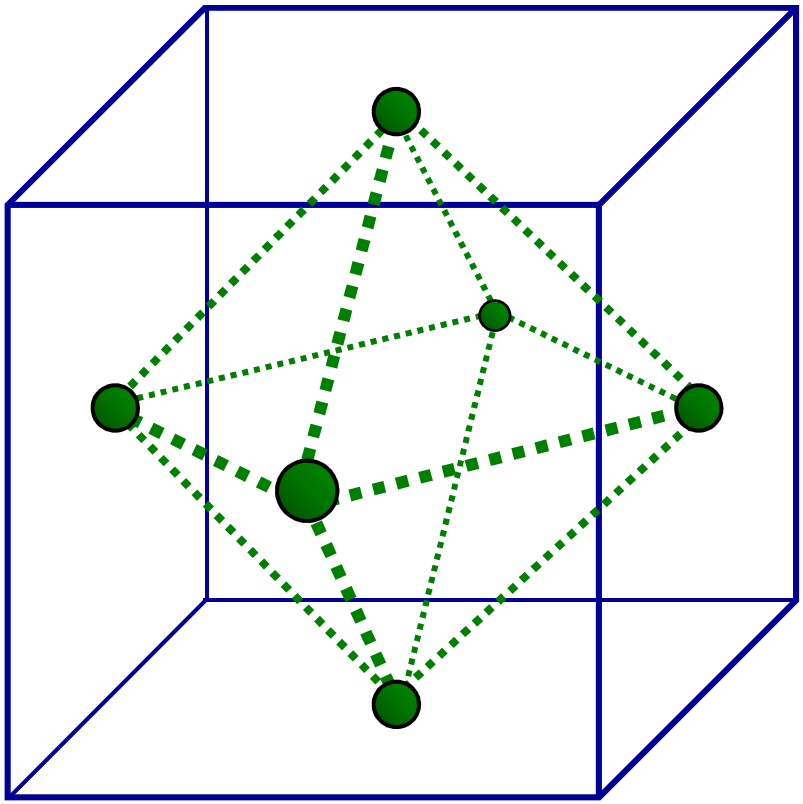


(Platonic Solids: Regular Polyhedra, Cube, 6 Squares)

Rainer Buerstinghaus

New MOFs for the Adsorptive Storage of Gases

Octahedron in a Hexahedron, Perspective View:

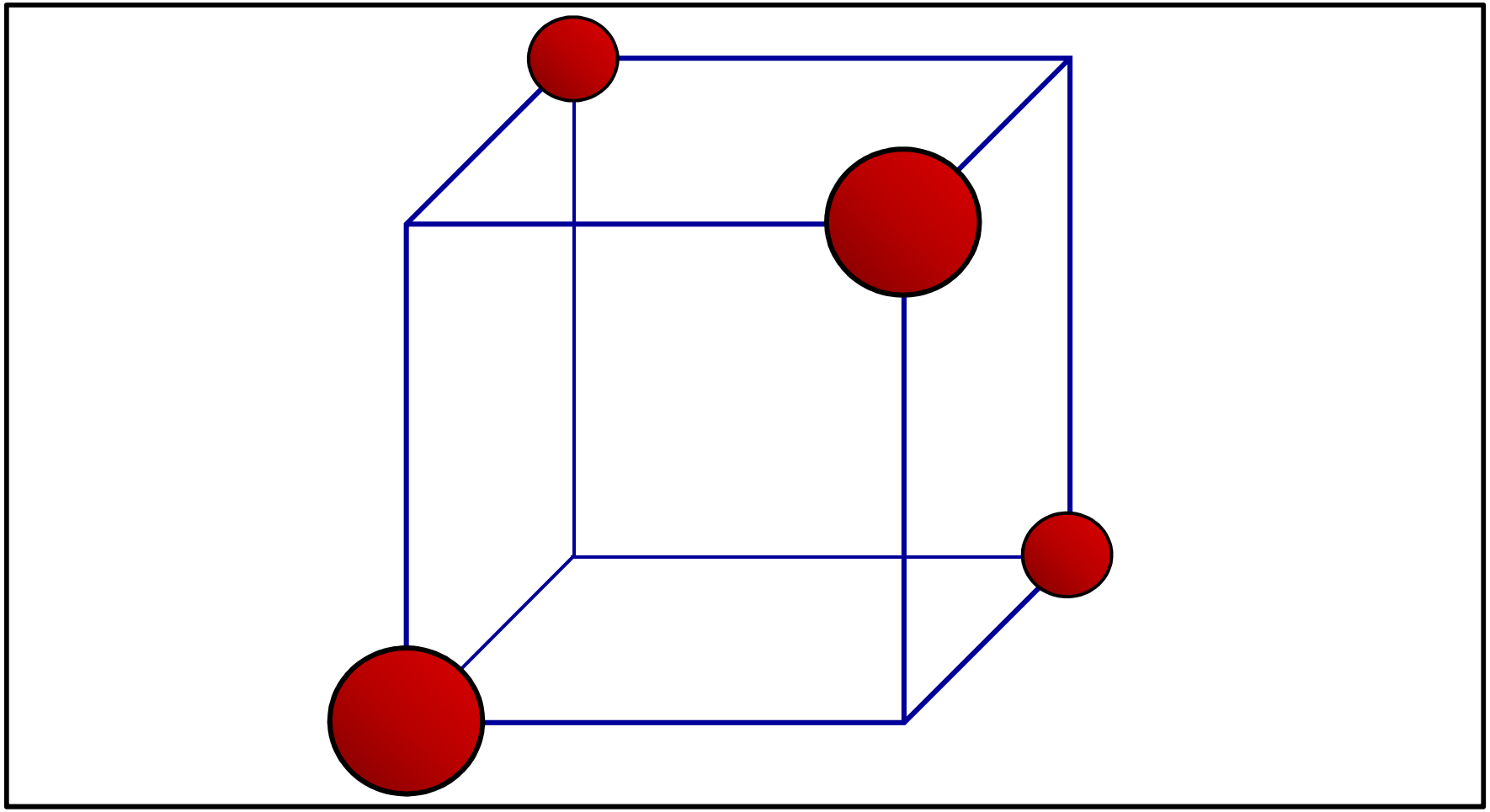


(Platonic Solids: Regular Polyhedra, Cube, 6 Squares)

Rainer Buerstinghaus

New MOFs for the Adsorptive Storage of Gases

Tetrahedron in a Hexahedron, Perspective View:

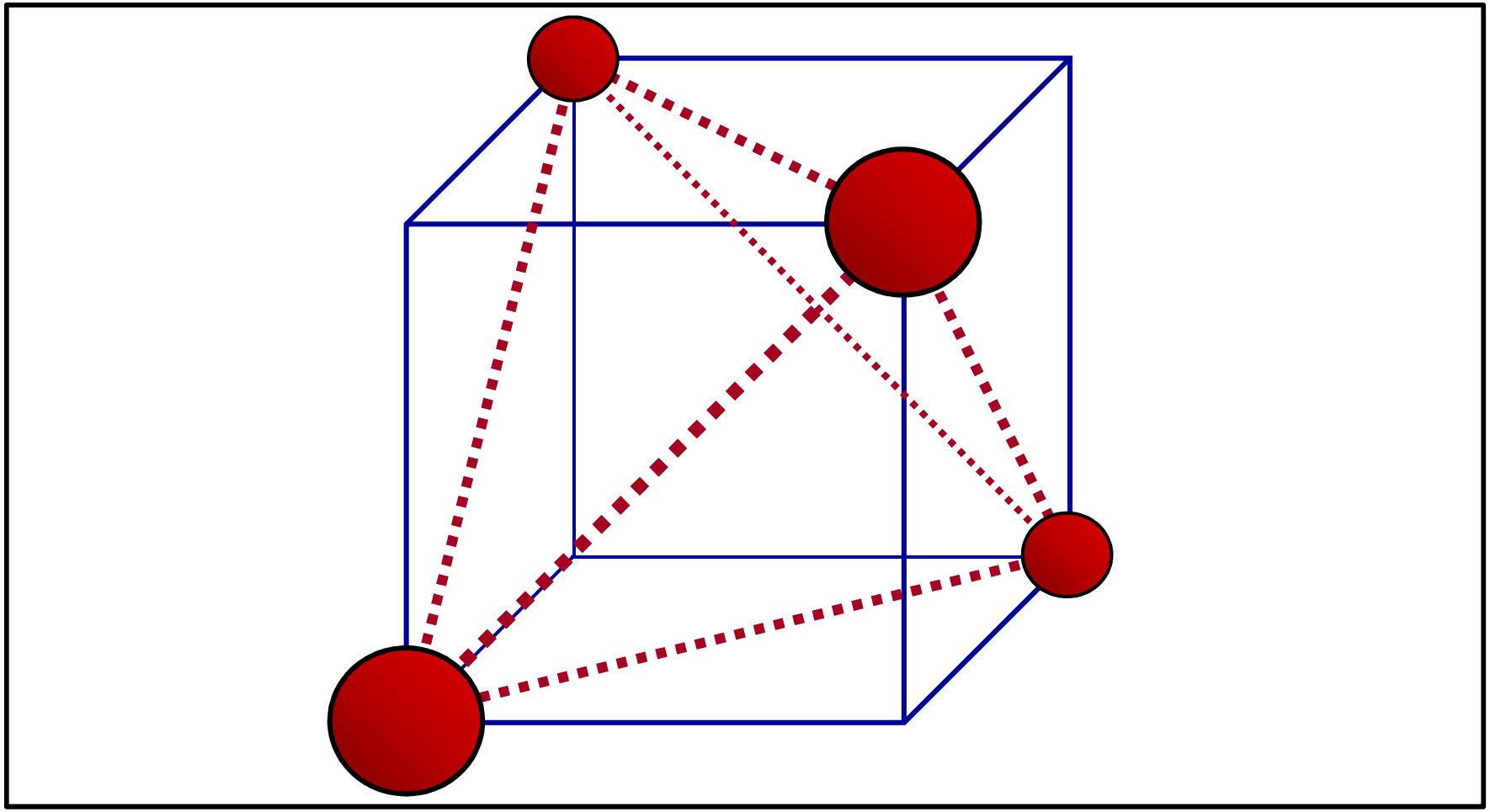


(Platonic Solids: Regular Polyhedra, Cube, 6 Squares)

Rainer Buerstinghaus

New MOFs for the Adsorptive Storage of Gases

Tetrahedron in a Hexahedron, Perspective View:

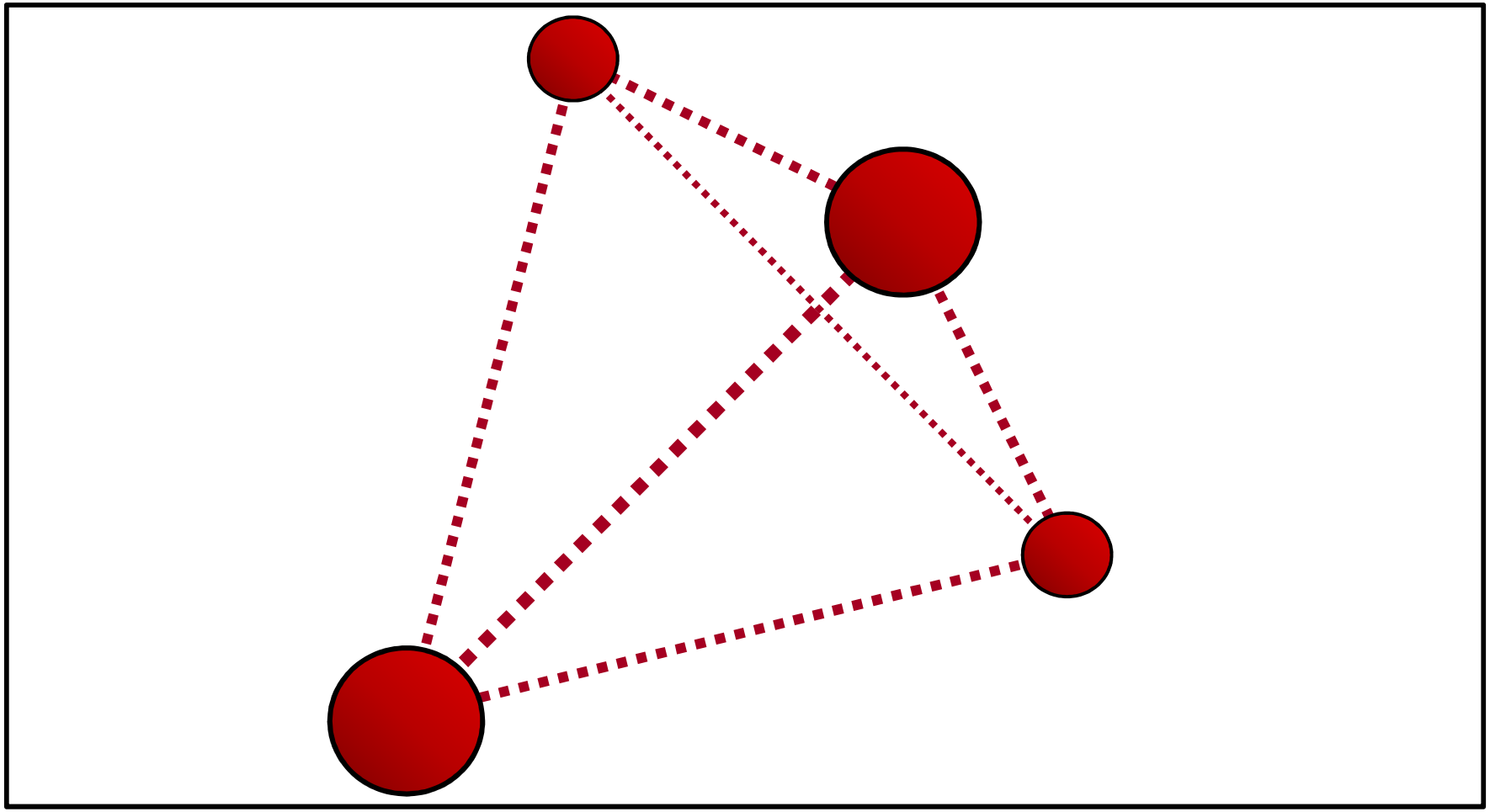


(Platonic Solids: Regular Polyhedra, Cube, 6 Squares)

Rainer Buerstinghaus

New MOFs for the Adsorptive Storage of Gases

Tetrahedron, Perspective View:

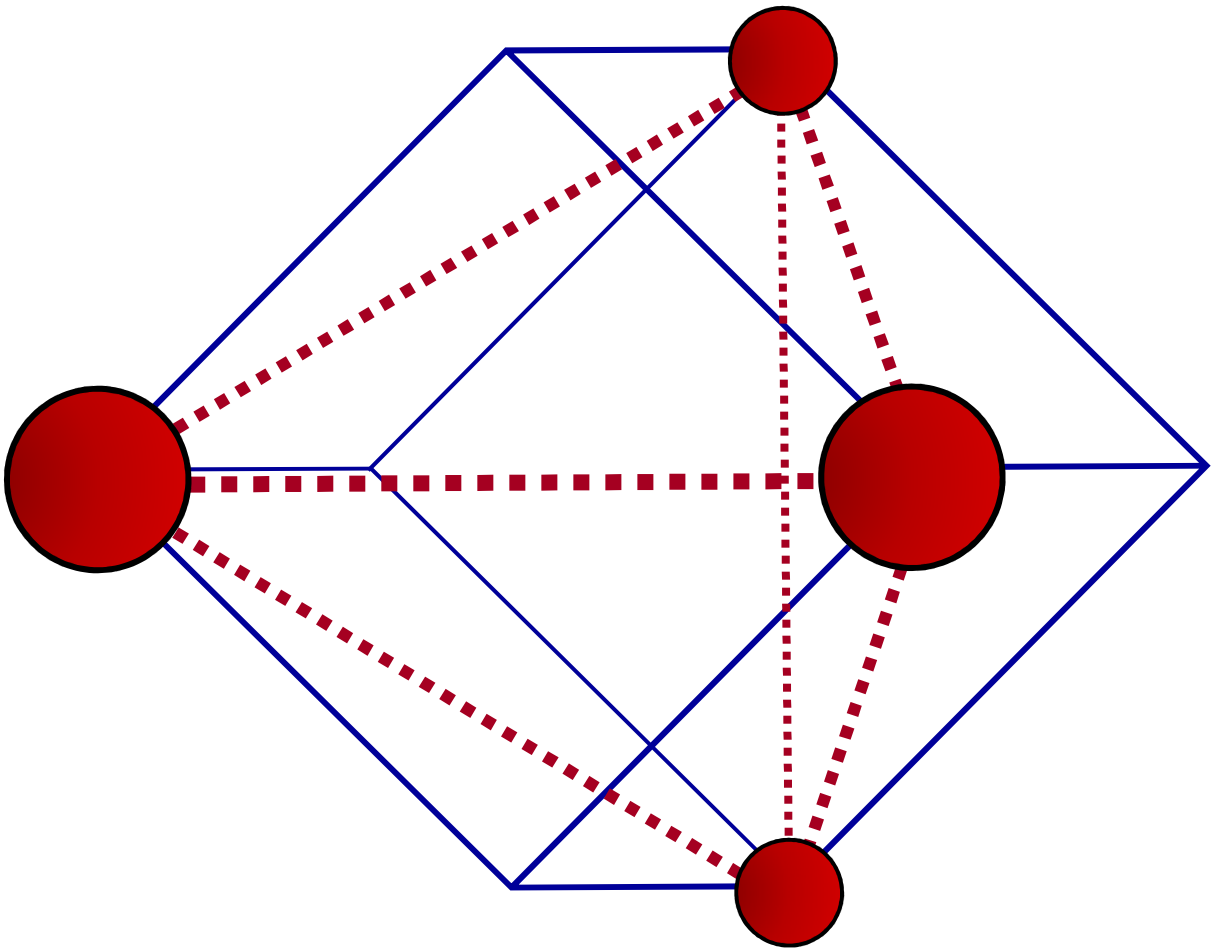


(Platonic Solids: Regular Polyhedra, 4 Equilateral Triangles)

Rainer Buerstinghaus

New MOFs for the Adsorptive Storage of Gases

Tetrahedron in a Hexahedron, Perspective View:

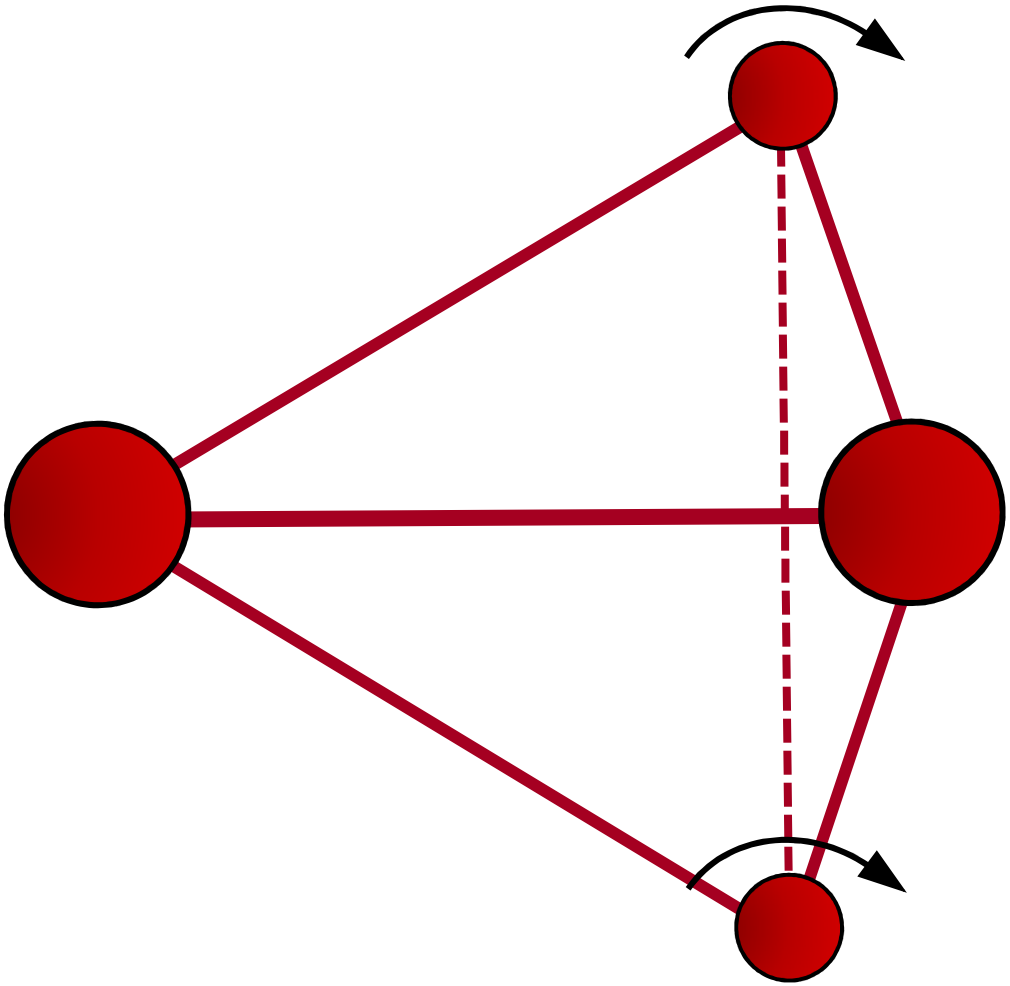


(Platonic Solids: Regular Polyhedra, Cube, 6 Squares)

Rainer Buerstinghaus

New MOFs for the Adsorptive Storage of Gases

Tetrahedron in a Hexahedron, Perspective View:

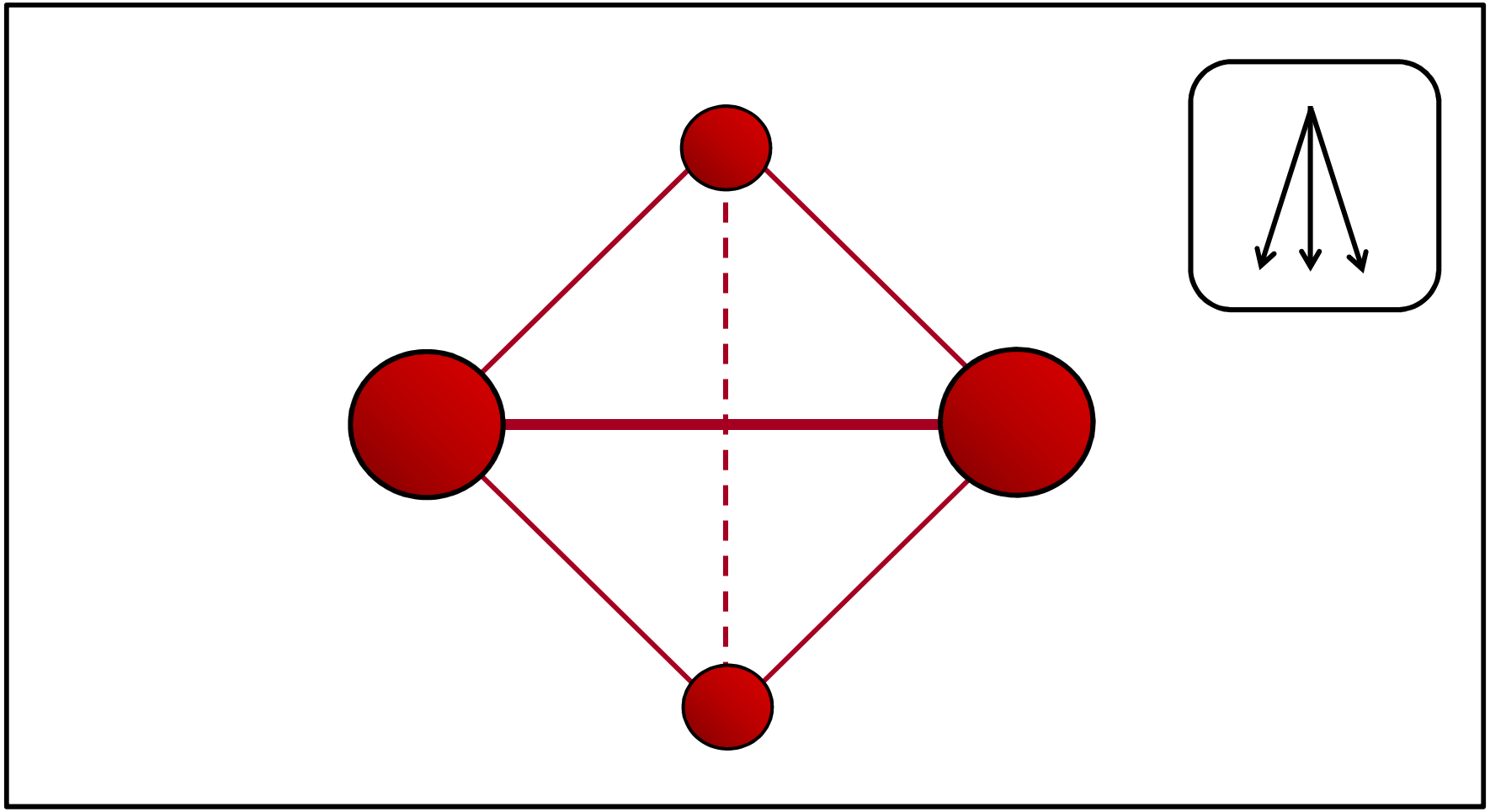


(Platonic Solids: Regular Polyhedra, Cube, 6 Squares)

Rainer Buerstinghaus

New MOFs for the Adsorptive Storage of Gases

Tetrahedron, Perspective View: 4 Vertices + 6 Edges.

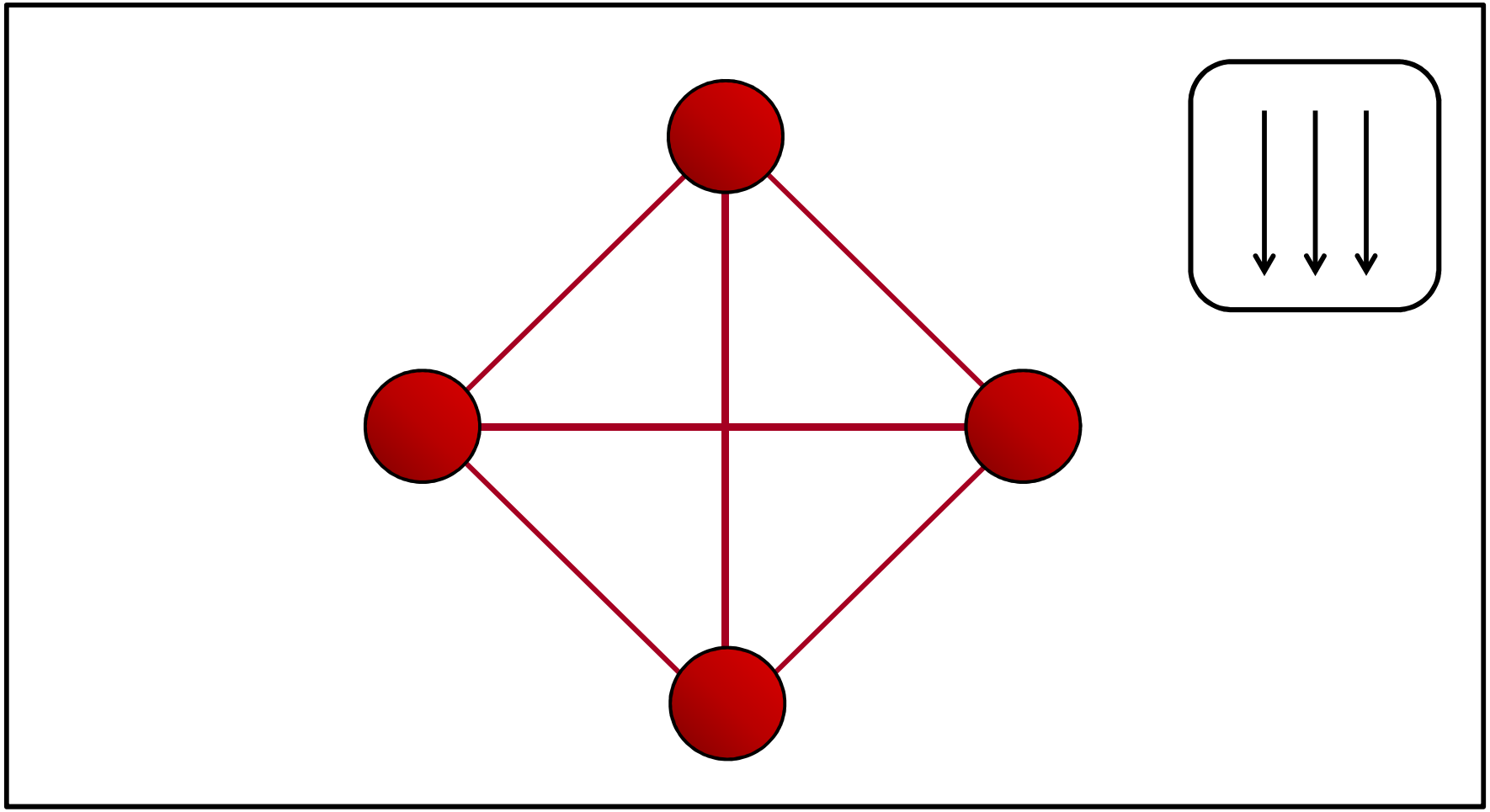


(Platonic Solids: Regular Polyhedra, 4 Equilateral Triangles)

Rainer Buerstinghaus

New MOFs for the Adsorptive Storage of Gases

Tetrahedron, Parallel Projection: 4 Vertices + 6 Edges.

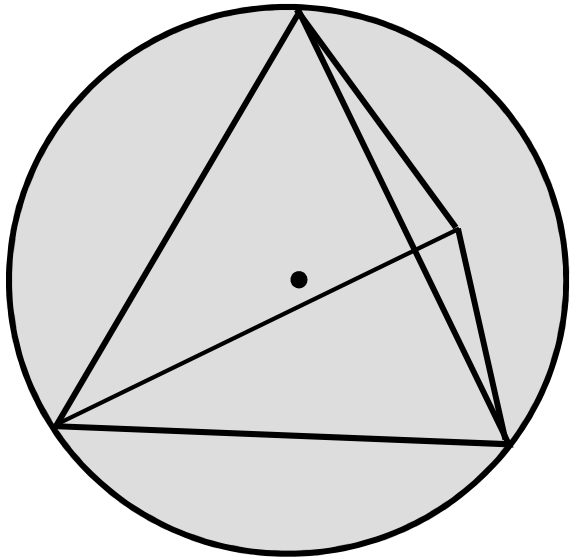


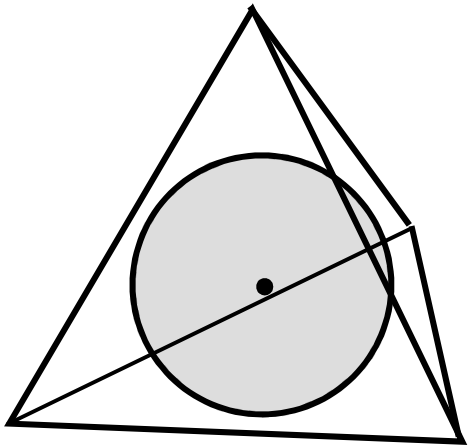
(Platonic Solids: Regular Polyhedra, 4 Equilateral Triangles)

Rainer Buerstinghaus

New MOFs for the Adsorptive Storage of Gases

Tetrahedron: Circumsribed Sphere, Incribed Sphere.





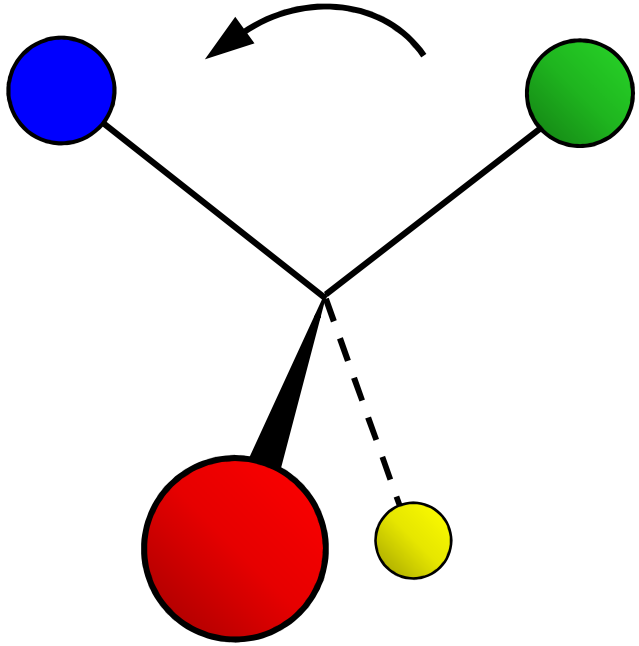
Circumsribed Sphere

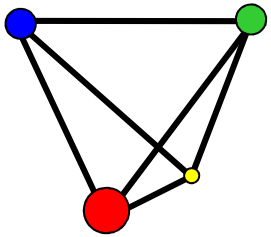
Inscribed Sphere

Rainer Buerstinghaus

Atoms in the Vertex Corners of a Tetrahedron:

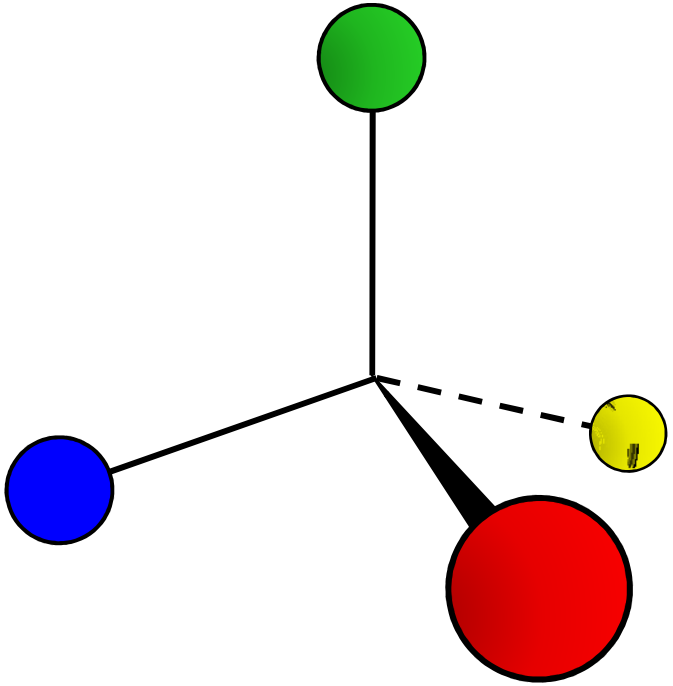
4 Vertex Corners
4 Outer Sphere Radii

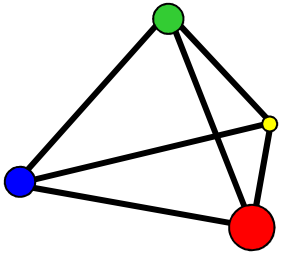




4 Corners
6 Edges

4 Vertex Corners
4 Outer Sphere Radii



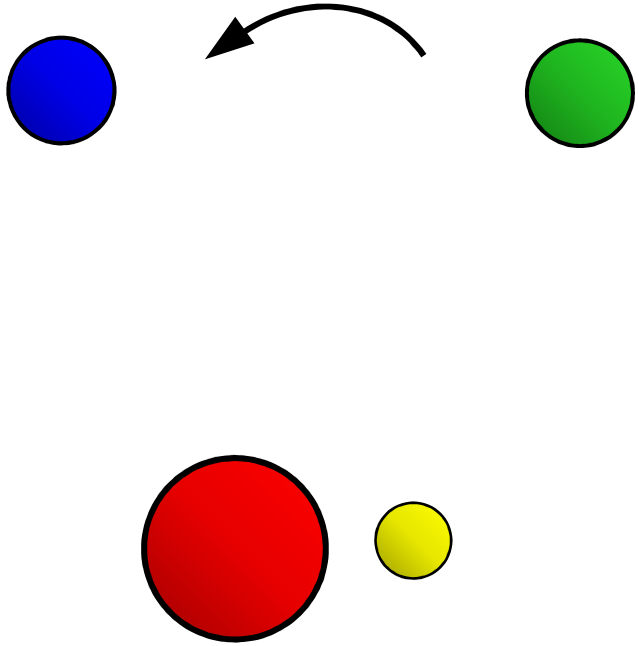


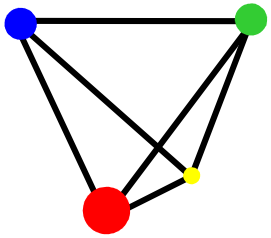
4 Corners
6 Edges

Rainer Buerstinghaus

Atoms in the Vertex Corners of a Tetrahedron:

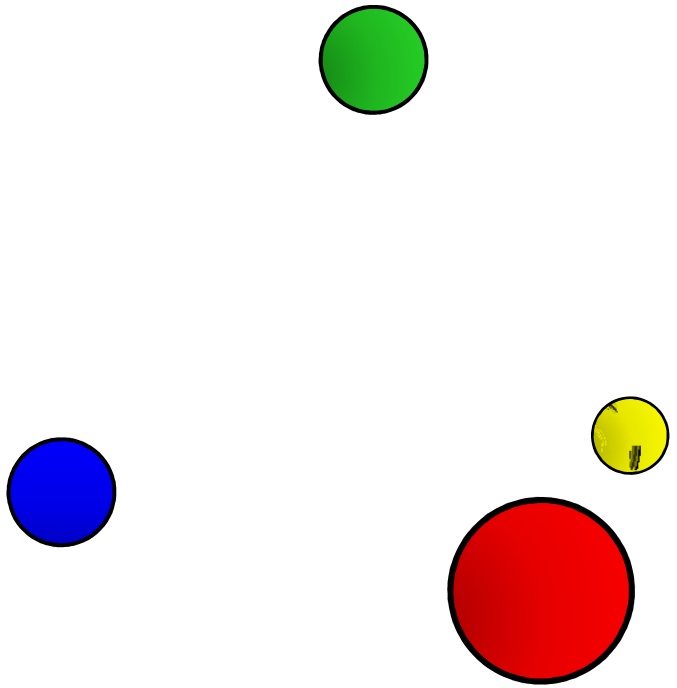
4 Different Vertex Corners

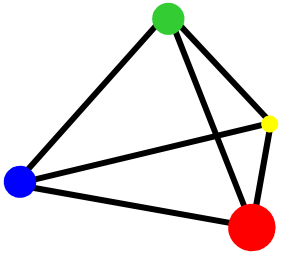




4 Corners
6 Edges

4 Different Vertex Corners



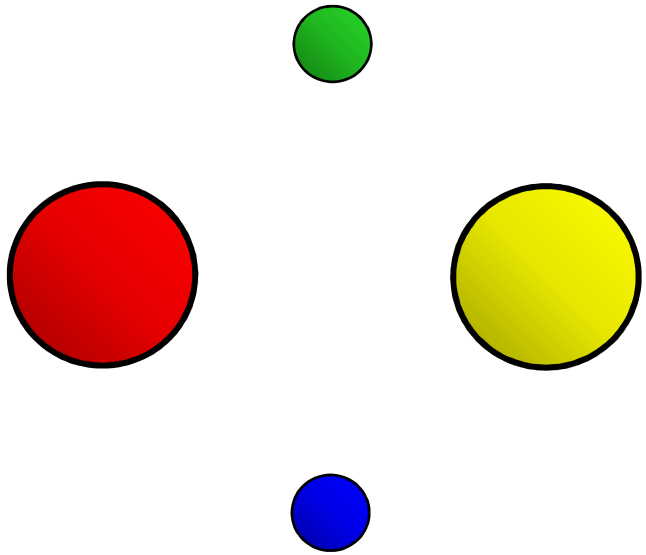


4 Corners
6 Edges

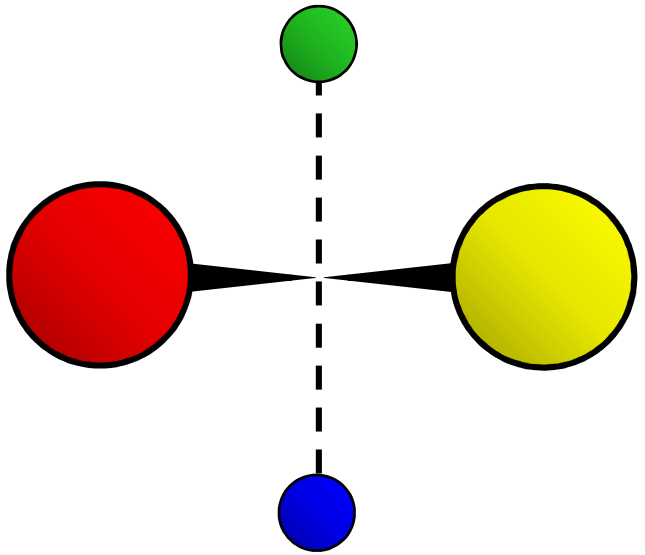
Rainer Buerstinghaus

New MOFs for the Adsorptive Storage of Gases

Structural Principle, Atoms in the Corners of a Tetrahedron:



4 Different Atoms,
Perspective View

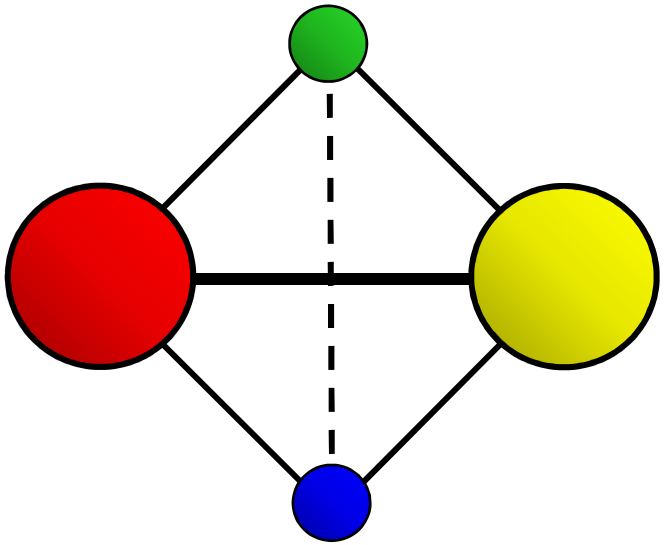


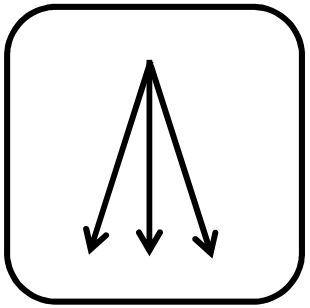
With the 4 Outer Sphere Radii,
Perspective View

Rainer Buerstinghaus

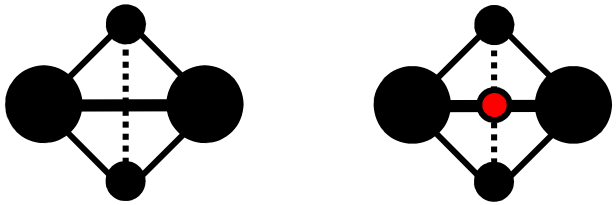
New MOFs for the Adsorptive Storage of Gases

Structural Principle, Atoms in the Corners of a Tetrahedron:





Perspective:
6 Edges, 4 Corners



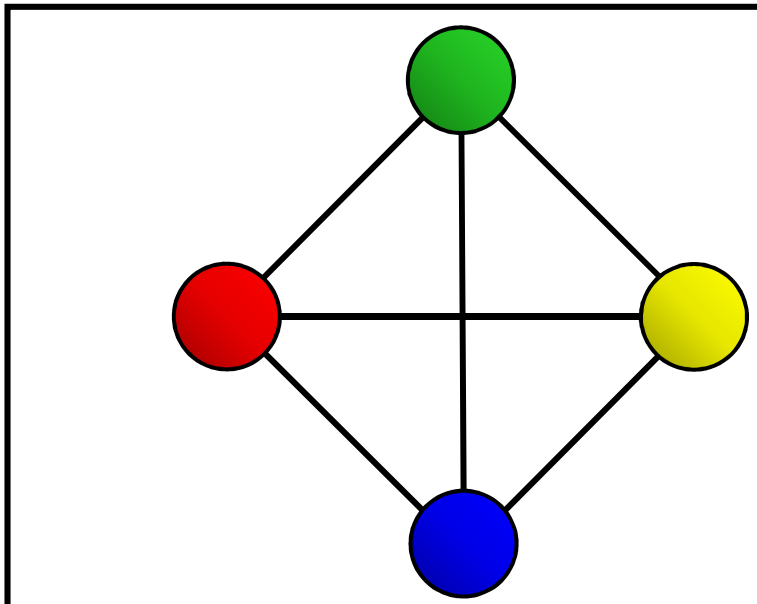
● = Zn^{2+}

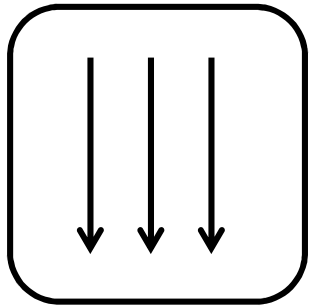
● = O^{2-}

Rainer Buerstinghaus

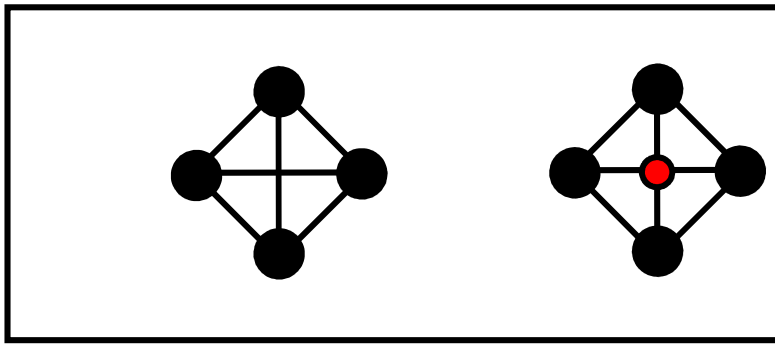
New MOFs for the Adsorptive Storage of Gases

Atoms in the Corners of a Tetrahedron, Parallel Projection:





Parallel Projection:
6 Edges + 4 Corners



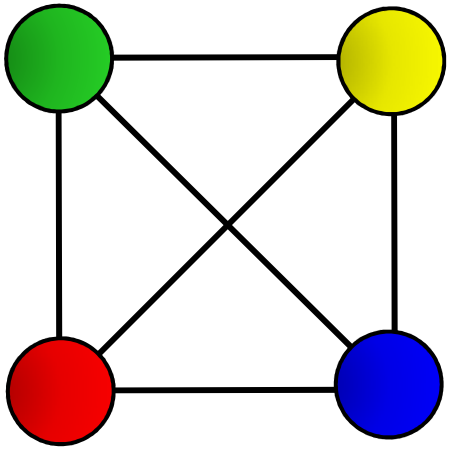
● = Zn^{2+}

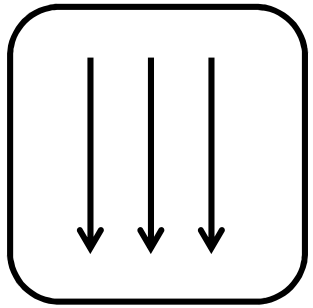
● = O^{2-}

Rainer Buerstinghaus

New MOFs for the Adsorptive Storage of Gases

Atoms in the Corners of a Tetrahedron, Parallel Projection:





Parallel Projection:
6 Edges + 4 Corners

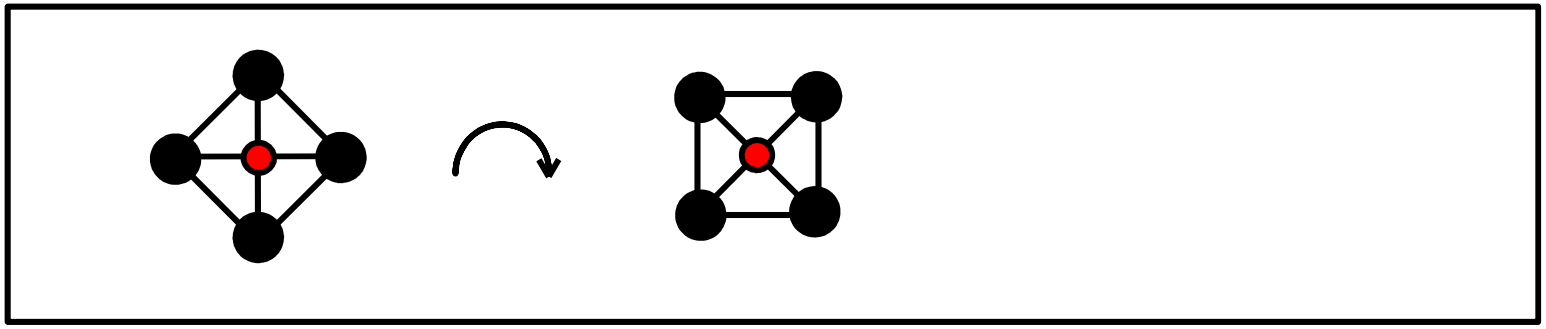
● = Zn^{2+}

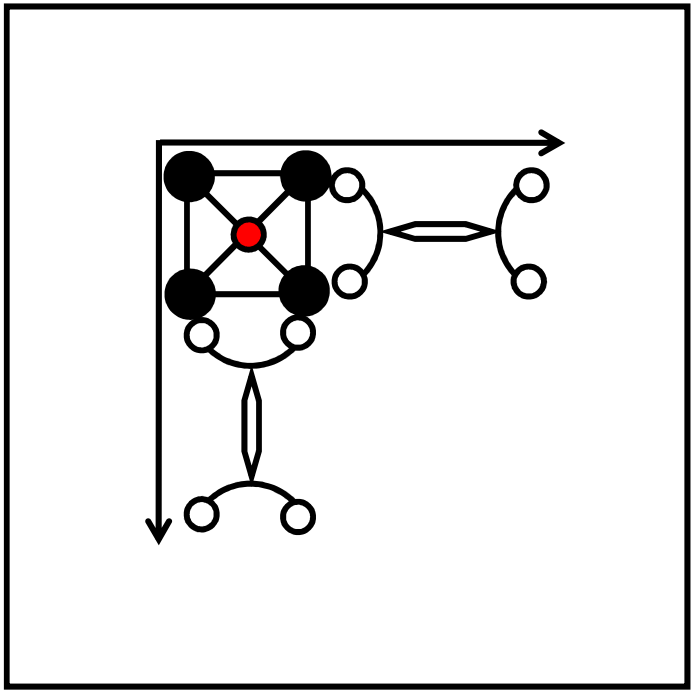
● = O^{2-}

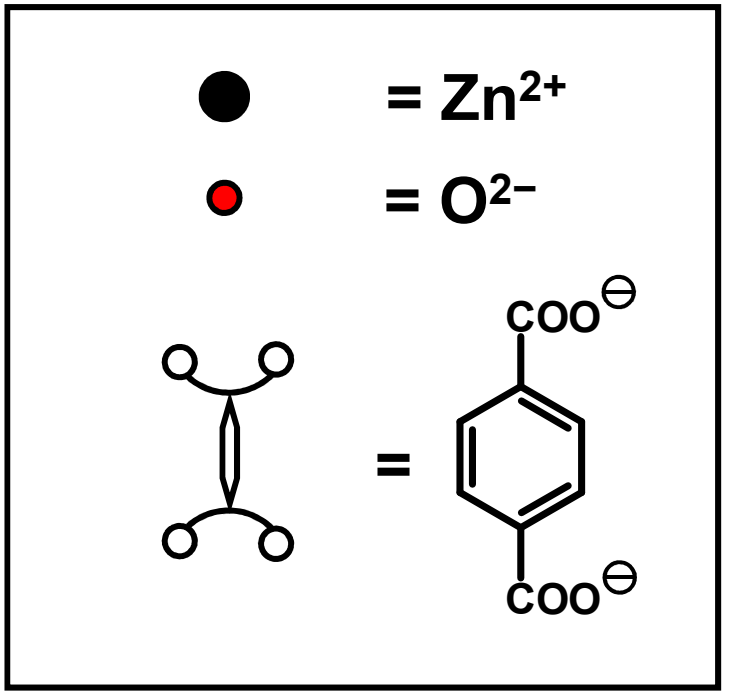
Rainer Buerstinghaus

New MOFs for the Adsorptive Storage of Gases

1,4-Benzene-dicarboxylic Acid as "Bridging Ligand":



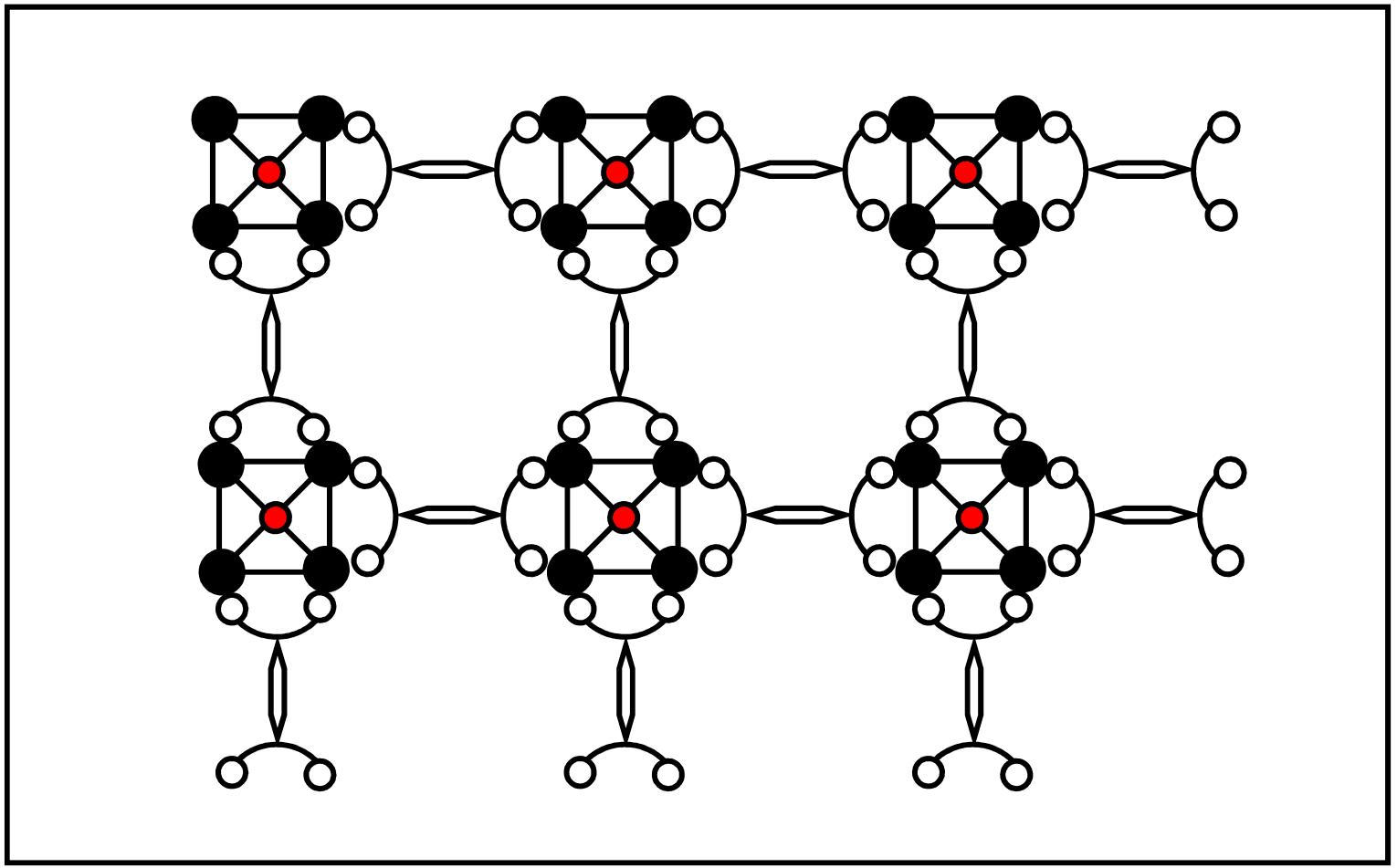




Rainer Buerstinghaus

New MOFs for the Adsorptive Storage of Gases

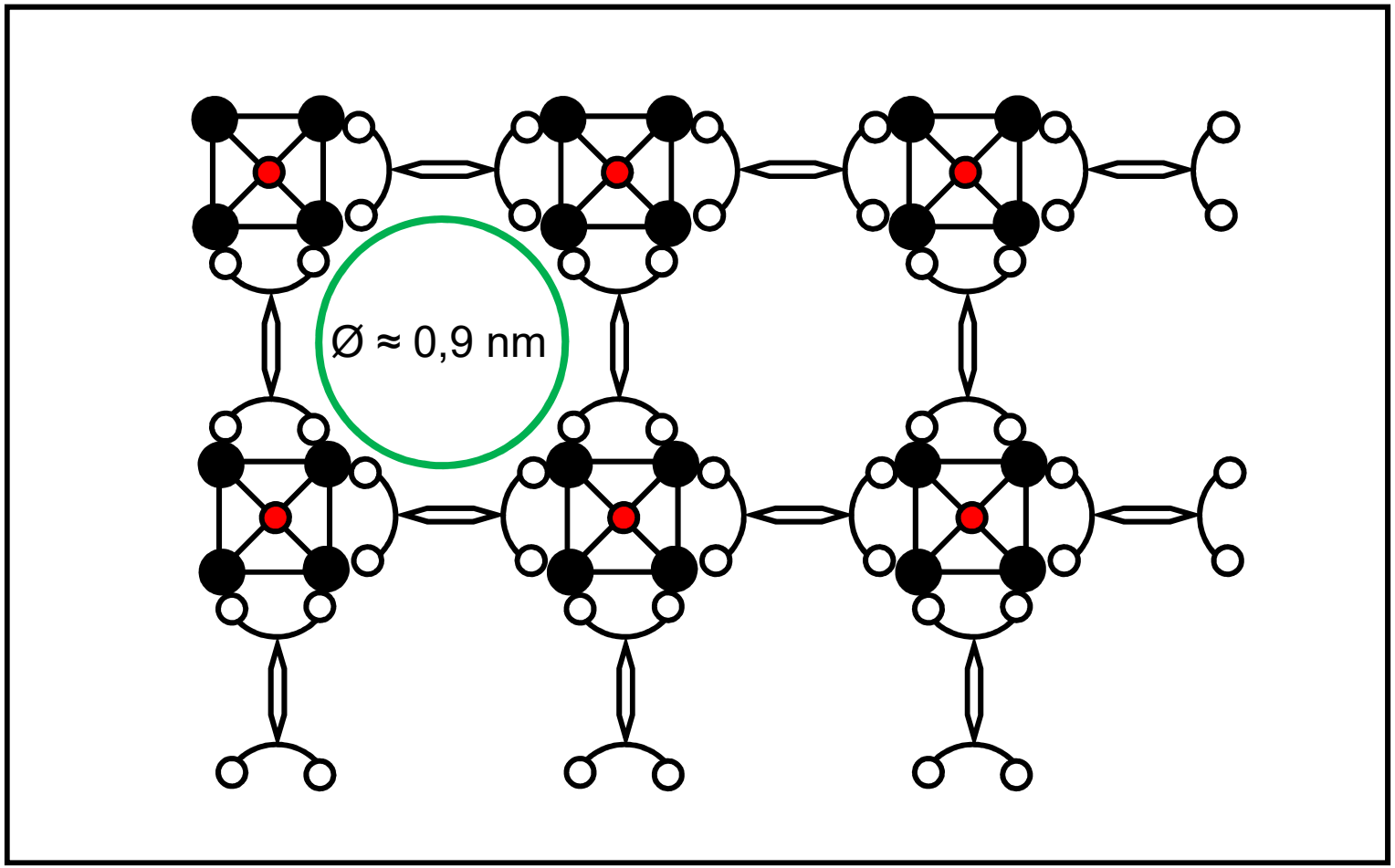
1,4-Benzene-dicarboxylic Acid as "Bridging Ligand":



Rainer Buerstinghaus

New MOFs for the Adsorptive Storage of Gases

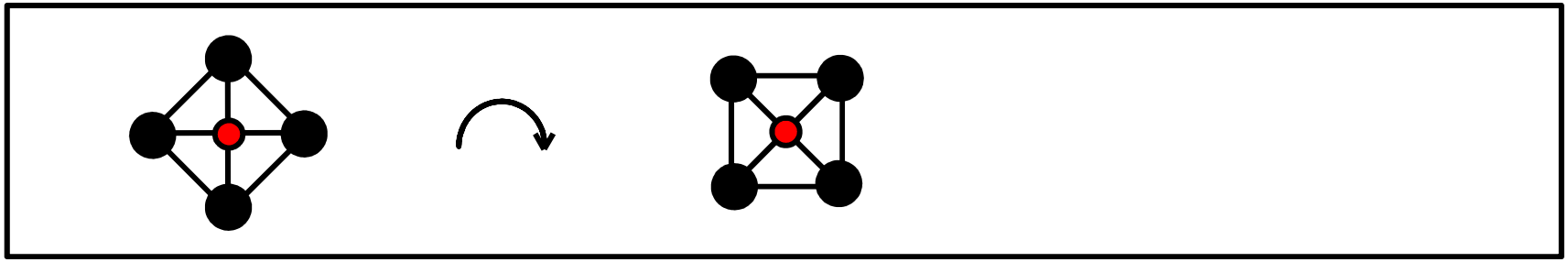
1,4-Benzene-dicarboxylic Acid as Bridging Ligand, Cavity:

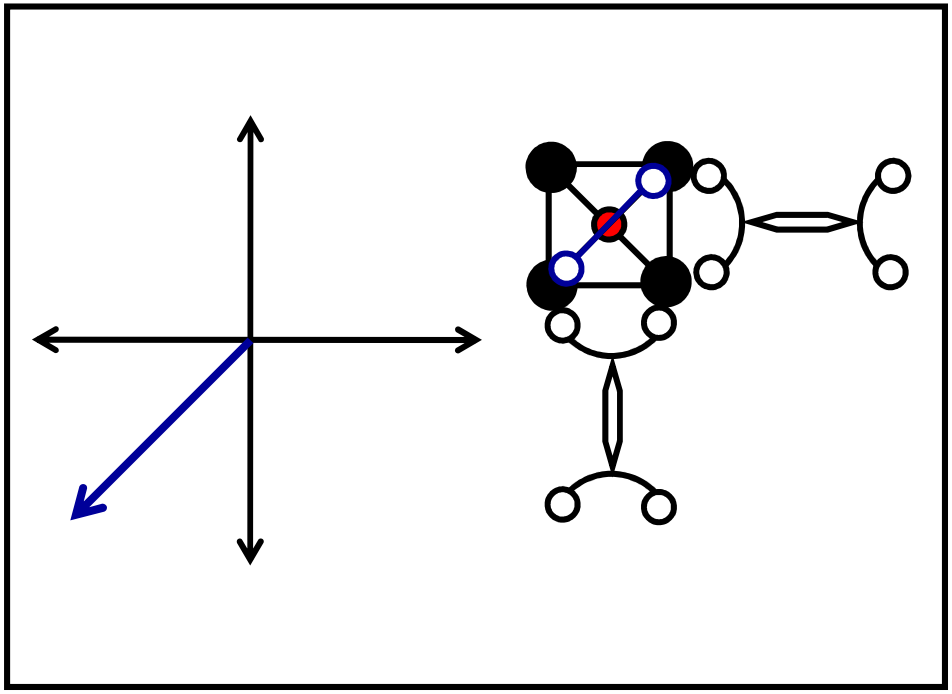


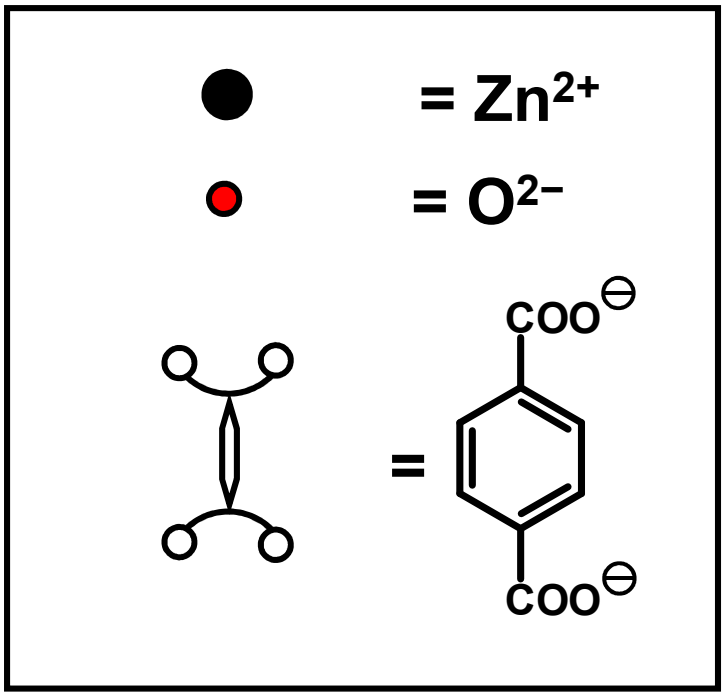
Rainer Buerstinghaus

New MOFs for the Adsorptive Storage of Gases

1,4-Benzene-dicarboxylic Acid as "Bridging Ligand":



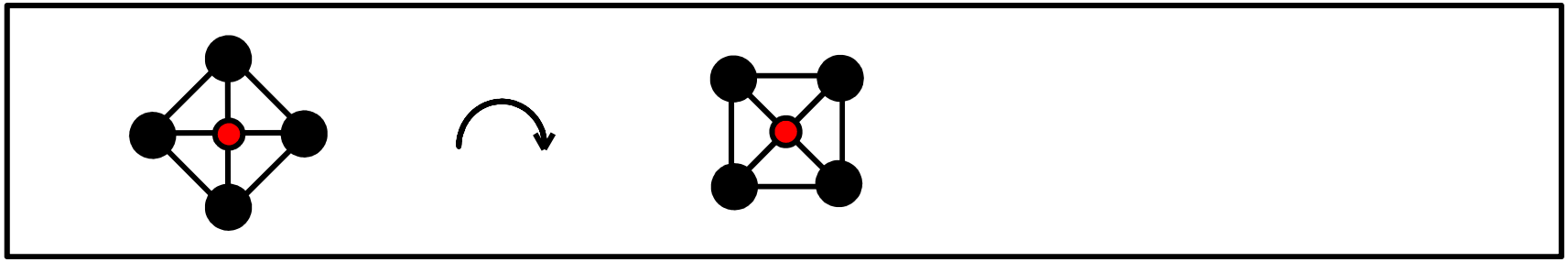


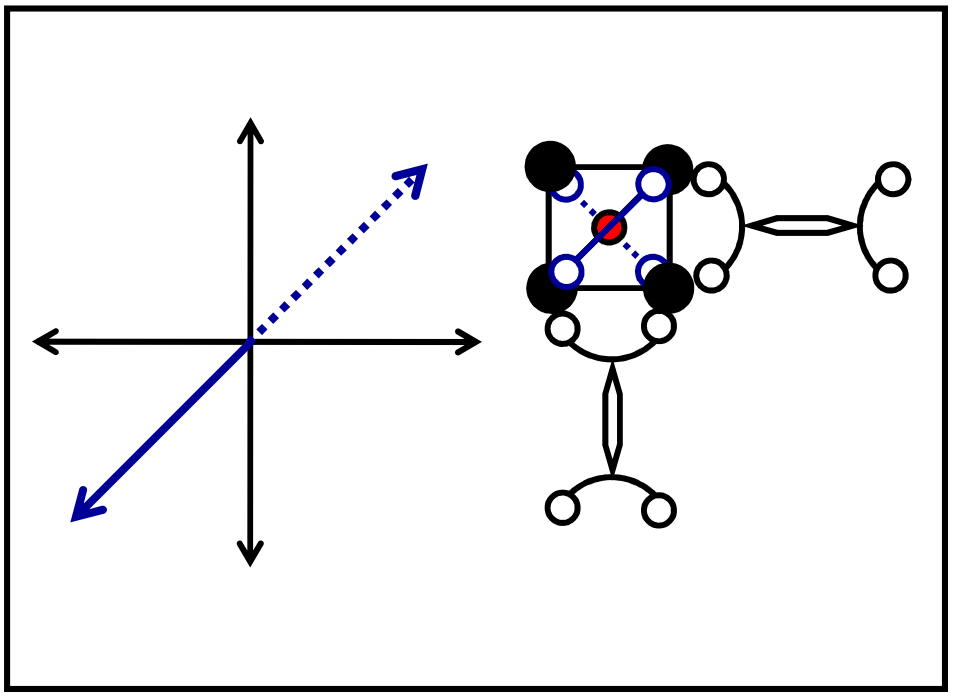


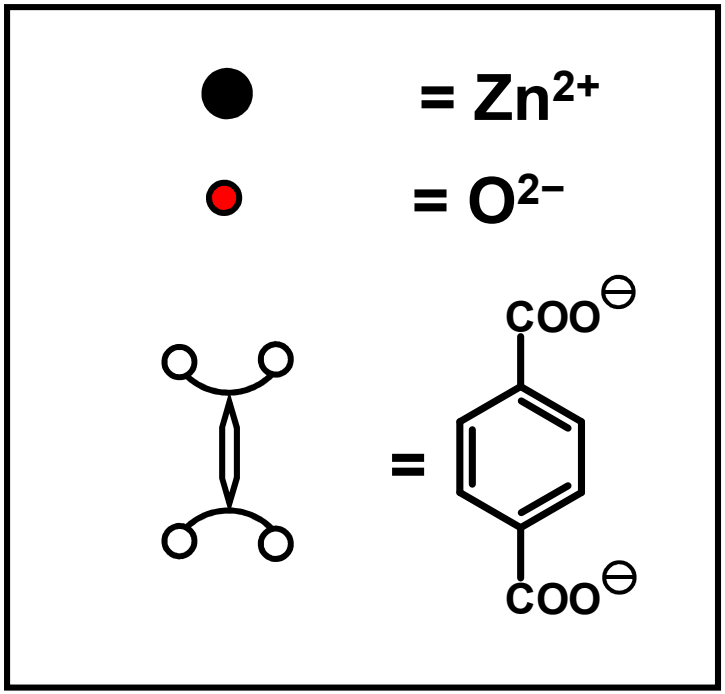
Rainer Buerstinghaus

New MOFs for the Adsorptive Storage of Gases

1,4-Benzene-dicarboxylic Acid as "Bridging Ligand":



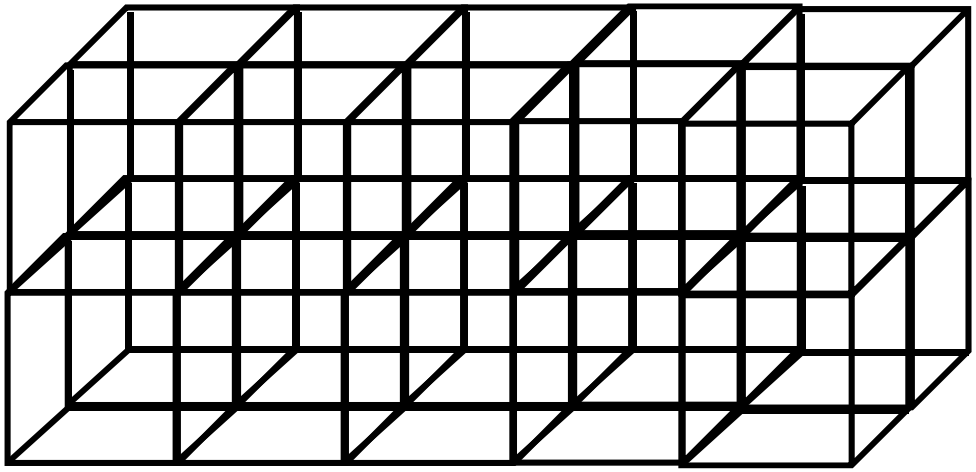




Rainer Buerstinghaus

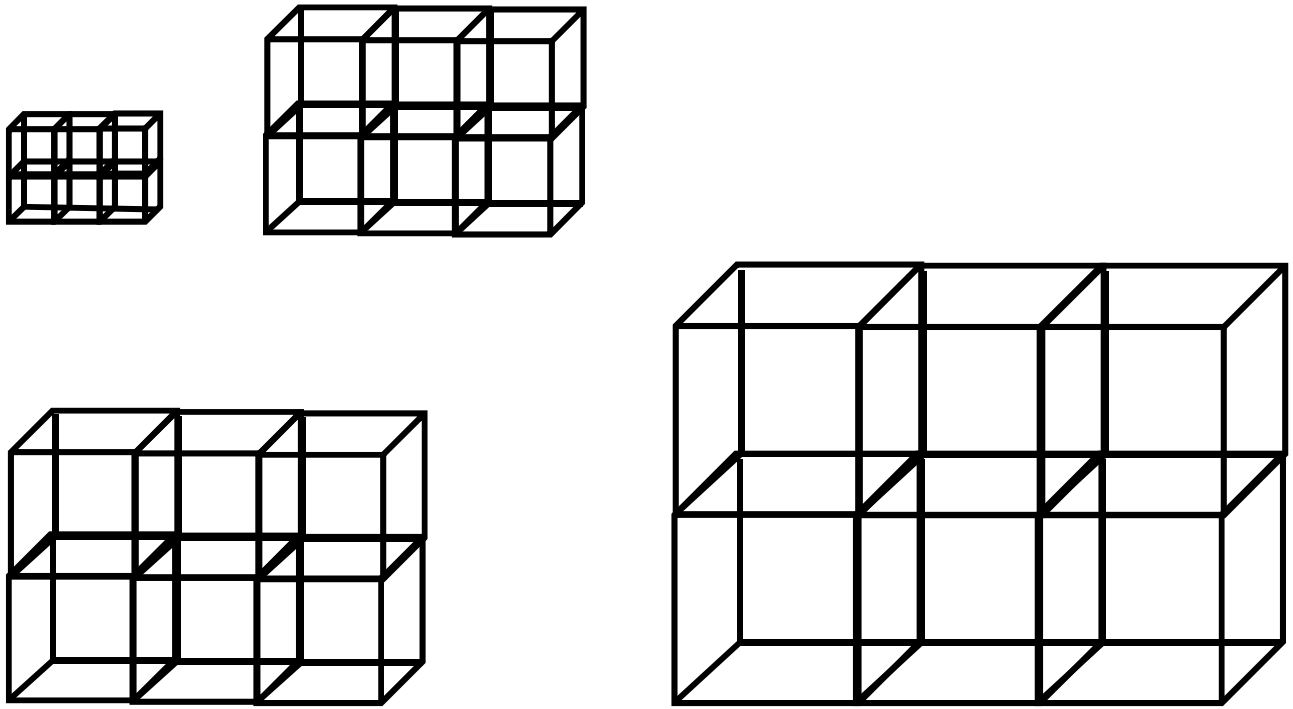
New MOFs for the Adsorptive Storage of Gases

Structural Principle: 3-Dimensional Grid, Detail.



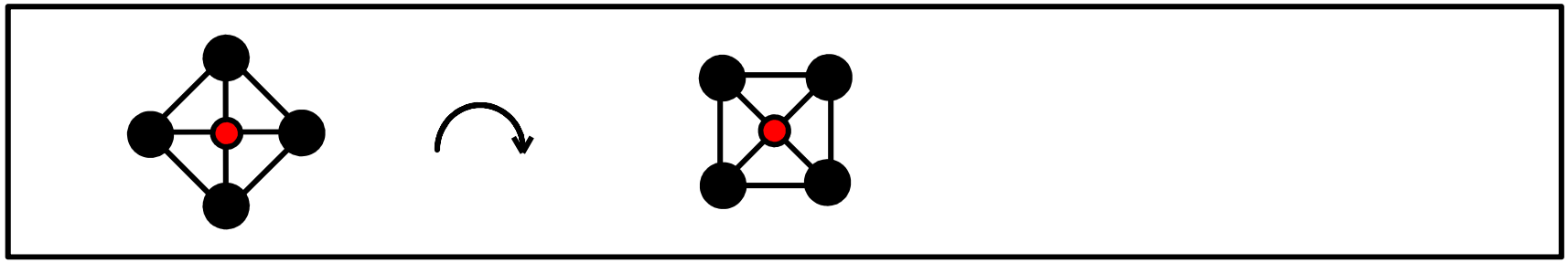
New MOFs for the Adsorptive Storage of Gases

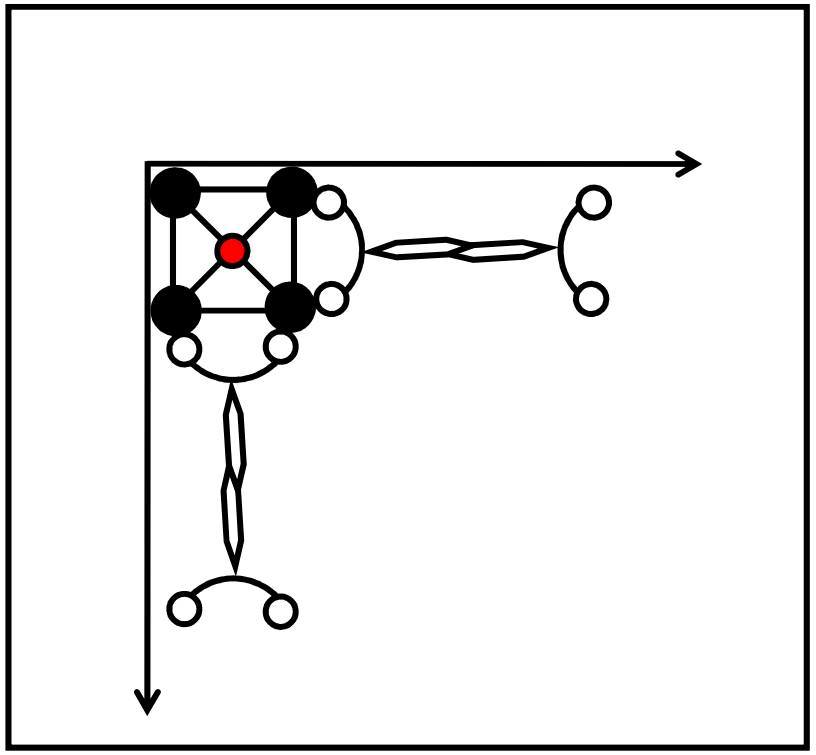
Structural Principle: Isoreticular Netzworks → "IRMOFs".

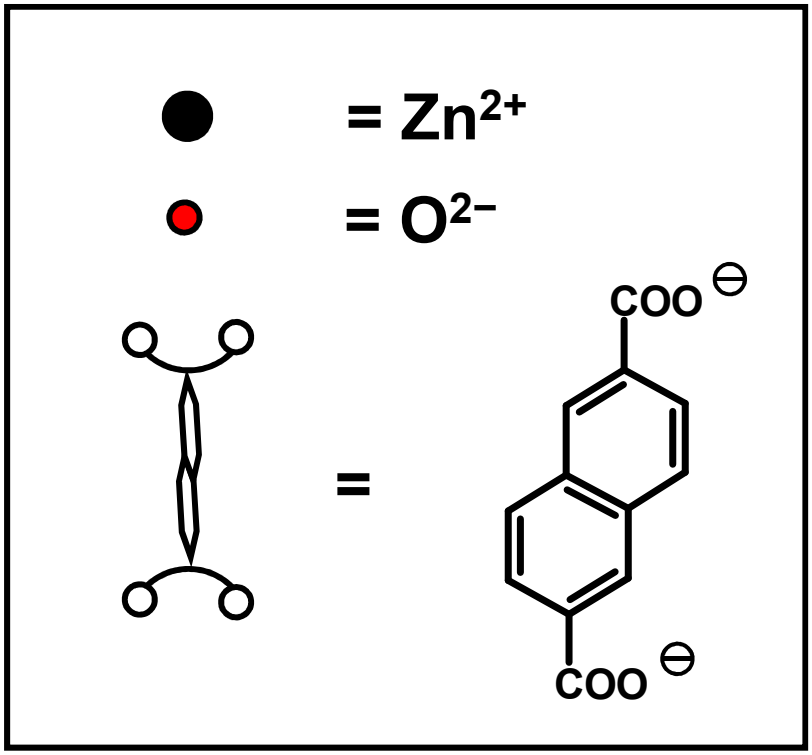


New MOFs for the Adsorptive Storage of Gases

2,6-Naphthalene-Dicarboxylic Acid as "Bridging Ligand":



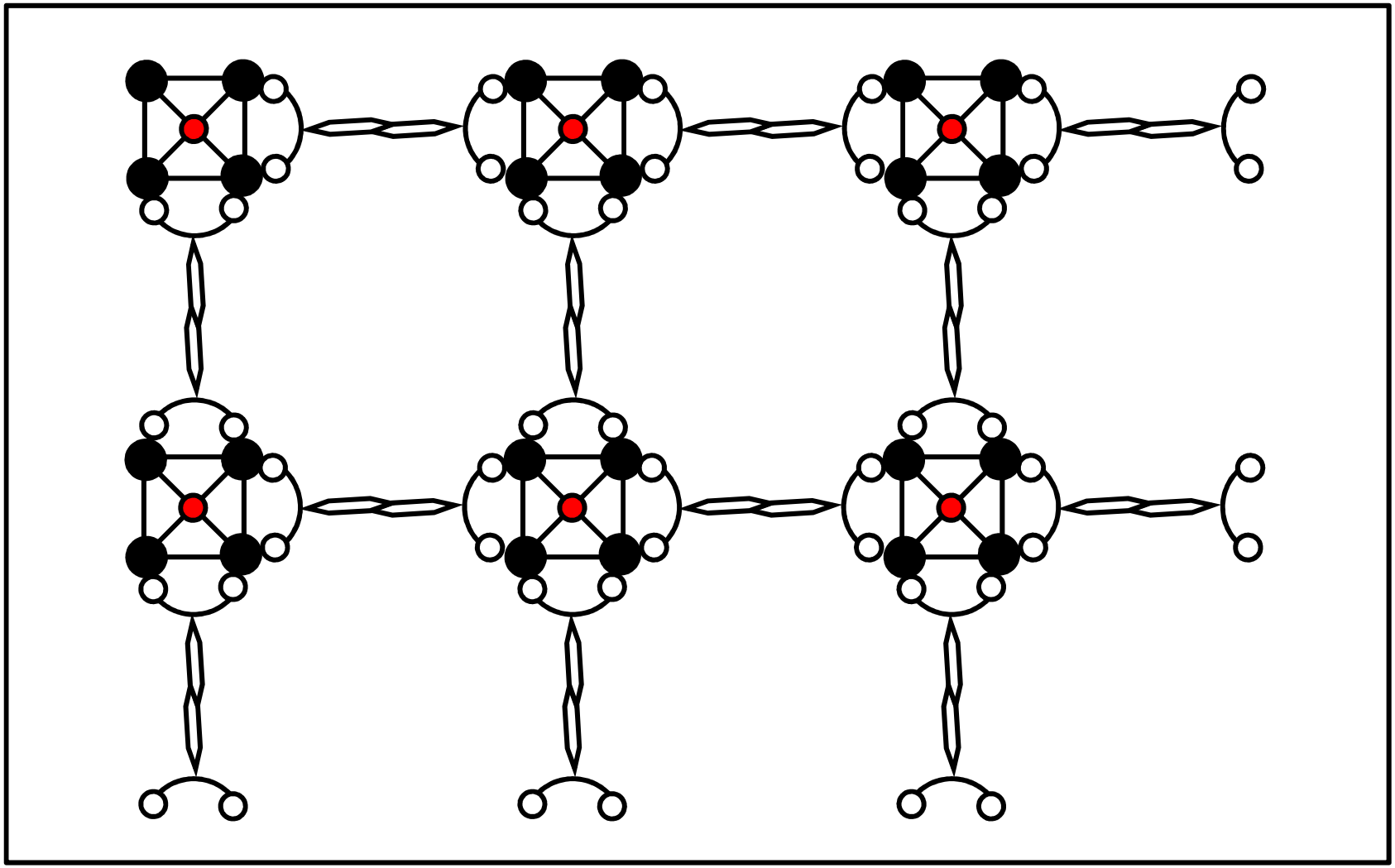




Rainer Buerstinghaus

New MOFs for the Adsorptive Storage of Gases

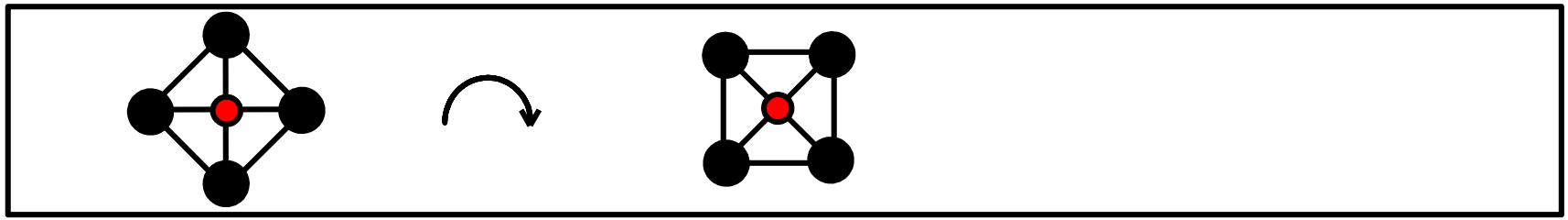
2,6-Naphthalene-Dicarboxylic Acid as "Bridging Ligand":

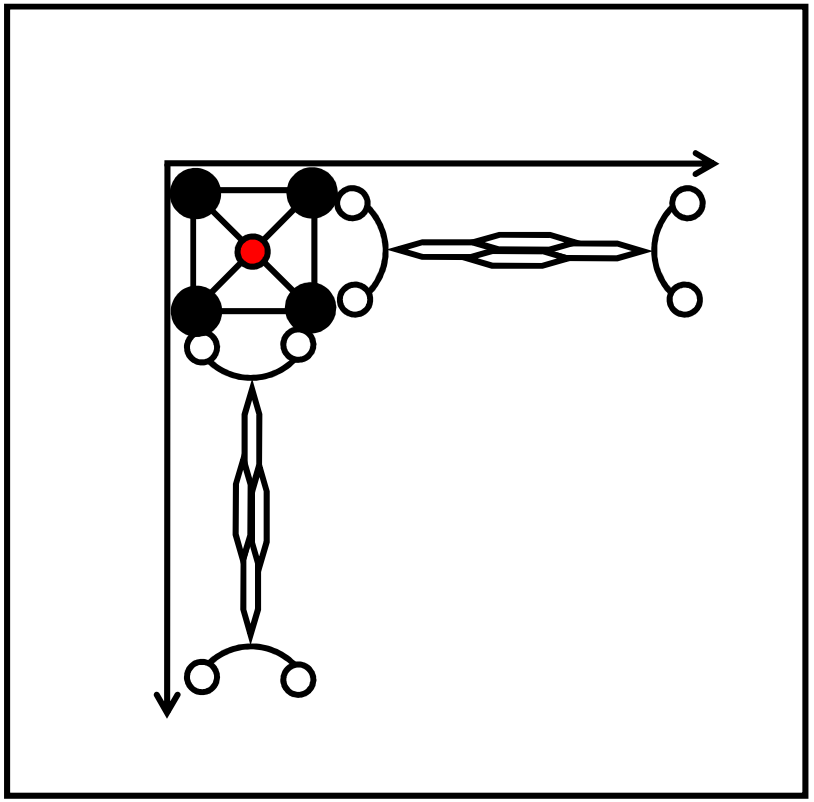


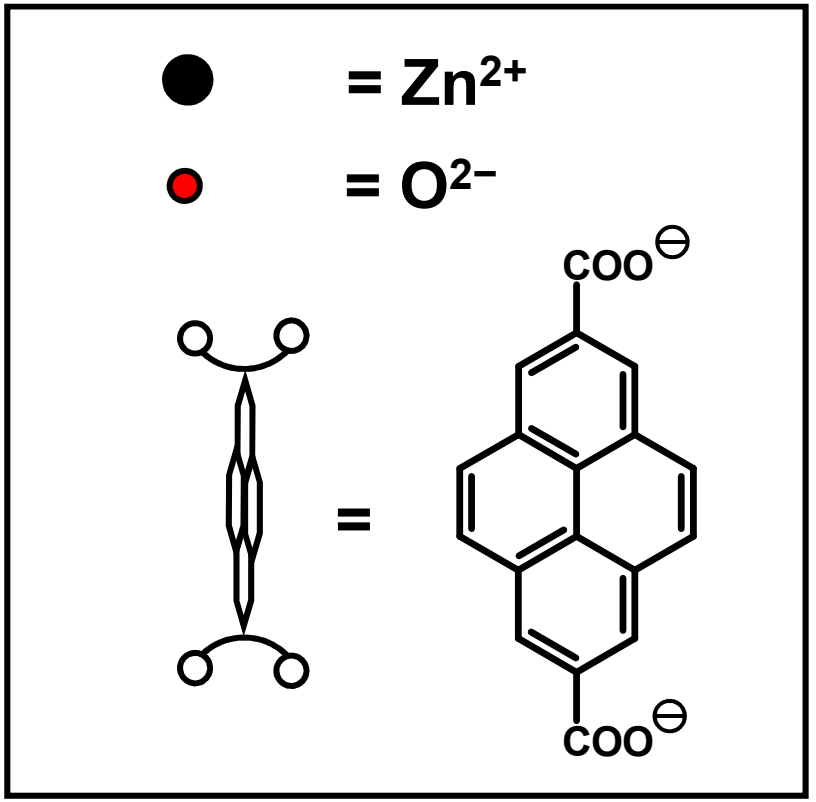
Rainer Buerstinghaus

New MOFs for the Adsorptive Storage of Gases

2,7-Pyrene-Dicarboxylic Acid as "Bridging Ligand":



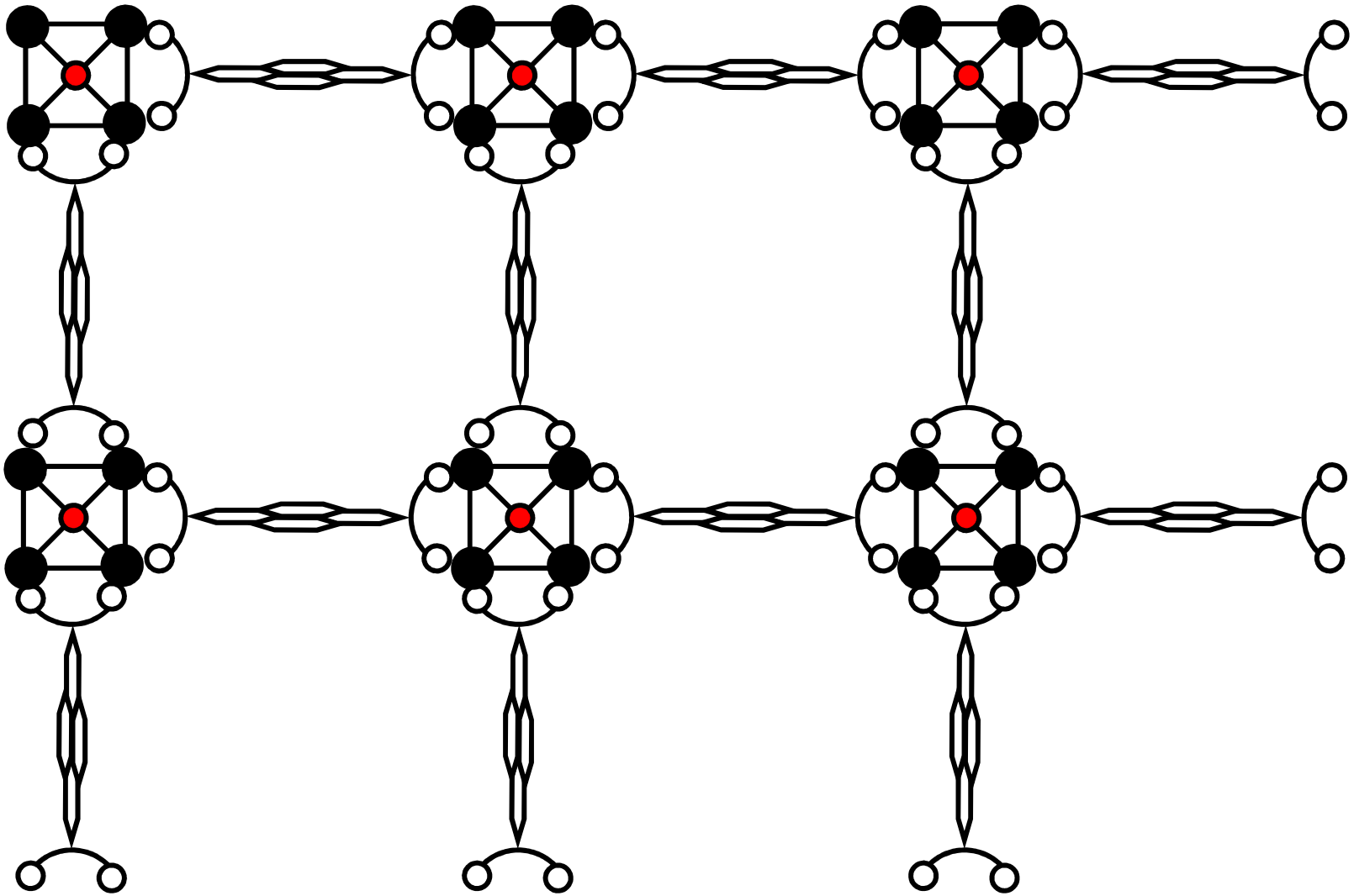




Rainer Buerstinghaus

New MOFs for the Adsorptive Storage of Gases

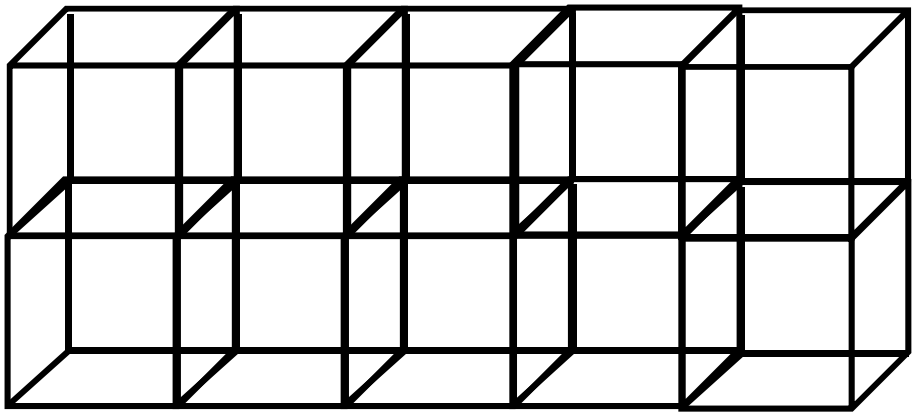
2,7-Pyrene-Dicarboxylic Acid as "Bridging Ligand":



Rainer Buerstinghaus

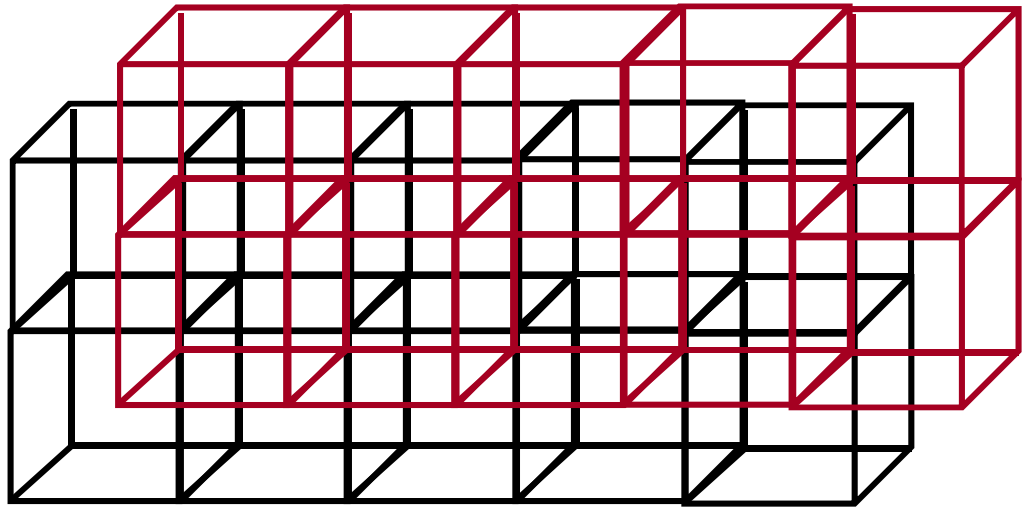
New MOFs for the Adsorptive Storage of Gases

Catenation of the Networks, Single Grid, 3-Dimensional:

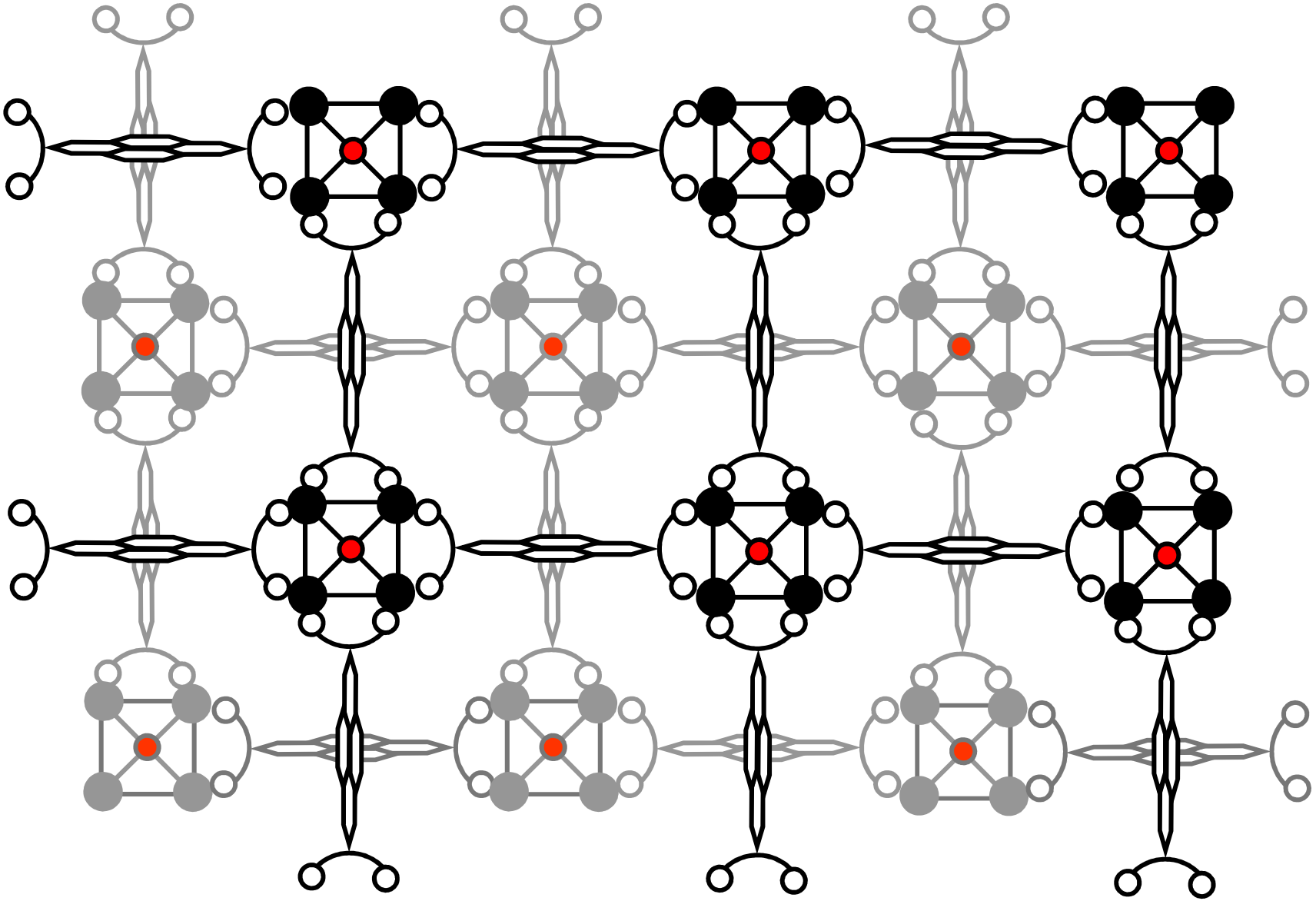


New MOFs for the Adsorptive Storage of Gases

Catenation of the Networks, Duplex Grid, 3-Dimensional:



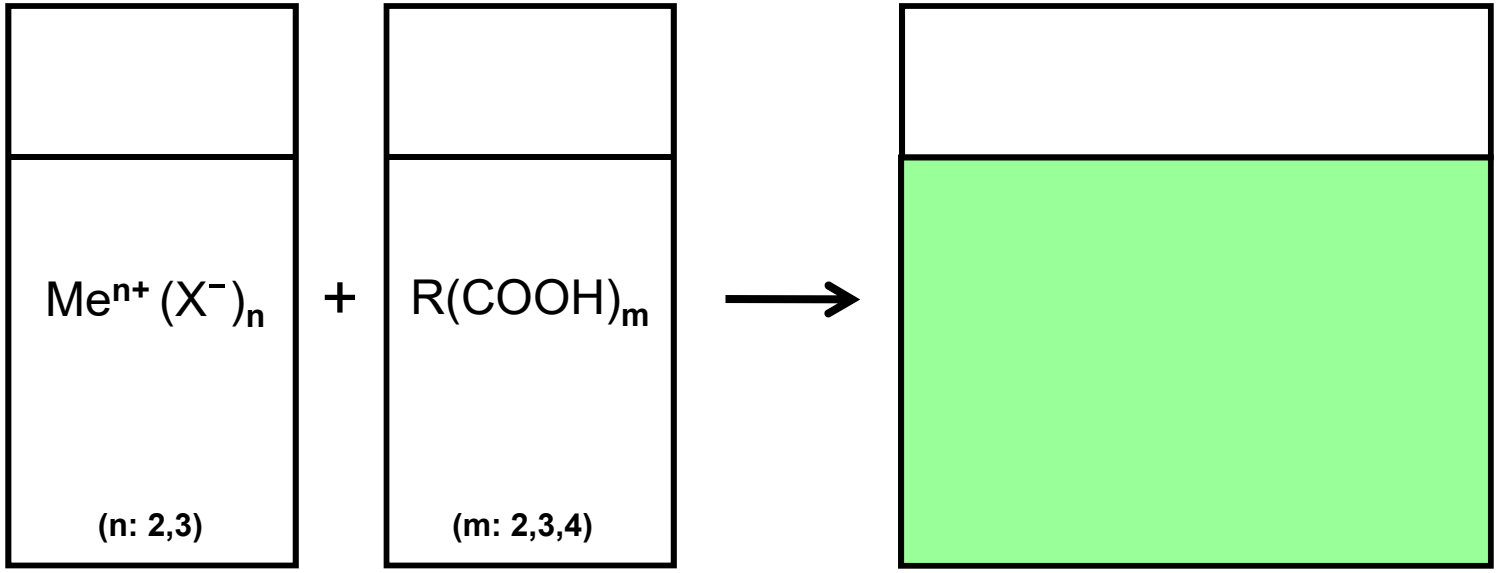
2,7-Pyrene-Dicarboxylic Acid as "Bridging Ligand", Catenation:



Rainer Buerstinghaus

New MOFs for the Adsorptive Storage of Gases

Metal-Organic Frameworks, Preparation (Laboratory):



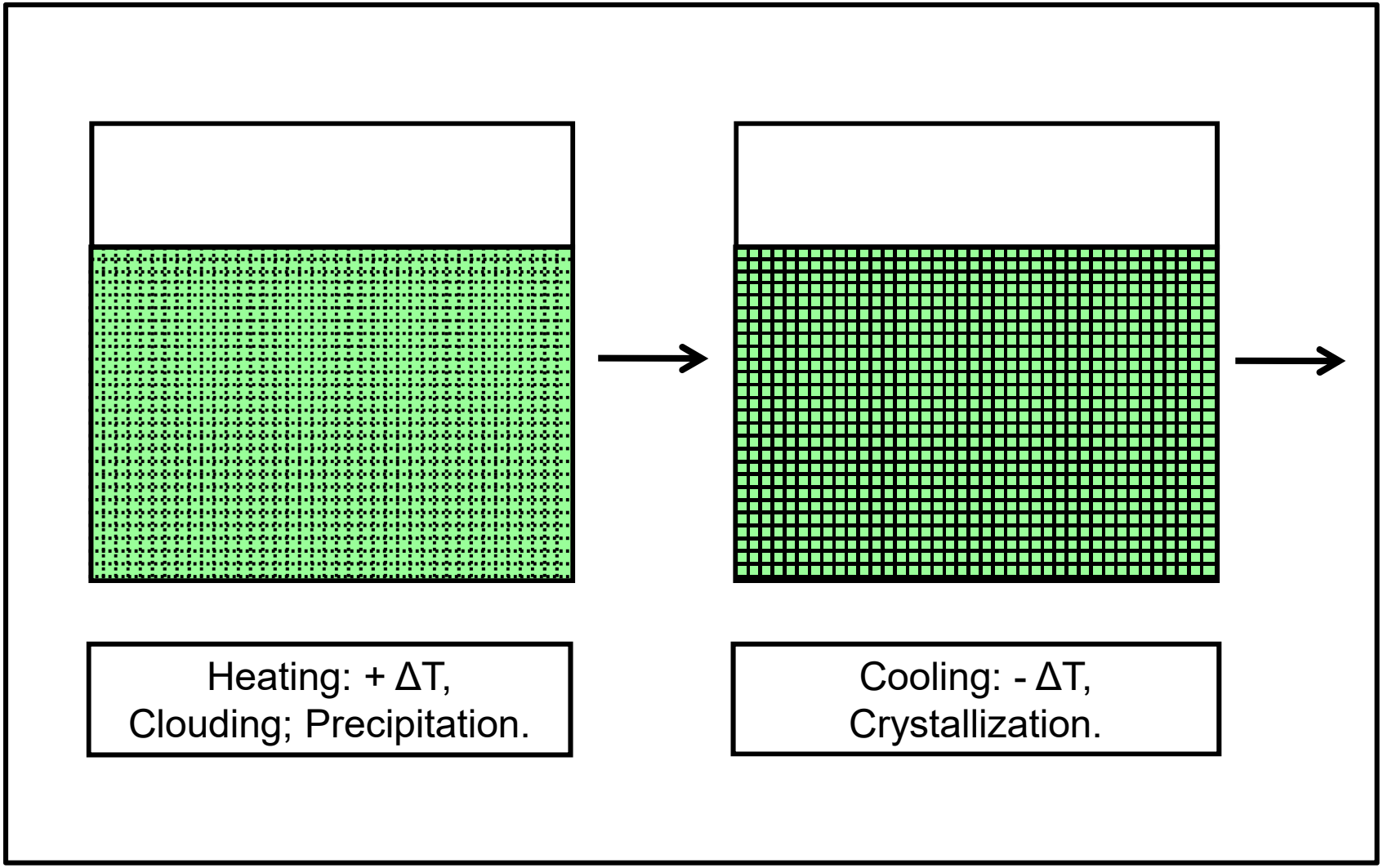
Starting materials:
Metal salt and oligofunctional bridging ligand in separated solutions.

Heating of the combined, homogeneous solutions:
+ ΔT (If needed.: Hydro-/ Solvothermal method).

Rainer Buerstinghaus

New MOFs for the Adsorptive Storage of Gases

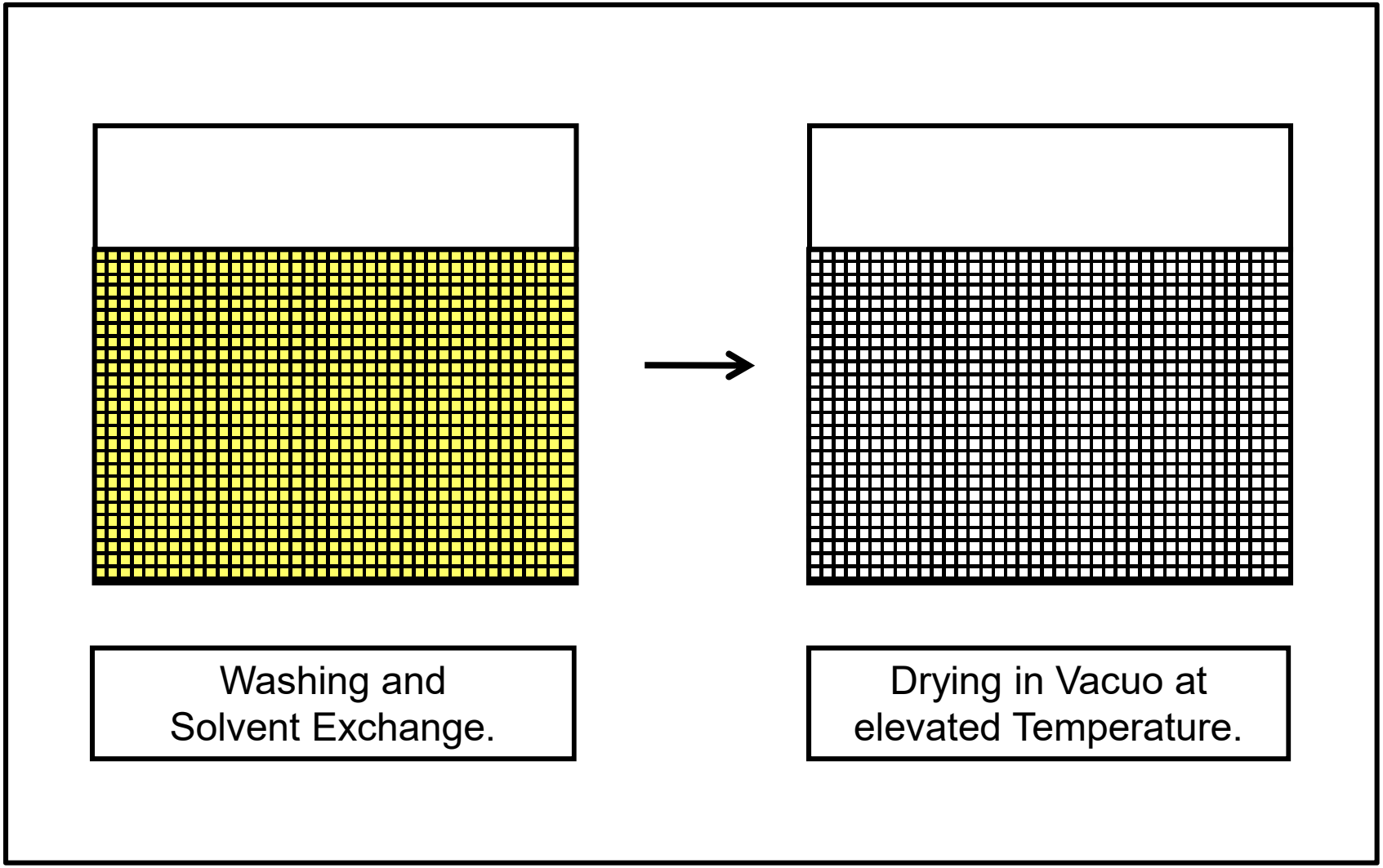
Metal-Organic Frameworks, Preparation (Laboratory):



Rainer Buerstinghaus

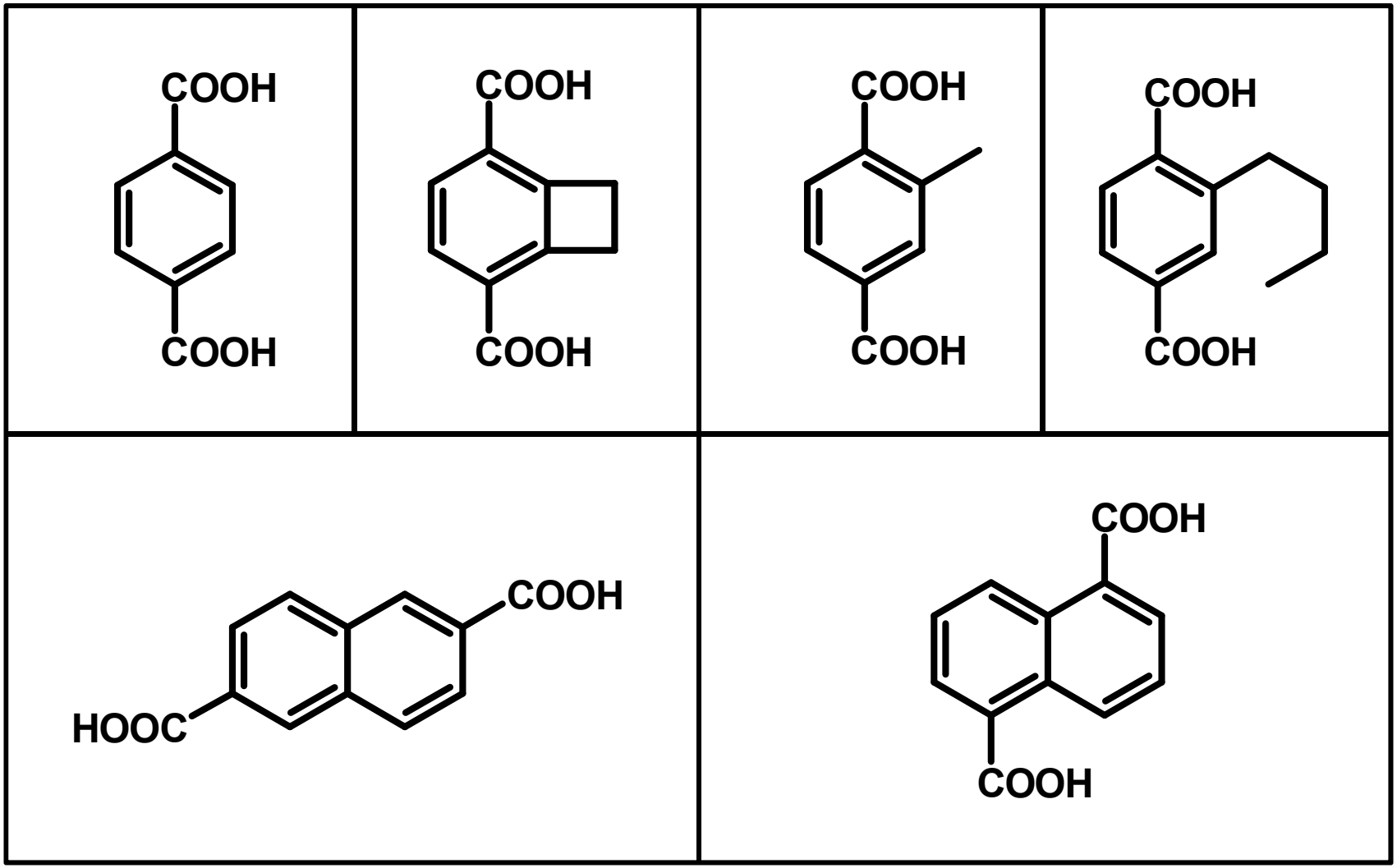
New MOFs for the Adsorptive Storage of Gases

Metal-Organic Frameworks, Preparation (Laboratory):



New MOFs for the Adsorptive Storage of Gases

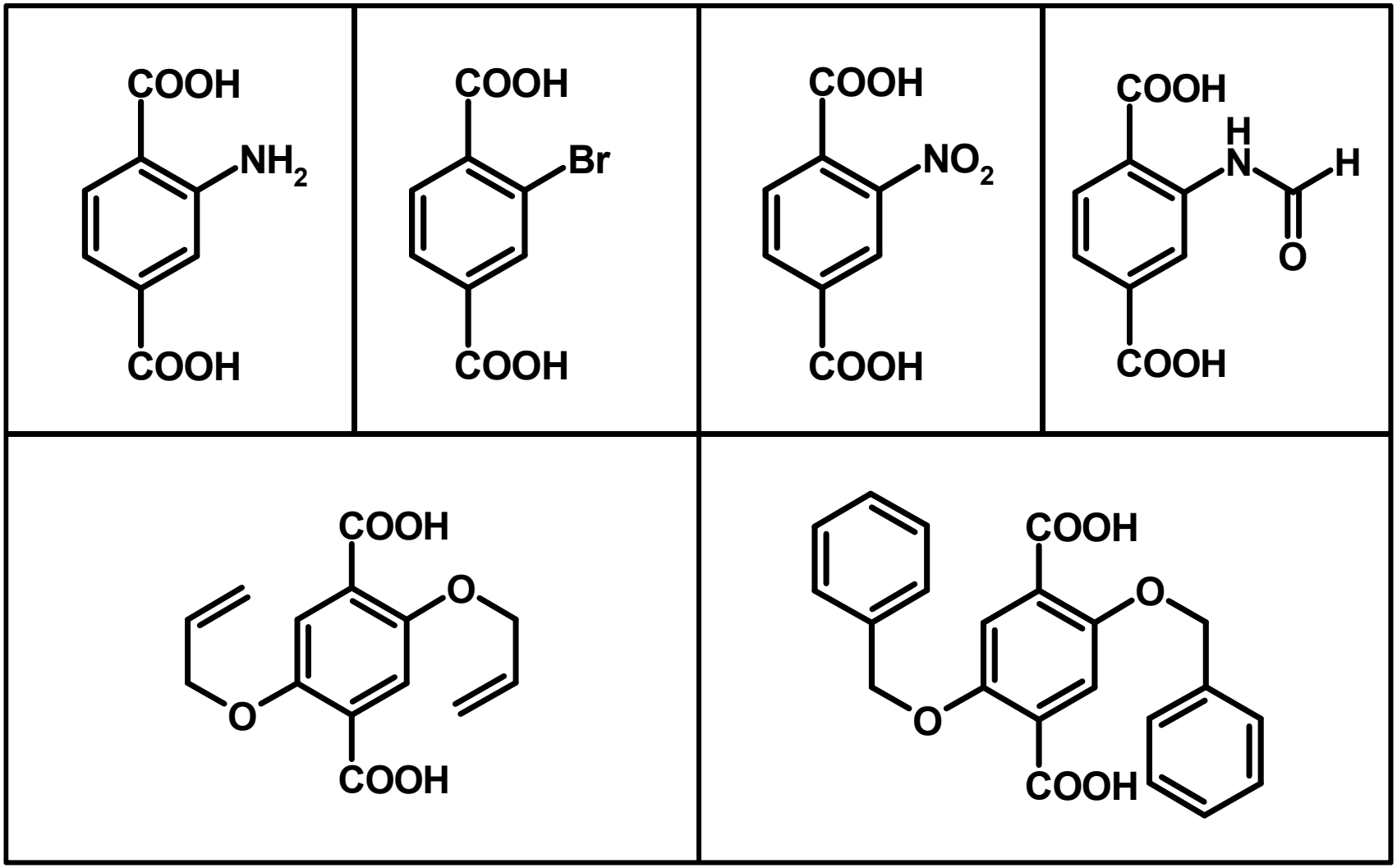
Dicarboxylic Acids as Rigid "Bridging Ligands":



Rainer Buerstinghaus

New MOFs for the Adsorptive Storage of Gases

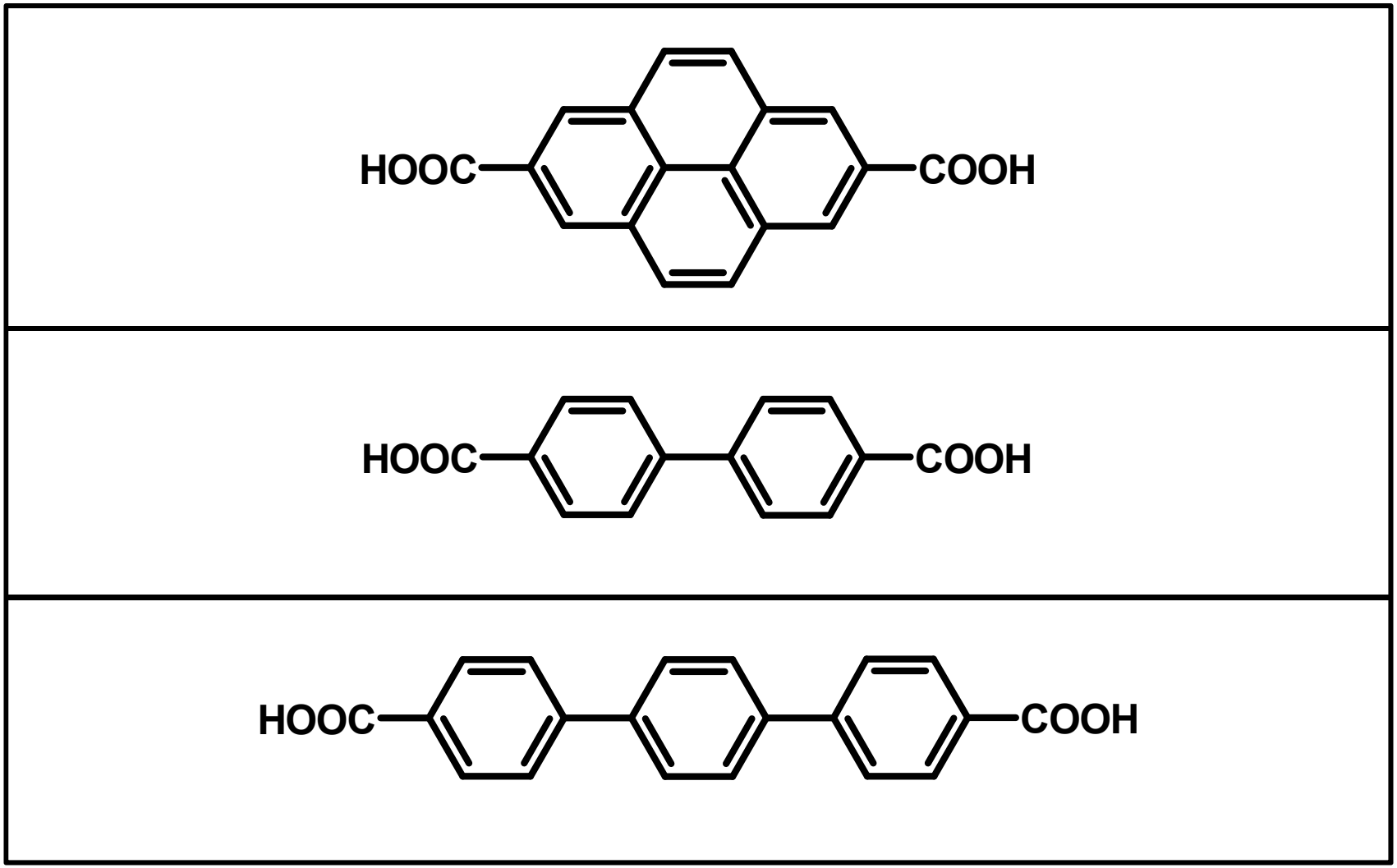
Dicarboxylic Acids as Rigid "Bridging Ligands":



Rainer Buerstinghaus

New MOFs for the Adsorptive Storage of Gases

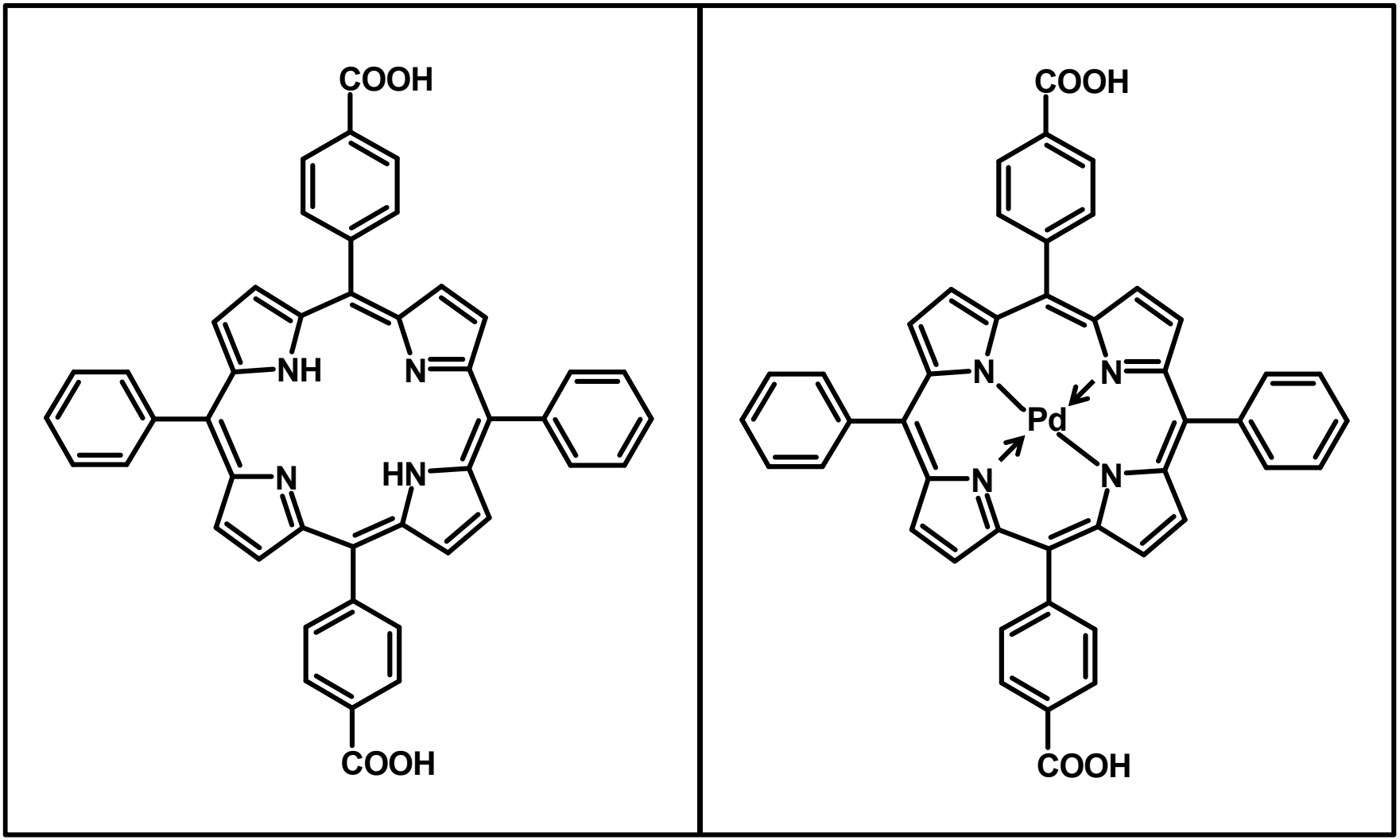
Dicarboxylic Acids as Rigid "Bridging Ligands":



Rainer Buerstinghaus

New MOFs for the Adsorptive Storage of Gases

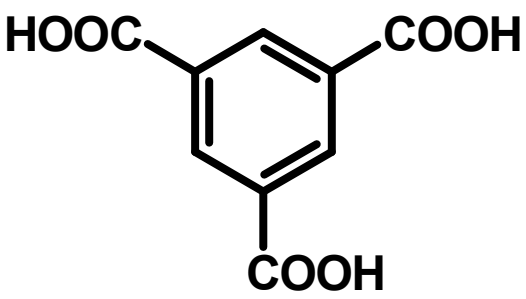
Dicarboxylic Acids as Rigid "Bridging Ligands":

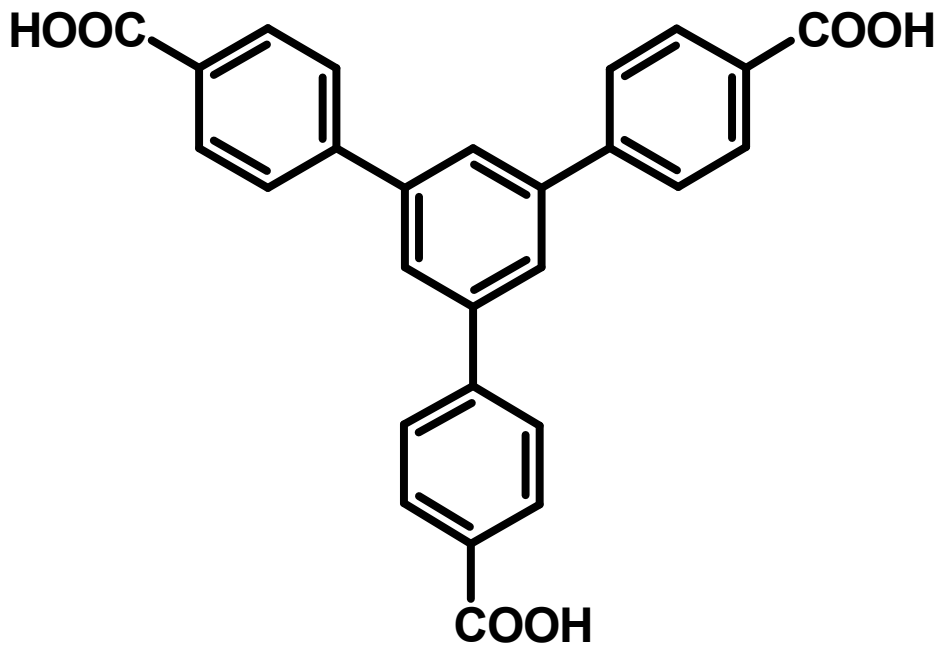


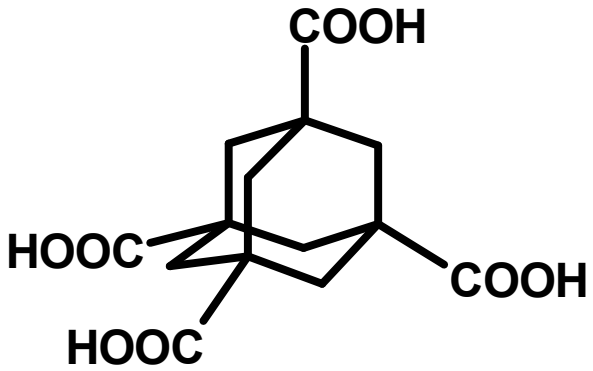
Rainer Buerstinghaus

New MOFs for the Adsorptive Storage of Gases

Typical Tricarboxylic Acids as "Bridging Ligands", Tetracarboxylic Acid as "Bridging Ligand":





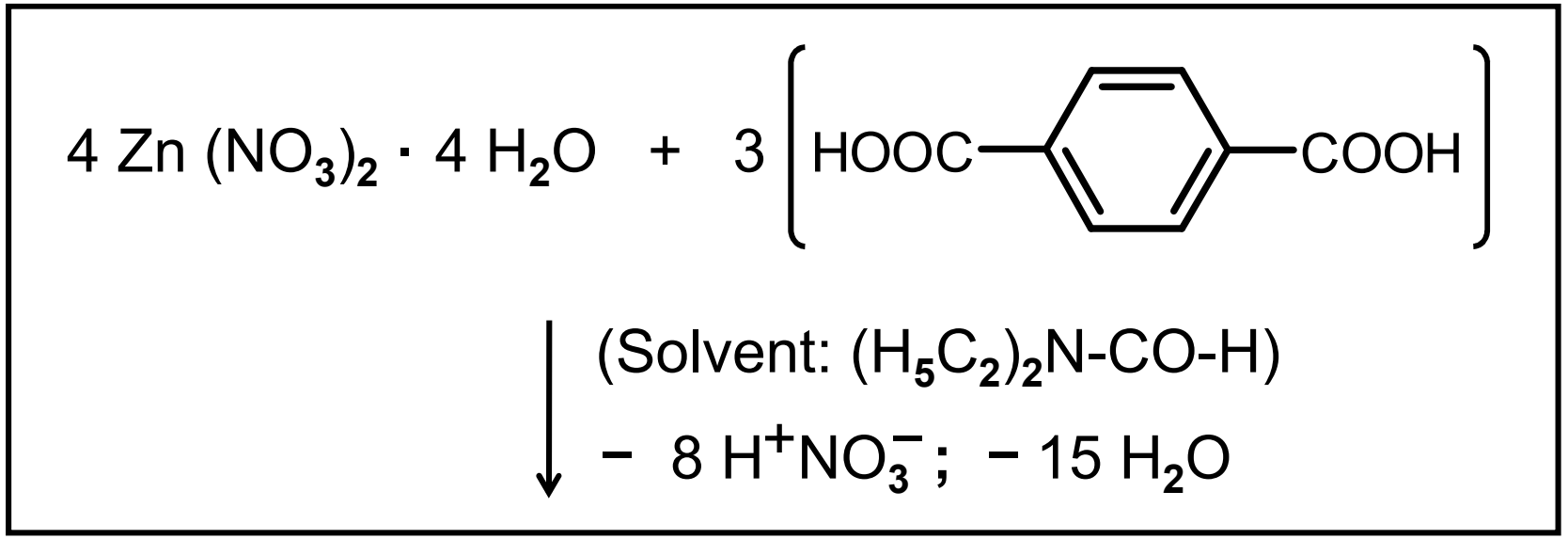


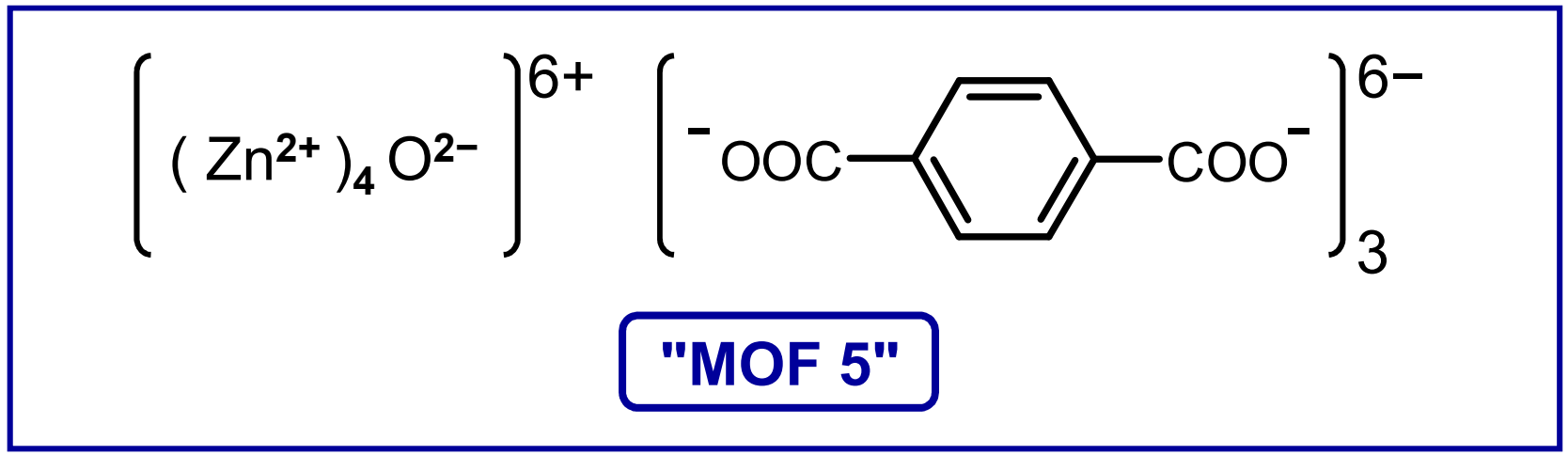
4,4´,4´´- Benzene -1,3,5-triyl - tribenzoic acid ("BTB")

Rainer Buerstinghaus

New MOFs for the Adsorptive Storage of Gases

Synthesis of MOF 5:

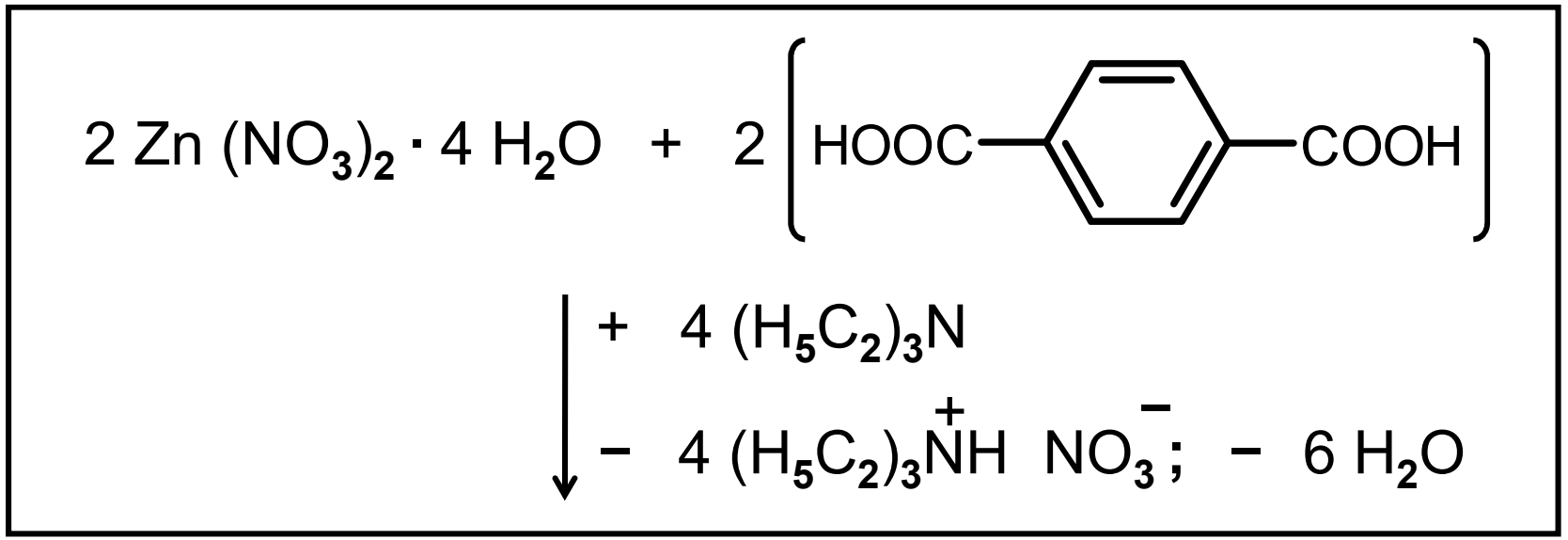


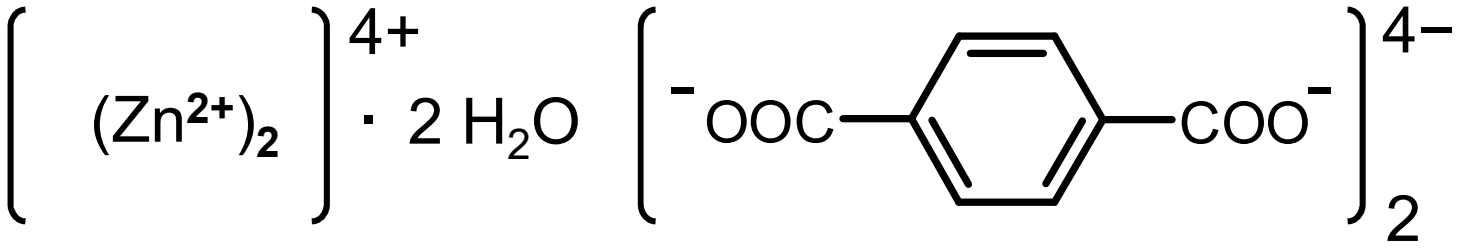


Rainer Buerstinghaus

New MOFs for the Adsorptive Storage of Gases

Synthesis of MOF 2:



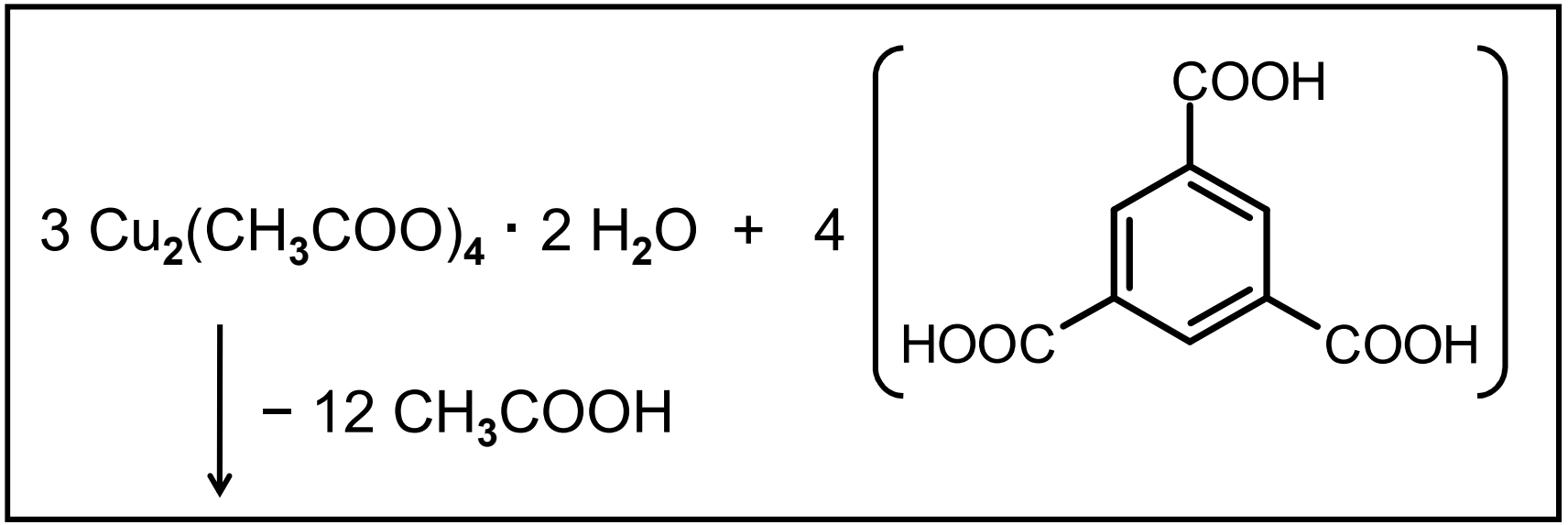


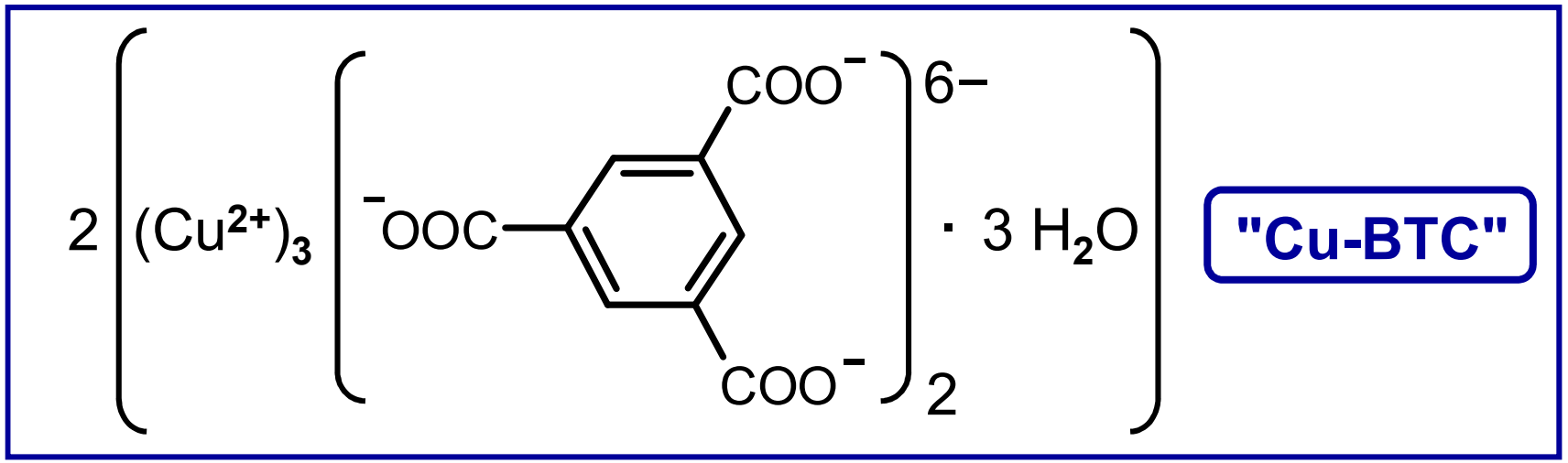
"MOF 2"

Rainer Buerstinghaus

New MOFs for the Adsorptive Storage of Gases

Synthesis of Cu-BTC-MOF:

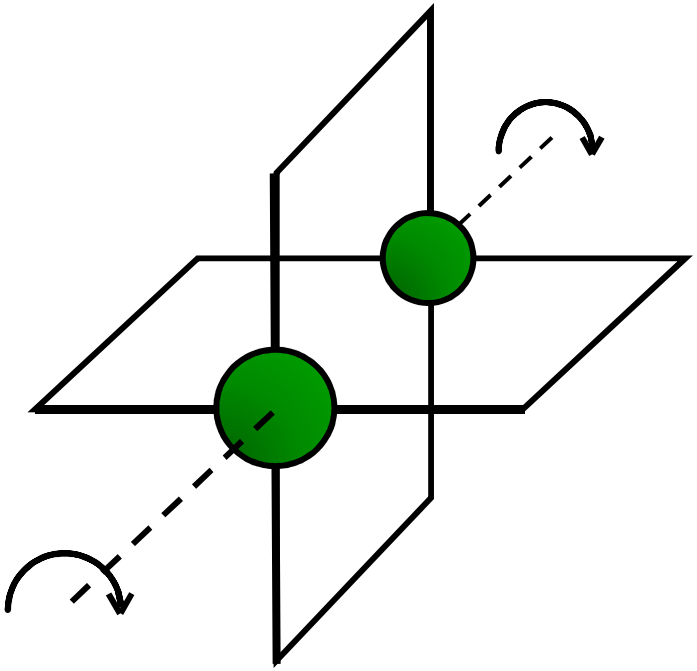




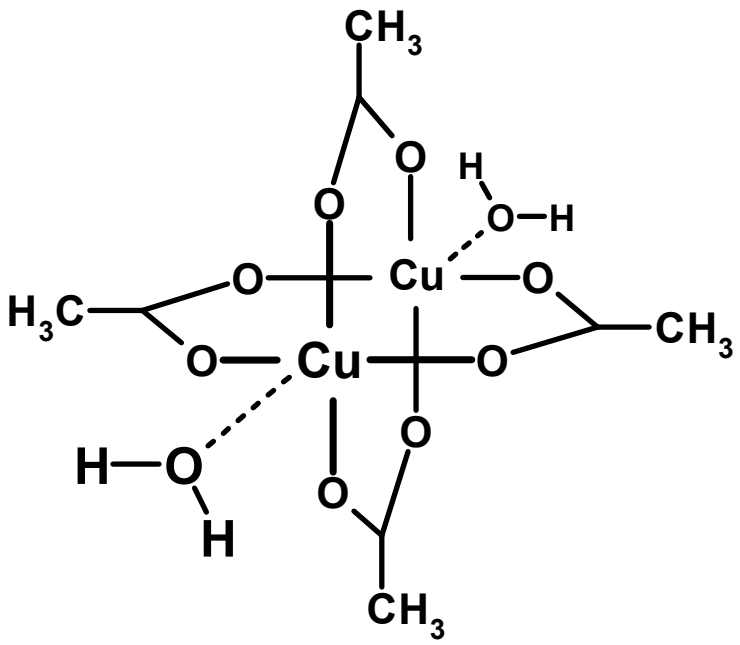
Rainer Buerstinghaus

Paddle Wheel Structure of Copper (II)-Acetate:

$Cu_2(CH_3COO)_4 \cdot 2\ H_2O$ (Hollemann Wiberg, Lehrbuch der Anorganischen Chemie, 103. Edition, de Gruyter, 2016).



"Paddle-Wheel"

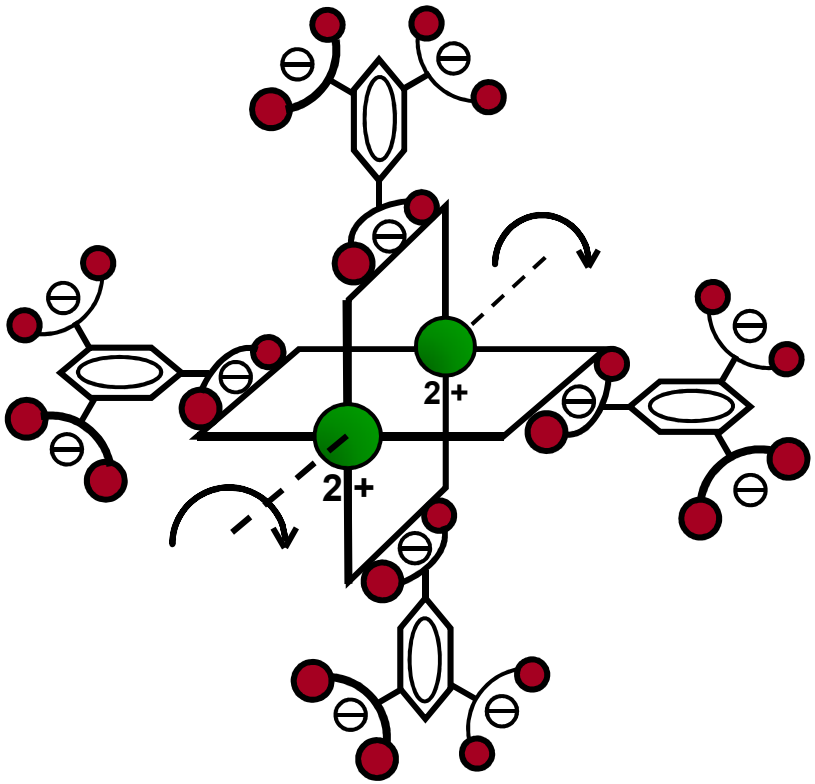


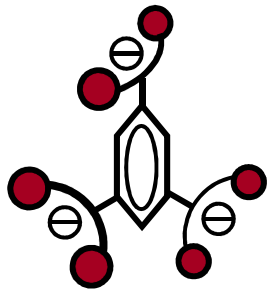
Copper (II)-acetate

Rainer Buerstinghaus

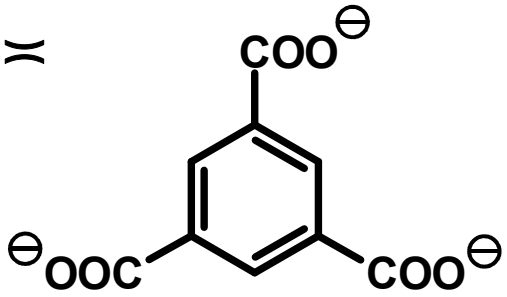
New MOFs for the Adsorptive Storage of Gases

Paddle wheel structure of building blocks of Cu-BTC, MOF 199, HKUST-1 (Hong Kong University of Science and Technology):





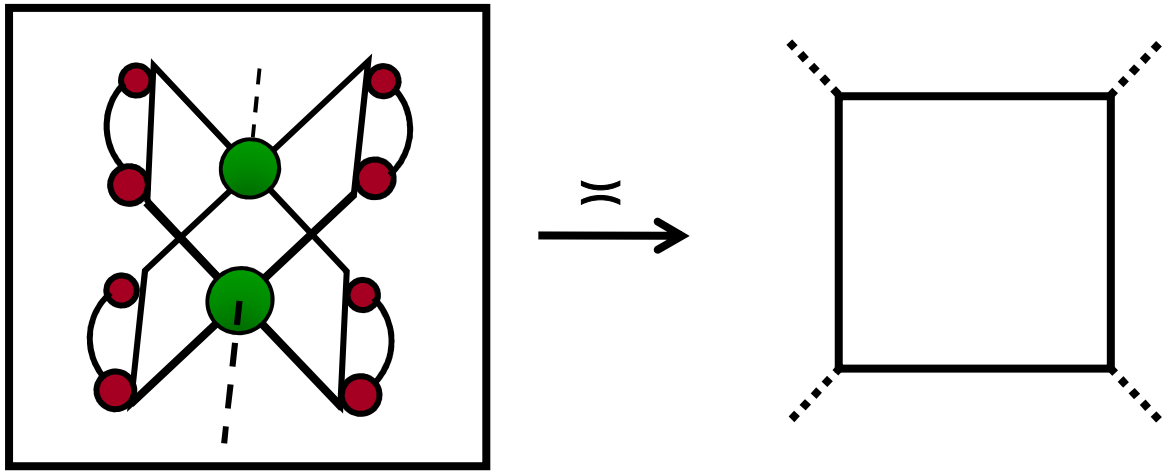
≃



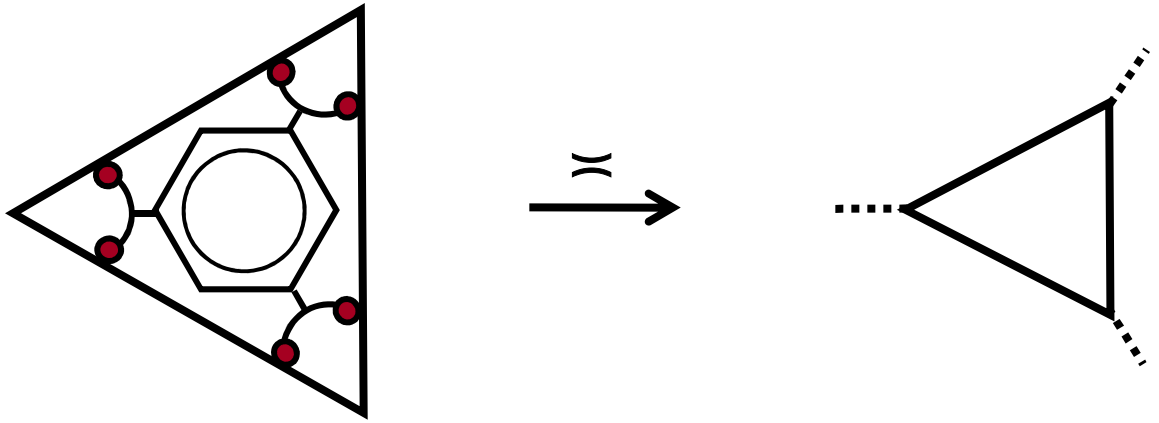
Rainer Buerstinghaus

New MOFs for the Adsorptive Storage of Gases

Paddle wheel structure of building blocks of Cu-BTC, MOF 199, HKUST-1 (Hong Kong University of Science and Technology):

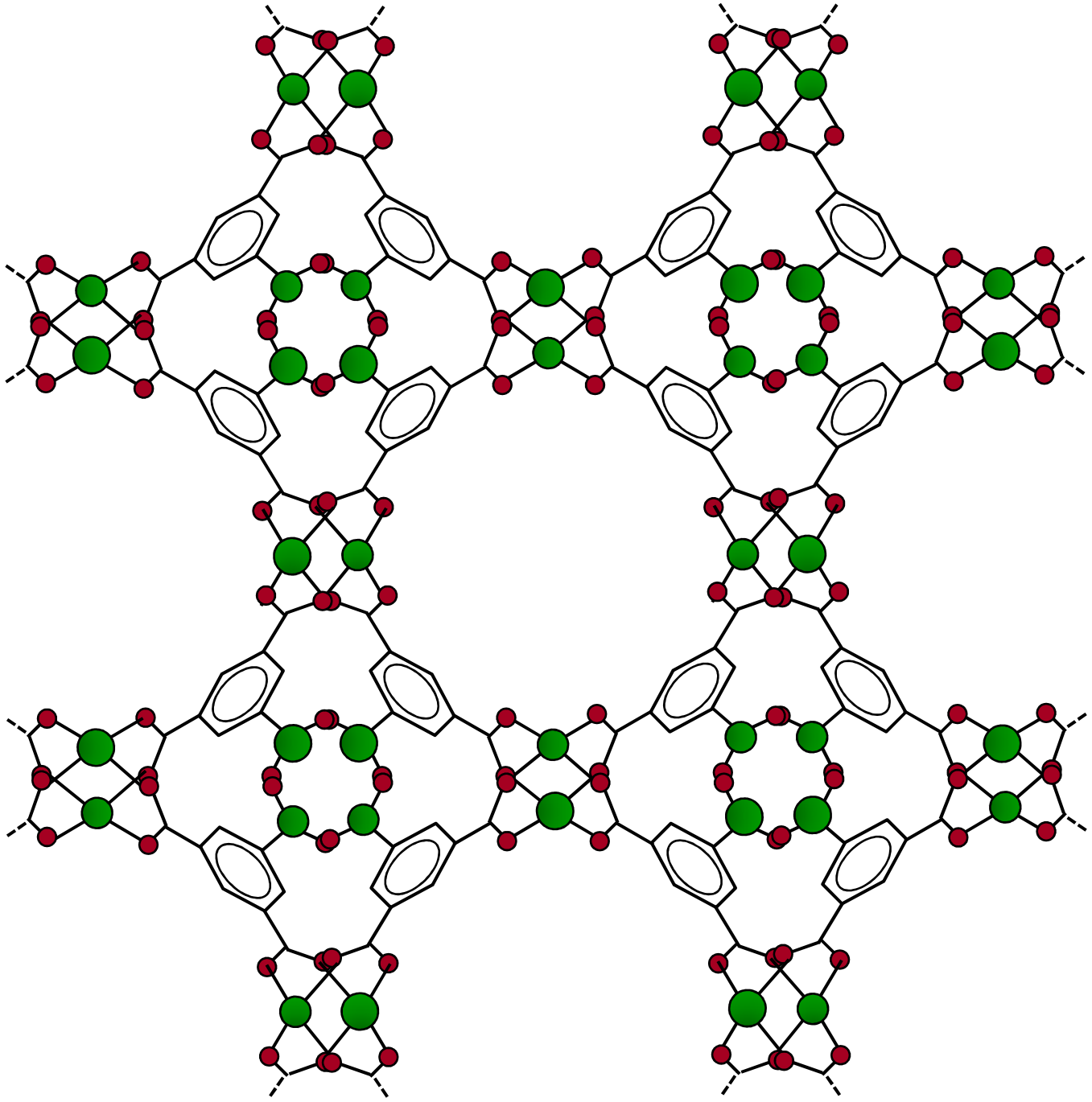


Orthogal Building Block



Trigonal Building Block

Rainer Bürstinghaus



Cu 2+

COO−

2+

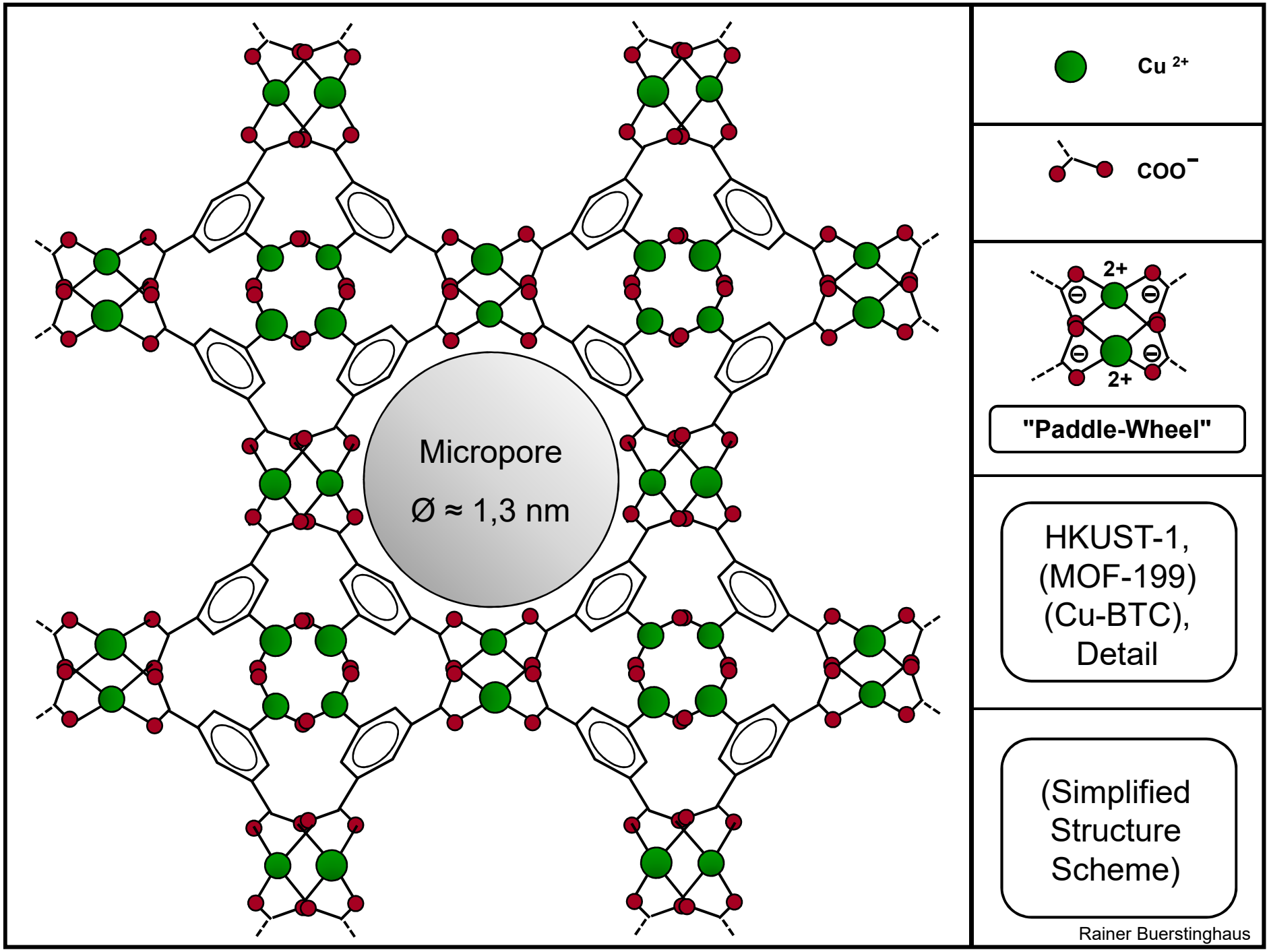
2+

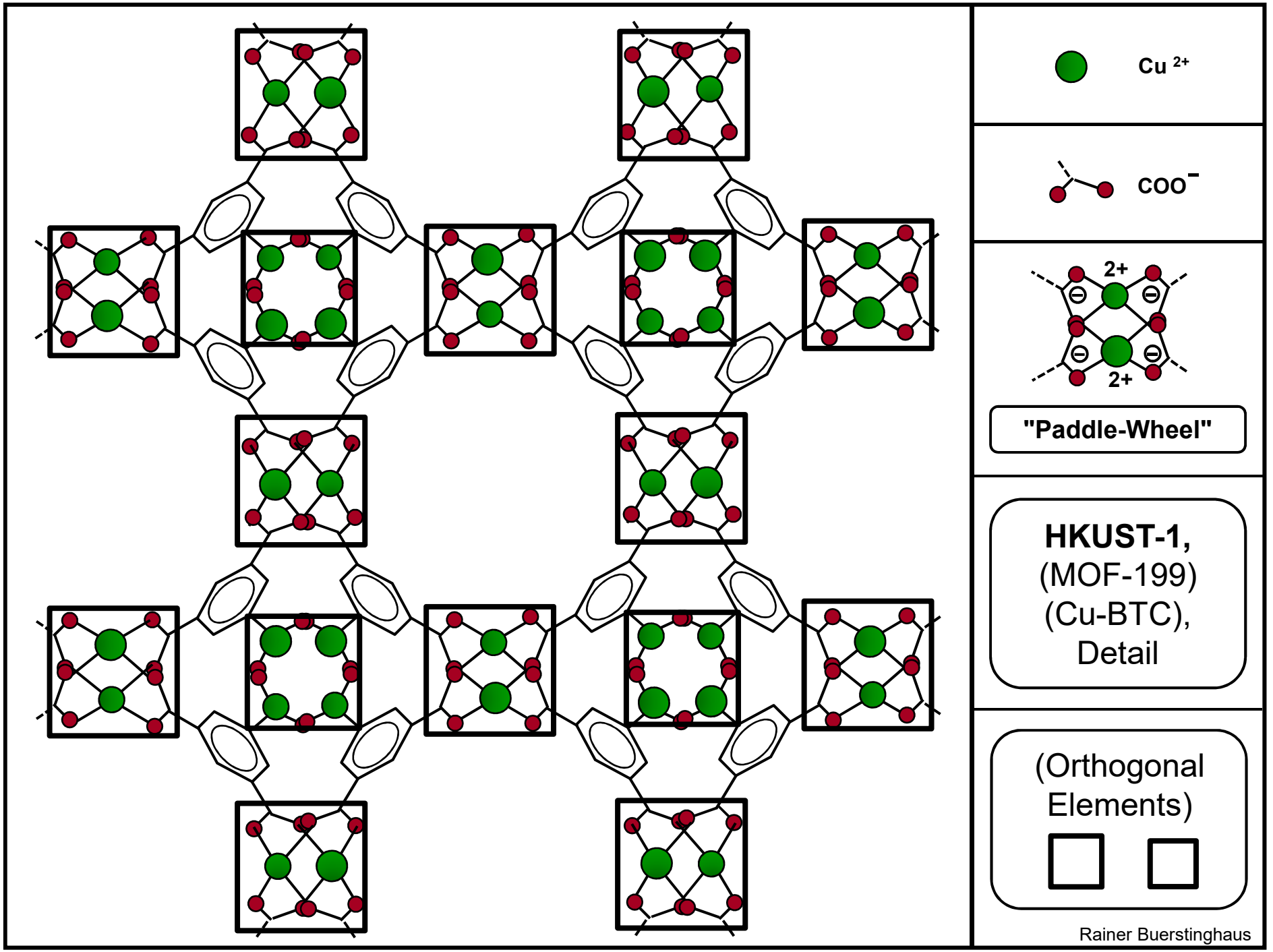
"Paddle-Wheel"

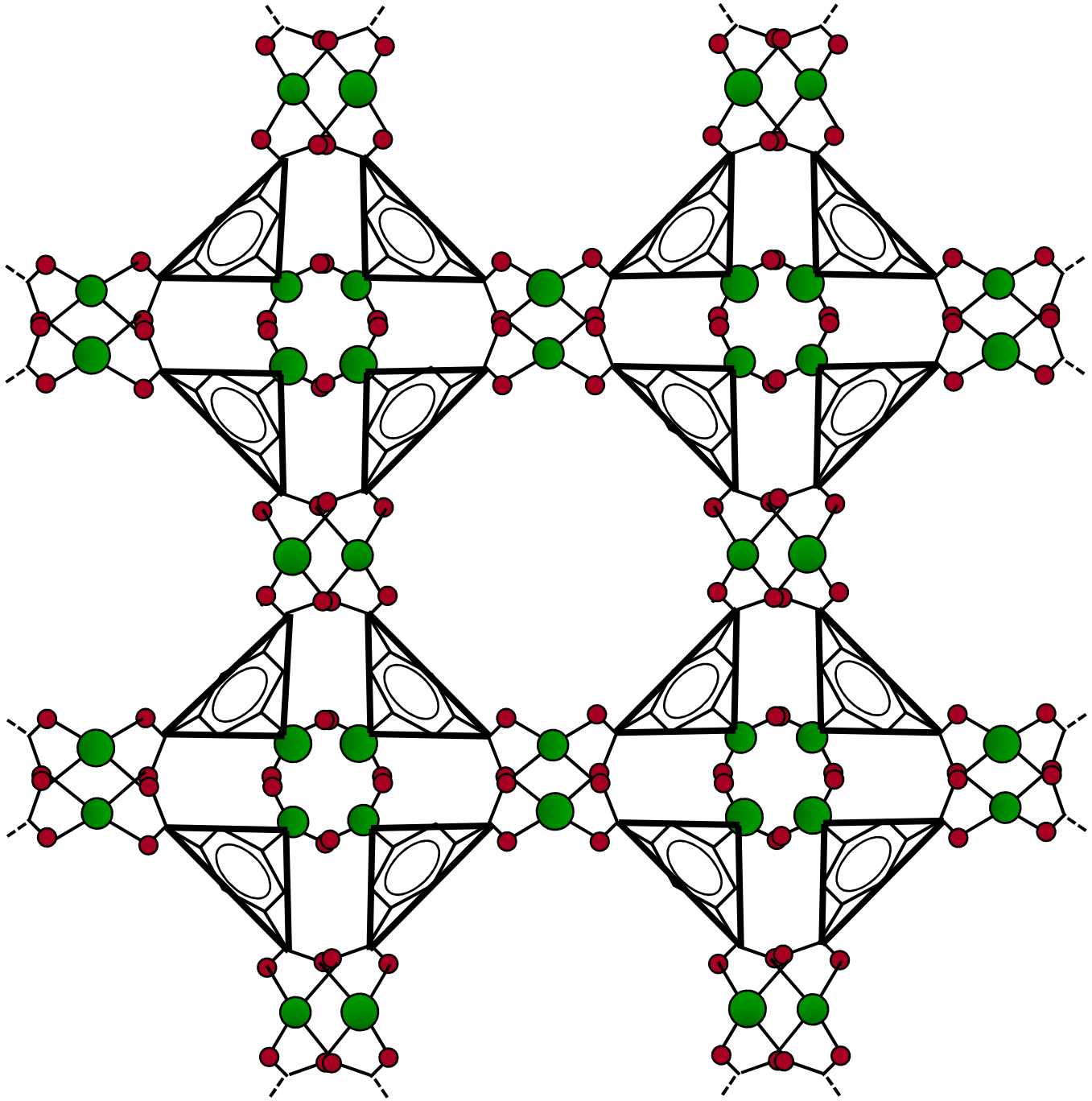
HKUST-1, (MOF-199) (Cu-BTC), Detail

(Simplified Structure Scheme)

Rainer Buerstinghaus


Micropore
Ø ≈ 1,3 nm
Cu 2+
COO−
2+
2+
"Paddle-Wheel"
HKUST-1,
(MOF-199)
(Cu-BTC),
Detail
(Simplified
Structure
Scheme)
Rainer Buerstinghaus


Cu 2+
COO−
2+
2+
"Paddle-Wheel"
HKUST-1,
(MOF-199)
(Cu-BTC),
Detail
(Orthogonal
Elements)
Rainer Buerstinghaus



Cu 2+

COO−

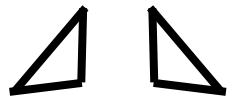
2+

2+

"Paddle-Wheel"

HKUST-1,
(MOF-199)
(Cu-BTC),
Detail

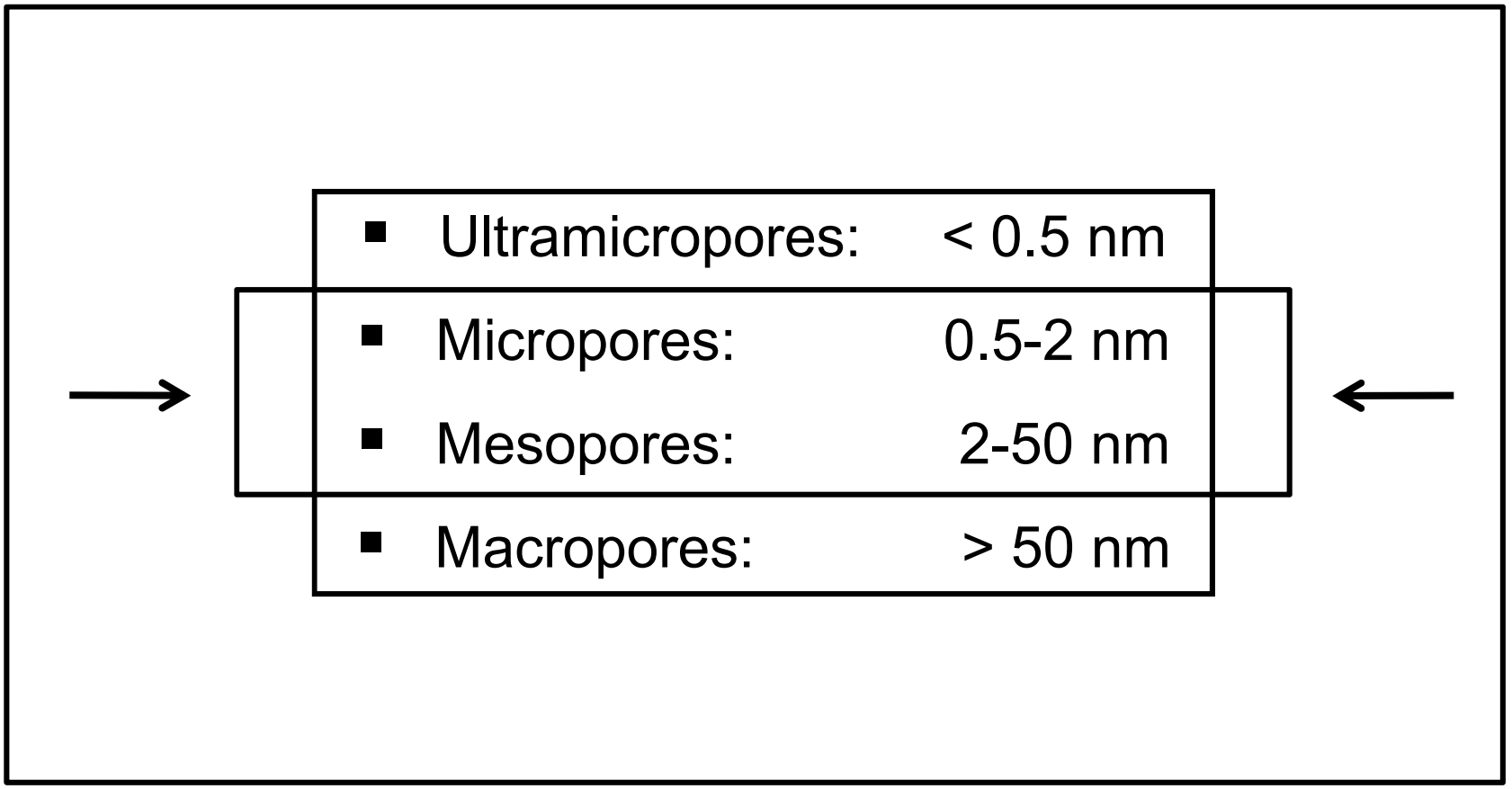
(Trigonal
Elements)



Rainer Buerstinghaus

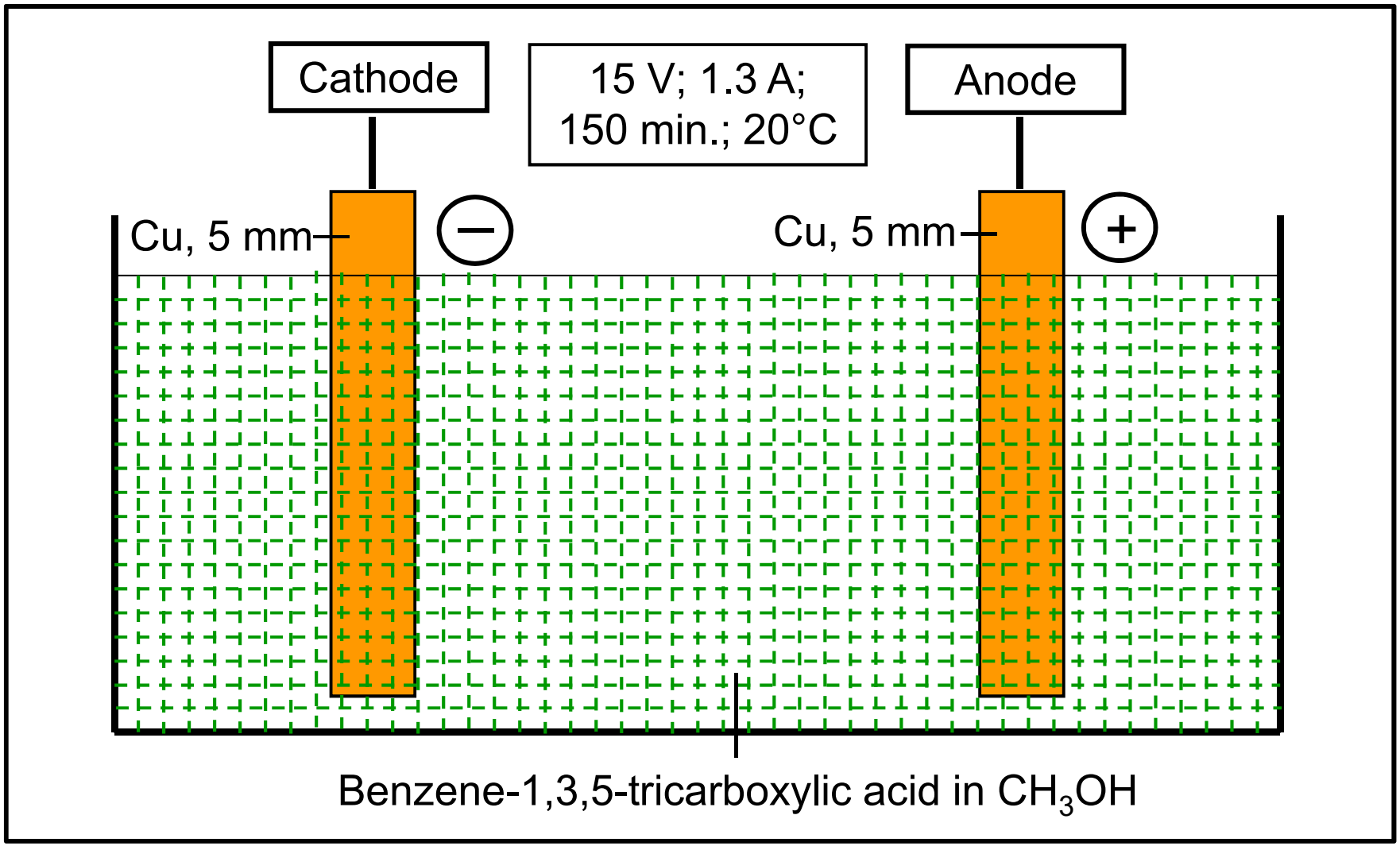
New MOFs for the Adsorptive Storage of Gases

Classification of Pores According to their Size.



New MOFs for the Adsorptive Storage of Gases

Electrochemical Synthesis of Cu-BTC-MOF:



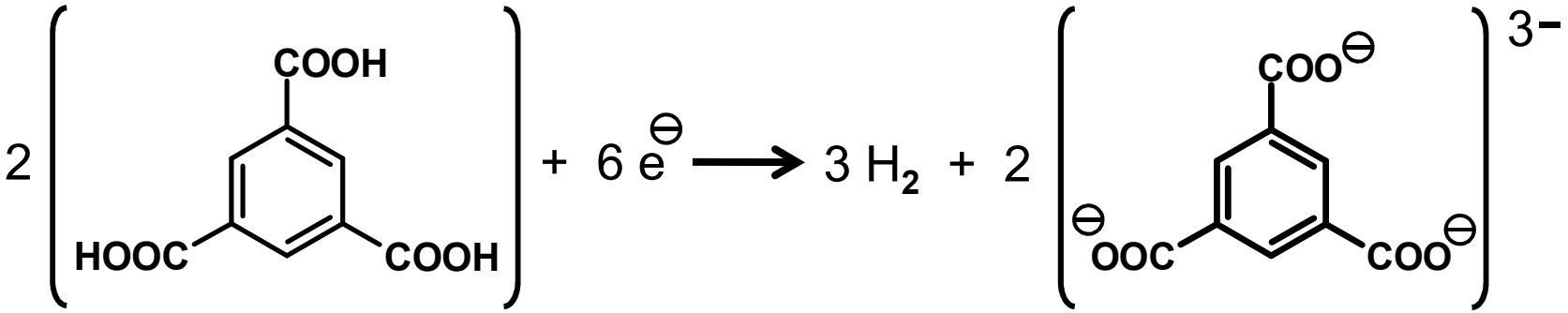
Rainer Buerstinghaus

New MOFs for the Adsorptive Storage of Gases

Electrochemical Synthesis of Cu-BTC-MOF:

Cathode Reactions

$$6\,H_2O + 6\,e^{\ominus} \longrightarrow 3H_2 + 6\,OH^{\ominus}$$



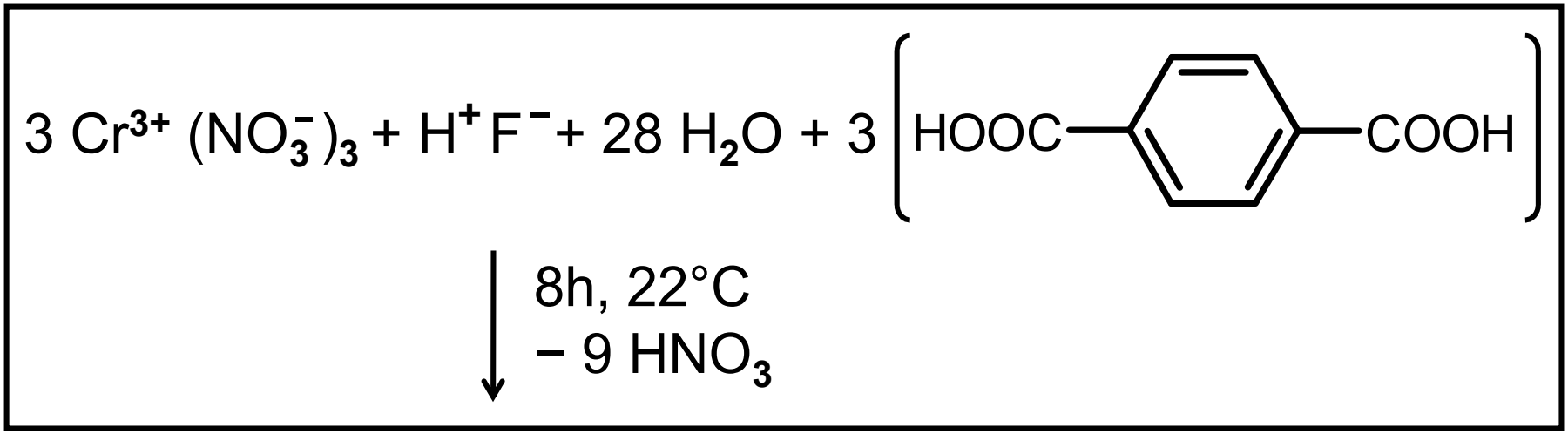
Anode Reaction

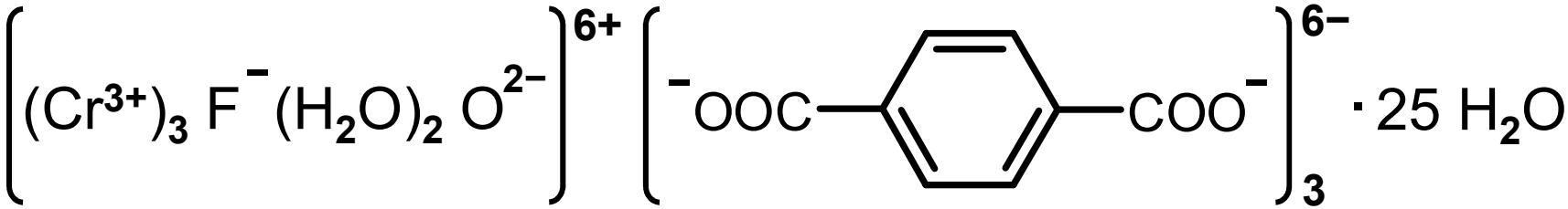
$$3\,Cu^{\pm 0} - 6\,e^{\ominus} \longrightarrow 3\,Cu^{2+}$$

Rainer Buerstinghaus

New MOFs for the Adsorptive Storage of Gases

Synthesis of "MIL 101",
"MIL": Matériaux de l´Institut Lavoisier, Versailles, France.

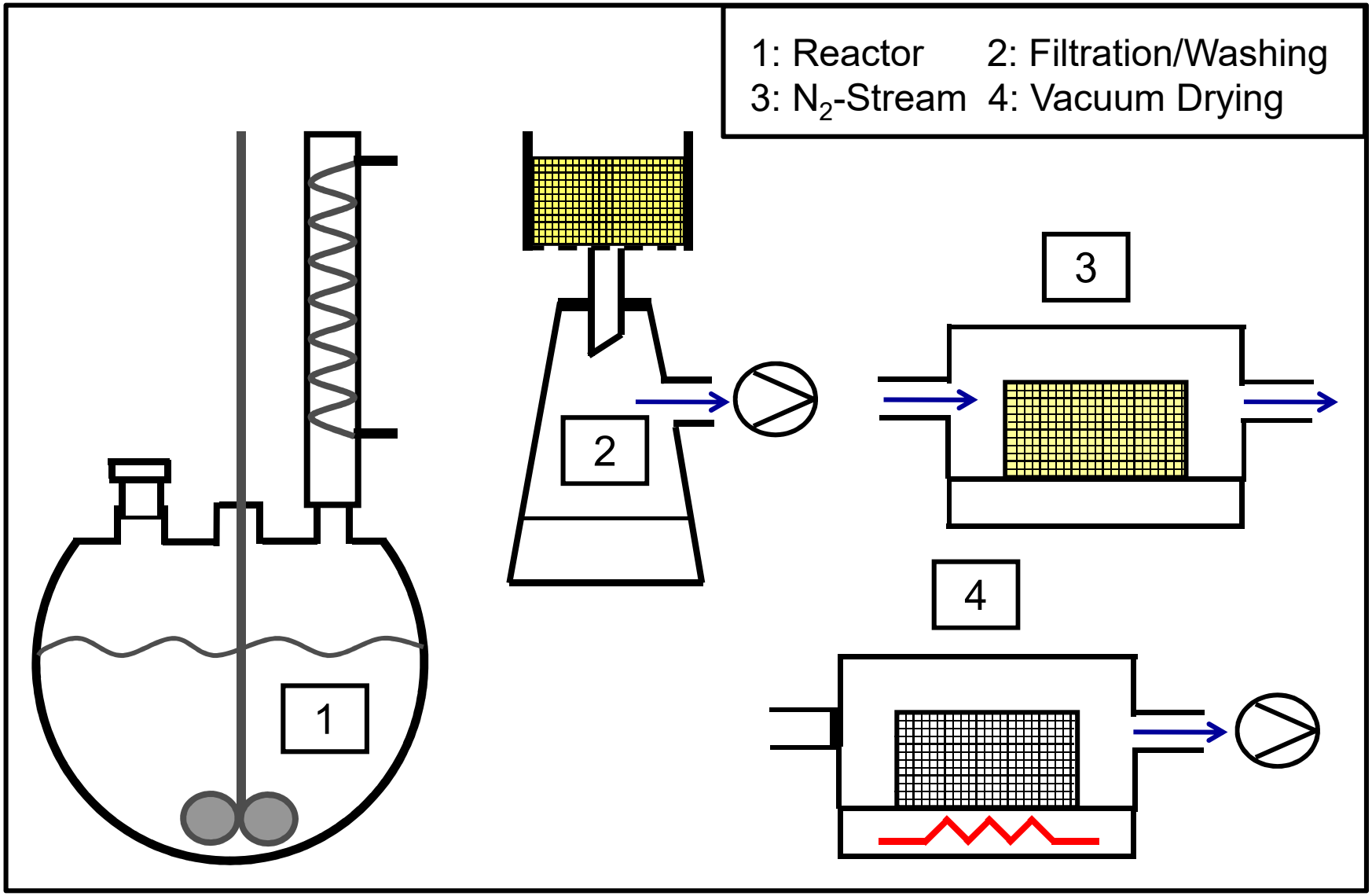




"MIL 101" shows mesopores with ø of ≈ 2,9−3.4 nm!

Rainer Buerstinghaus

Metal-Organic Frameworks, Synthesis (Laboratory):



Rainer Buerstinghaus

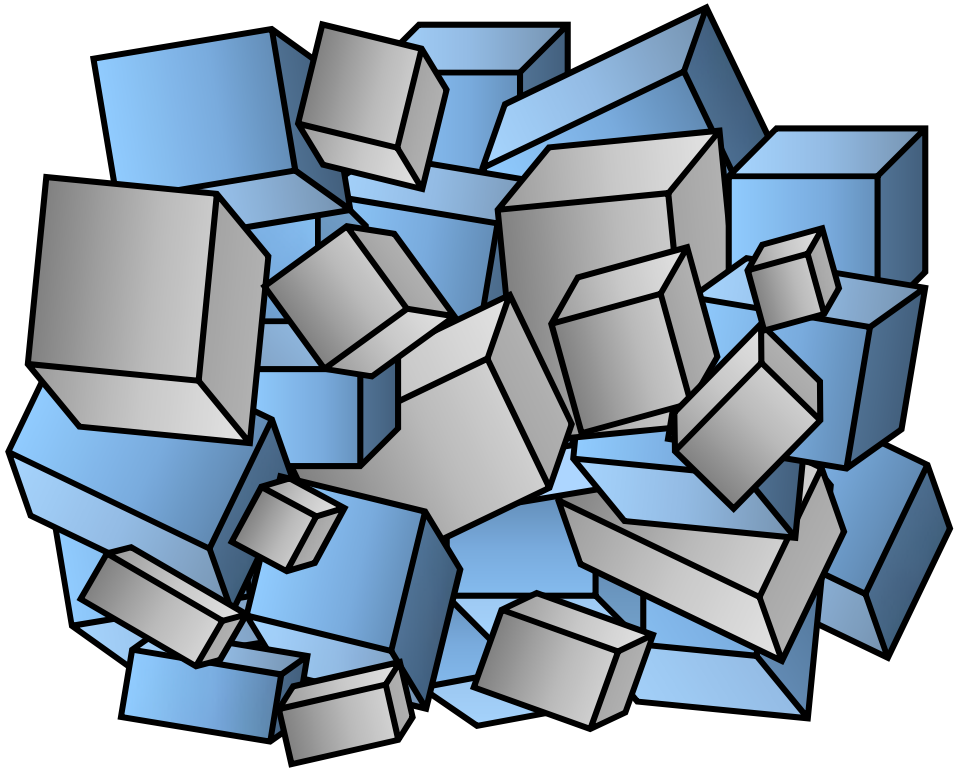
New MOFs for the Adsorptive Storage of Gases

Synthesis of MOF 5, Working Instructions:

In a glass reactor equipped with a reflux condenser and a teflon-lined strirrer, 41g of terephthalic acid and 193g of zinc nitrate tetrahydrate (Merck) were dissolved in 5.650g of diethylformamide (BASF, < 100 ppm water) and heated up to 130°C for 4 hours. After 45 minutes, crystallization started and the formerly clear solution turned slightly opaque.

After a total of 4 hours, the reaction product wass cooled down to room temperature. The solid was filtered off, washed three times with 1 liter of dry acetone and dried under a stream of flowing nitrogen. Finally, the product was activated at 60°C for at least 3 hours under a reduced pressure of < 0.2 mbar.

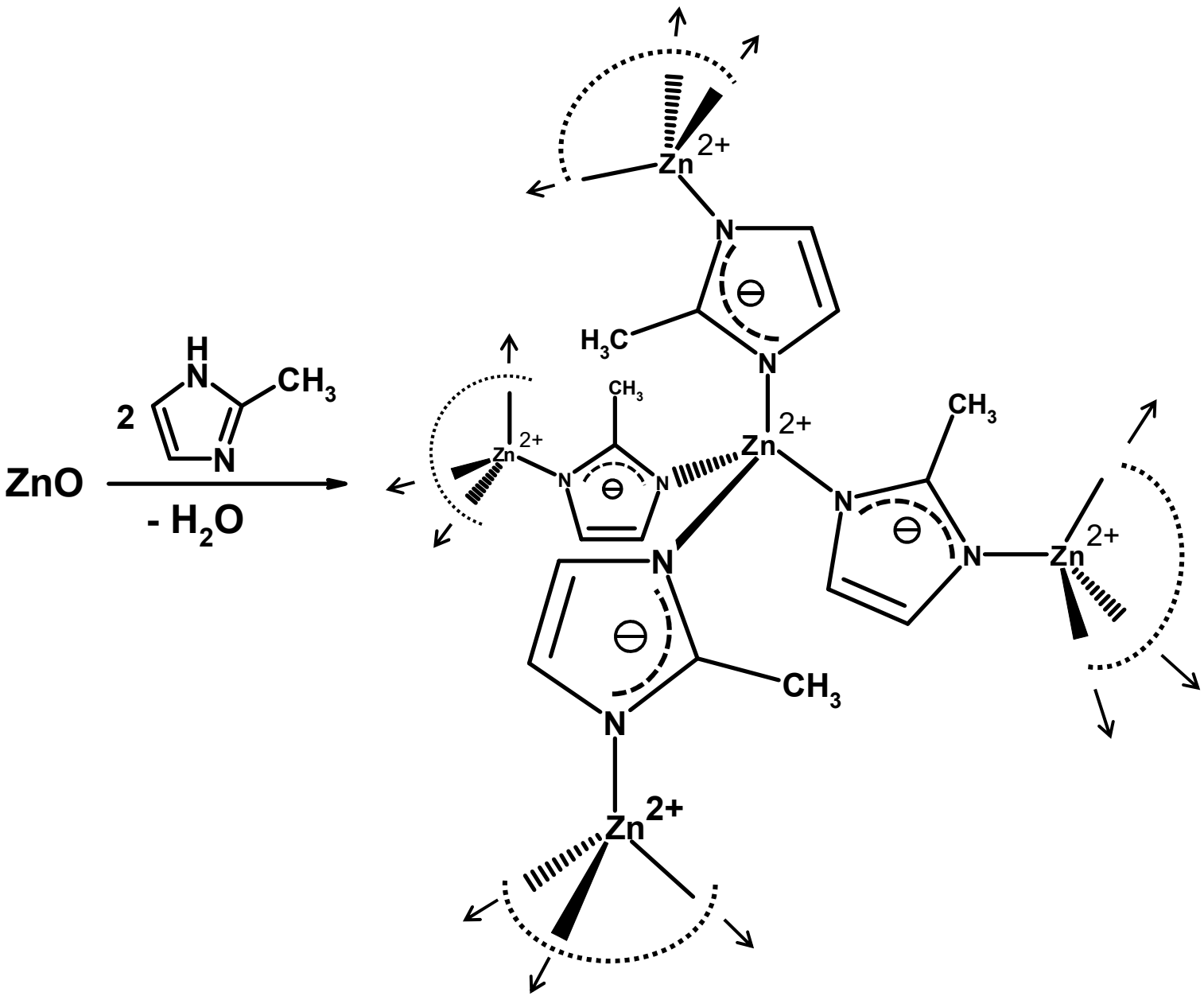
New MOFs for the Adsorptive Storage of Gases



MOF 5: View under the Electron Microscope (Sketch).

Rainer Buerstinghaus

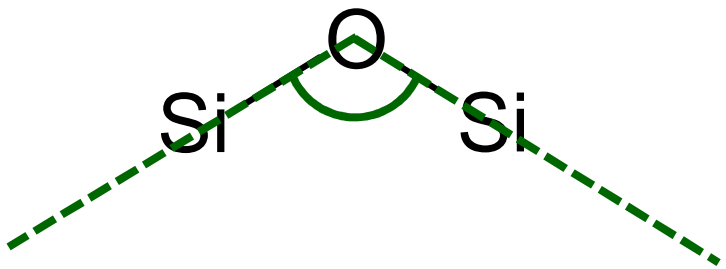
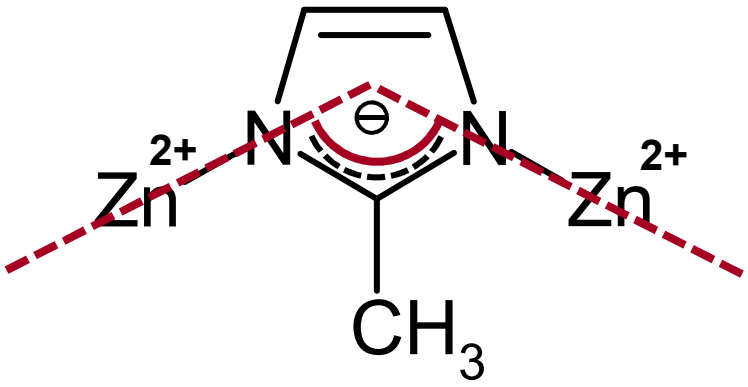
Zeolitic Imidazolate Framework, ZIF-8, Structural Detail:



Rainer Buerstinghaus

New MOFs for the Adsorptive Storage of Gases

Zeolitic Imidazolate Framework (ZIF) ; Structural Similarity with Inorganic Zeolites:

Zeolite-Fragment	ZIF-8-Fragment
	
∢ Si-O-Si: **145°**	∢ Zn^{2+}-Im^{-}-Zn^{2+}: **145°**

Rainer Buerstinghaus

New MOFs for the Adsorptive Storage of Gases

Technical Applications of these Porous Materials:

- Carrier materials for heterogeneous catalysis.
- Immobilization of (chiral) homogeneous catalysts.
- Nanoreactors.
- "Templates" on the nanoscale.
- Slow release formulations, controlled drug release.
- Luminescent lamps.
- Gas cleaning.
- Gas separation.
- Gas storage.

New MOFs for the Adsorptive Storage of Gases

Technical Applications of these Porous Materials:

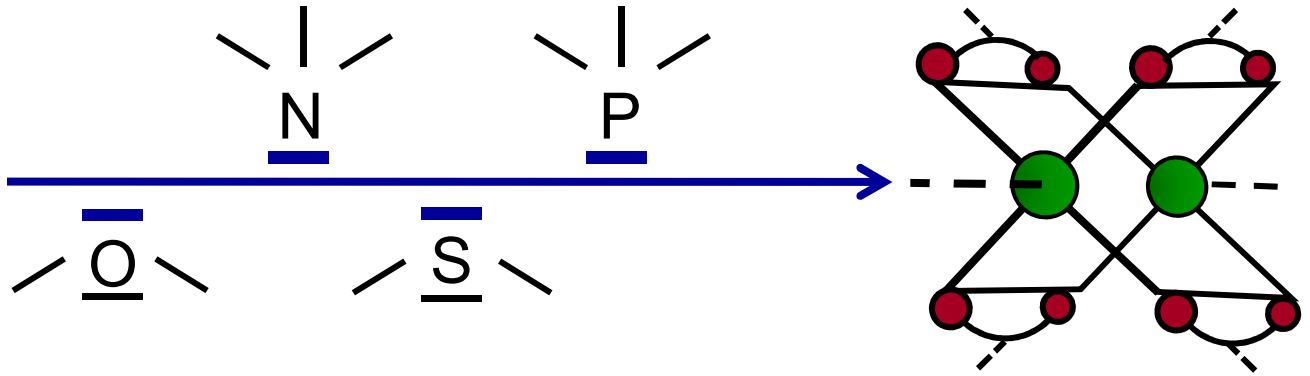
- Carrier materials for heterogeneous catalysis.
- Immobilization of (chiral) homogeneous catalysts.
- Nanoreactors.
- "Templates" on the nanoscale.
- Slow release formulations, controlled drug release.
- Luminescent lamps.
- Gas cleaning.
- Gas separation.
- Gas storage.

Rainer Buerstinghaus

Metal-Organic Frameworks ⟶ Technical Applications

Gas Purification:

- Continuous gas purification by selective adsorption of (polar) impurities on the surfaces of MOFs.
- Detectability by color change (blue ⟶ green ⟶ blue).
- Regenerability of Cu-BTC MOFs.
- Purification of natural gas / methane with Cu-BTC-MOFs. Removal of sulphurous impurities.

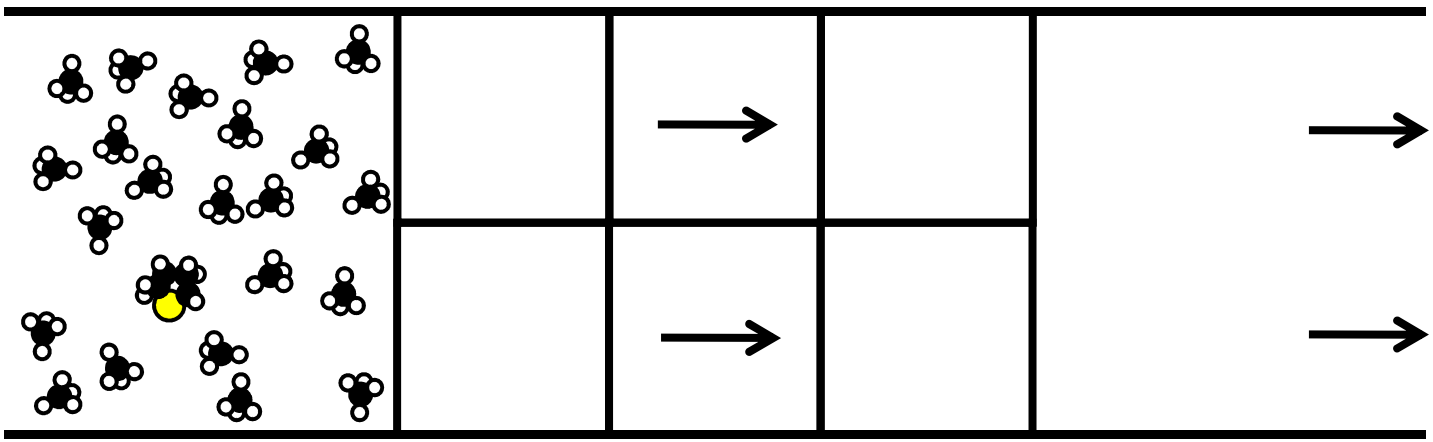


Contaminations: NR_3; NH_3; H_2O; ROH; R_1OR_2; R_1OOR_2

Rainer Buerstinghaus

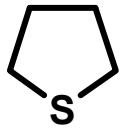
Metal-Organic Frameworks ⟶ Technical Applications

Gas Purification with HKUST-1: $Cu_3[BTC]_2 \cdot 3\,H_2O$



Tetrahydrothiophene

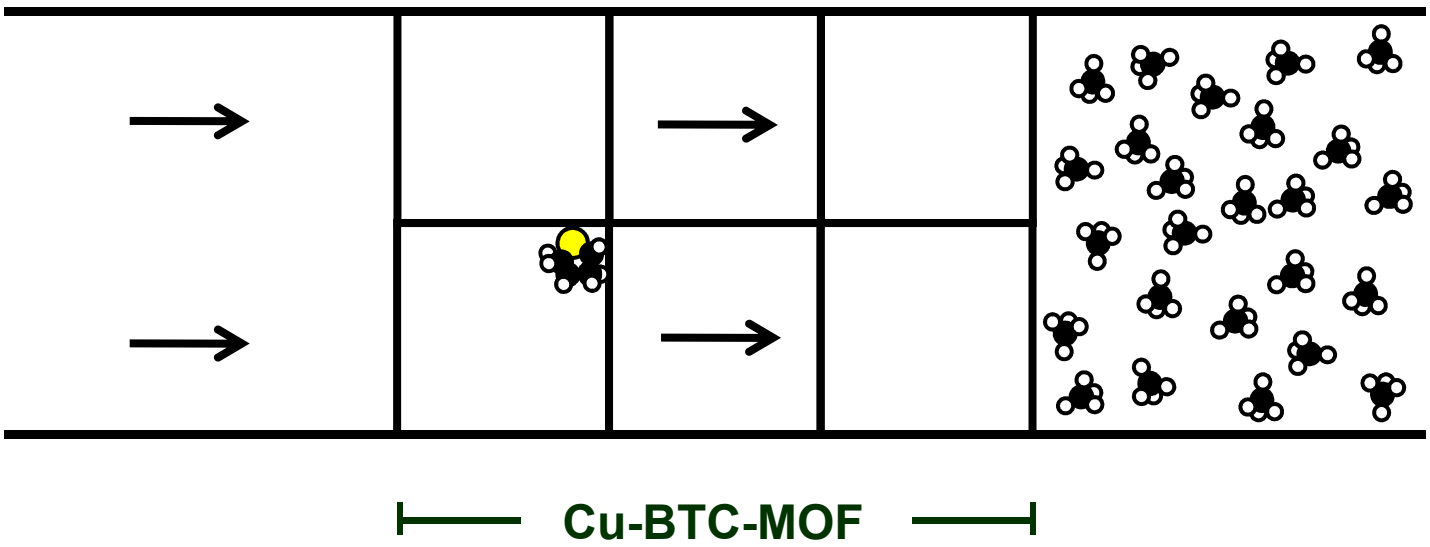
Methane, Natural Gas



13 ppm, 25°C

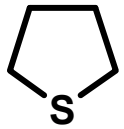
Metal-Organic Frameworks ⟶ Technical Applications

Gas Purification with HKUST-1: $Cu_3[BTC]_2 \cdot 3\,H_2O$



Tetrahydrothiophene

Methane, Natural Gas



0 ppm, 25°C

Rainer Buerstinghaus

Metal-Organic Frameworks ⟶ Technical Applications

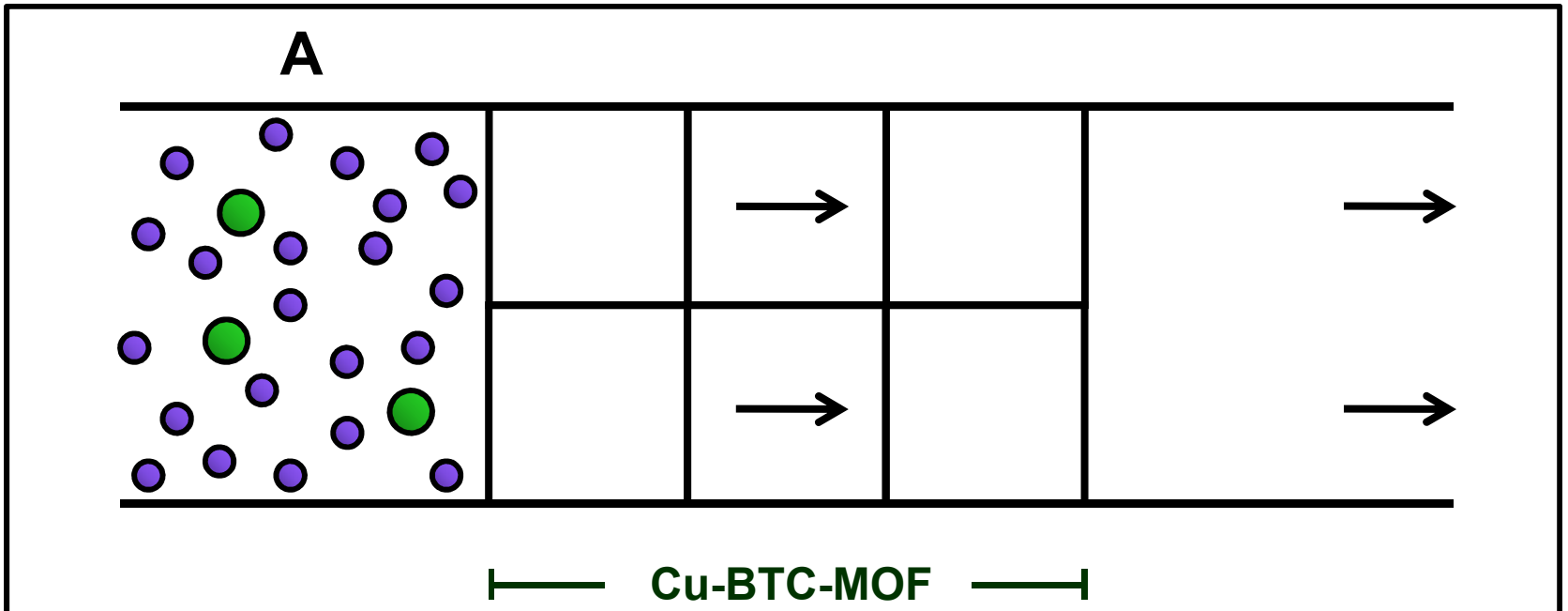
Gas Separation:

- Gas separations by means of cryogenic distillation can be highly cumbersome.
- Pressure swing adsorption on MOFs (HKUST-1) as "atomic sieves" are much simpler and cheaper.
- Separation of krypton and xenon by "pressure-swing separation".

  (Xenon: Anesthetic gas in the operating room)
  (Krypton: Inert gas in bulbs / lamps).

Metal-Organic Frameworks ⟶ Technical Applications

Gas Separation of Krypton (●) and Xenon (●):



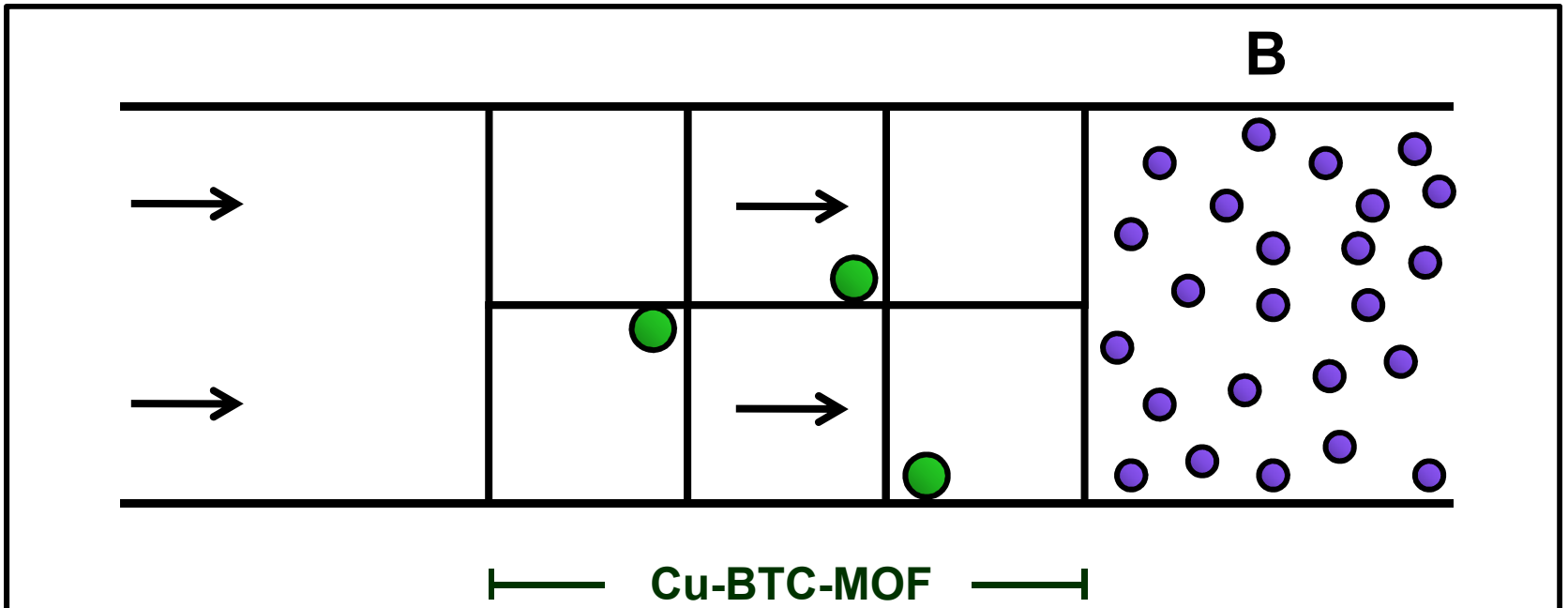
A: 94 Mol-% Krypton, 6 Mol-% Xenon

Separation Conditions: 55°C, 40 bar, Flow Rate: 60l/h

Rainer Buerstinghaus

Metal-Organic Frameworks ⟶ Technical Applications

Gas Separation of Krypton (●) and Xenon (●):



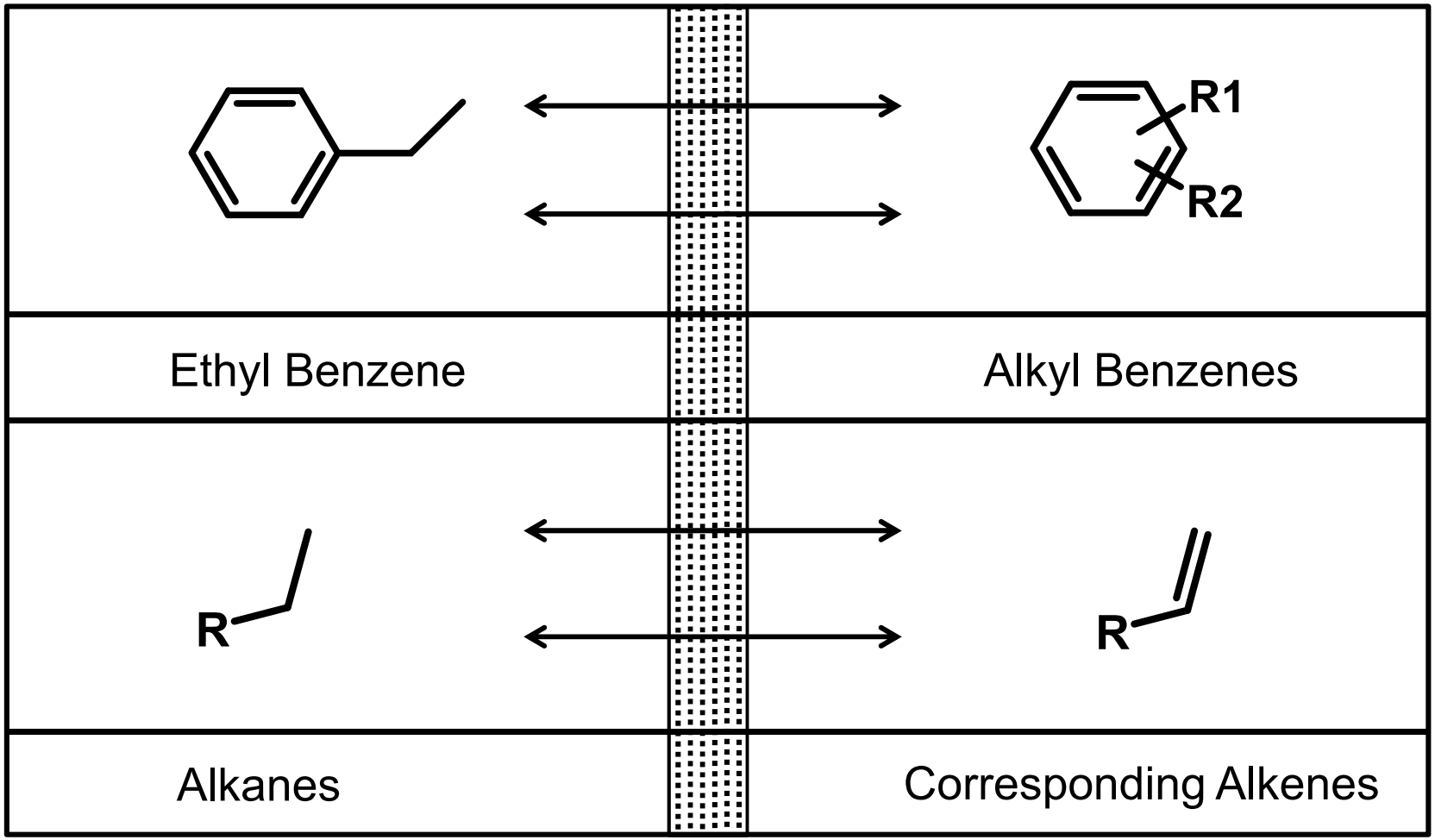
B: Krypton with a maximum of 0,01% Xenon

Separation Conditions: 55°C, 40 bar, Flow Rate: 60l/h

Rainer Buerstinghaus

Metal-Organic Frameworks ⟶ Technical Applications

Other Material Separations via MIL- 47 or MIL- 53:



New MOFs for the Adsorptive Storage of Gases

Technical Applications of these Porous Materials:

- Carrier materials for heterogeneous catalysis.
- Immobilization of (chiral) homogeneous catalysts.
- Nanoreactors.
- "Templates" on the nanoscale.
- Slow release formulations, controlled drug release.
- Luminescent lamps.
- Gas cleaning.
- Gas separation.
- Gas storage.

Metal-Organic Frameworks ⟶ Technical Applications

Target Application "Hydrogen Economy": H_2-Storage for the Operation of Vehicles under (Low) Pressure through Efficient H_2-Adsorption within Pores or the Interior of Molecular Channels, if Possible at Ambient Temperature.

- Pressure gas storage of H_2 in the appropriate container at **p ≈ 500-700 bar**: This is disadvantageous for automotive drives: **Risk of explosion in the event of a crash!** ⊖

- **Cryo-Storage** of liquid H_2 at p ≈ 200 bar and T ≈ 50-75 K.

- Pressure-free, adsorptive **cryogenic storage** of hydrogen **in porous materials**, such as MOFs, even at 50 K (T_s H_2: 20 K). ?

Rainer Buerstinghaus

Metal-Organic Frameworks ⟶ Technical Applications

Target Application "Hydrogen Economy": H_2-Storage for the Operation of Vehicles under (Low) Pressure through Efficient H_2-Adsorption within Pores or the Interior of Molecular Channels, if Possible at Ambient Temperature.

Setpoint for H_2-storage in 2017, according to "US Department of Energy (DOE)"

→ The **volumetric capacity** of the storage materials used should be **between 30g and 70g H_2 per liter.**

→ MOFs that can be used for hydrogen storage in fuel cells of motor vehicles should work in the **temperature range of −20°C to + 40°C** and **pressures between 1 and 100 bar**. Such physical conditions are considered safe for automotive applications.

Metal-Organic Frameworks ⟶ Technical Applications

Gas Storage of Hydrogen, H_2.

Hydrogen-Fuel Cell, Basic Reaction:

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O \qquad (\Delta H = -572\ kJ/Mol)$$

Advantages	⊕

- Complete reaction with O_2 to water.
- Efficiency about 50% higher than that of the gasoline combustion engine.
- High gravimetric energy density: Approx. 120 MJ/kg.

Rainer Buerstinghaus

Metal-Organic Frameworks ⟶ Technical Applications

Gas Storage of Hydrogen, H_2.

Hydrogen-Fuel Cell, Partial Reactions, Overall Balance:

$$2\ H_2 + 4\ H_2O \xrightarrow{[Pt]} 4\ H_3O^{\oplus} + 4\ ^{\ominus}$$

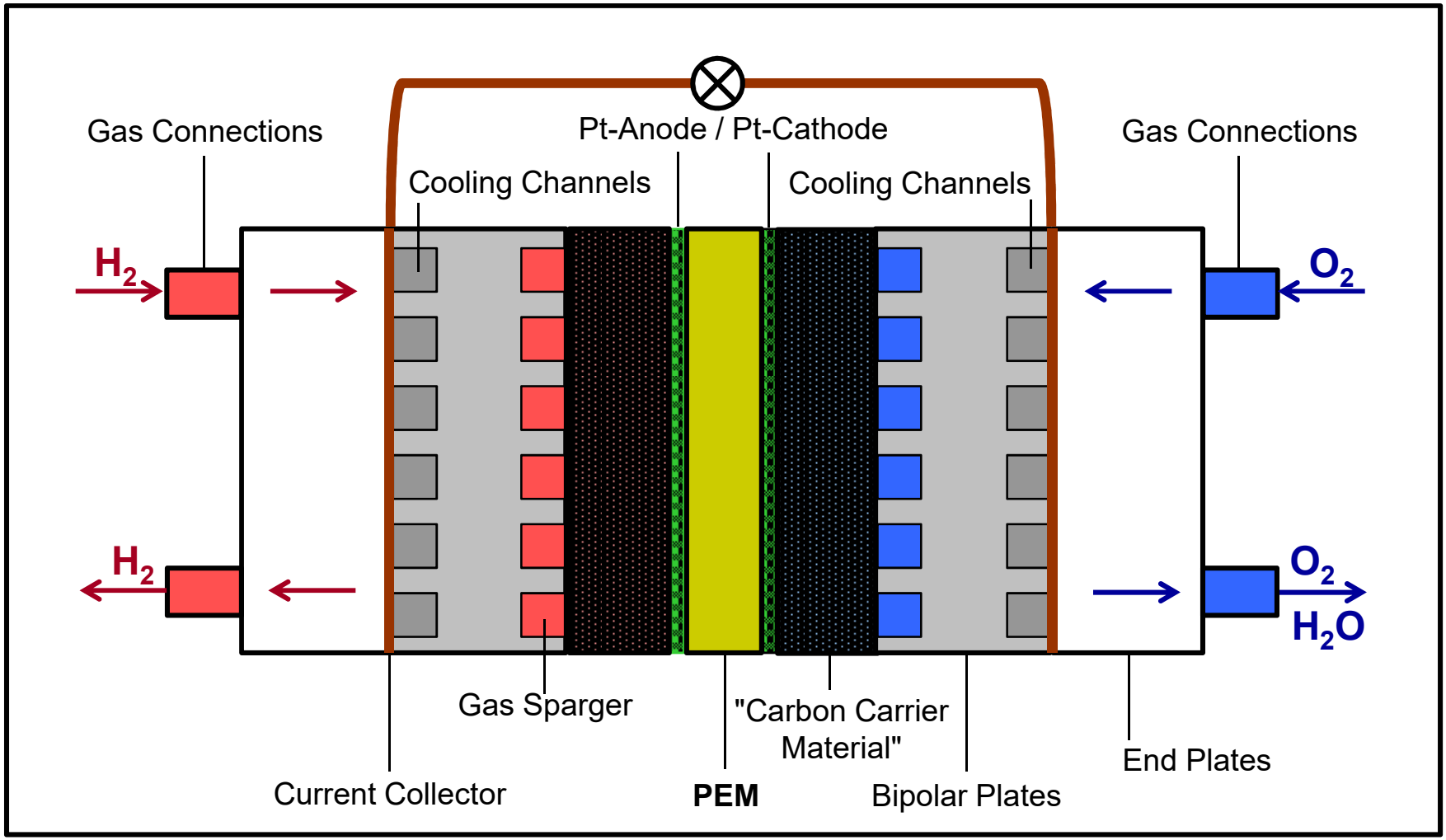
$$O_2 + 4\ H_3O^{\oplus} + 4\ ^{\ominus} \xrightarrow{[Pt]} 6\ H_2O$$

$$\Sigma: \quad 2\ H_2 + O_2 \xrightarrow{[Pt]} 2\ H_2O \quad (\Delta H = -572\ kJ/Mol)$$

Rainer Buerstinghaus

Metal-Organic Frameworks ⟶ Technical Applications

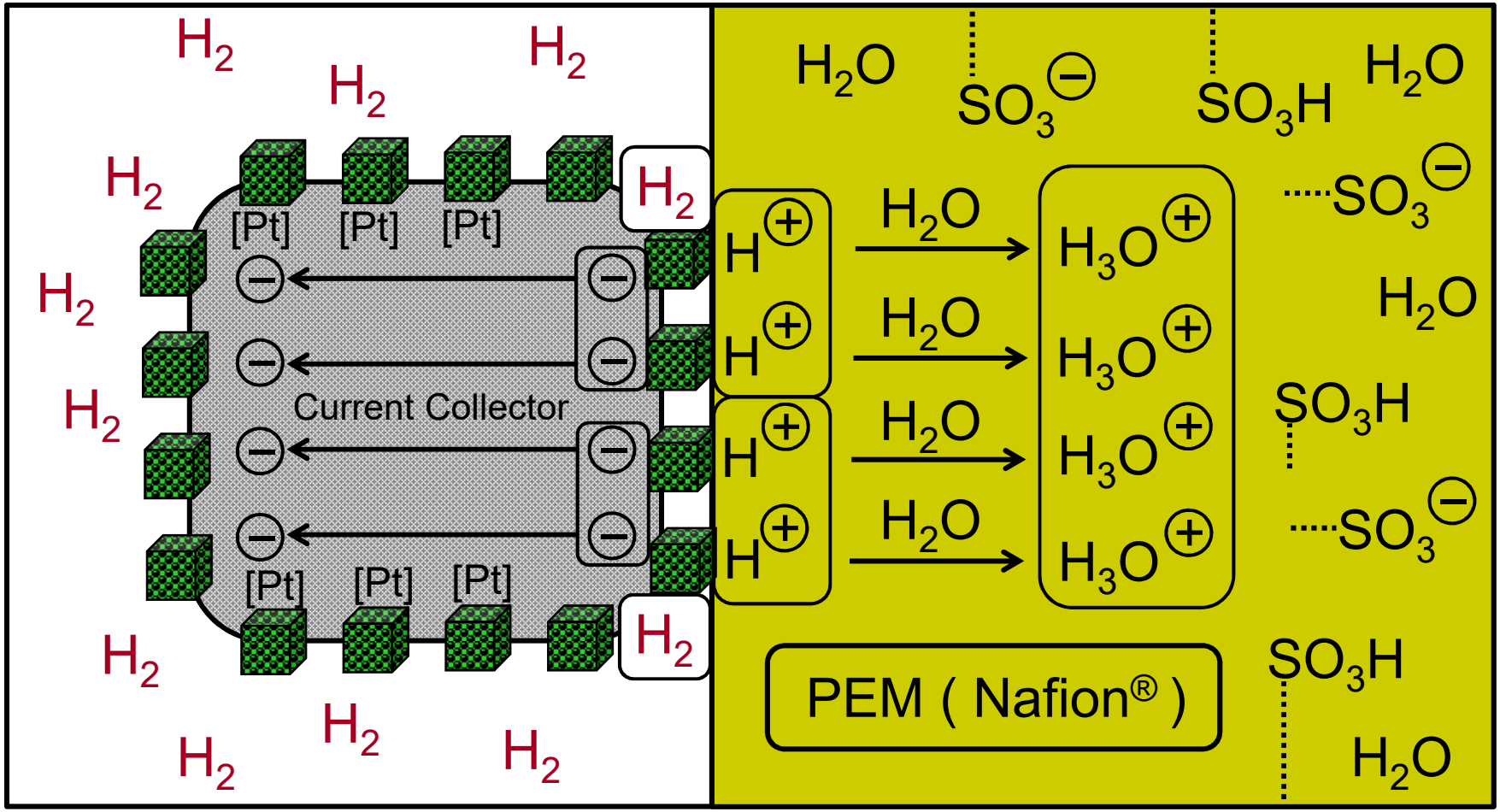
Proton Exchange Membrane (PEM) Fuel Cell , Structure:



Rainer Buerstinghaus

PEM Fuel Cell, Anode: Oxidation of Hydrogen.

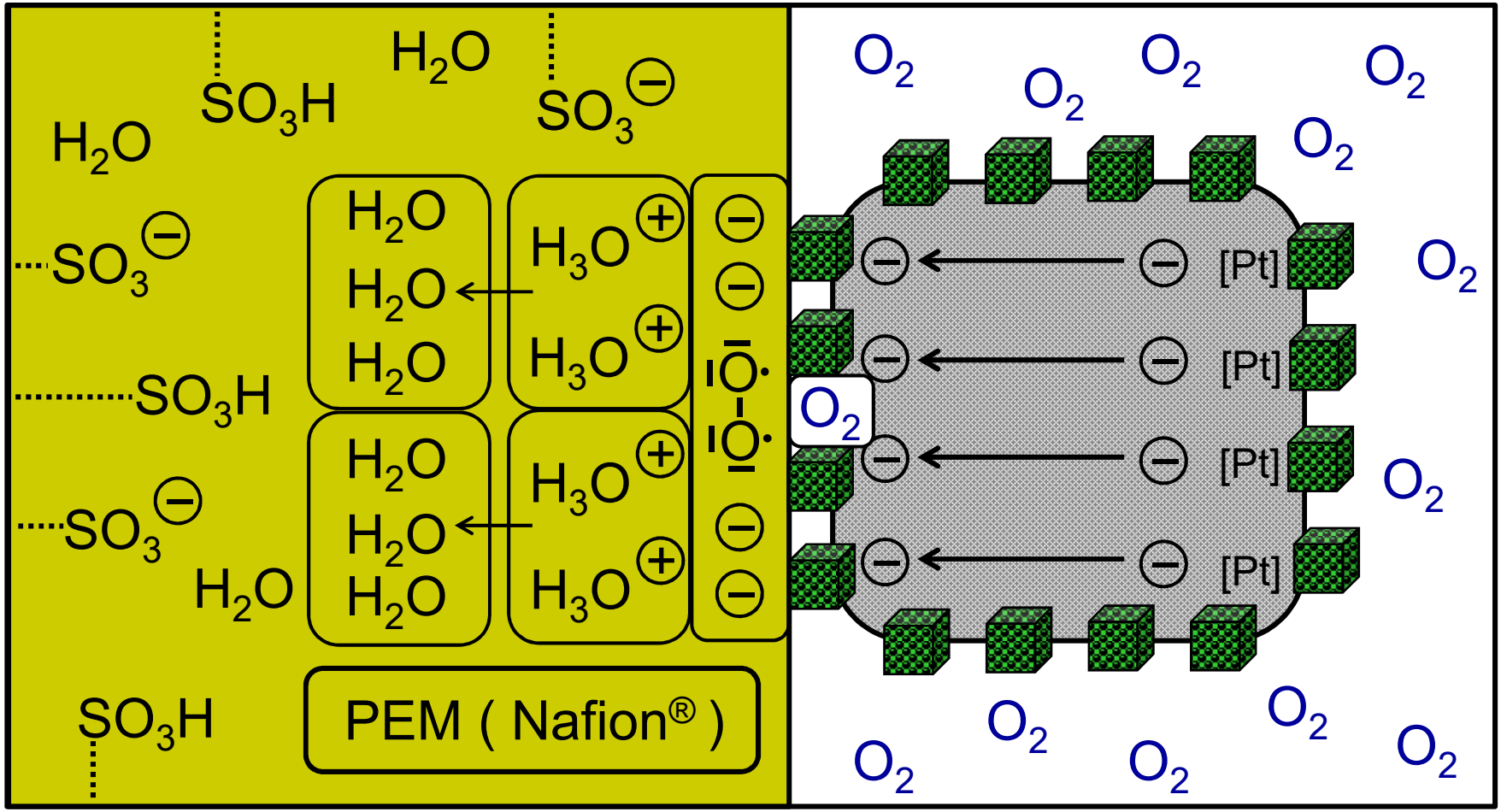
Single Particle of a Porous "Carbon Carrier" (ø ≈ 40nm) with Pt-Nanoparticles (ø ≈ 4nm) on its Surface (Scheme):



Rainer Buerstinghaus

PEM Fuel Cell, Cathode: Reduction of Oxygen.

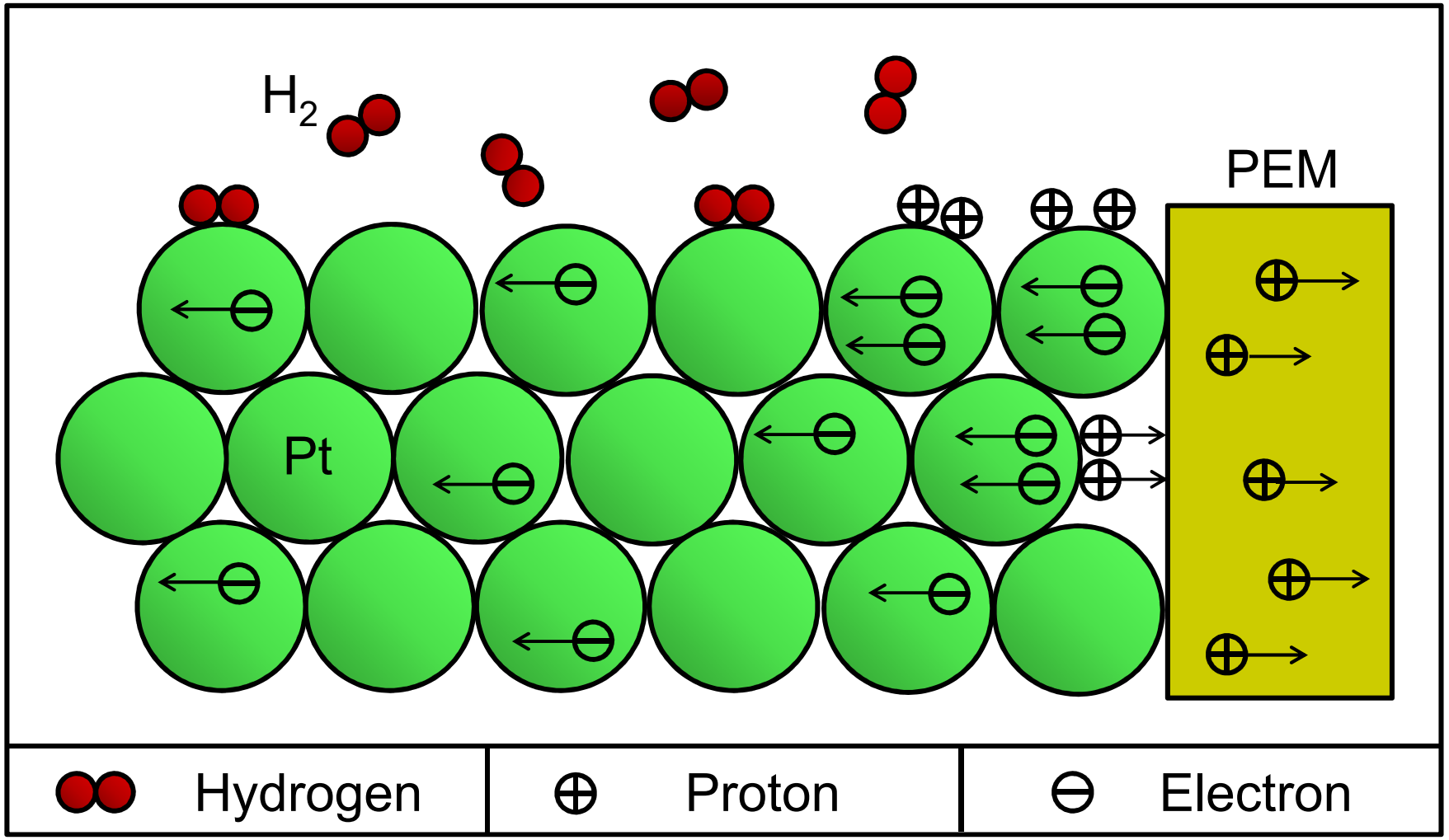
Single Particle of a Porous "Carbon Carrier" (ø ≈ 40nm) with Pt-Nanoparticles (ø ≈ 4nm) on its Surface (Scheme):



Rainer Buerstinghaus

PEM Fuel Cell, Anode: Oxidation of Hydrogen.

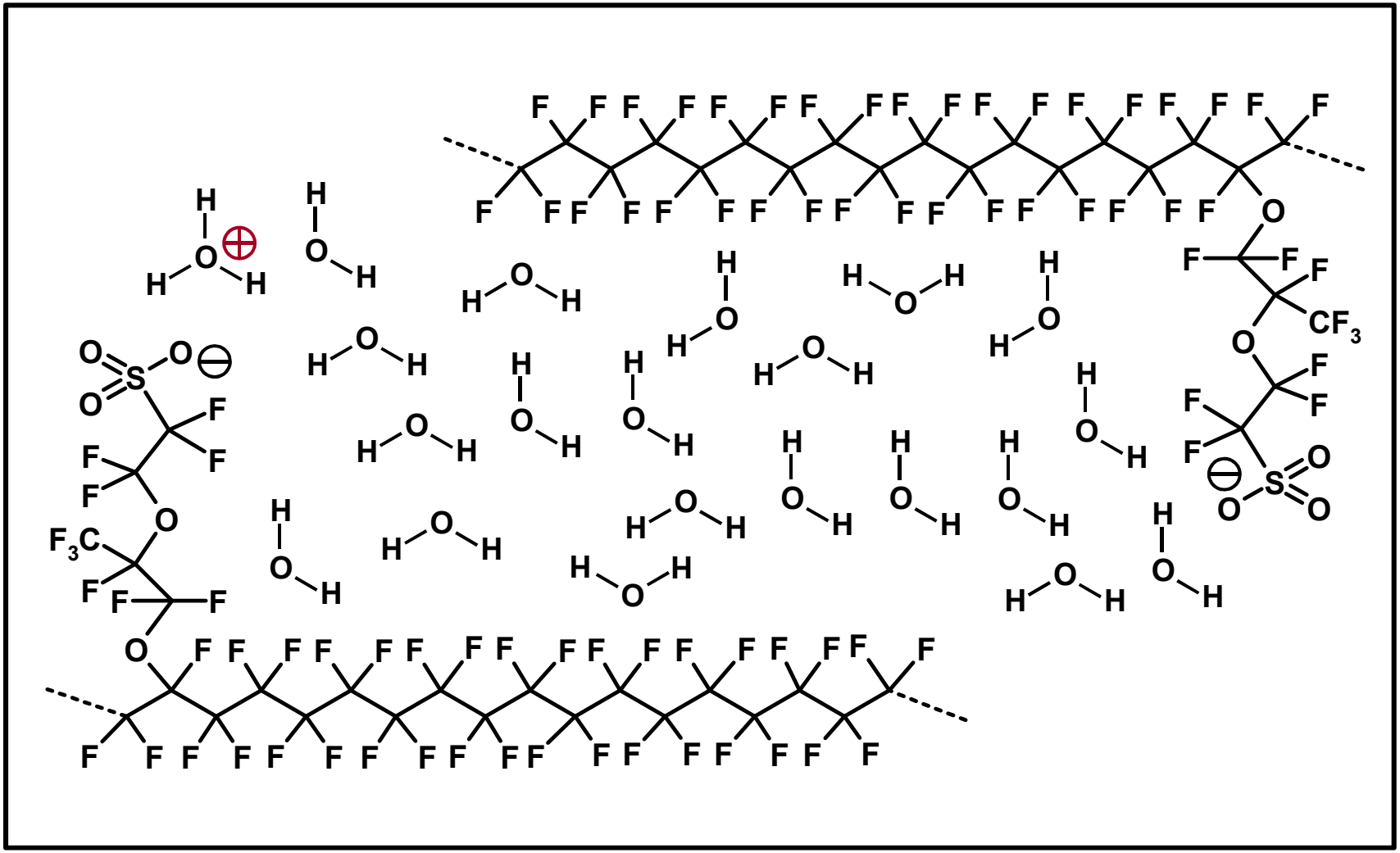
Platinum Nanoparticles, Electron / Proton Transfer (Scheme):



Rainer Buerstinghaus

Proton Exchange Membrane Fuel Cell (PEMFC), PEM.

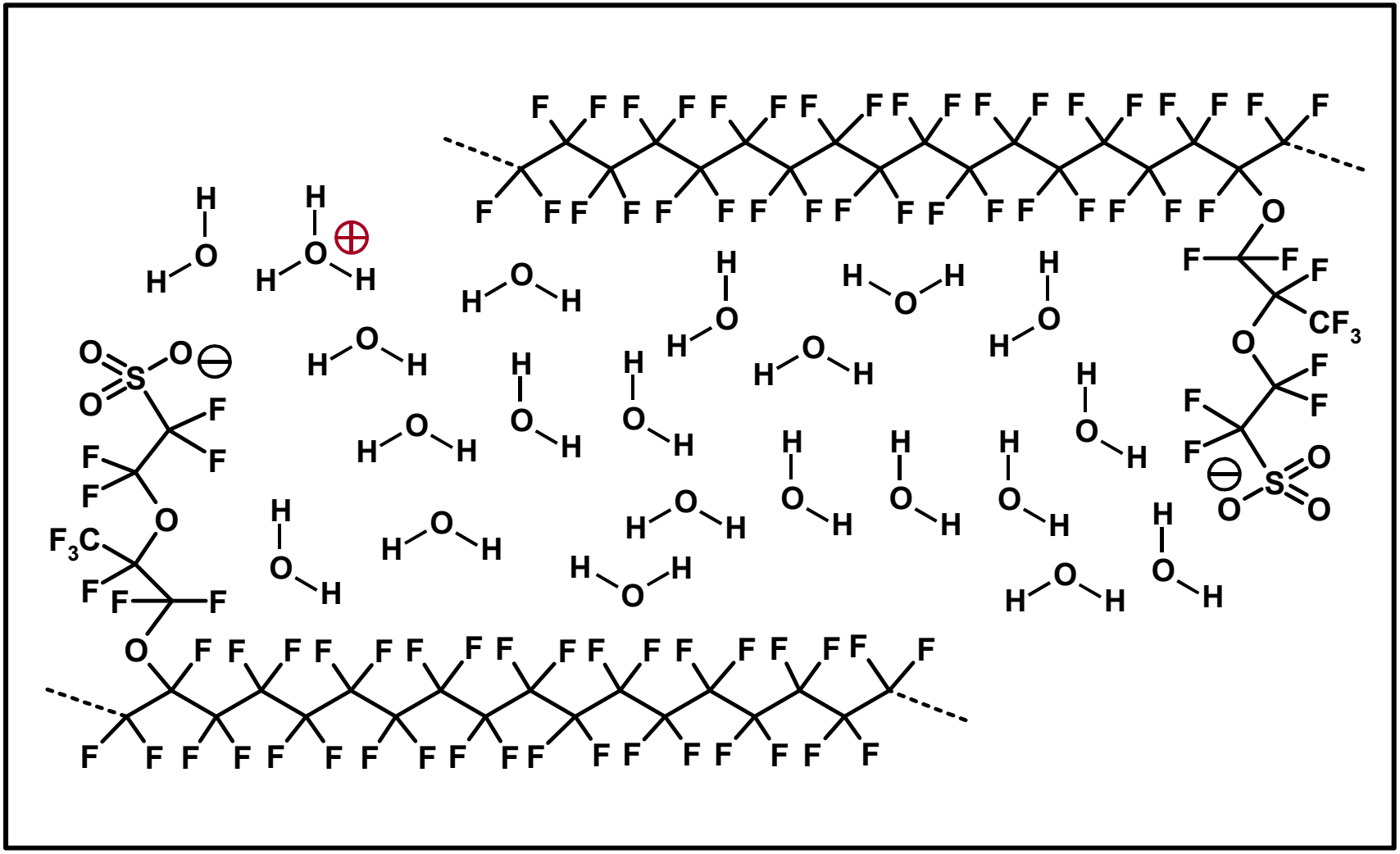
Proton Conduction in a Water Domain From Nafion® (Idealized):



Rainer Buerstinghaus

Proton Exchange Membrane Fuel Cell (PEMFC), PEM.

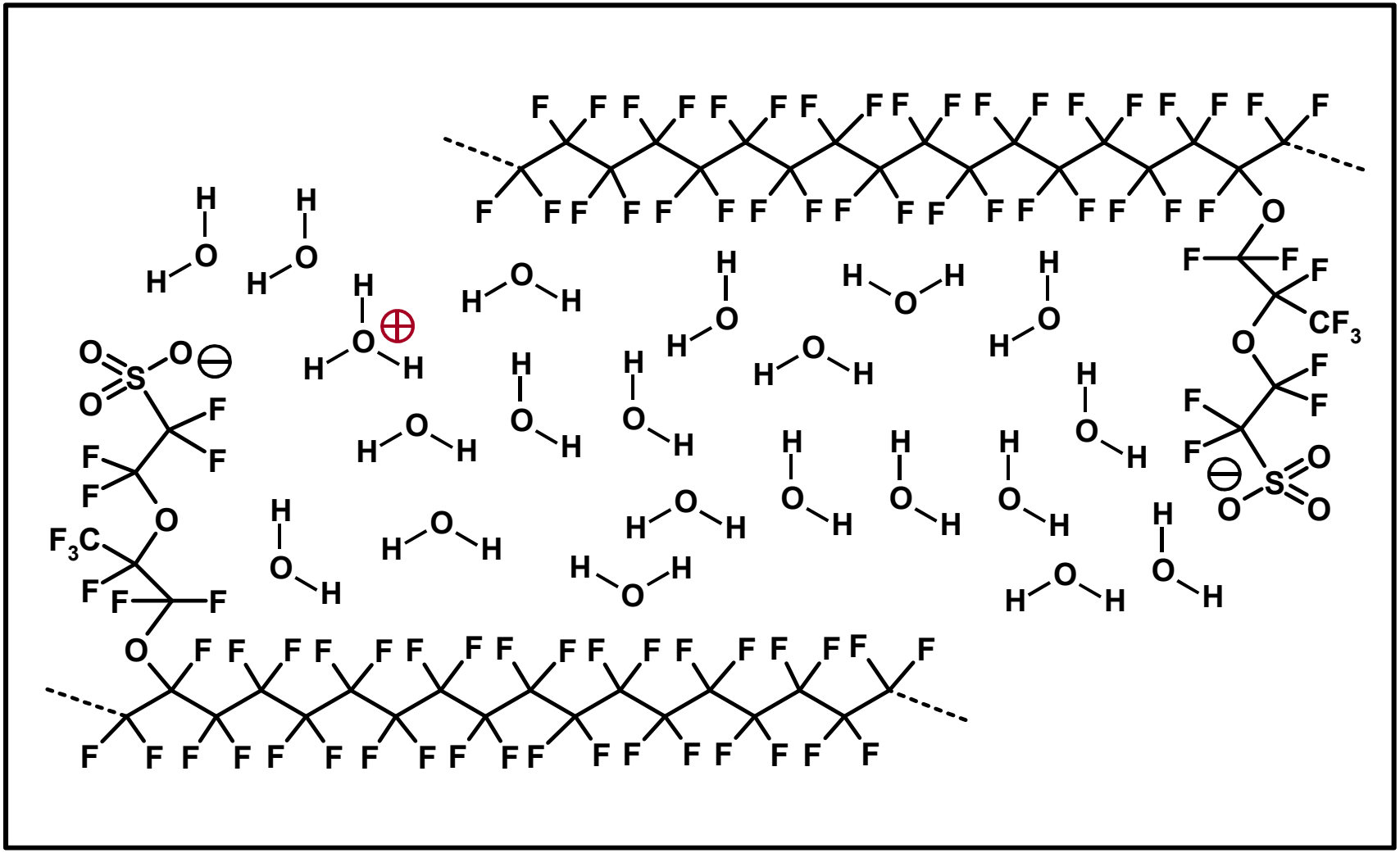
Proton Conduction in a Water Domain From Nafion® (Idealized):



Rainer Buerstinghaus

Proton Exchange Membrane Fuel Cell (PEMFC), PEM.

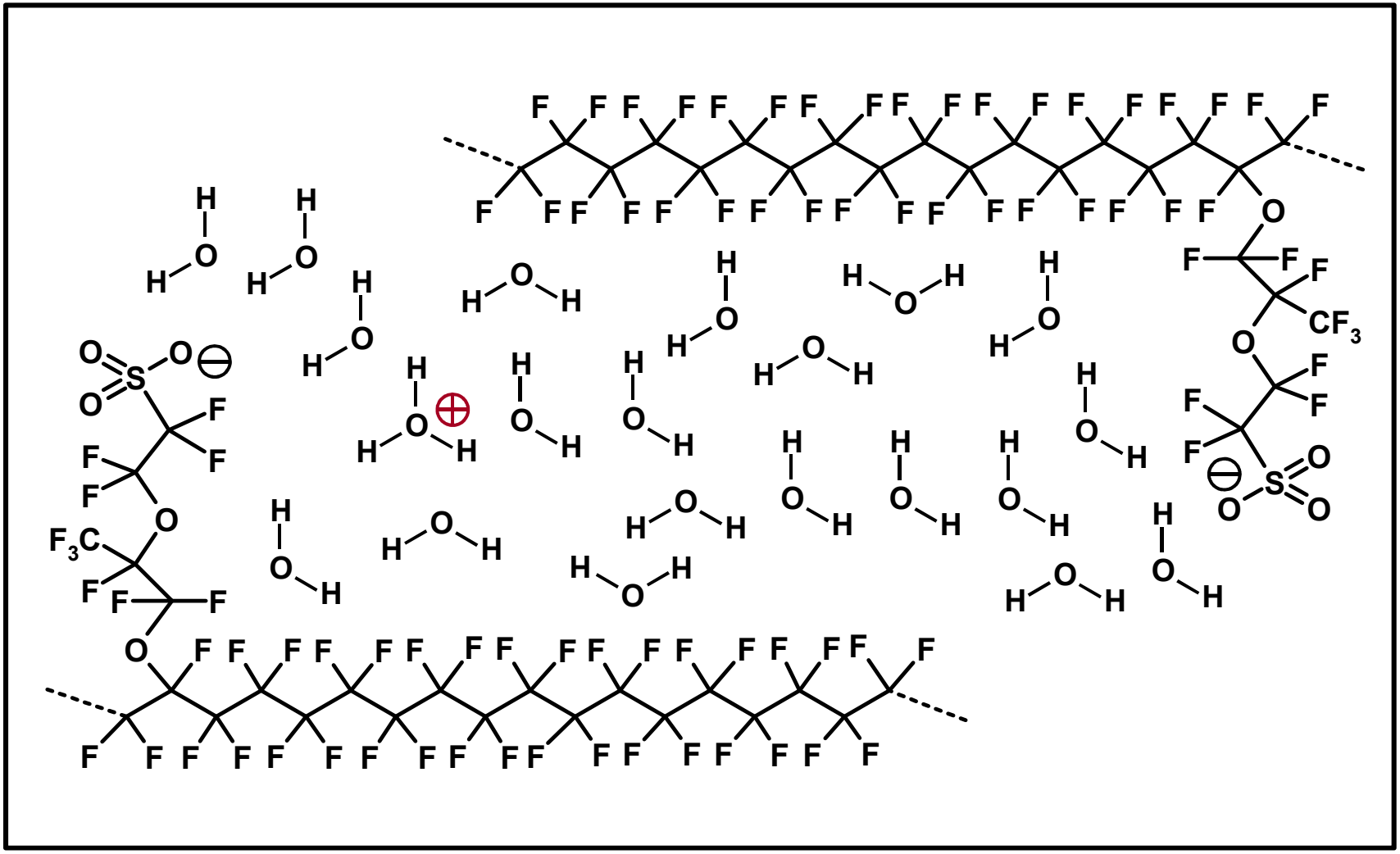
Proton Conduction in a Water Domain From Nafion® (Idealized):



Rainer Buerstinghaus

Proton Exchange Membrane Fuel Cell (PEMFC), PEM.

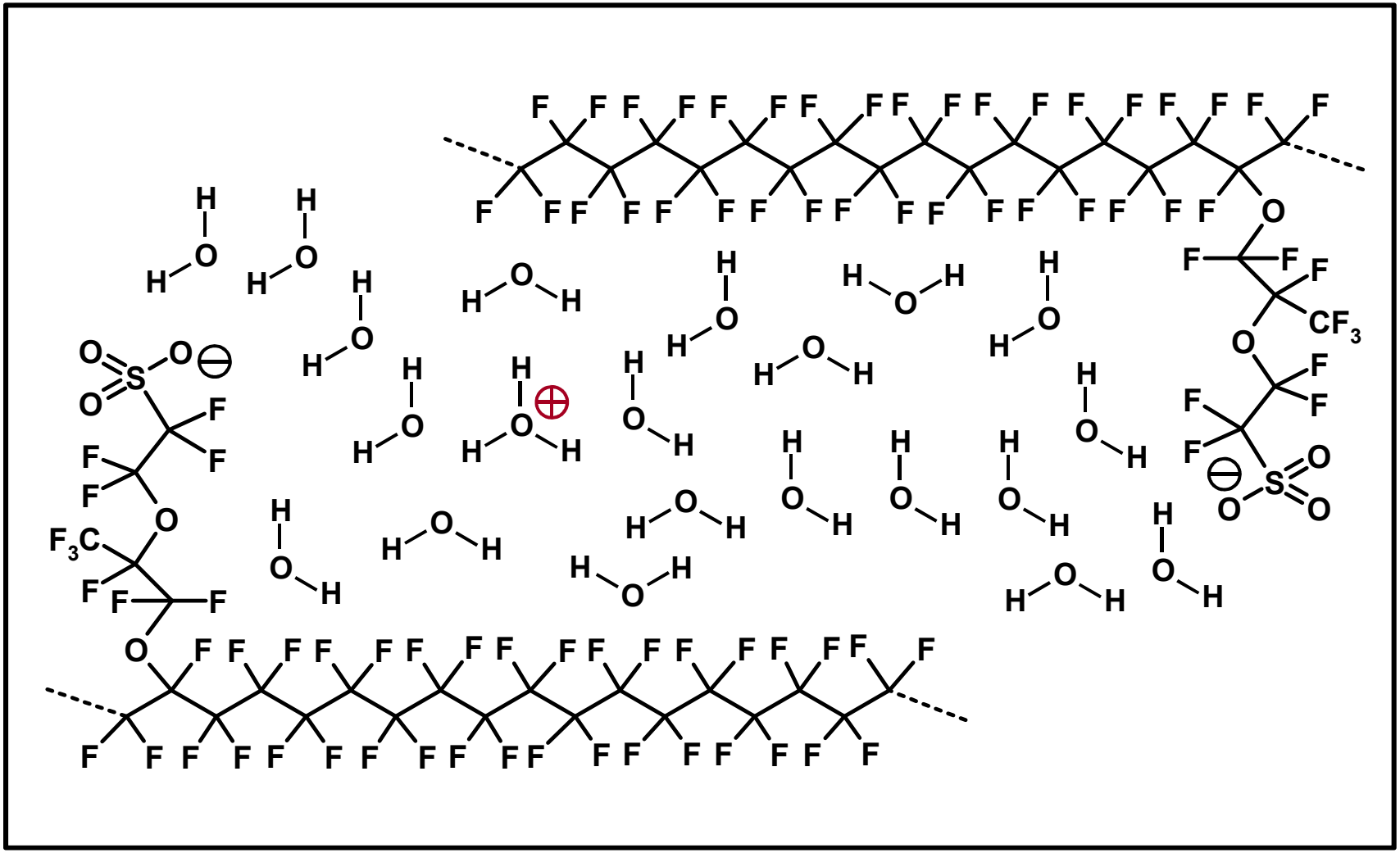
Proton Conduction in a Water Domain From Nafion® (Idealized):



Rainer Buerstinghaus

Proton Exchange Membrane Fuel Cell (PEMFC), PEM.

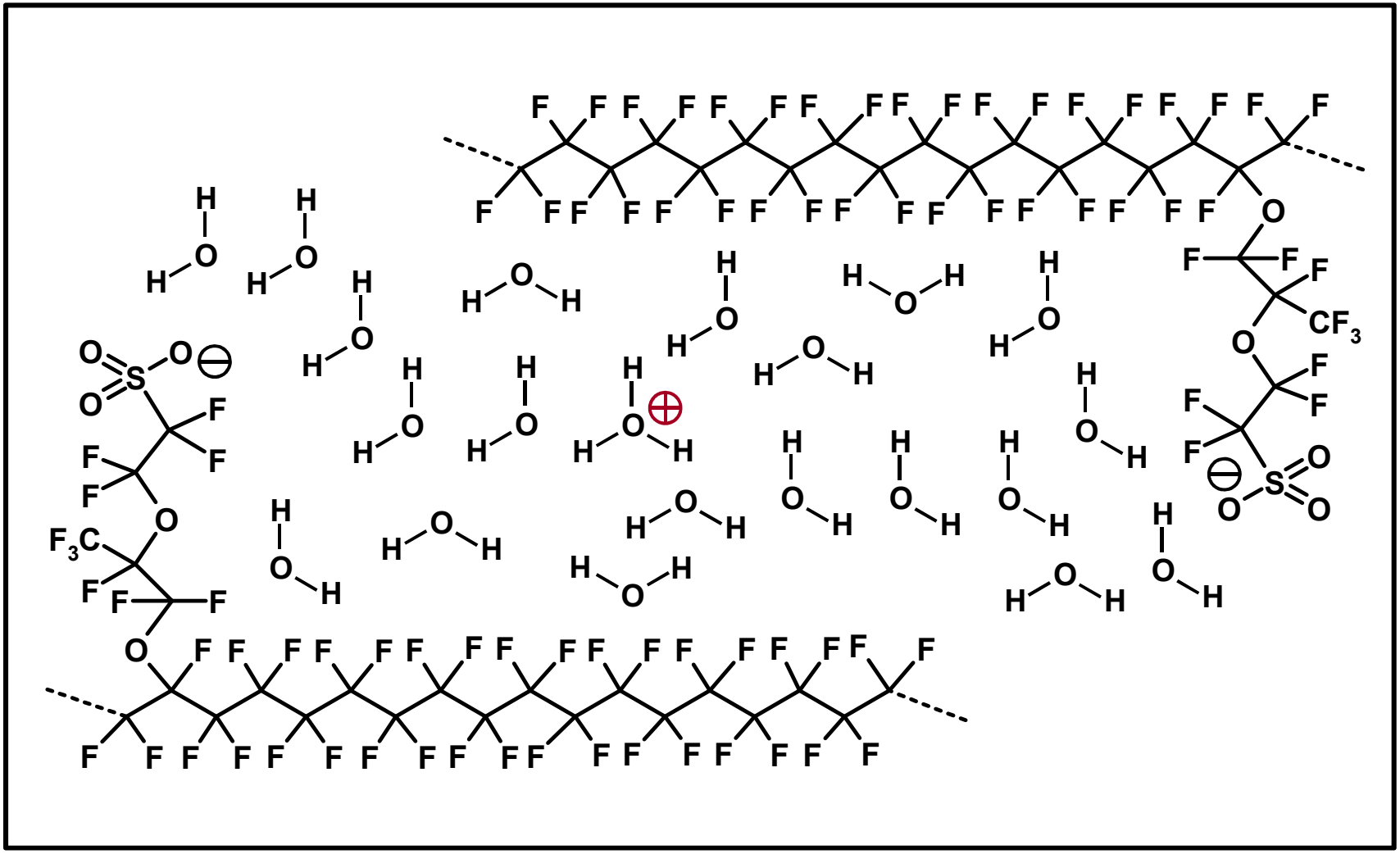
Proton Conduction in a Water Domain From Nafion® (Idealized):



Rainer Buerstinghaus

Proton Exchange Membrane Fuel Cell (PEMFC), PEM.

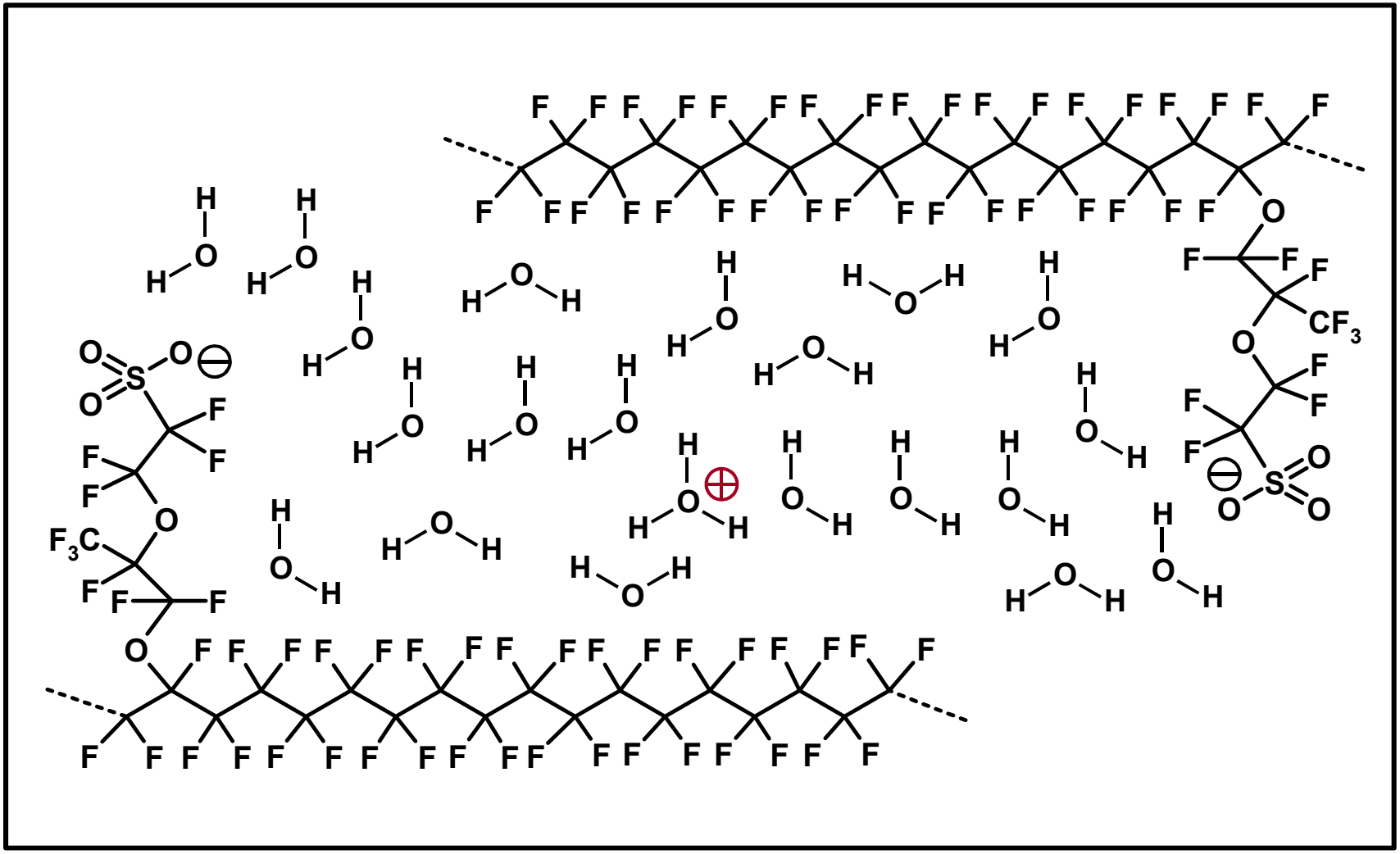
Proton Conduction in a Water Domain From Nafion® (Idealized):



Rainer Buerstinghaus

Proton Exchange Membrane Fuel Cell (PEMFC), PEM.

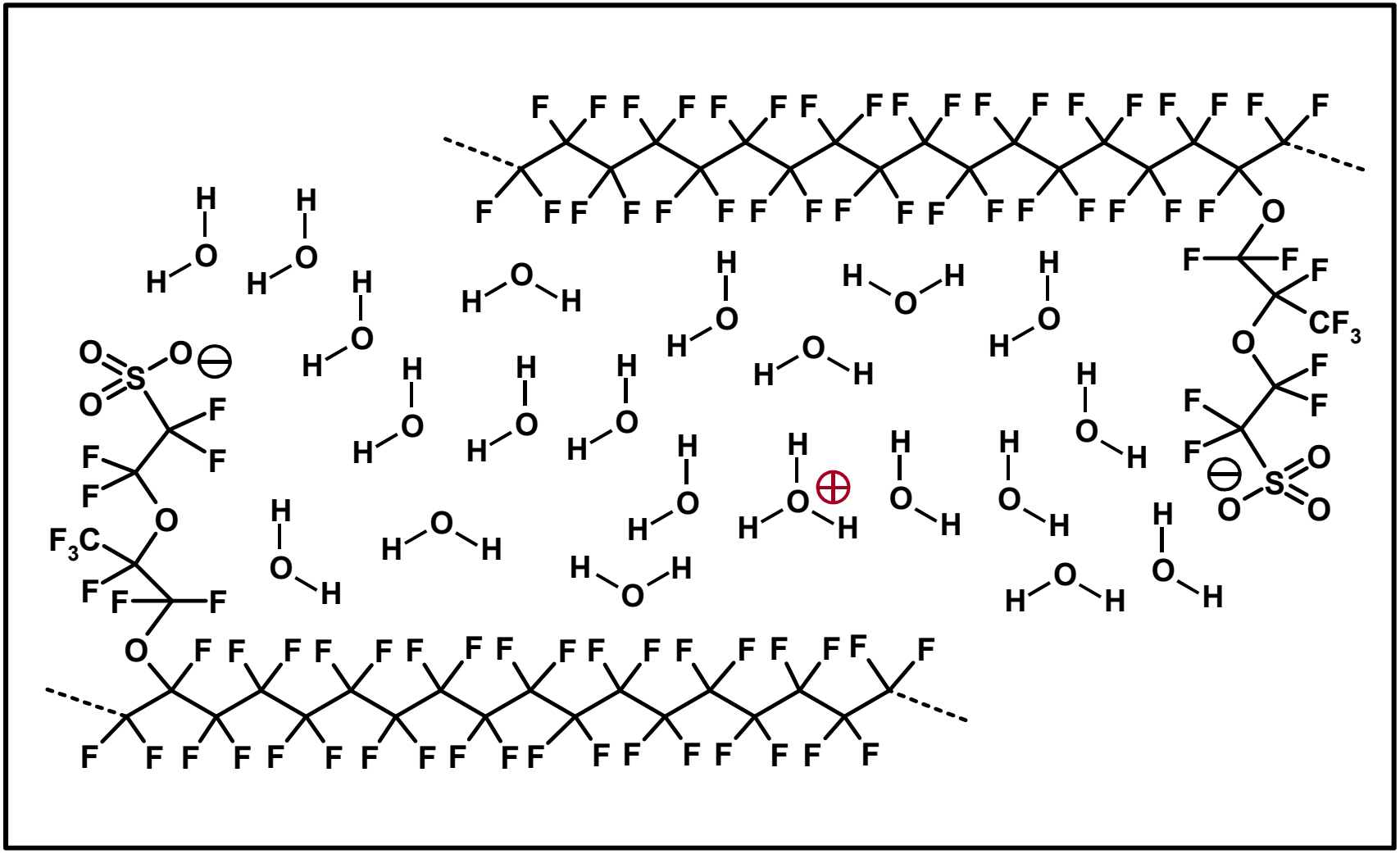
Proton Conduction in a Water Domain From Nafion® (Idealized):



Rainer Buerstinghaus

Proton Exchange Membrane Fuel Cell (PEMFC), PEM.

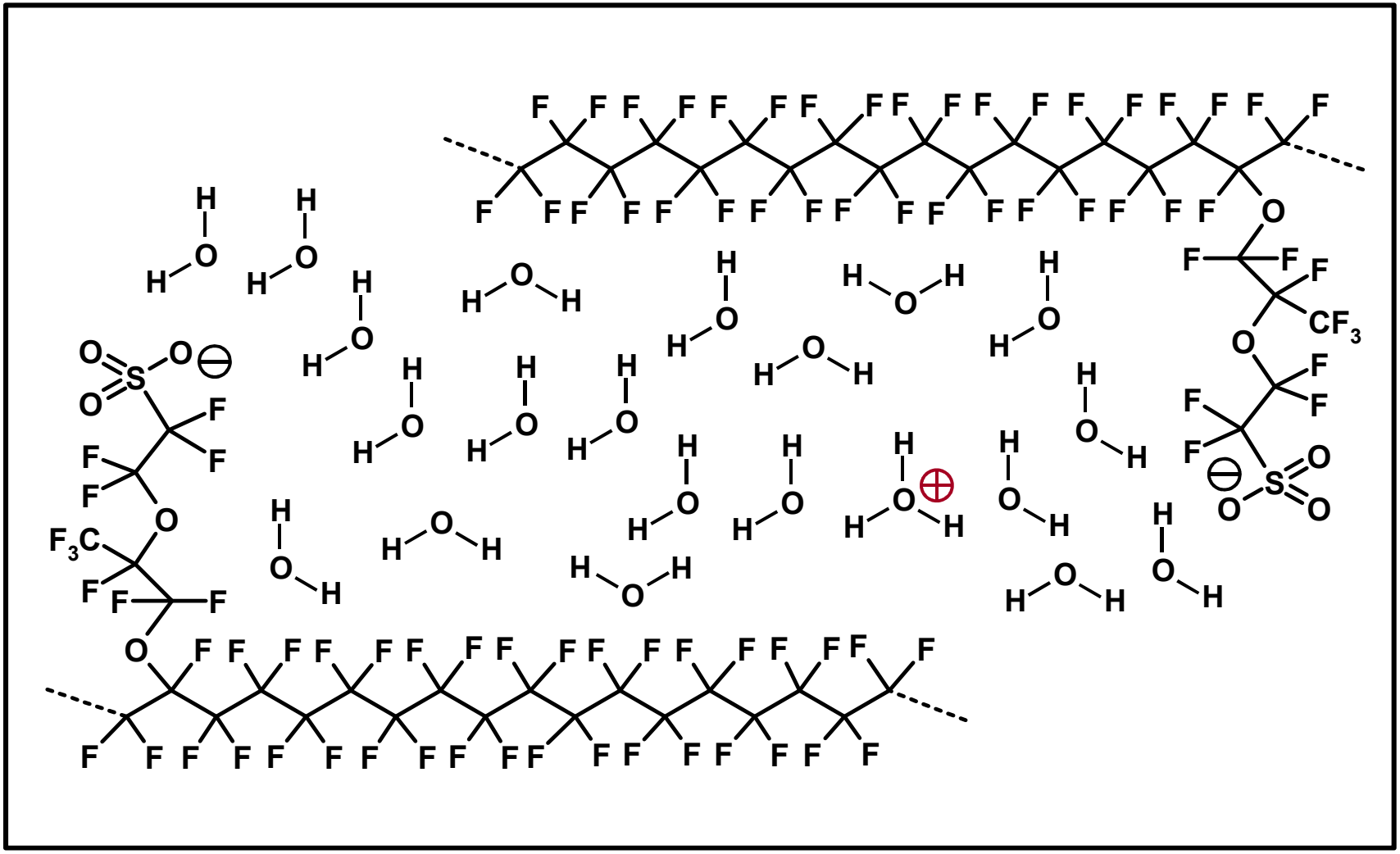
Proton Conduction in a Water Domain From Nafion® (Idealized):



Rainer Buerstinghaus

Proton Exchange Membrane Fuel Cell (PEMFC), PEM.

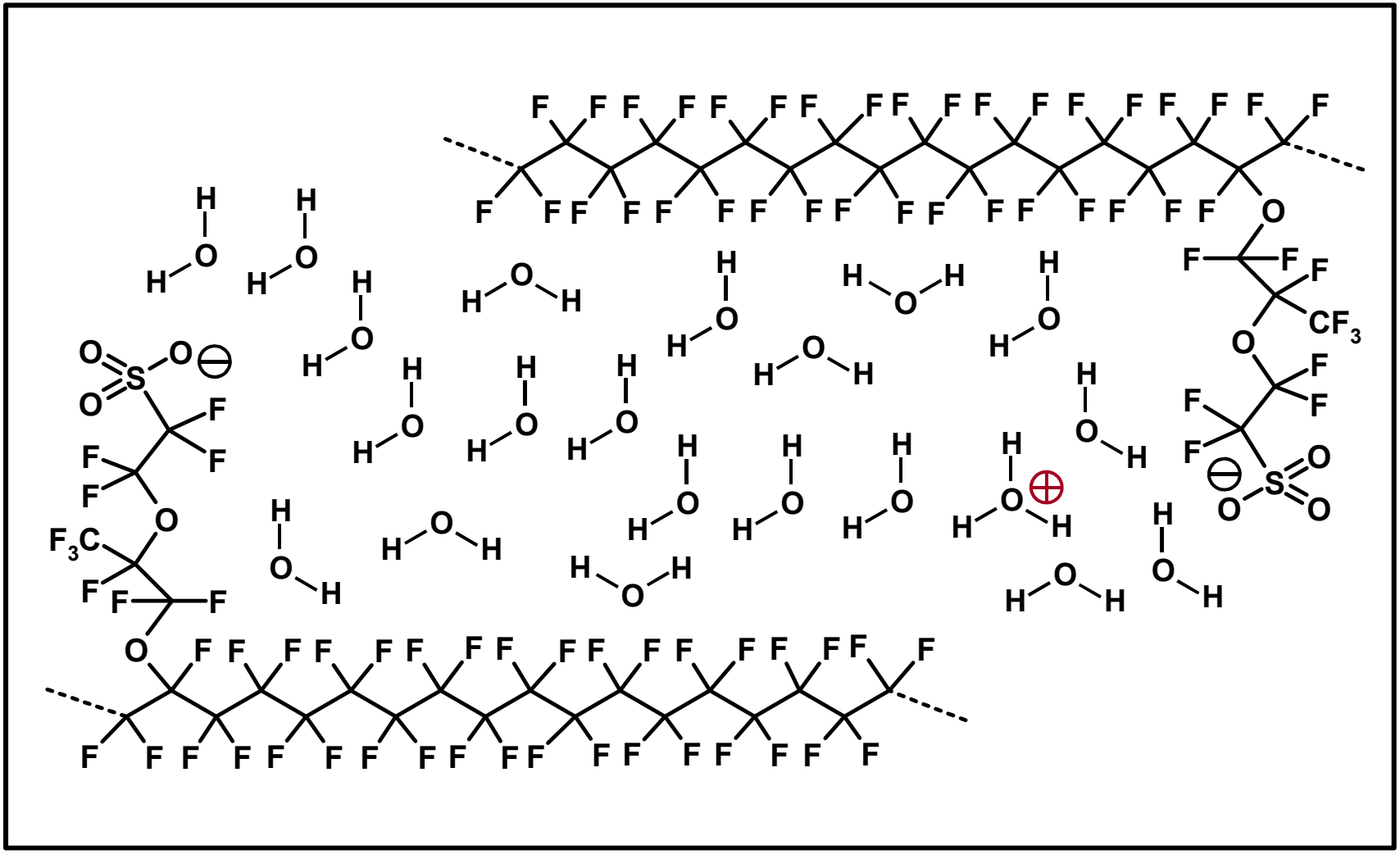
Proton Conduction in a Water Domain From Nafion® (Idealized):



Rainer Buerstinghaus

Proton Exchange Membrane Fuel Cell (PEMFC), PEM.

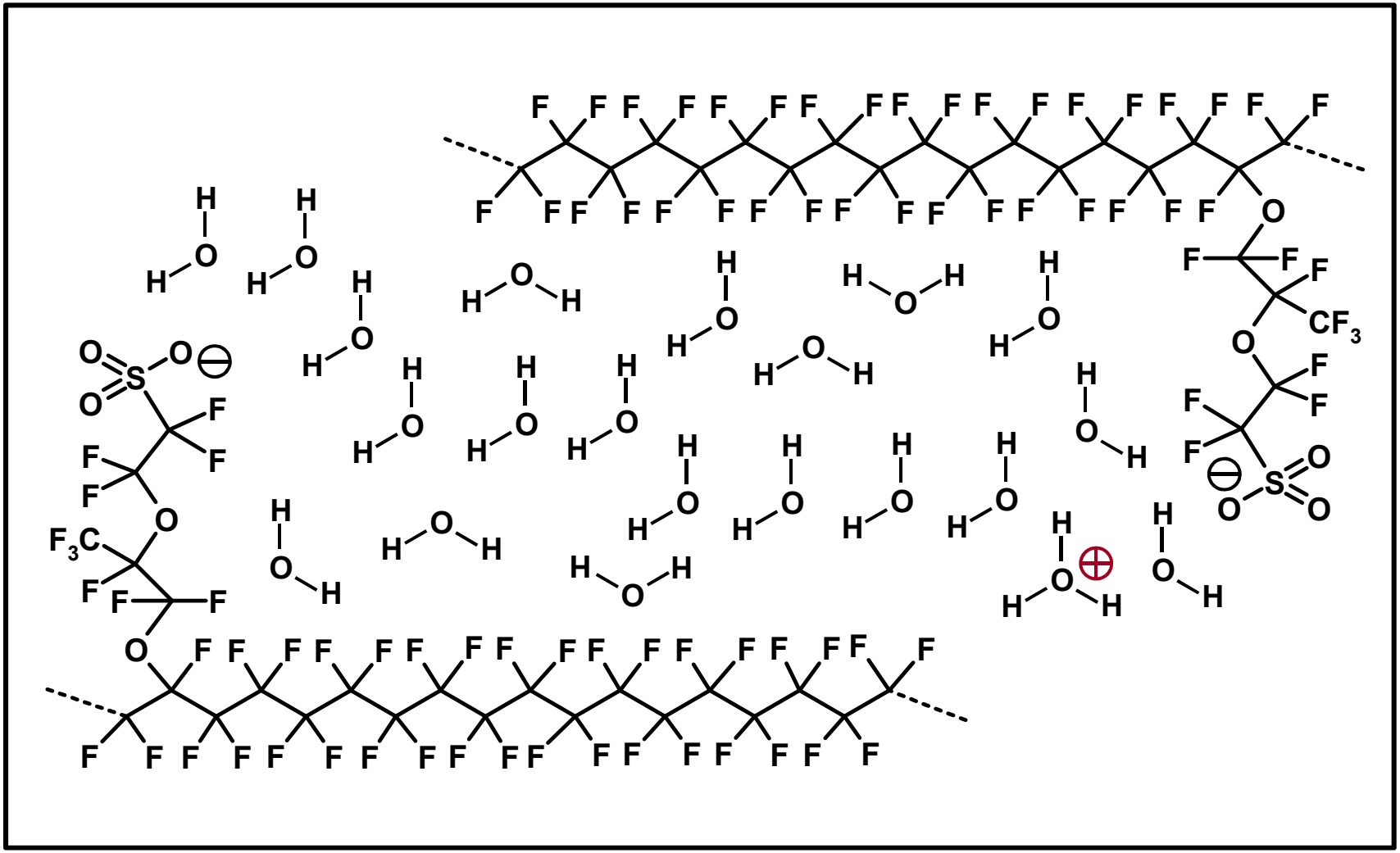
Proton Conduction in a Water Domain From Nafion® (Idealized):



Rainer Buerstinghaus

Proton Exchange Membrane Fuel Cell (PEMFC), PEM.

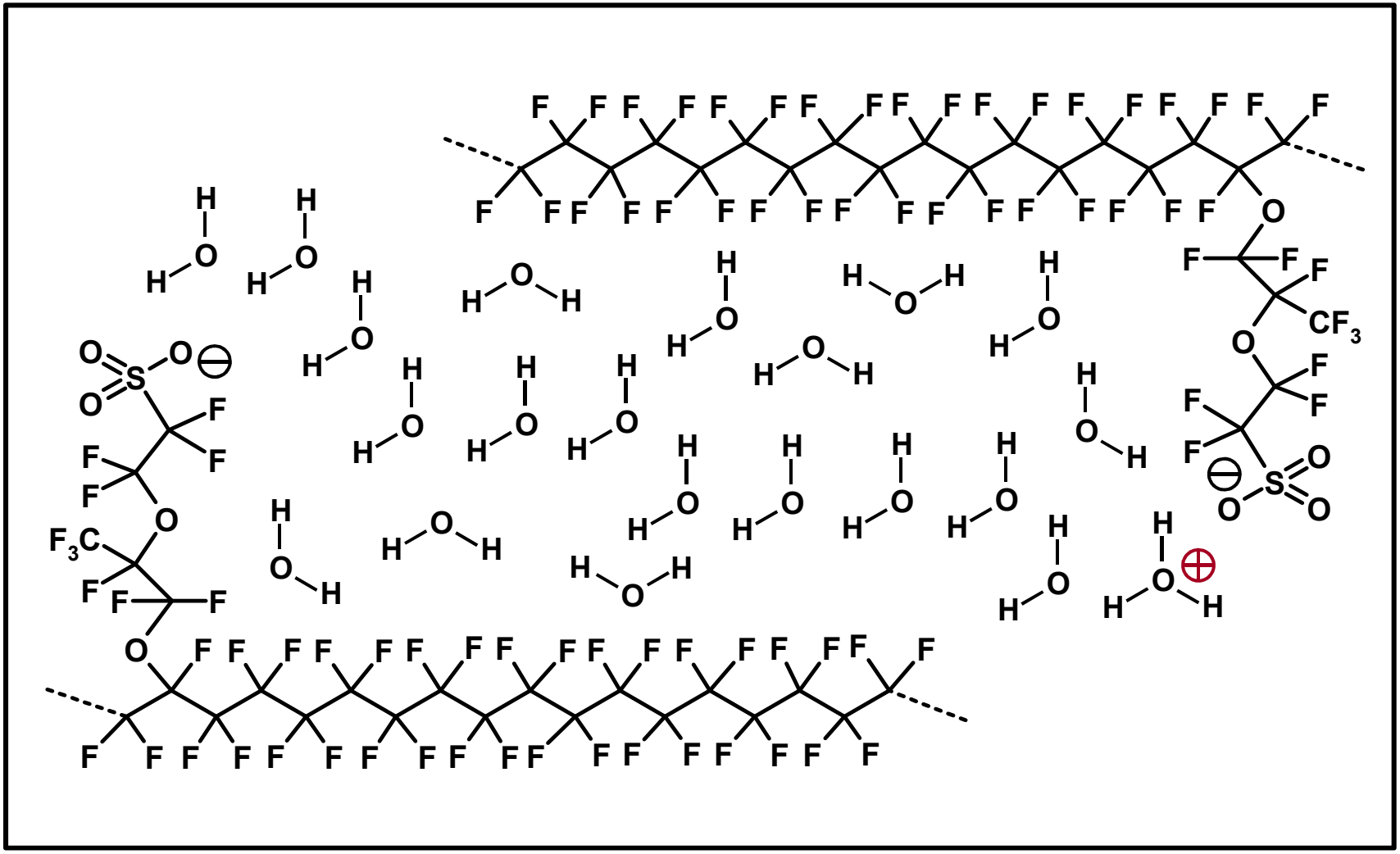
Proton Conduction in a Water Domain From Nafion® (Idealized):



Rainer Buerstinghaus

Proton Exchange Membrane Fuel Cell (PEMFC), PEM.

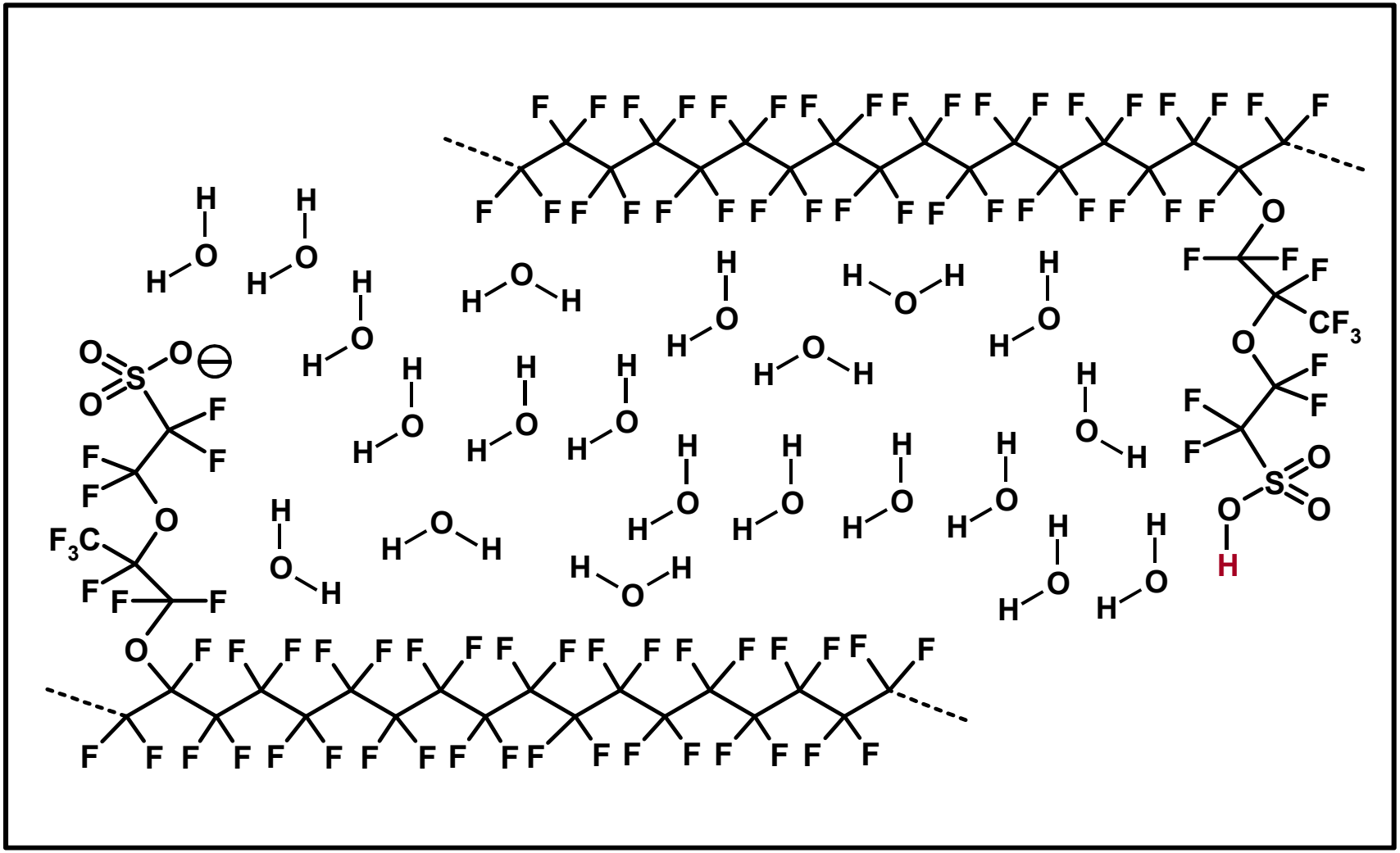
Proton Conduction in a Water Domain From Nafion® (Idealized):



Rainer Buerstinghaus

Proton Exchange Membrane Fuel Cell (PEMFC), PEM.

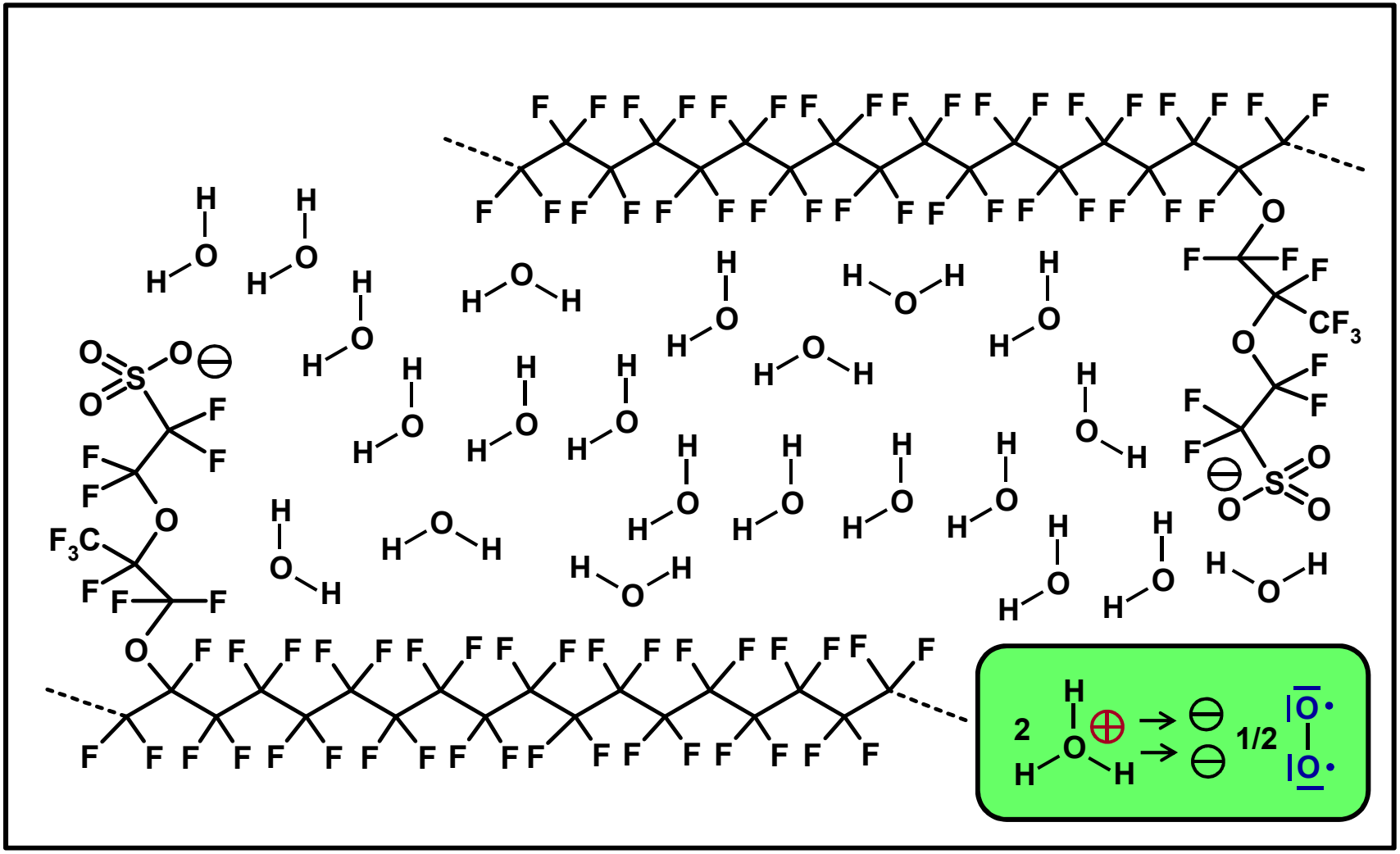
Proton Conduction in a Water Domain From Nafion® (Idealized):



Rainer Buerstinghaus

Proton Exchange Membrane Fuel Cell (PEMFC), PEM.

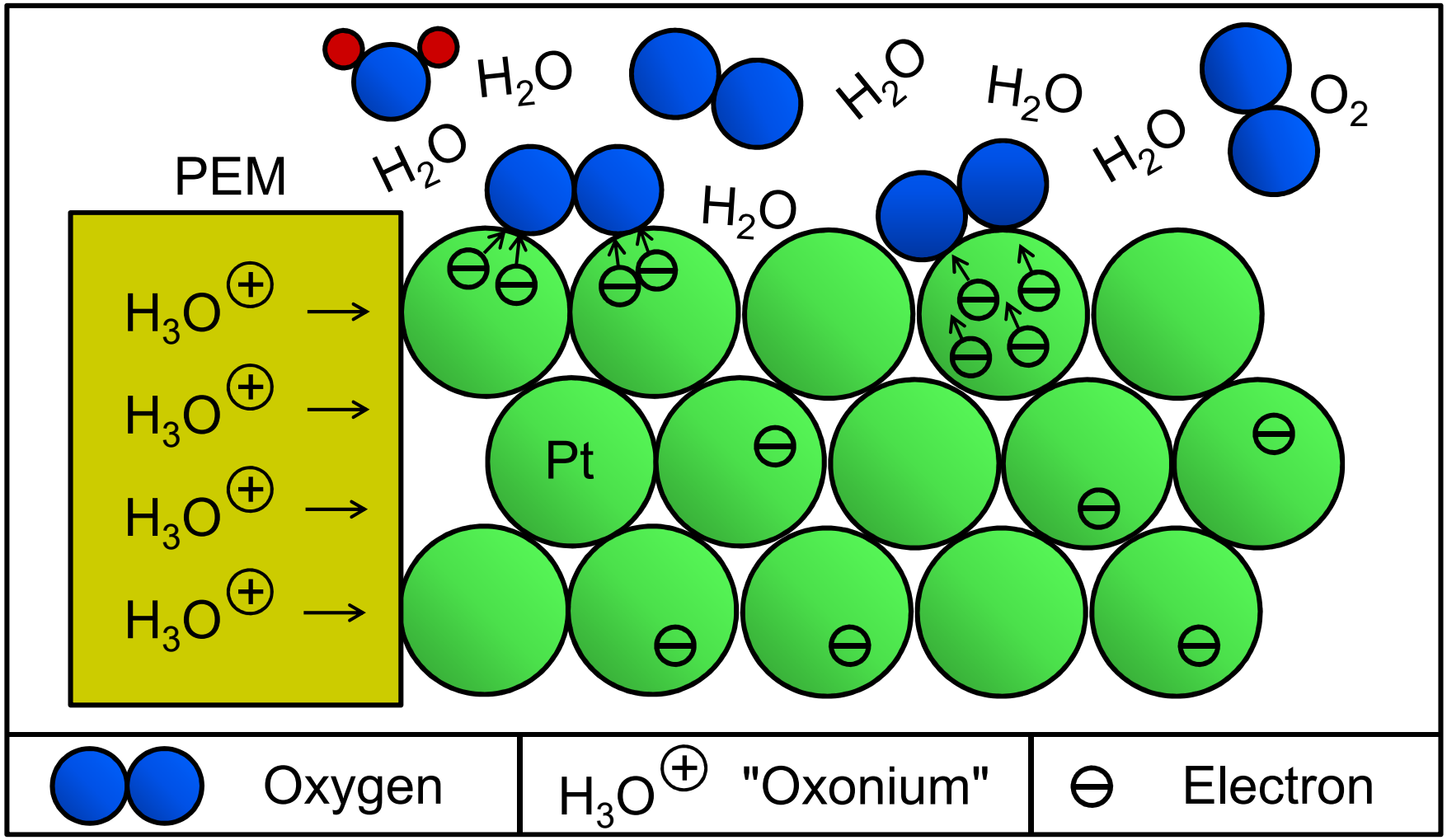
Proton Conduction in a Water Domain From Nafion® (Idealized):



Rainer Buerstinghaus

PEM Fuel Cell, Cathode: Reduction of Oxygen.

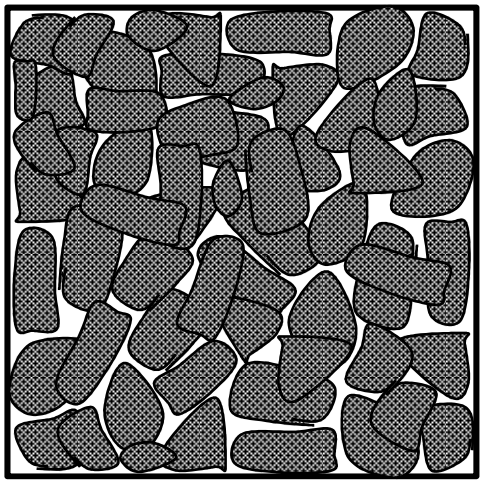
Platinum Nanoparticles, Electron / Proton Transfer (Scheme):



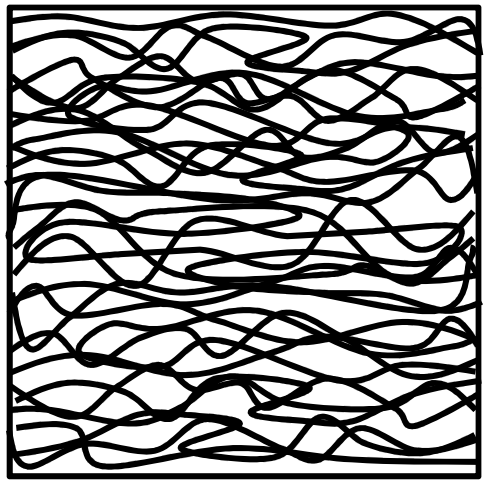
Rainer Buerstinghaus

Proton Exchange Membrane Fuel Cell (PEMFC), PEM.

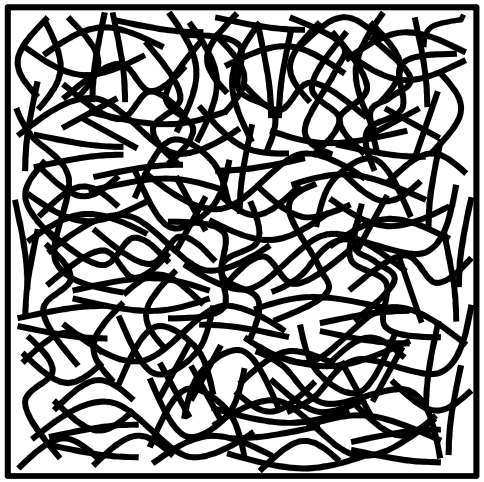
Gas-Permeable Carrier Materials for the Platinum Nanoparticles:



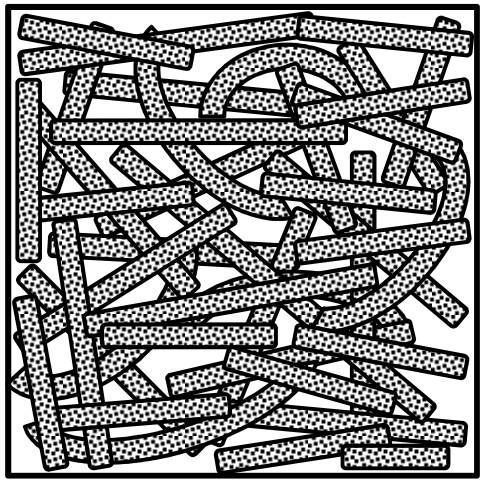
Pressed Activated Carbon



Carbon Fibers, Pressed



Carbon Fibers, Nonwoven

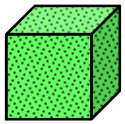
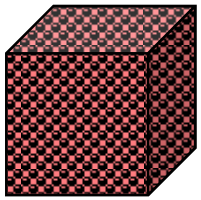
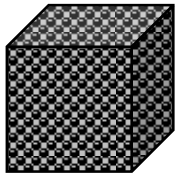
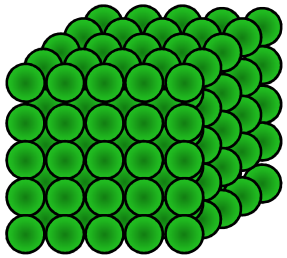


Carbon Nano Tubes

Rainer Buerstinghaus

Proton Exchange Membrane Fuel Cell (PEMFC), PEM.

Effective Alternatives to the Platinum Catalyst Metal:

Ni	Ru	Pd	Pt
			

These particles have edge lengths between ≈ 1.0 nm and 5.0 nm.
A platinum particle with an edge length of 1nm contains approx.
40 platinum atoms.

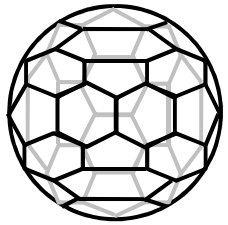
Rainer Buerstinghaus

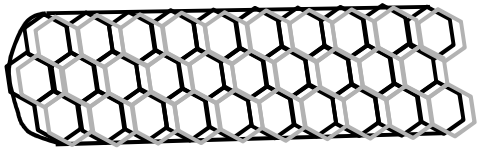
Metal-Organic Frameworks ⟶ Technical Applications

Reversible Gas Storage of Hydrogen, H_2 .

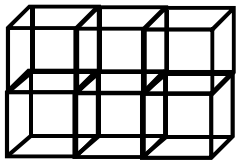
⟶ **Reversible Hydrogen Storage by Adsorption:**

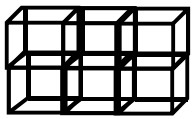
- Carbon Modifications:
  e.g. Fullerenes, Graphene-Nanotubes.





- Metal-Organic Frameworks: e.g. Cu-BTC-**MOF**s.





Rainer Buerstinghaus

Metal-Organic Frameworks ⟶ Technical Applications

Hints and Additions ⟶

Chemical alternative for the hydrogen economy: "Partly reversible" chemical storage of hydrogen, H_2 , by means of **"Hydride Storage Materials"**. Release of H_2 from finely ground metal hydride (Ball mill, transition metal catalysis, temperatures between 35°C and 150°C).

⟶ Hydrides as "Partly Reversible" Hydrogen Storages

- Metal hydrides: e.g. Mg_2NiH_4 , $NaAlH_4$, $Mg[AlH_4]_2$
- Complex hydrides: e.g. , $NaBH_4$, $LiBH_4$

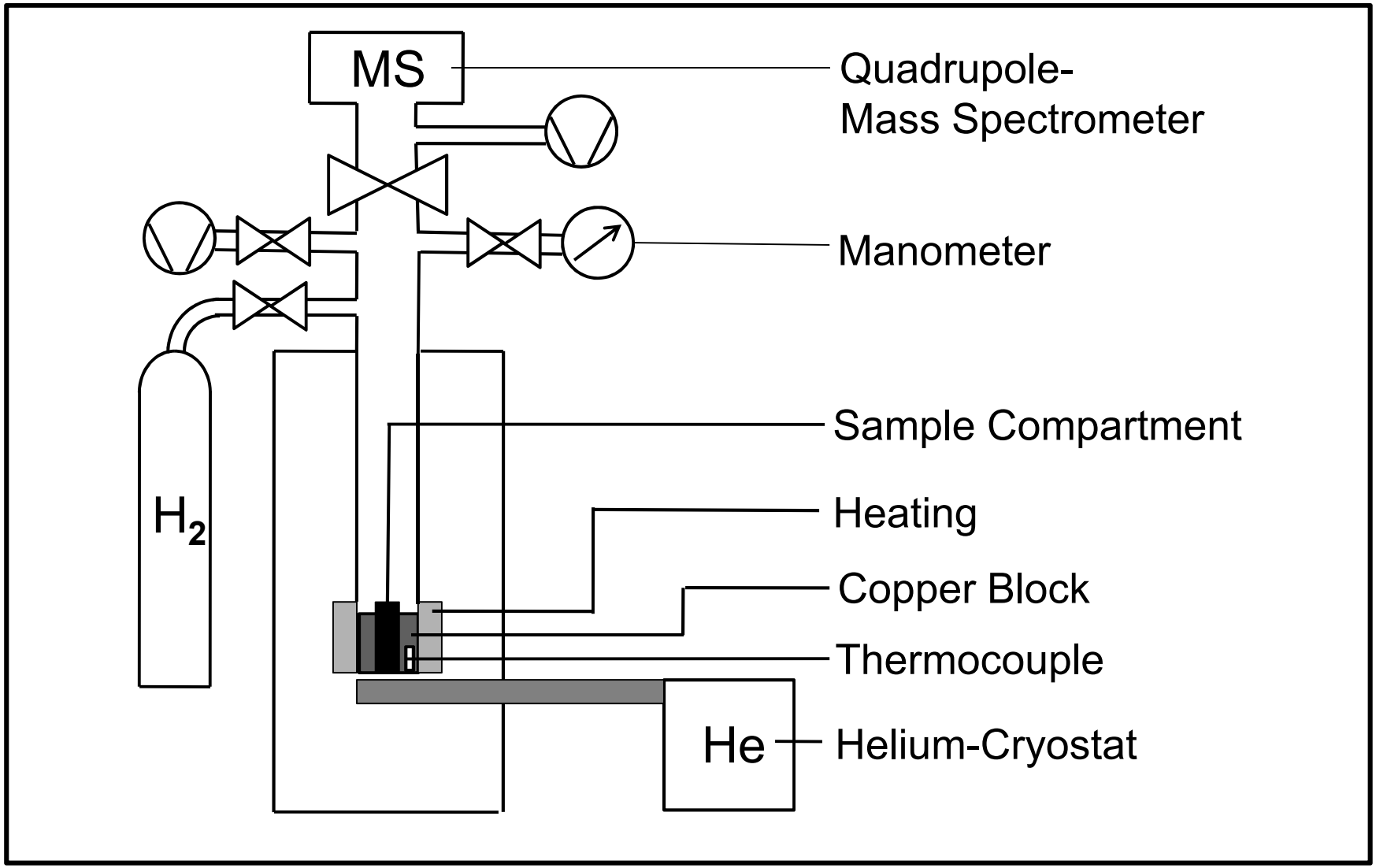
⟶ Hydrogen Release

$$3\ NaAlH_4 \overset{(Ti)}{\rightleftarrows} Na_3AlH_6 + 2\ Al + 3H_2 \rightleftarrows 3NaH + 3\ Al + \boxed{4{,}5\ H_2}$$

$$2\ LiBH_4 + MgH_2 \rightleftarrows 2\ LiH + MgB_2 + \boxed{4\ H_2}$$

Rainer Buerstinghaus

MOFs, Measurement of the Hydrogen-Adsorption by Thermal Desorption Spectroscopy , TDS-Equipment:



Rainer Buerstinghaus

Metal-Organic Frameworks ⟶ Technical Applications

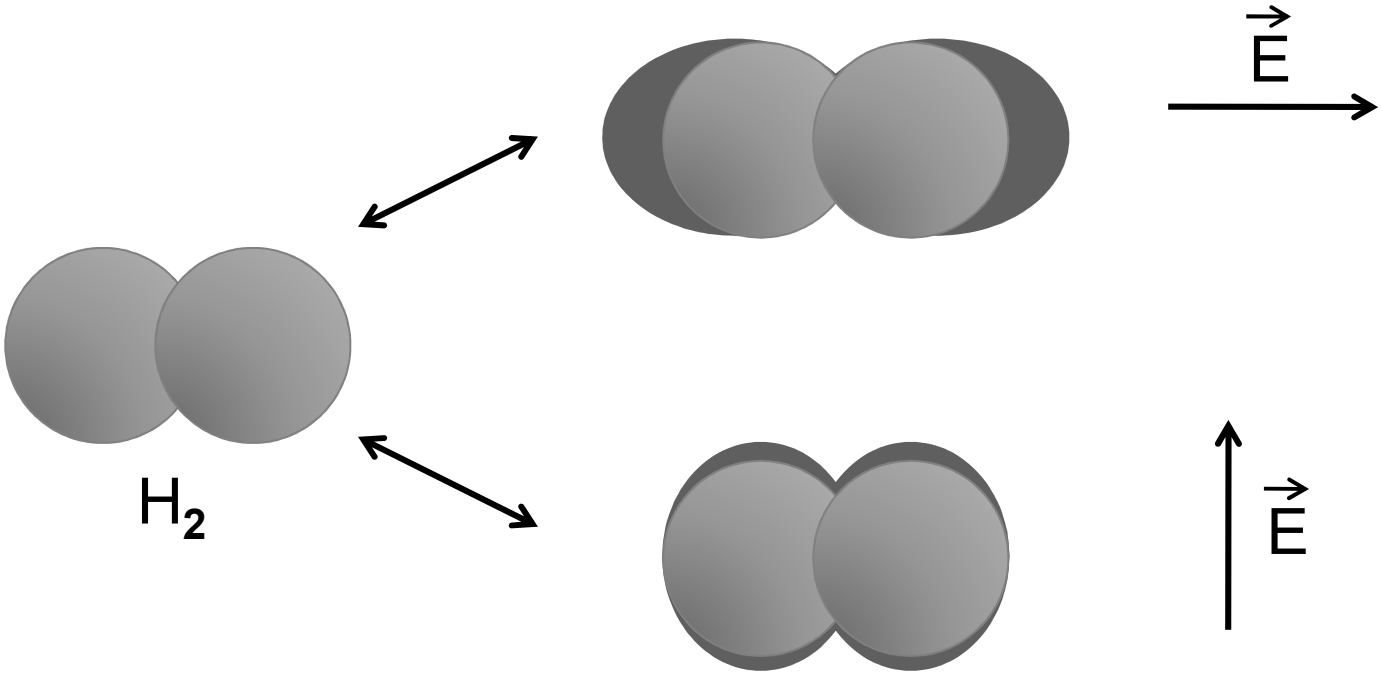
MOFs, Measurement of Hydrogen Adsorption by Thermal Desorption Spectroscopy (TDS), Procedure:

1. At 20°C, adjustment of an H_2-pressure of 25 mbar in the sample chamber.
2. Cooling down to 20K.
3. Keep these p- and T-conditions for 30 minutes.
4. Evacuation to remove excess, not adsorbed H_2.
5. Start of the heating program with 0.1K/s.
6. Measurement of the ionization current in the mass spectrometer (~ H_2-desorption rate).

(Source: B. Panella, K. Hönes, U. Müller, N. Trukhan, M. Schubert, H. Pütter, M. Hirscher, "Desorption Studies of Hydrogen in Metal-Organic Frameworks", Angewandte Chemie International Edition, **47**, 2138-2142, 2008.

Metal-Organic Frameworks ⟶ Technical Applications

MOFs, Measurement of Hydrogen Adsorption by Raman Spectroscopy (Anisotropic Polarizability of H_2):

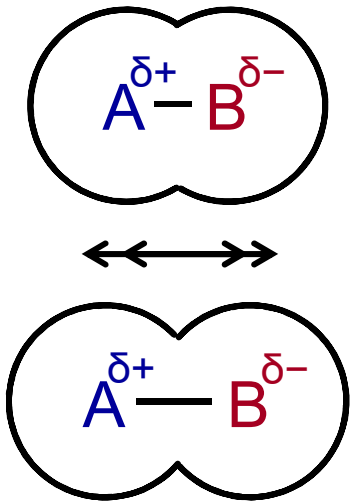


$\vec{p} = \alpha \cdot \vec{E}$: Dipole Moment = Polarizability · Electric Field Strength

Rainer Buerstinghaus

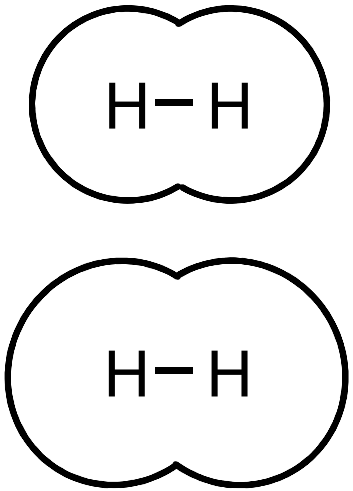
Metal-Organic Frameworks ⟶ Technical Applications

Measurement of Hydrogen Adsorption by Raman Spectroscopy, Raman Effect, Physical Principles:



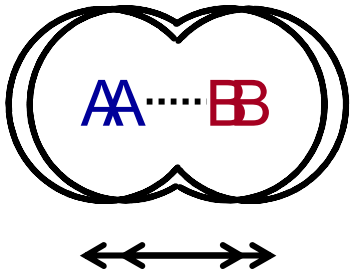
IR:

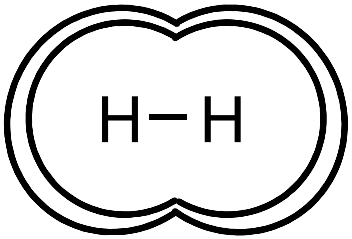
$\Delta\vec{p}$

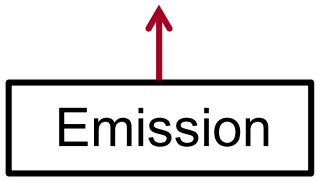


Raman:

Δα







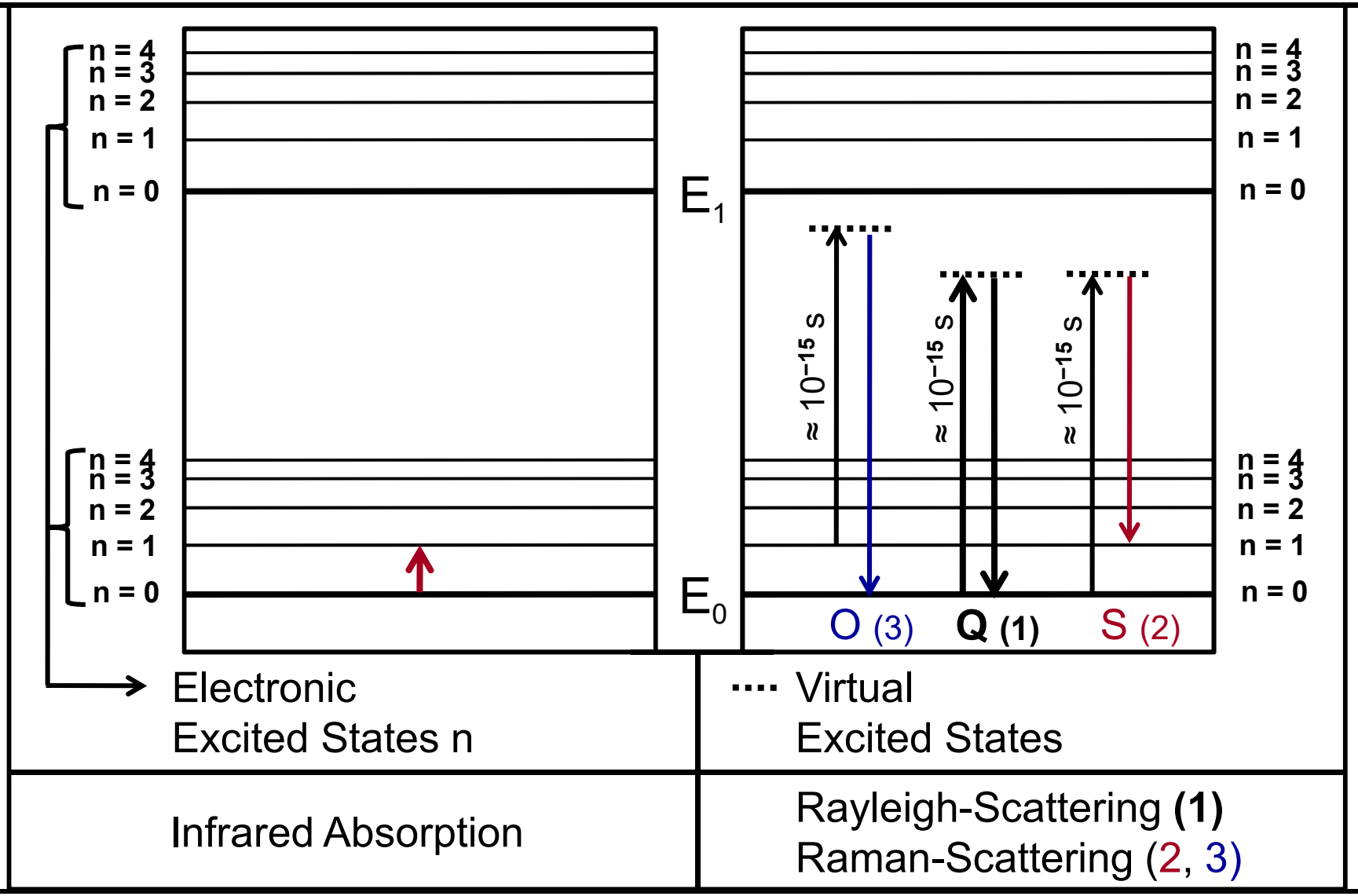
IR **Absorption,** Δ dipole moment: $\Delta\vec{p}$, **distance** changes **d** A–B

Raman **Emission,** Δ polarization: Δα, **no distance** changes **d** H–H

Rainer Buerstinghaus

Metal-Organic Frameworks ⟶ Technical Applications

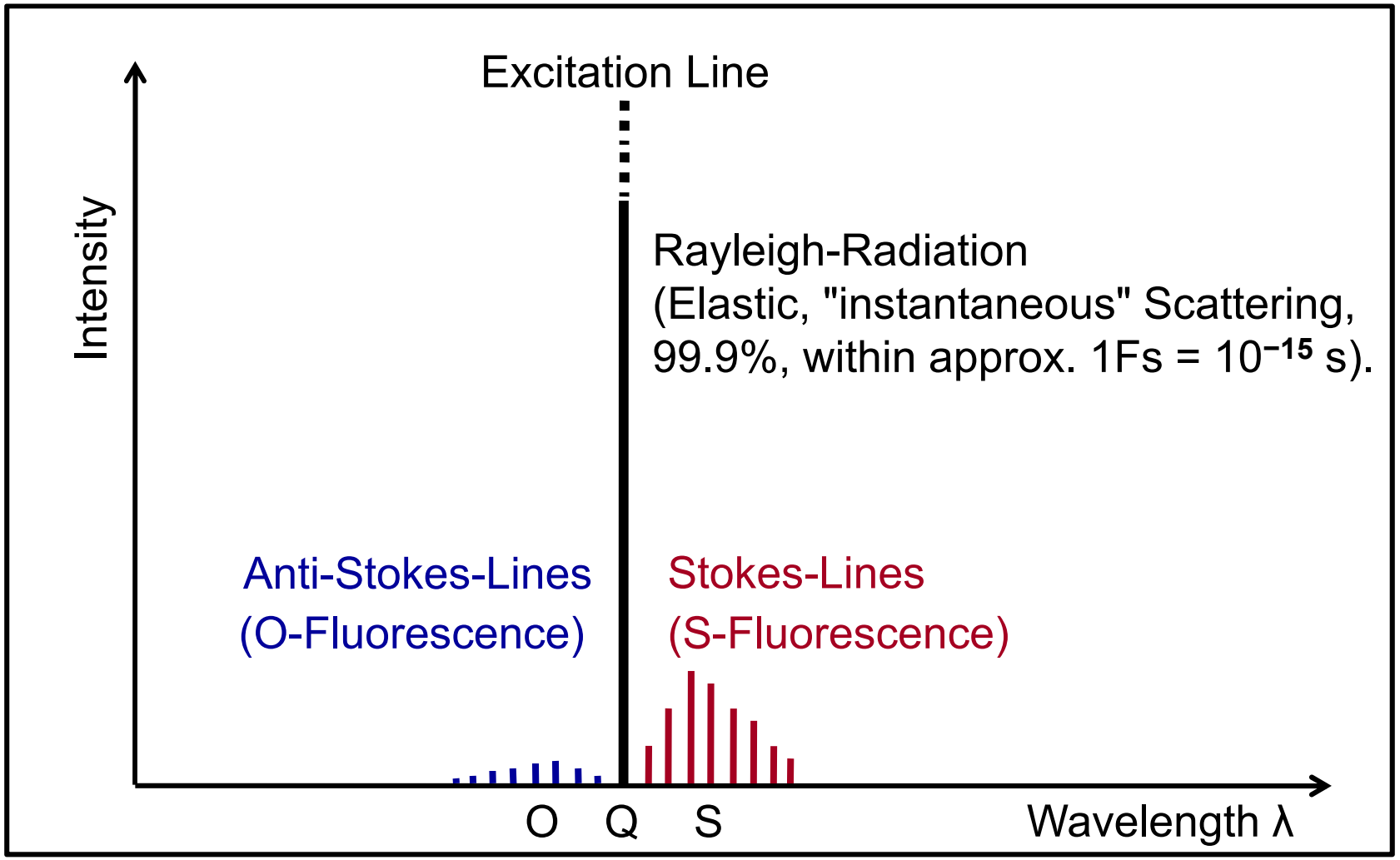
Measurement of Hydrogen Adsorption by Raman Spectroscopy, Raman Effect, Physical Principles:



Rainer Bürstinghaus

Metal-Organic Frameworks ⟶ Technical Applications

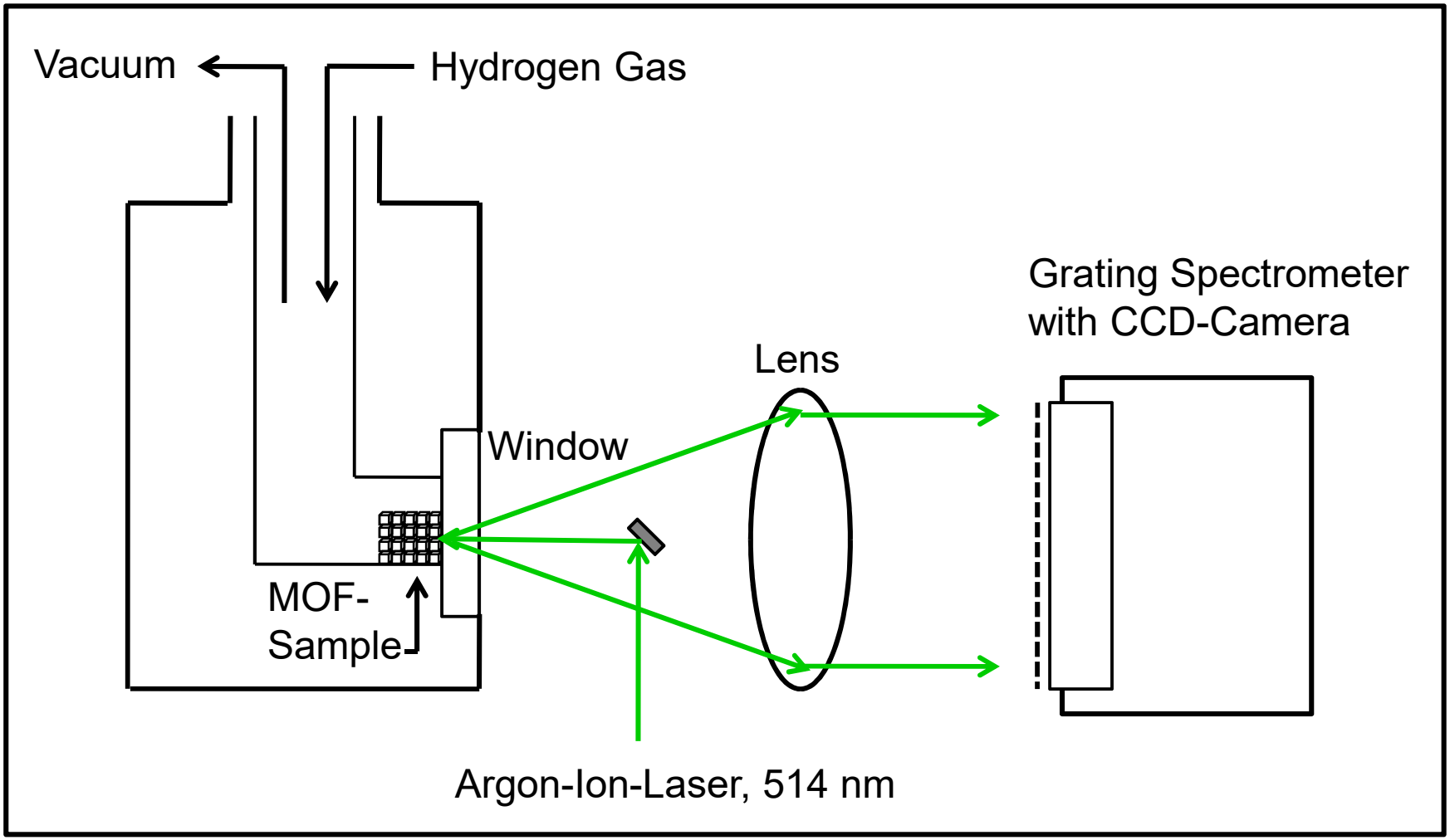
Measurement of Hydrogen Adsorption by Raman Spectroscopy, Raman Effect:



Rainer Buerstinghaus

Metal-Organic Frameworks ⟶ Technical Applications

Measurement of Hydrogen Adsorption by Raman Spectroscopy, Apparatus:



Rainer Buerstinghaus

Metal-Organic Frameworks ⟶ Technical Applications

Measurement of Hydrogen Adsorption by Means of Raman Spectroscopy, Result with Cu-BTC:

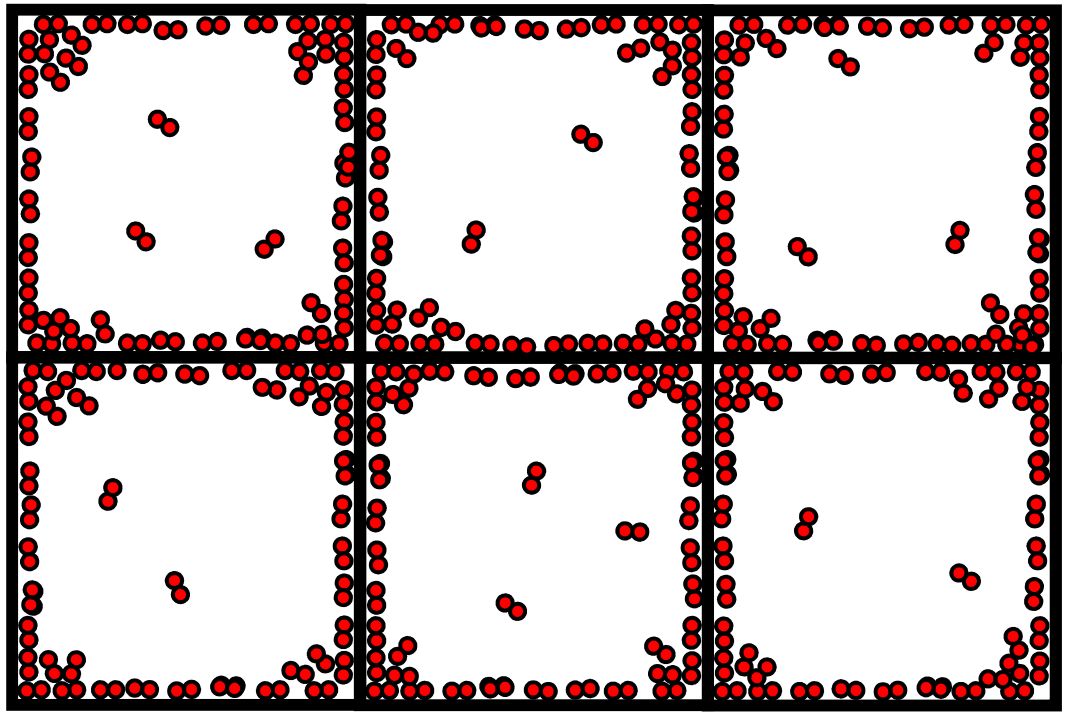
- The Q-line of molecular hydrogen adsorbed on Cu-BTC is shifted (only) by 1.5 cm^{-1} toward higher wavenumbers.

- This small shift shows that in MOFs, hydrogen storage is due to weak van der Waals forces and that charge transfer between H_2-molecules and MOF can be neglected.

(Source: Doctoral Thesis from B. Panella, University of Stuttgart, 2006).

Metal-Organic Frameworks ⟶ Technical Applications

Gas Storage: ⟶ Hydrogen, H_2 ( ), Simplified Sketch:



MOF 5: H_{ads} = 3,8 kJ/Mol H_2

Mg Formate: H_{ads} = 7,0 kJ/Mol H_2

Rainer Buerstinghaus

Metal-Organic Frameworks ⟶ Technical Applications

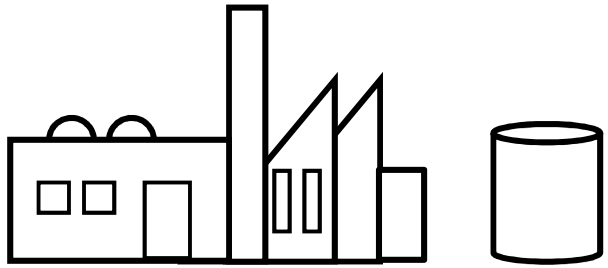
Gas Storage by Adsorption:

Other gases that can be stored using MOFs ⟶

- Methane (Cu-MOFs, MIL 101).
- Carbon Dioxide (ZIFs: Zeolitic Imidazolate Frameworks).
- Carbon Monoxide.
- Ammonia.
- Chlorine.
- Sulphur Dioxide.

The company in which new MOFs for gas storage are to be created.

R&D-Project "New Metal-Organic Frameworks…"



The Chemical Company […GmbH 3]:

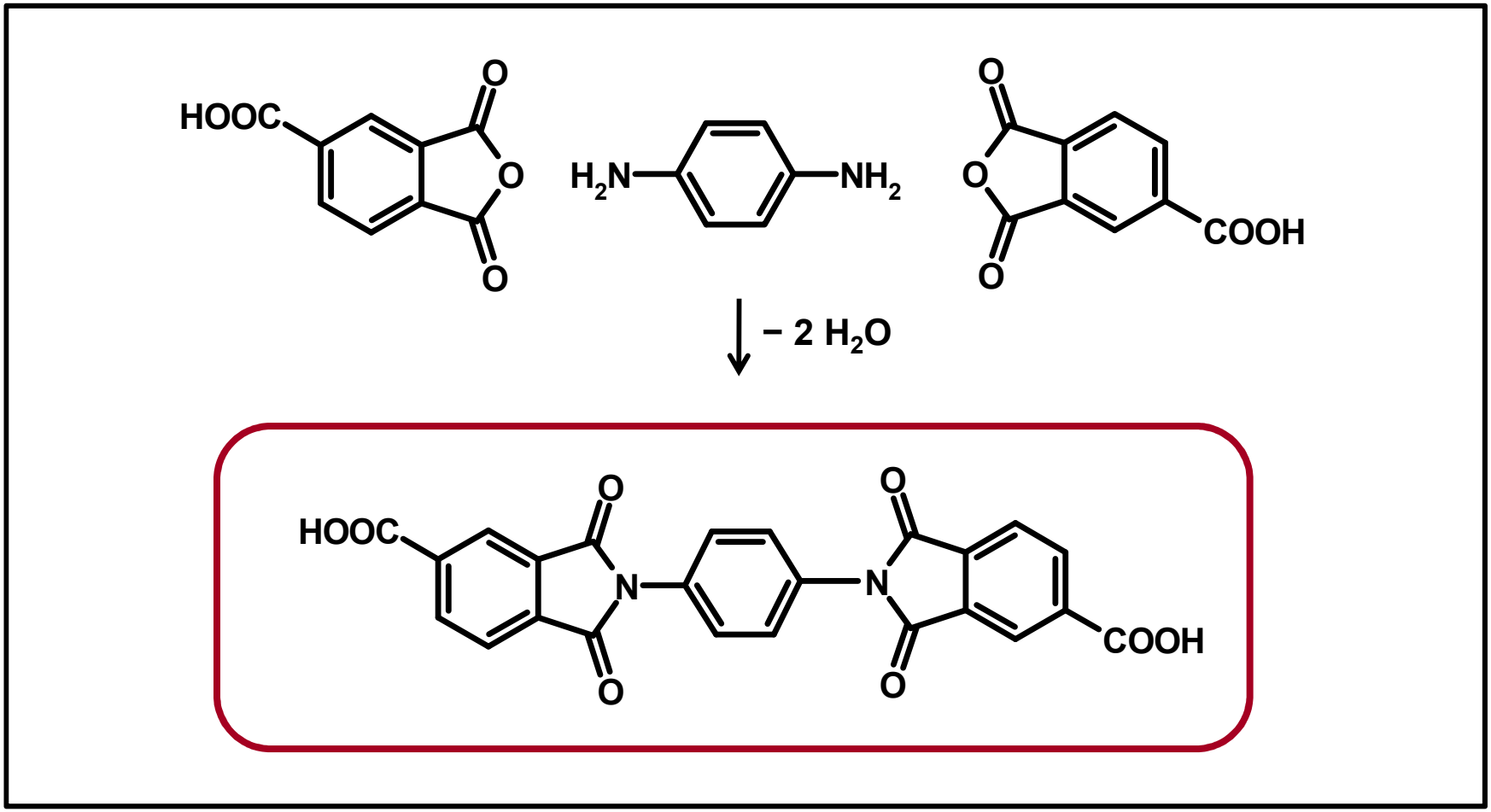
Smaller medium-sized enterprise: 127 employees throughout Europe, including 11 chemists, 17 engineers (FH), 5 engineers (TU).
Manufacturer and distributor of special metalorganic compounds.

Own research and development, own production.
Active for 12 years in R & D, scale-up and contract manufacturing of metalorganic compounds.

Organic specialty chemicals: Production and distribution of TMA (trimellitic anhydride) and PMA, (pyromellitic anhydride).

New Metal-Organic Frameworks for the Hydrogen Storage

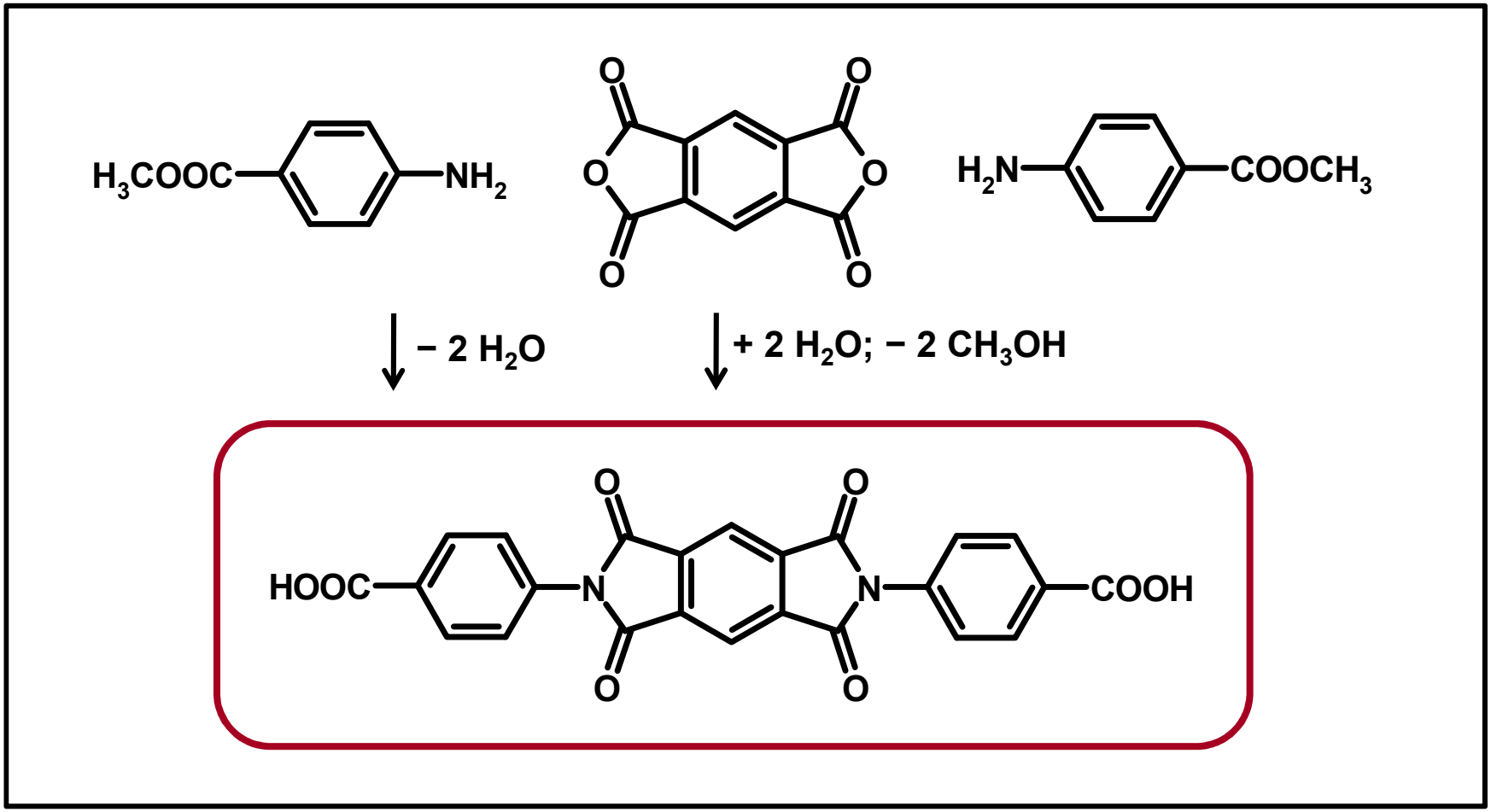
Thermostable Dicarboxylic Acids, Bridging Ligands in MOF`s. Potential Storage Materials for Compressed Hydrogen.



Rainer Buerstinghaus

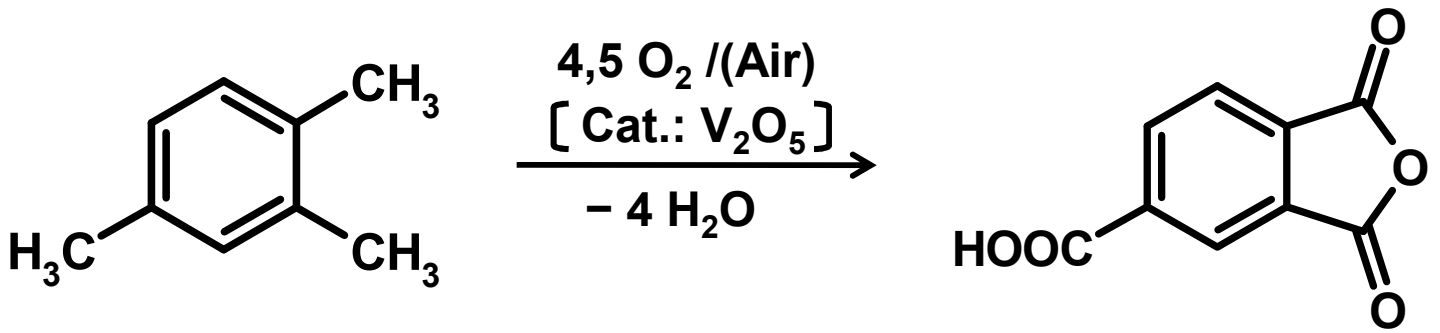
New Metal-Organic Frameworks for the Hydrogen Storage

Thermostable Dicarboxylic Acids, Bridging Ligands in MOF`s. Potential Storage Materials for Compressed Hydrogen.



New Metal-Organic Frameworks for the Hydrogen Storage

Industrial Synthesis of Trimellitic Anhydride, TMA:

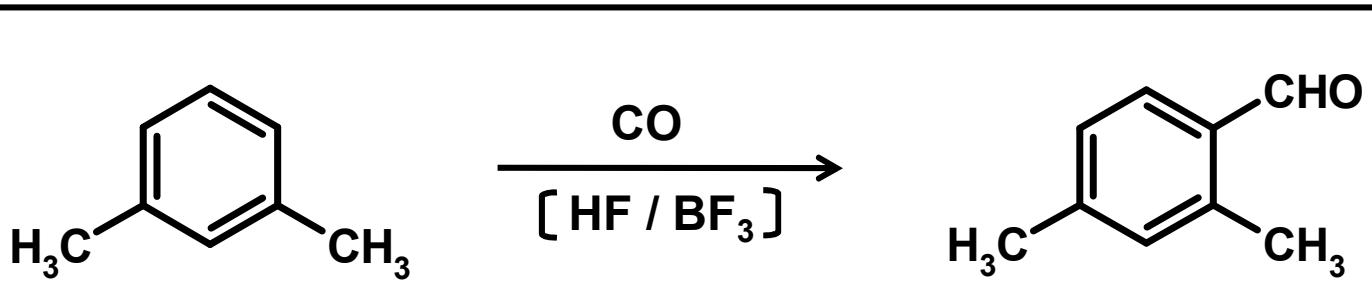


1,2,4-Trimethylbenzene (Pseudo Cumene)

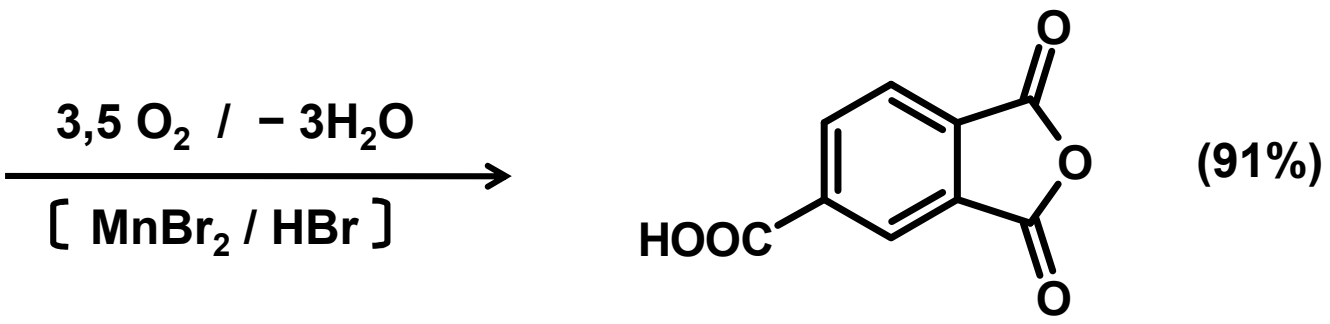
World Production: ≈ 100.000 tonnes a year.

Rainer Buerstinghaus

Industrial Synthesis of Trimellitic Anhydride, TMA. Process Chemistry: Mitsubishi Gas Chemical.



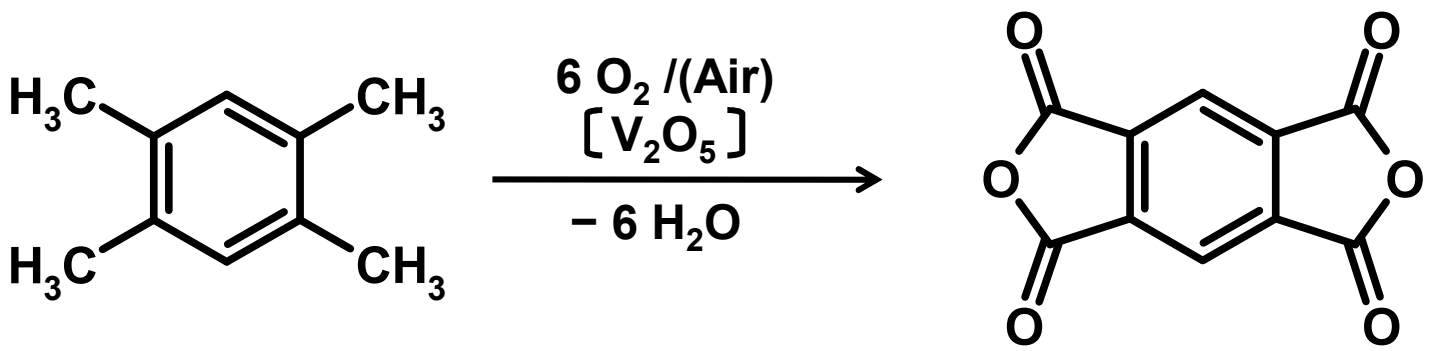
m-Xylene



(91%)

New Metal-Organic Frameworks for the Hydrogen Storage

Industrial Synthesis of Pyromellitic Anhydride, PMA:

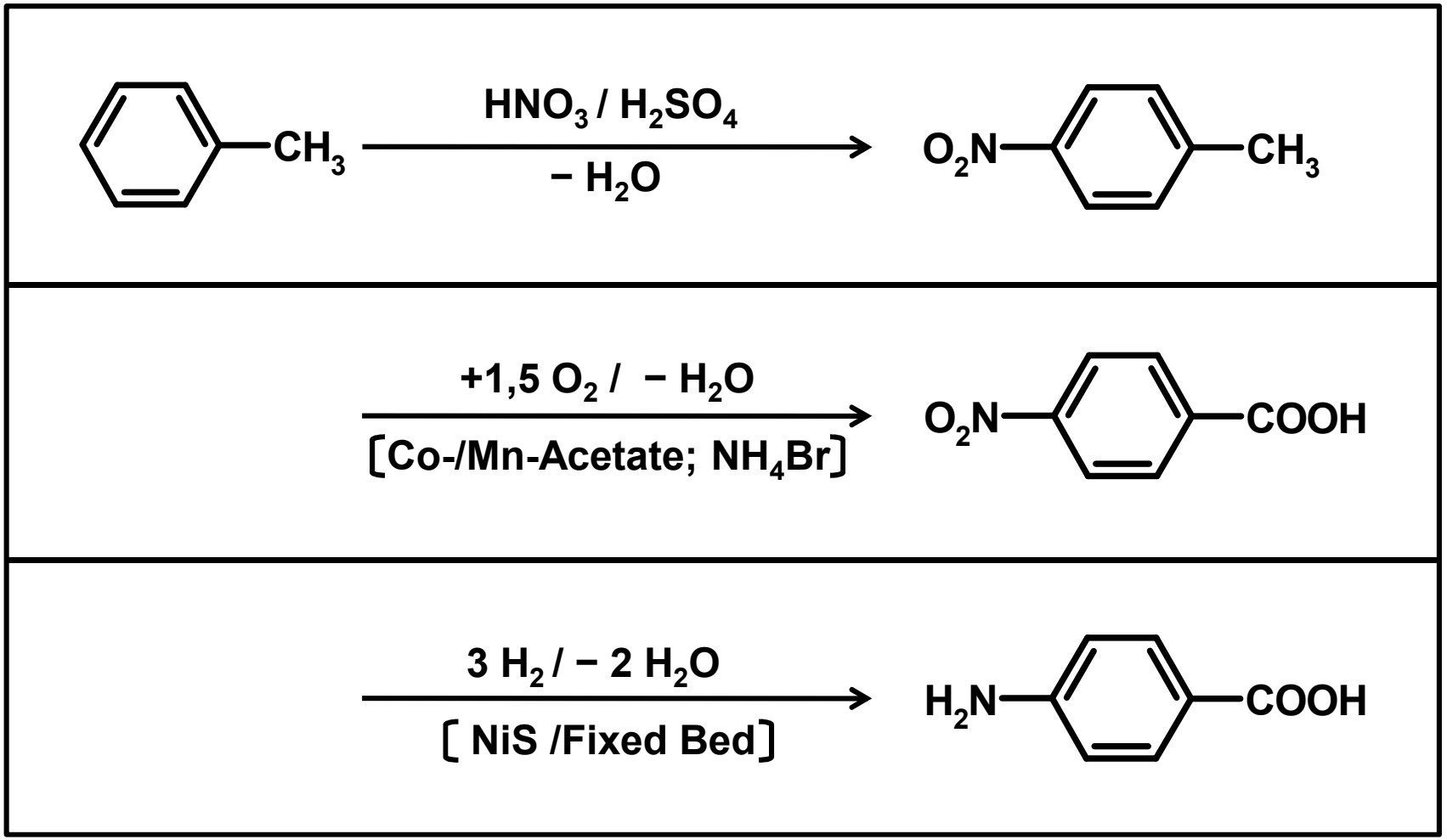


1,2,4,5-Tetramethylbenzene
(Durene)

World production:
≈ 8.000 tonnes a year.

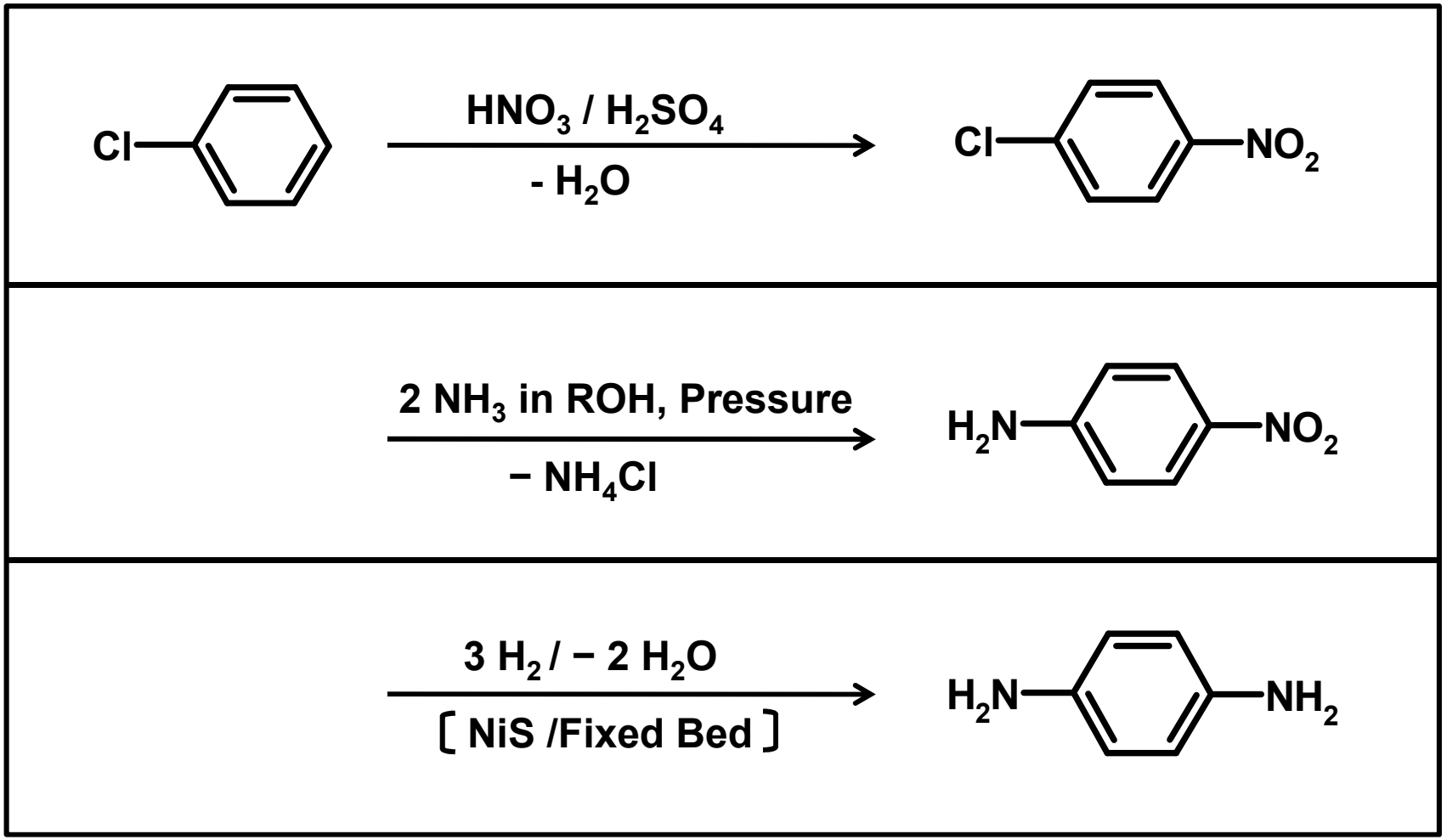
New Metal-Organic Frameworks for the Hydrogen Storage

Industrial Synthesis of 4-Aminobenzoic Acid (PABA):



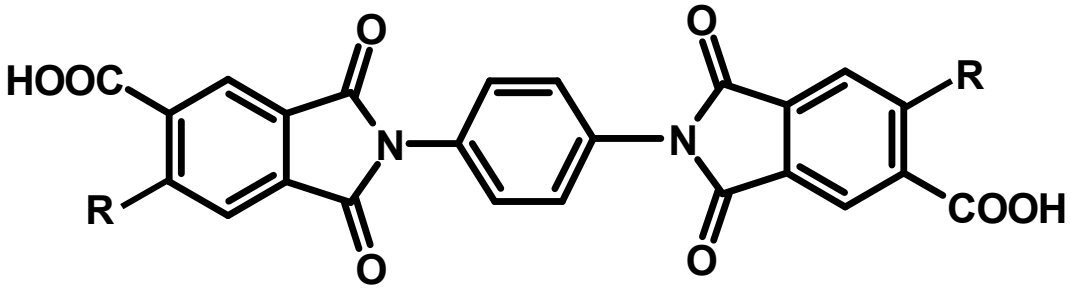
New Metal-Organic Frameworks for the Hydrogen Storage

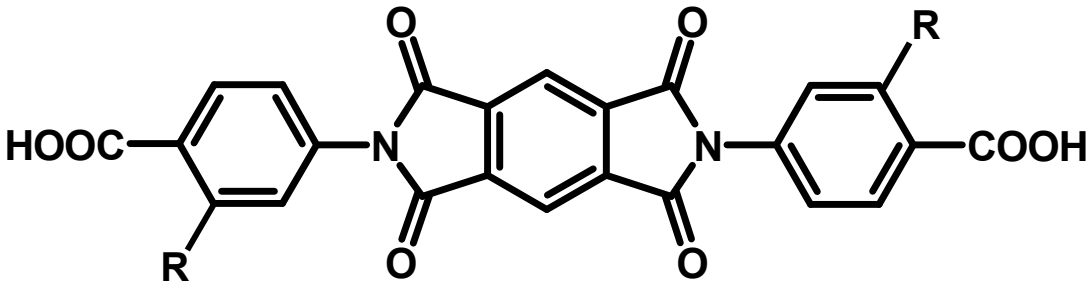
Industrial Synthesis of p-Phenylene Diamine:



New Metal-Organic Frameworks for the Hydrogen Storage

Linkers and connectors for MOFs whose storage capacities for hydrogen (198K−373K/10−50 bar) are to be investigated:





Dicarboxylic Acids as Linkers: R = H, OH (Type: CPO-27)

Zn^{2+}	
Co^{2+}	
Ni^{2+}	Mg^{2+}
Mn^{2+}	Ca^{2+}
Fe^{2+}	Sr^{2+}
Cu^{2+}	Ba^{2+}
Cd^{2+}	

Connectors M^{2+}

Rainer Buerstinghaus

New Metal-Organic Frameworks… → H_2-Storage

Technical Crystallization Procedures for Testing the Scale Up of Hydrogen-Storing Metal-Organic Frameworks:

Evaporation Crystallization

- With interior radiator.
- With external evaporator.

Cooling Crystallization

- Cold stirrer, vertical stirrer.
- Cooling cylinder crystallizer.
- Rotary tube crystallizer.
- Weighing crystallizer.
- Column crystallizer.

Vacuum Crystallization

- Vacuum circulation crystallizer.
- Vacuum agitator crystallizer.
- Multi-stage vacuum crystallizer.

Rainer Buerstinghaus

New Metal-Organic Frameworks… → H_2-Storage

Technical Drying Procedures for Testing the Scale Up of Hydrogen-Storing Metal-Organic Frameworks:

Convection Drying, Contact Drying, Radiation Drying

- Chamber Dryer.
- Tunnel Dryer.
- Belt Dryer.
- Rack Dryer.
- Rotary Dryer.

- Plate Dryer.
- Paddle Dryer.
- Fluidized Bed Dryer.
- Spray Dryer.
- Roller Dryer.

Vacuum Drying

Vacuum Freeze-Drying

Rainer Buerstinghaus

Further literature on the subject of "R&D project management in the chemical industry". Selection of purchasable monographs and publications in journals or in internet.

- Leker, Gelhard, von Delft, Business Chemistry, Wiley & Sons Ltd., Oxford U. K., 2018.
- Hauschildt, Salomo, Schultz, Kock, Innovationsmanagement, Verlag Franz Vahlen, München, 2021.
- Vahs, Brem, Innovationsmanagement, Schäffer-Poeschel Verlag, Stuttgart, 2015.
- Gausemeier, Dumitrescu, et al., Innovationen für die Märkte von morgen, Carl Hanser Verlag, München, 2019.
- Cooper, Top oder Flop in der Produktentwicklung, WILEY-VCH Verlag, Weinheim, 2002.
- Russo, Gleich, Strascheg, Von der Idee zum Markt, Verlag Franz Vahlen, München, 2008.
- Loch, Kavadias, Handbook of New Product Development, Elsevier, Oxford, 2008.
- Bullinger, Fokus Innovation, Carl Hanser Verlag, München, 2006.
- Offermanns, "Steinheimer Gespräche" within the FCI, personal communications, Steinheim, 2002.

- Münch, Patente, Marken, Design von A bis Z, WILEY-VCH Verlag, Weinheim, 2012.

- Gassmann, Praxiswissen Projektmanagement, Carl Hanser Verlag, München, 2006.
- Kerzner, Projekt Management, Ein systemorientierter Ansatz, mitp, Redline Verlag, Heidelberg, 2008.
- Gessler, Kompetenzbasiertes Projektmanagement, GPM-Publikation, Nürnberg, 2016.
- Patzak, Rattay, Projektmanagement, Linde-Verlag, Wien, 2014.
- Jenny, Projektmanagement - Das Wissen für den Profi, vdf Hochschulverlag an der ETH, Zürich, 2020.
- Jenny, Projektmanagement - Das Wissen für eine erfolgreiche Karriere, vdf Hochschulverlag an der ETH, Zürich, 2020.
- Drees, Lang, Schöps, Praxisleitfaden Projektmanagement, Carl Hanser Verlag, München, 2014.
- Burghardt, Projektmanagement, Publicis MCD Verlag, Erlangen, 2018.

Further literature on the subject of "R&D project management in the chemical industry". Selection of purchasable monographs and publications in journals or in internet.

- Hesseler, Projektmanagement, Verlag Franz Vahlen, München, 2015.
- Stöger, Wirksames Projektmanagement, Schäffer- Poeschel, Stuttgart, 2019.
- Litke, Projektmanagement, Carl Hanser Verlag, München, 2007, new edition announced for 2023.
- Litke, Kunow, Schulz-Wimmer, Projektmanagement, Haufe-Lexware, Freiburg, 2018.
- Madauss, Projektmanagement, Theorie und Praxis aus einer Hand, Springer Gabler, Berlin, 2020.
- Bea, Scheurer, Hesselmann, Projektmanagement, UVK-Verlag, München, 2020.
- Braehmer, Projektmanagement für kleine und mittlere Unternehmen, Carl Hanser Verlag, München, 2009.
- Klein, Projektmanagement in der Praxis, Ebook, Verlag Interna, Bonn, 2012.
- Weichselbaumer, Bley, MS-Project 2013 in 13 Stunden, epubli GmbH, Stuttgart, Berlin, 2014.
- Dittmann, Dirbanis, Projektmanagement (IPMA®), Haufe, Freiburg, 2020.
- Schels, Seidel, Projektmanagement mit Excel, Carl Hanser Verlag, München, 2016.
- Tumuscheit, Überleben im Projekt, Redline Wirtschaft, Heidelberg, 2014.
- Tumuscheit, 55 Mythen des Projektmanagements, Orell Füssli Verlag, Zürich, 2013.
- Meyer, Reher, Projektmanagement, Springer Fachmedien, München, 2020.
- Drews, Hillebrand, Kärner, Praxishandbuch Projektmanagement, Haufe, Freiburg, 2015.
- Pautsch, Steininger, Lean Project Management – Projekte exzellent umsetzen, Carl Hanser Verlag, München, 2014.
- Cole, Barker, Brilliant Project Management, Pearson Education Ltd., London, 2015.
- Andler, Tools für Projektmanagement, Workshops und Consulting, Publicis Publishing, Erlangen, 2015.
- Hüsselmann, Lean Project Management, Schäffer-Poeschel Verlag, Stuttgart, 2021

Further literature on the subject of "R&D project management in the chemical industry". Selection of purchasable monographs and publications in journals or in internet.

- Schröder, Agile Produktentwicklung, Carl Hanser Verlag, München, 2018.
- Kuster et al., Handbuch Projektmanagement, Agil – Klassisch – Hybrid, Springer Gabler, Wiesbaden, 2019.
- Ziegler, Agiles Projektmanagement mit Scrum für Einsteiger, Independ. Published, ISBN 9781729408353, 2021.
- Cooper, Edgett, Kleinschmidt, Optimizing the Stage Gate Process, Res. Technol. Management, 45, 2002.
- Cooper, What`s Next After Stage-Gate? Res. Technol. Management, 157, 2014.
- Hirzel, Alter, Niklas, Projektportfolio-Management, Springer Gabler, Wiesbaden, 2019.
- Timinger, Modernes Projektmanagement, WILEY-VCH Verlag, Weinheim, 2017.
- www.projektmanagementhandbuch.de, PMH, 2021.
- www.projektmanagement-definitionen.de, 2021.
- www.projektmagazin.de, 2021.
- GPM Deutsche Gesellschaft für Projektmanagement e.V., Kompetenzbasiertes Projektmanagement (PM4), Handbuch für Praxis und Weiterbildung im Projektmanagement, Band 1, Band 2, Nürnberg, 2019.
- Lang, Wagner, Der Weg zum projektorientierten Unternehmen, Carl Hanser Verlag, München, 2019.

- Helm, Pfeifer, Ohser, Mathematik für Wirtschaftswissenschaftler, Carl Hanser Verlag, München, 2015.
- Grieser, Mathematisches Problemlösen und Beweisen, Springer Fachmedien, Wiesbaden, 2017.
- Krischke, Röpcke, Graphen- und Netzwerktheorie, Carl Hanser Verlag, München, 2015.
- Tittmann, Graphentheorie, eine anwendungsbezogene Einführung, Fachbuchverlag, Leipzig, 2003.
- Nitzsche, Graphen für Einsteiger, Vieweg + Teubner Verlag, Wiesbaden, 2009.
- Stegbauer, Häußling, Handbuch Netzwerkforschung, Springer Fachmedien, Wiesbaden, 2010.

Further literature on the subject of "R&D project management in the chemical industry". Selection of purchasable monographs and publications in journals or in internet.

- Festel, Hassan, Leker, Bamelis, Betriebswirtschaftslehre für Chemiker, Springer, Berlin, 2001.
- Festel, Söllner, Bamelis, Volkswirtschaftslehre für Chemiker, Springer, Berlin, 2000.
- Mühlbradt, Wirtschaftslexikon, Scriptor Reihe, Cornelsen Verlag, Berlin, 2008.
- Malik, Unternehmenspolitik und Corporate Governance, Campus-Verlag, Frankfurt/Main, 2013.
- Schierenbeck, Wöhle, Grundzüge der Betriebswirtschaftslehre, Oldenbourg Verlag, München, 2016.
- Wöhe, Einführung in die Allgemeine Betriebswirtschaftslehre, Verlag Franz Vahlen, München, 2020.

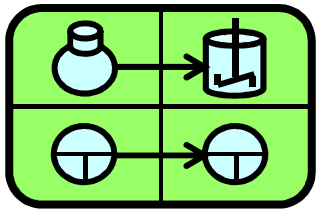
- Drucker, Die Kunst des Managements, Econ Verlag, München, 2000.
- Drucker, Alles über Management, Redline Wirtschaft, Heidelberg, 2007.
- Drucker, The Effective Executive, Verlag Franz Vahlen, München, 2014.
- Malik, Management, Das A und O des Handwerks, Campus-Verlag, Frankfurt/Main, 2013.
- Malik, Führen, Leisten, Leben, Campus-Verlag, Frankfurt/Main, 2019.
- Roth, Fühlen, Denken, Handeln, Suhrkamp Verlag, Frankfurt/Main, 2007.
- Sprenger, Mythos Motivation, Campus-Verlag, Frankfurt/Main, 2014.
- Sprenger, Vertrauen führt, Campus-Verlag, Frankfurt/Main, 2007.
- Freitag, Kommunikation im Projektmanagement, Springer-Gabler, Wiesbaden, 2016.
- Schulz von Thun, Miteinander Reden, Rowohlt Verlag, Reinbeck, 2019.
- Riemann, Grundformen der Angst, Reinhardt Verlag, München, 2019.
- Csikszentmihalyi, Flow im Beruf, Klett-Cotta Verlag, Stuttgart, 2012.

Further literature on the subject of "R&D project management in the chemical industry". Selection of purchasable monographs and publications in journals or in internet.

- Horx, Das Zukunftsmanifest, Ullstein Taschenbuch Verlag, Berlin, 2002.
- Bürkle, Aktive Karrierestrategie, Springer Gabler, Wiesbaden, 2013.
- Hesse, Schrader, Das große Bewerbungshandbuch, Stark Verlag, München, 2015.
- Hesse, Schrader, 1X1 - Das erfolgreiche Vorstellungsgespräch, Stark Verlag, München, 2014.
- Püttjer, Schnierda, Trainingsmappe Vorstellungsgespräch, Campus-Verlag, Frankfurt/Main, 2019.
- Püttjer, Schnierda, Das überzeugende Bewerbungsgespräch für Führungskräfte, Campus-Verlag, Frankfurt/M, 2019.
- Püttjer, Schnierda, Das große Bewerbungshandbuch, Campus-Verlag, Frankfurt/Main, 2019.
- Stärk, Erfolgreich im Vorstellungsgespräch und Jobinterview, GABAL, Offenbach, 2018.
- Hesse, Schrader, Die hundert häufigsten Fragen im Vorstellungsgespräch, Stark Verlag, München, 2013.
- Lüdemann, Lüdemann, Die 111 wichtigsten Fragen im Vorstellungsgespräch, Redline Wirtschaft, München, 2018.
- Rohrschneider, Lorenz, Müller-Thurau, Vorstellungsgespräche, Haufe, Freiburg und Planegg, 2018.
- Engst, Willmann, Professionelles Bewerben, Bibliografisches Institut, Berlin, 2019.

- Drewermann, Glauben in Freiheit oder Tiefenpsychologie und Dogmatik, Band 1, Walter-Verlag, Olten, 1994.
- Schuler, Psychologische Personalauswahl, Hogrefe Verlag, Göttingen, 2014.
- Kanning, Personalauswahl zwischen Anspruch und Wirklichkeit, Springer-Verlag, Berlin, 2015.
- Herrmann, Die Auswahl, Wiley-VCH Verlag, Weinheim, 2016.
- Riedel, Agile Personalauswahl, Haufe Fachbuch, Freiburg, 2017.
- Autorenkollektiv „Diagnostik- und Testkuratorium“, Personalauswahl kompetent gestalten, Springer, Berlin, 2018.

R&D Project Management
in the Chemical Industry



End of Lecture Module 03

Rainer Buerstinghaus