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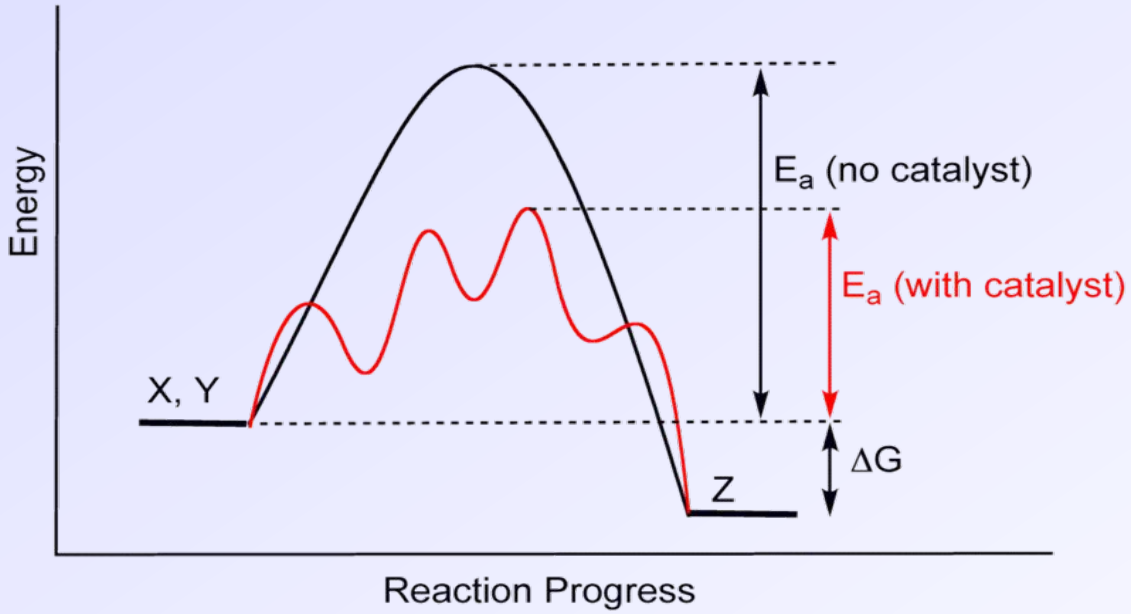
New aspects for technical textiles: Immobilization of organometallic catalysts on textile carriers for heterogeneous catalysis

Deutsches Textilforschungszentrum Nord-West e.V.
Institut an der Universität Duisburg-Essen
Eckhard Schollmeyer, Thomas Mayer-Gall, Klaus Opwis
Adlerstr. 1, D-47798 Krefeld, Germany

Catalysts

- catalysts decrease the activation energy of chemical reactions
- therefore, they increase the reaction rate extremely
- they are used in most large-scale industrial processes
  (more than 80% of all chemical products are synthesized by catalytic reactions)



no consumption
of the catalyst itself !!!

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Catalysts

- bio-catalysts (enzymes)
- organo-catalysts
- **organometallic catalysts**
- inorganic catalysts

Process Control

- homogeneous
- **heterogeneous (immobilized catalysts)**

Homogeneous vs. heterogeneous process control

homogeneous:

- 1 phase (mostly liquid)
- rapid formation of the educt-catalyst complex
- rapid product formation

→ rapid

heterogeneous:

- 2 phase (mostly liquid/gaseous - solid)
- controlled by transport processes
  - → mass transport: educt(s) → carrier
  - → pore diffusion: educt(s) → catalyst
  - → adsorption on the catalyst´s surface
  - → reaction
  - → desorption of product(s)
  - → pore diffusion: catalyst → product(s)
  - → mass transport: carrier → product(s)

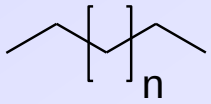
→ less rapid

Why Immobilization ?

Advantages of heterogeneous process control:

- catalysts are reusable
- use in continuous processes possible (flow-through-reactor)
- products free from catalysts

Typical large-scale heterogeneous catalyzed reactions

$3\ H_2 + N_2$	$\rightleftharpoons$ $2\ NH_3$	T = 550°C, 250-350 bar	Haber-Bosch-Process
$CH_4 + H_2O$	$\rightleftharpoons$ $CO + 3\ H_2$	T = 700-1000 °C, 100 bar	Steam Reforming
	$\rightleftharpoons$ alkanes, alkenes, cycloalkanes ...	T = 300 °C, 3 bar	Catalytic Cracking

$n\ CO + x\ H_2$ $\xrightleftharpoons{Ni}$ $C_nH_{2n+2} + x\ H_2O$ T = 160-200 °C — Fischer-Tropsch-Process

$n\ CO + x\ H_2$ $\xrightleftharpoons{Cu/Cr}$ CH_3OH T = 250-300 °C, 200 bar — Methanol-Synthesis

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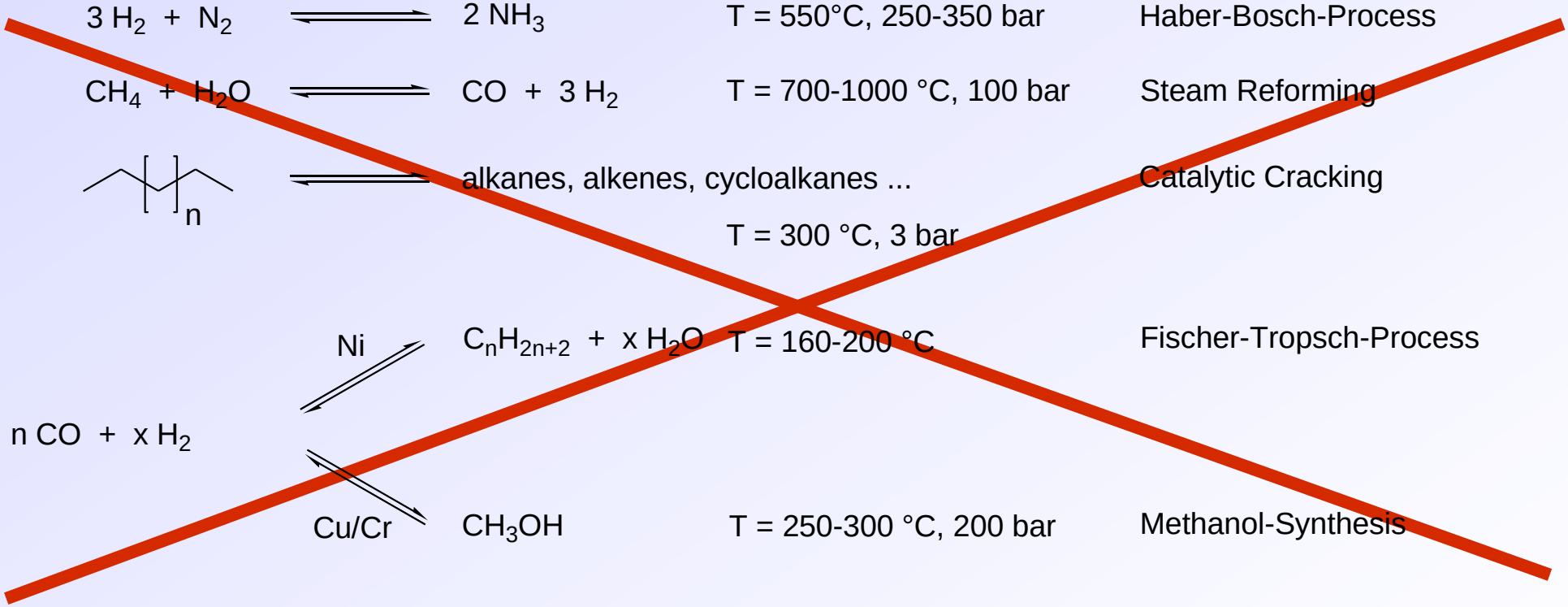
Why Textile Carrier Materials ?

Advantages/Properties

- textile materials are inexpensive (cotton, polyamide, polyester)
- high chemical resistance
- active surface area can be easily adjusted/optimized by the fiber diameter
- excellent flow through
- flexible construction, easy to drape
- simple and rapid removal from the reactor without any residues

BUT: Limitation to low-temperature processes (T < 100 °C)



Typical low-temperature catalysts

- bio-catalysts (enzymes)

→ former investigations

→ see, e.g.:

K. Opwis, D. Knittel, E. Schollmeyer, Immobilization of Catalase on Textile Carrier Materials, AATCC Review **4** (2004) 11, 25-28.

K. Opwis, D. Knittel, E. Schollmeyer, Quantitative Analysis of Immobilized Metalloenzymes by Atomic Absorption Spectroscopy, Analytical and Bioanalytical Chemistry **380** (2004) 937-941.

K. Opwis, D. Knittel, T. Bahners, E. Schollmeyer, Photochemical Enzyme Immobilization on Textile Carrier Materials, Engineering in Life Sciences **5** (2005) 1, 63-67.

K. Opwis, D. Knittel, T. Bahners, E. Schollmeyer, Verfahren zur photochemischen Immobilisierung von Proteinen an polymeren Trägermaterialien, German Patent DE 10 2005 011 926 A1 2005.10.06.

K. Opwis, D. Knittel, T. Bahners, E. Schollmeyer, Thin film coating of textile materials. Part II: Enzyme immobilization on textile carrier materials, in: Contact Angle, Wettability and Adhesion, Vol. 4, K.L. Mittal (Ed.), 447-460, VSP, Leiden (2006), ISBN 9-6764-436-6.

K. Opwis, D. Knittel, E. Schollmeyer, Functionalization of Catalase for a Photochemical Immobilization on Poly(ethylene terephthalate), Biotechnology Journal **2** (2007) 347-352.

NEW FIELD:

- organometallic catalysts

K. Opwis, D. Knittel, E. Schollmeyer, Immobilization of (Bio-) Catalysts on Textile Carrier Materials, 3rd International Textile, Clothing & Design Conference, Dubrovnik, October 2006.

K. Opwis, E. Schollmeyer, Technical Textiles with Catalytic Properties, Avantex, Frankfurt, June 2007.

K. Opwis, T. Mayer-Gall, E. Schollmeyer, Immobilization of Organometallic Catalysts on Textile Carrier Materials, Autex 2007, Tampere, Finnland, June2007.

K. Opwis, E. Schollmeyer, T. Mayer-Gall, G. Dyker, Textile Materialien mit daran fixierten metallorganischen Katalysatoren, German Patent DE 10 2007 006 874 A1 2008.08.14.

K. Opwis, T. Mayer-Gall, E. Schollmeyer, Immobilization of organometalllic catalysts on textile carrier materials, 2nd Aachen-Dresden International Textile Conference, Dresden, November 2008.

K. Opwis, T. Mayer-Gall, T. Textor, E. Schollmeyer, Immobilization of Organometallic Catalysts on Textile Carrier Materials, in: Polymer Surface Modification: Relevance to Adhesion, Vol. 5, K.L. Mittal (Ed.), 177-185, Brill, Leiden (2009).

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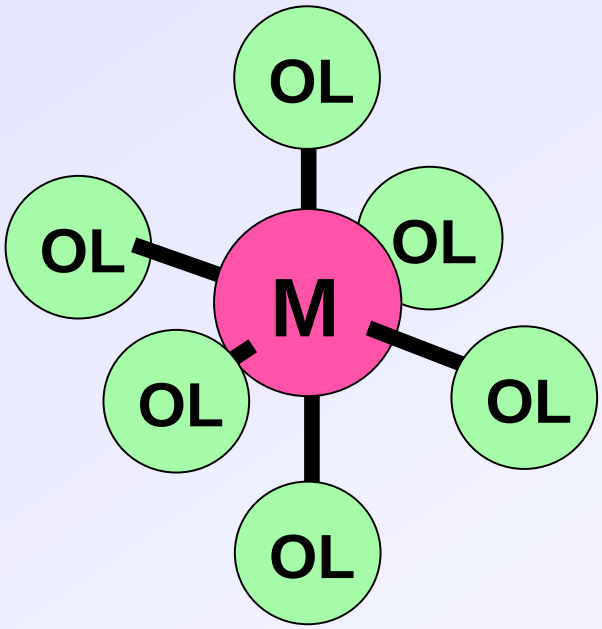
Organometallic Catalysts

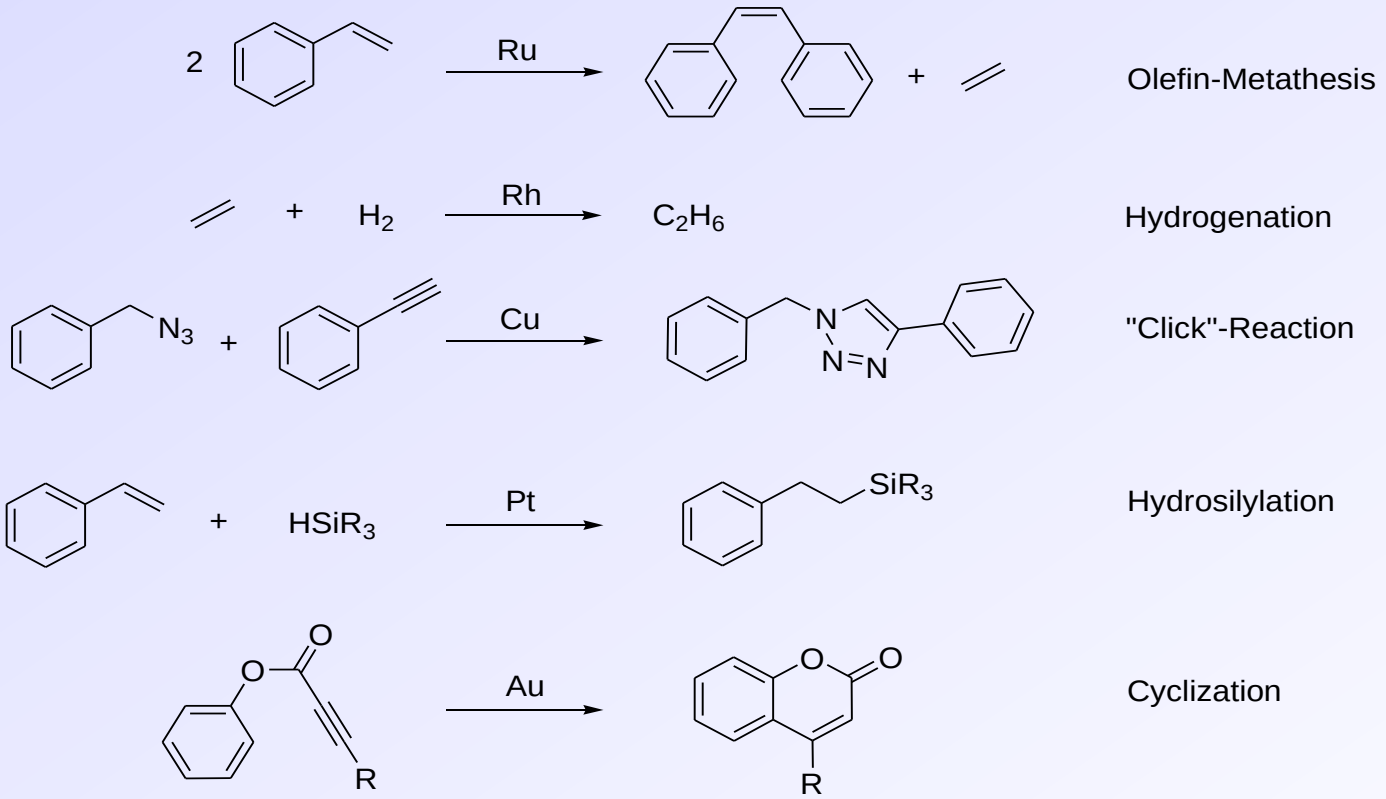


- organometallic compounds
  (direct Carbon-Metal-Bond) with catalytic properties

- metal centre is surrounded by so-called organic ligands

- most important class of catalysts besides the classical heterogeneous, inorganic catalysts

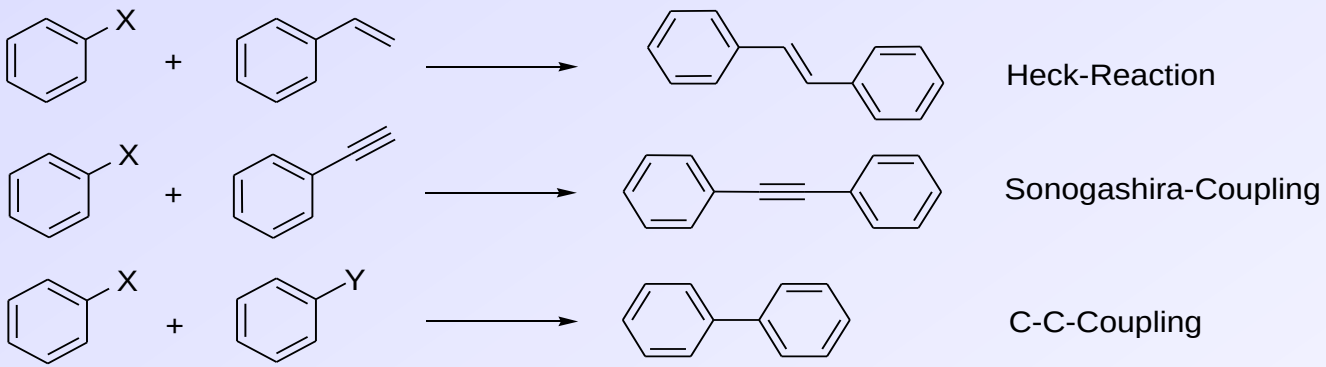
Typical industrial used organometallo-catalyzed reactions



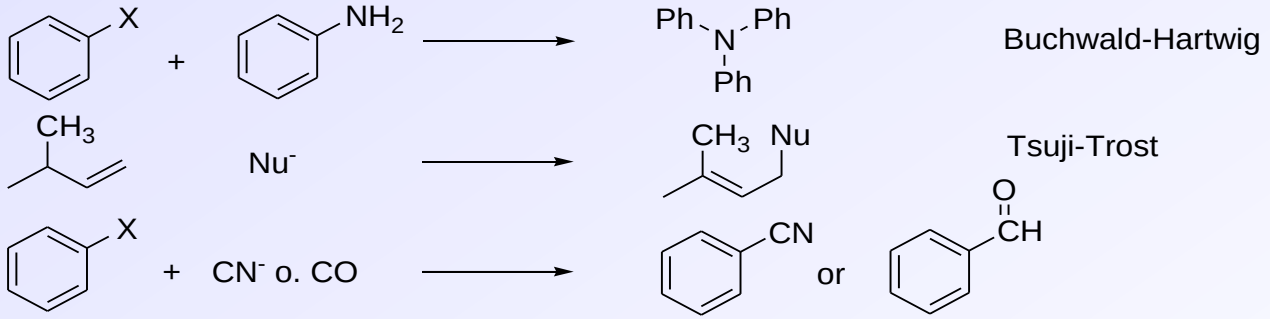
mostly at low temperatures (< 100 °C)
→ textile materials are applicable as carriers!!!

Typical industrial used organometallo- catalyzed reactions

Palladium Catalysis



Y= SnR_3 (Stille), $B(OMe)_2$ (Suzuki), ZnR (Negishi), MgR (Kumada), $Si(OR)_3$ (Hiyama)



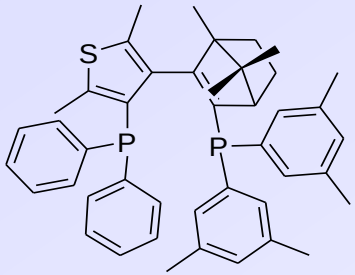
X = Br, I, F, Cl, OTf, N_2BF_4, BF_3K, OTs

mostly at low temperatures (< 100 °C)

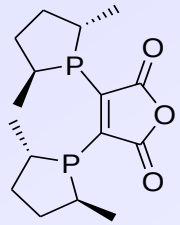
→ textile materials are applicable as carriers!!!

Advantages “heterogenization”

- highly specialized ligands, synthesized in multiple reaction steps
- therefore, high prices!!!
- noble metals used → high prices!!!
- discussion with chemical industry: **keen demand on recycling/reuse strategies!!!**



1 g 740 €



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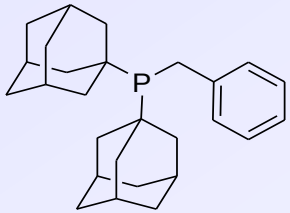

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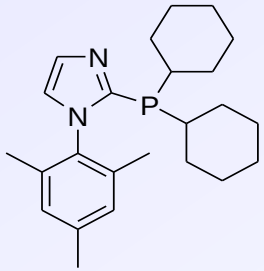

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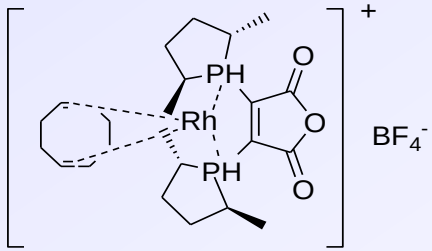
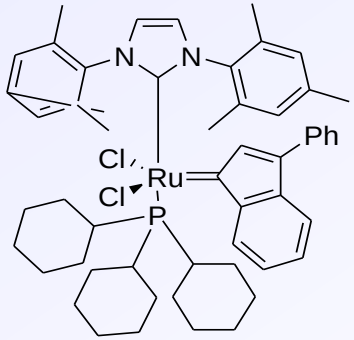


1 g 900 €



1 g 400 €

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German Project IGF No. 15691 N

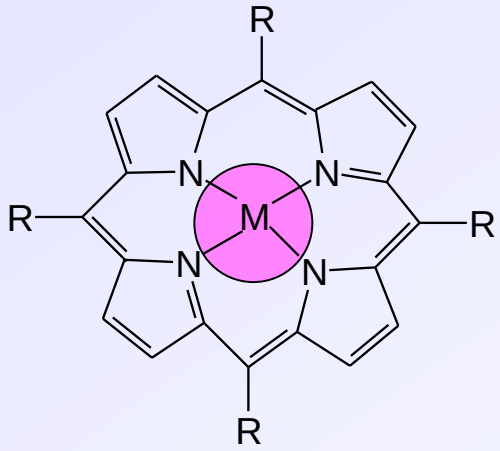
„Immobilization of organometallic Catalysts on textile carrier materials“

Partners

Deutsches Textilforschungszentrum Nord-West e.V., Krefeld
Prof. Dr. E. Schollmeyer
Dr. Klaus Opwis
Dipl.-Chem. Thomas Mayer-Gall

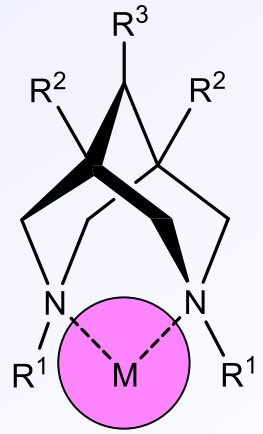
Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr
Prof. Dr. Klaus-Richard Pörschke
Dr. Huiling Cui

Model Systems



- organometallic porphyrin complexes
  - → easy to synthesize
  - → easy to modify (on demand)
  - → rich variety of active species (e.g. Fe, Mn, Ru, Zn)
  - → rich variety of catalyzed reactions

- organometallic bispidine complexes
  - → project partner MPI



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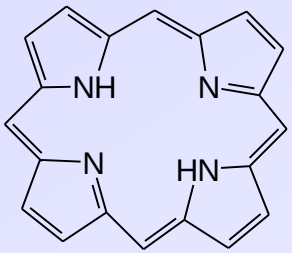
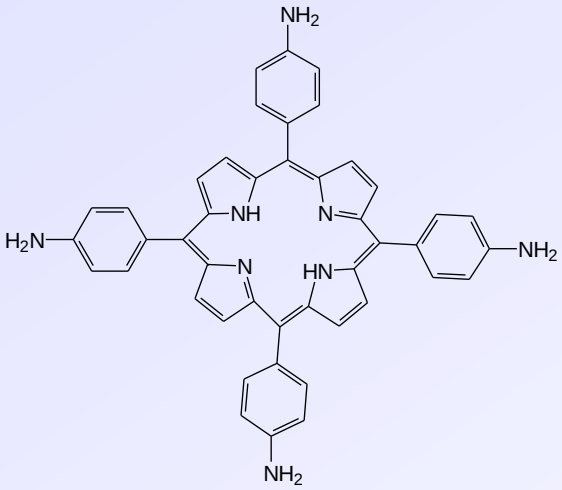
Porphyrins/modified Porphyrins

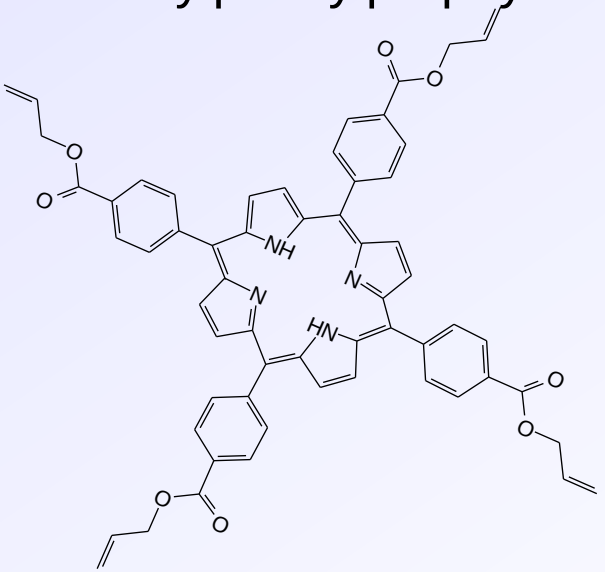
Porphyrin



Tetraaminophenylporphyrin



5,10,15,20-Tetrakis-*p*-allyloxy-carbonylphenylporphyrin



- in nature porphyrins are widespread pigments
- substituted tetrapyrrol ring system
- organometallic porphyrin complexes with metal centre catalyze many chemical reactions (e.g. epoxidations, synthesis of cyclopropane, peptide syntheses)

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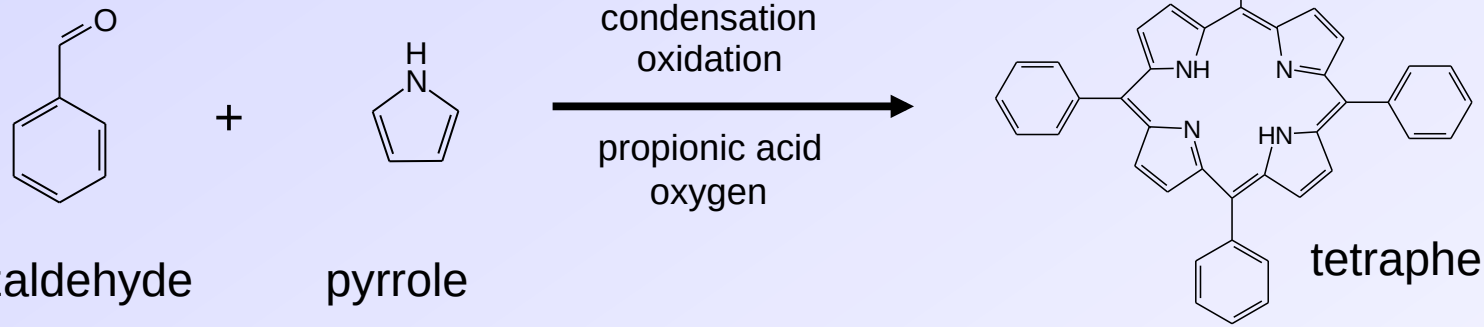
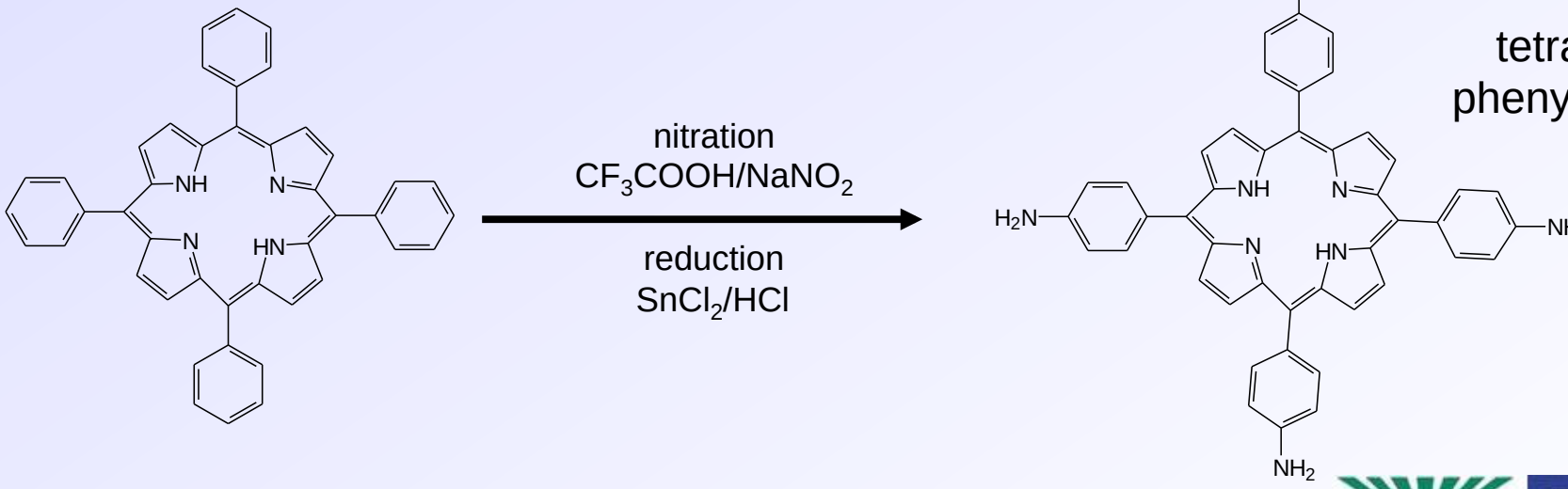
Synthesis of amino-modified Porphyrins



benzaldehyde pyrrole

tetraphenylporphyrin



tetraamino-phenylporphyrin

tetraphenylporphyrin

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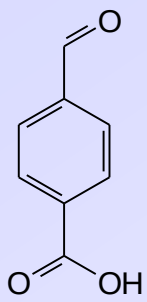
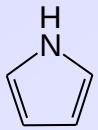
Synthesis of allyl-modified Porphyrins



p-carboxy-benzaldehyde

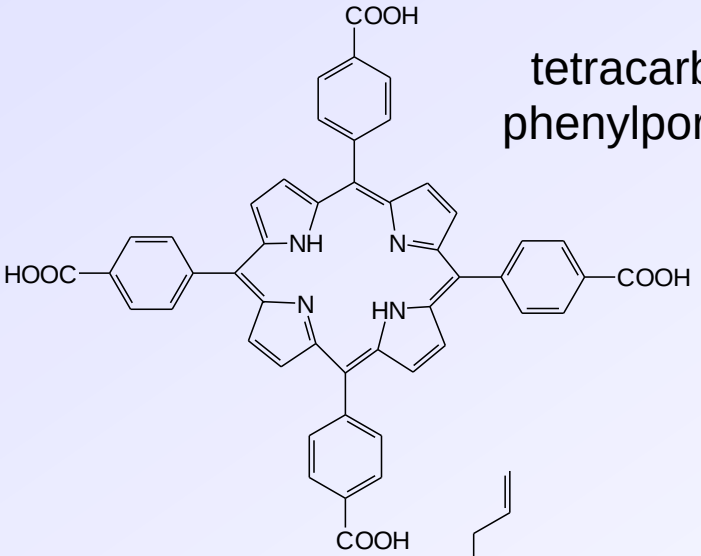
+



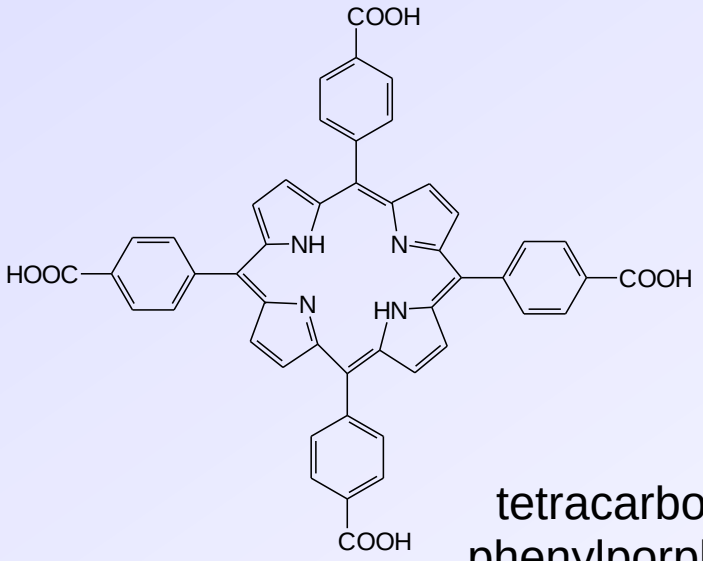
pyrrole

condensation
oxidation

propionic acid
oxygen

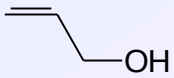


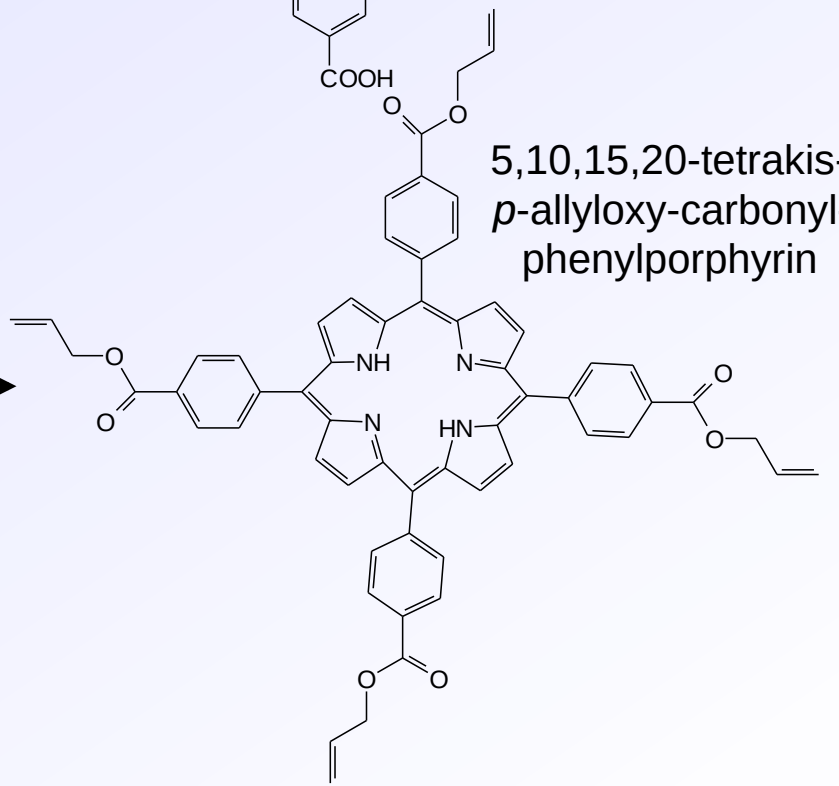
tetracarboxy-phenylporphyrin



tetracarboxy-phenylporphyrin

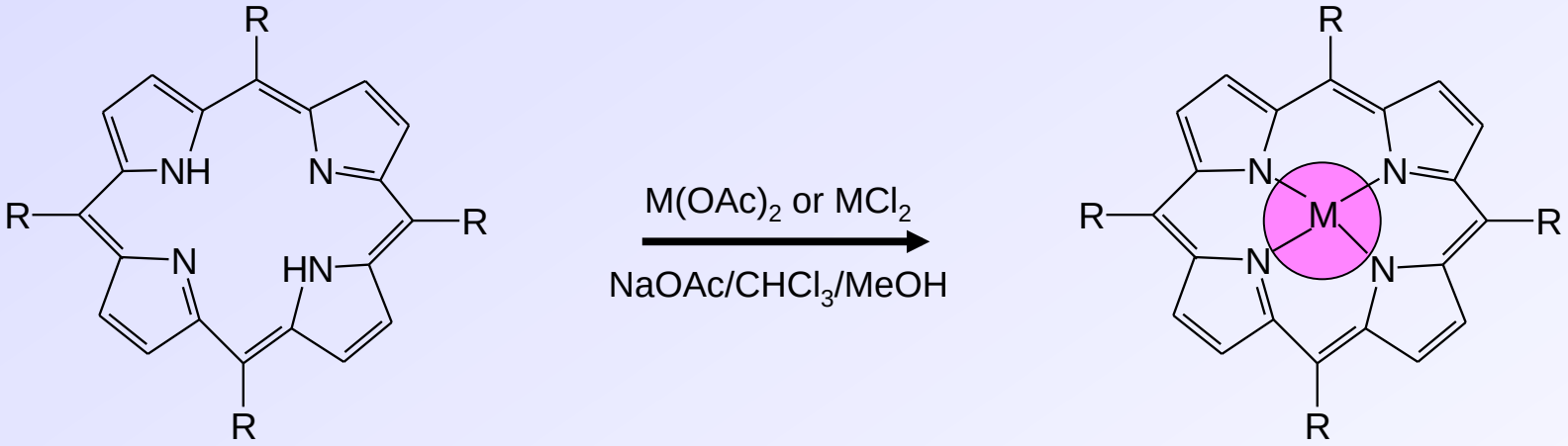
esterification
allyl alcohol





5,10,15,20-tetrakis-*p*-allyloxy-carbonyl-phenylporphyrin

Complex Formation



free porphyrin

active catalyst

Metallocomplexes of Porphyrins

pure porphyrin	iron porphyrin (Fe)	manganese porphyrin (Mn)	zinc porphyrin (Zn)

Immobilization Strategies (I)

Photochemical Route:

- use of UV-absorbing polymers (e.g. polyester)
- synthesis of adequate functionalized porphyrins for grafting reactions (e.g. allyl-modified)
- UV-irradiation → generation of surface radicals (e.g. use of excimer-UV-lamps)
- covalent porphyrin attachment by photo-induced grafting

Wet Chemical Route:

- use of polymers with functional groups (e.g. polyamide: amino groups)
- synthesis of adequate functionalized porphyrins (e.g. amino-modified)
- use of bifunctional anchor molecules for covalent attachment (e.g. glutaraldehyde (GDA), cyanuric chloride, diisocyanates or thioisocyanates)

Thermal Route:

- independent from textile substrate (e.g. polyamide **or** polyester)
- synthesis of adequate functionalized porphyrins (e.g. amino-modified or carboxy-modified)
- use of polymeric cross-linking agents
- thermal fixation

Immobilization Strategies (II)

Route I:

Step 1: immobilization of the free porphyrin

Step 2: subsequent complex formation

Advantage: individual choice of the active catalyst possible

Disadvantage: cleaning of the carriers from excess metal necessary

Route II:

Step 1: complex formation

Step 2: subsequent immobilization of the active porphyrin

Advantage: optimized catalyst-ligand system for one reaction

Disadvantage: limited application depending on the metal used

Photo-chemical immobilization of allyl-modified porphyrins (UV)

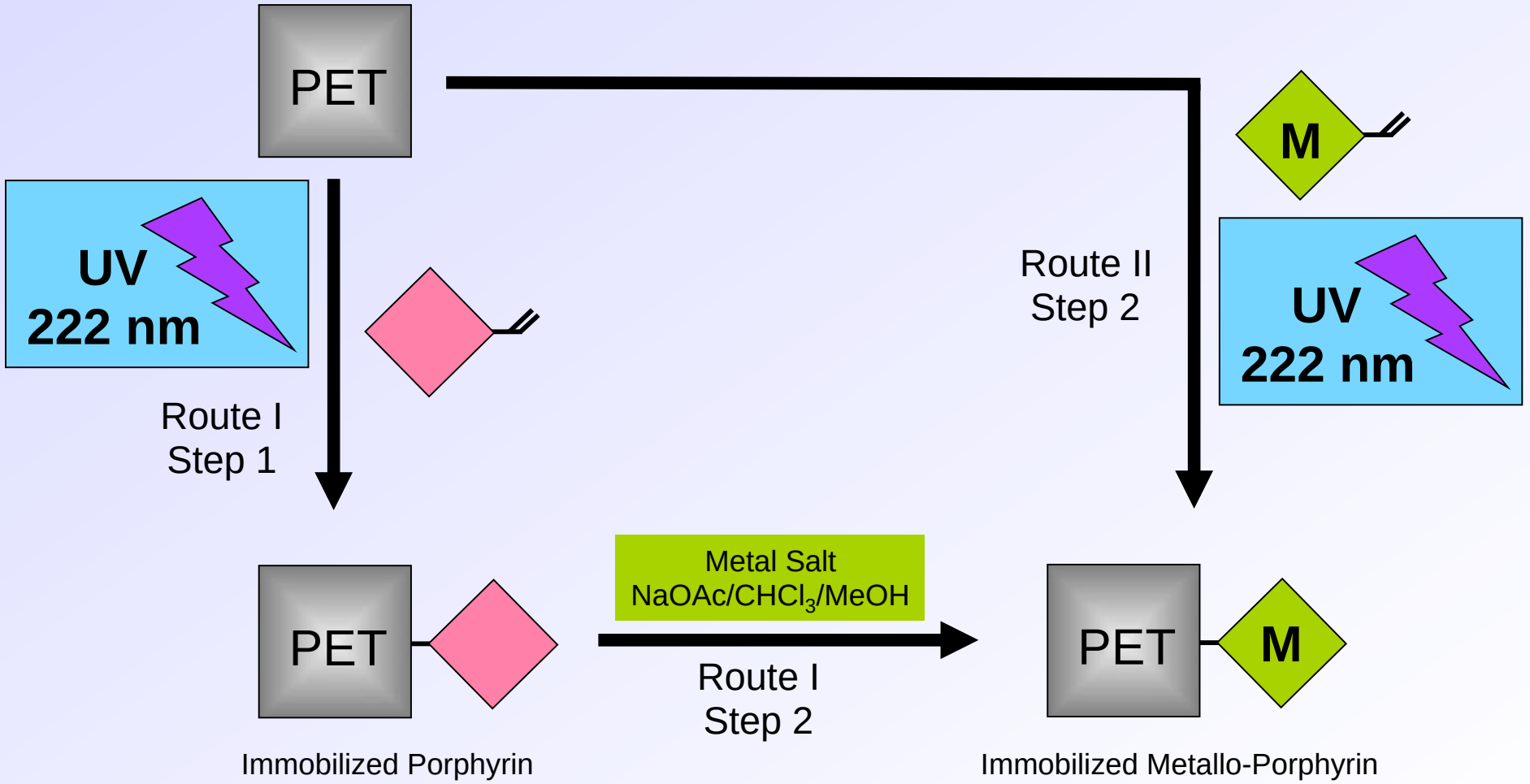
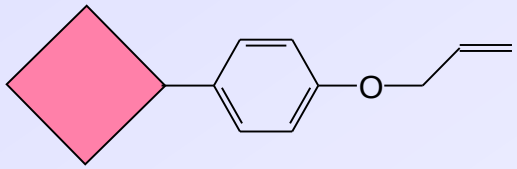
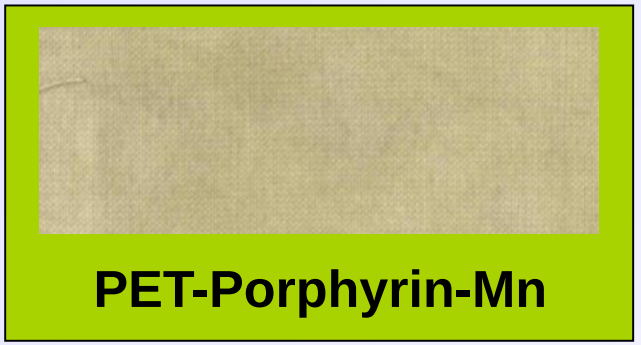


Photo-chemical immobilization of allyl-modified porphyrins

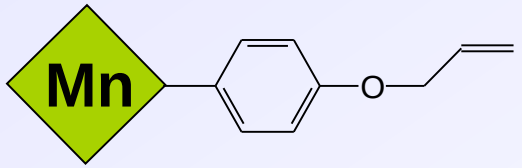
Photographs

PET-Porphyrin

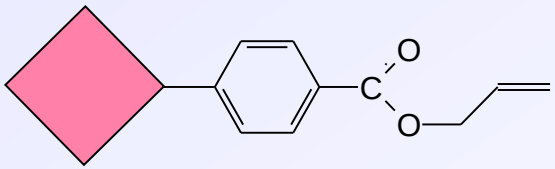


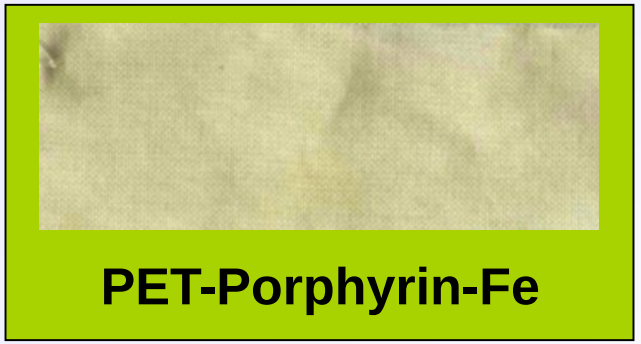


PET-Porphyrin-Mn

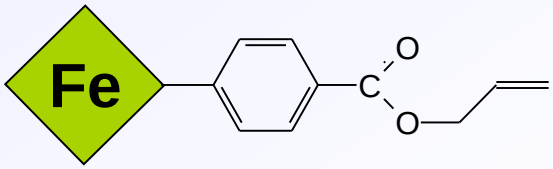


PET-Porphyrin

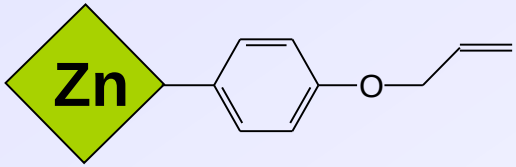


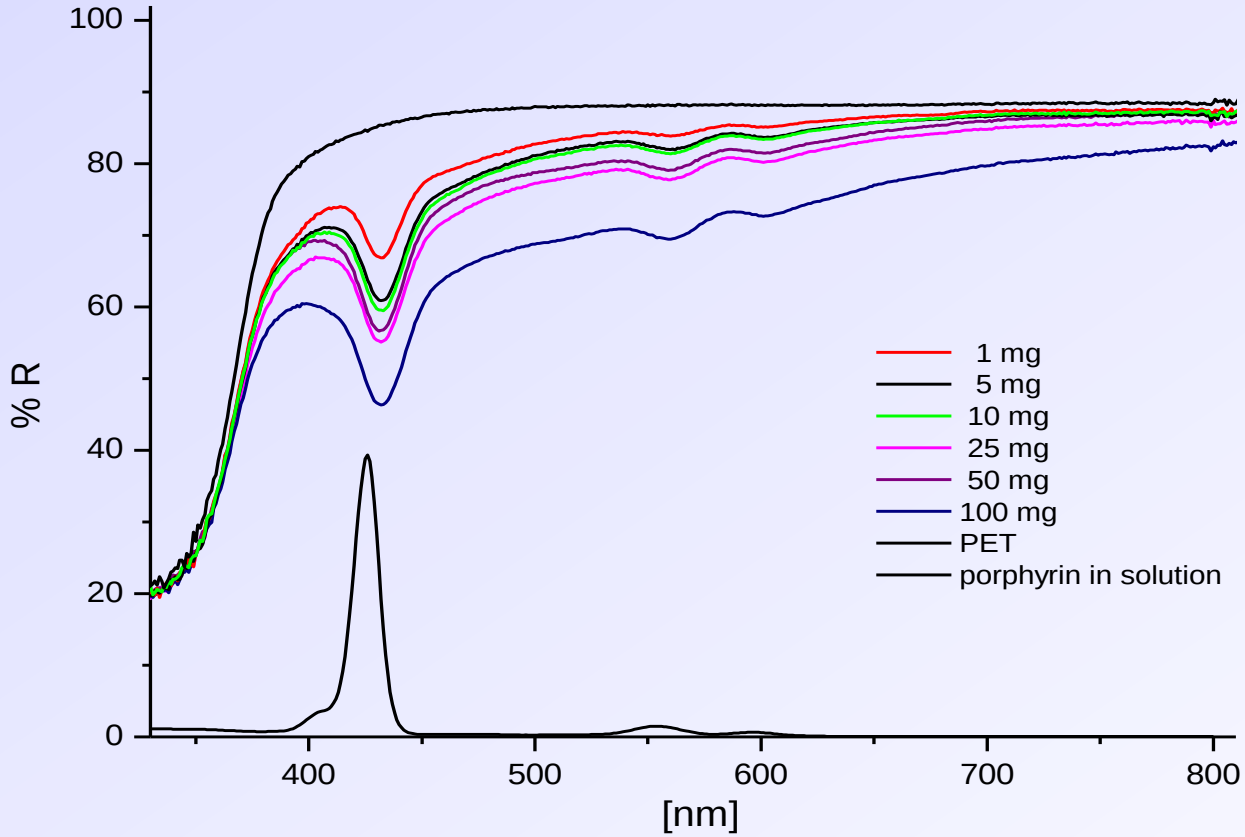


PET-Porphyrin-Fe



Vis-Spectra of immobilized allyl-modified porphyrins





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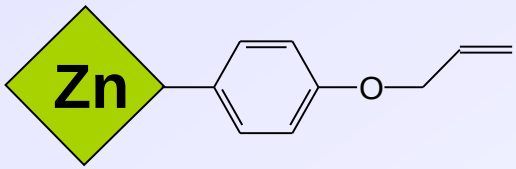
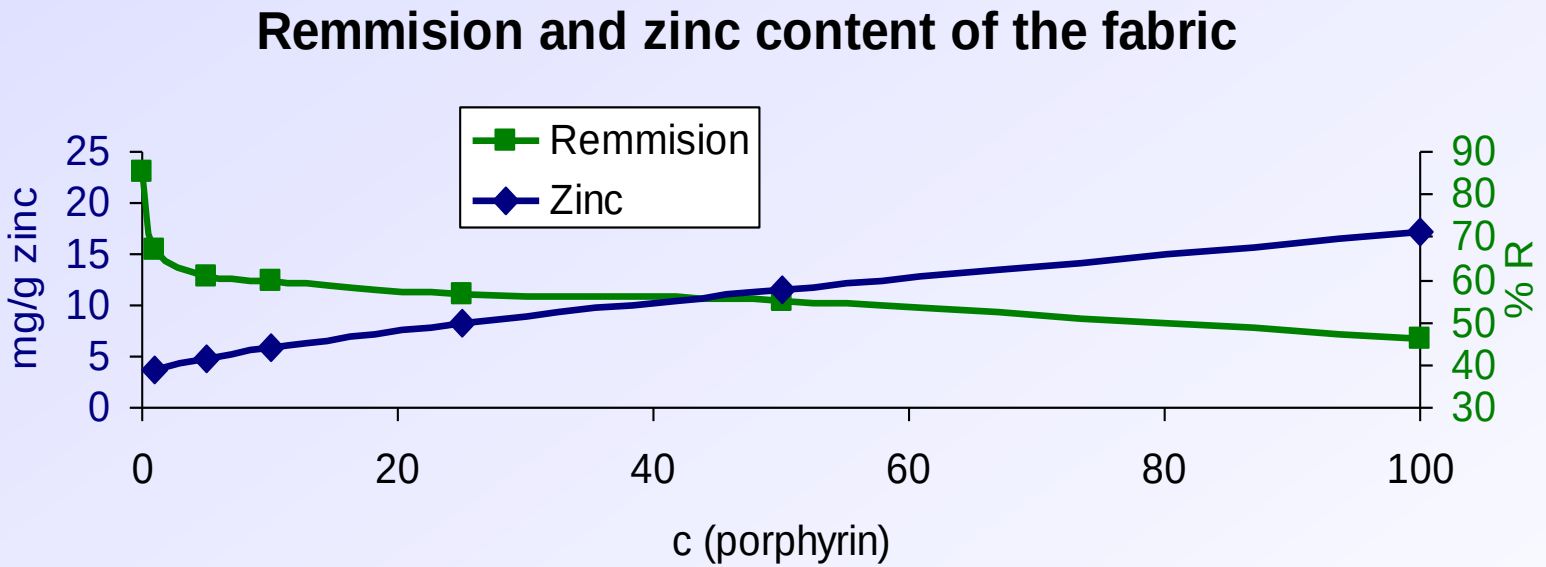
Vis-Spectra of immobilized allyl-modified porphyrins





433 nm

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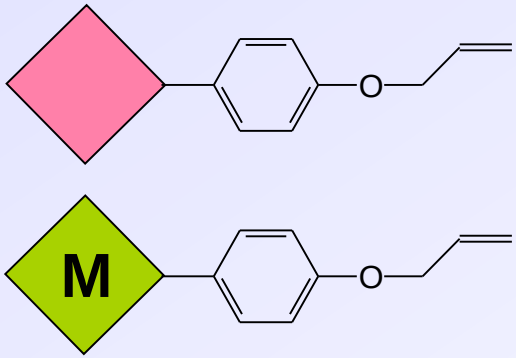
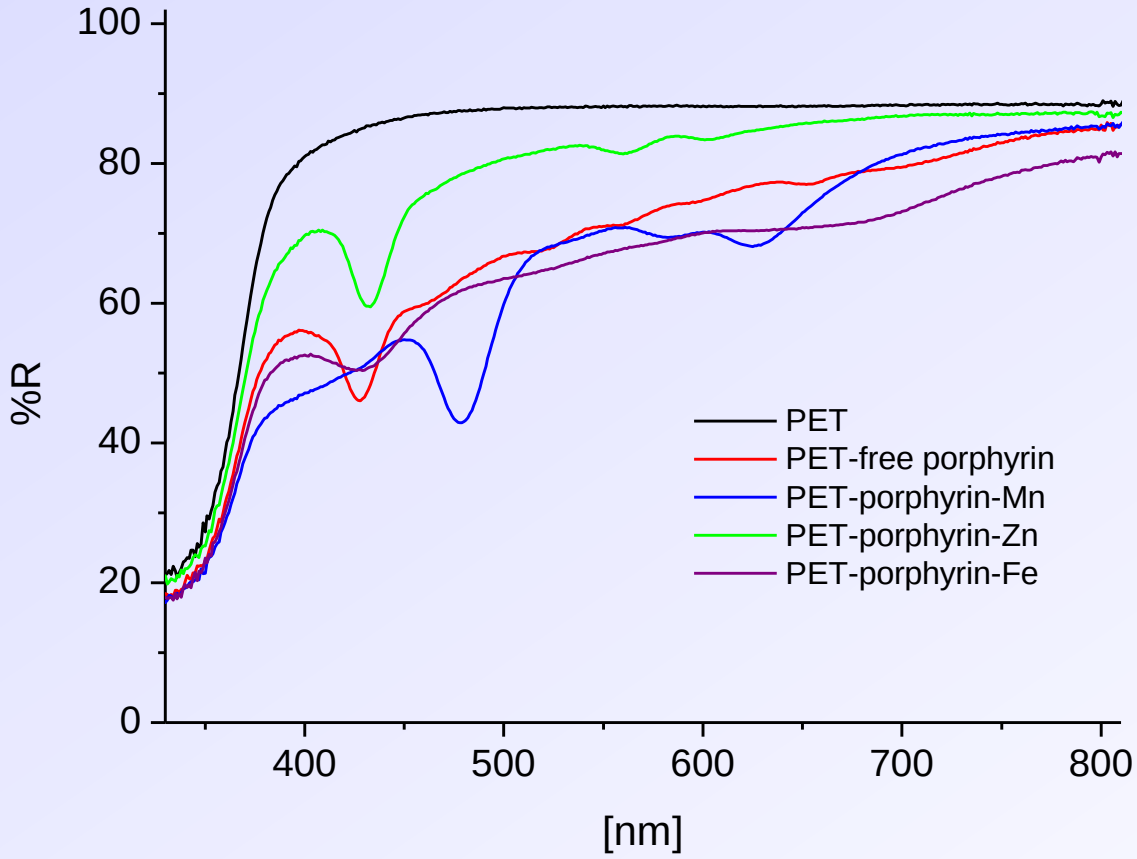
Vis-Spectra of immobilized allyl-modified porphyrins



M = **Manganese**
Zinc
Iron



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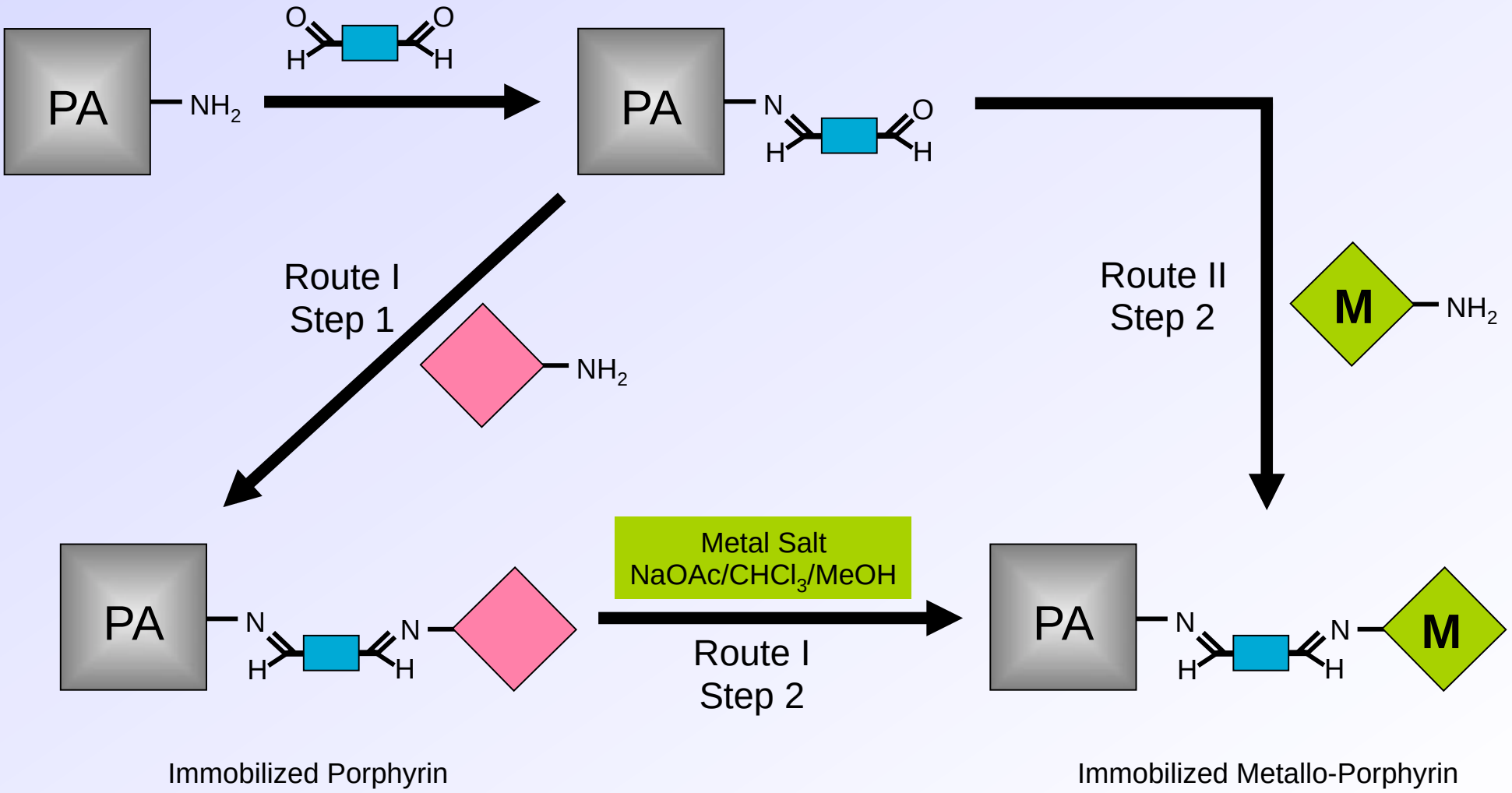
Wet chemical immobilization of amino-modified porphyrins (via GDA)

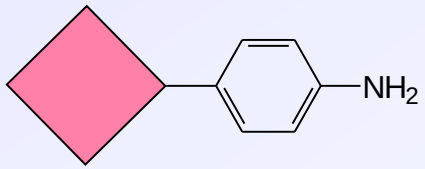


Wet chemical immobilization of amino-modified porphyrins

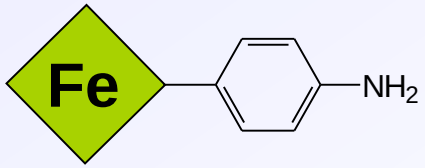
Photographs

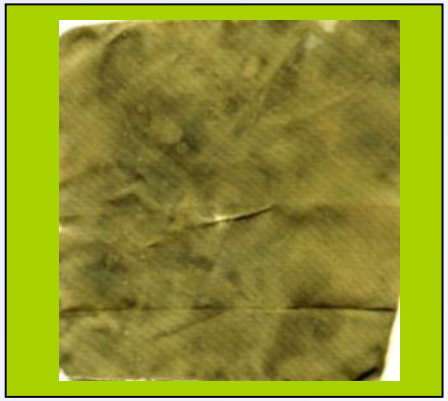
PA blank

PA Porphyrin

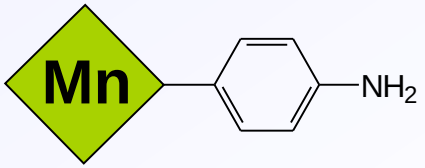


PA Porphyrin-Fe





PA Porphyrin-Mn



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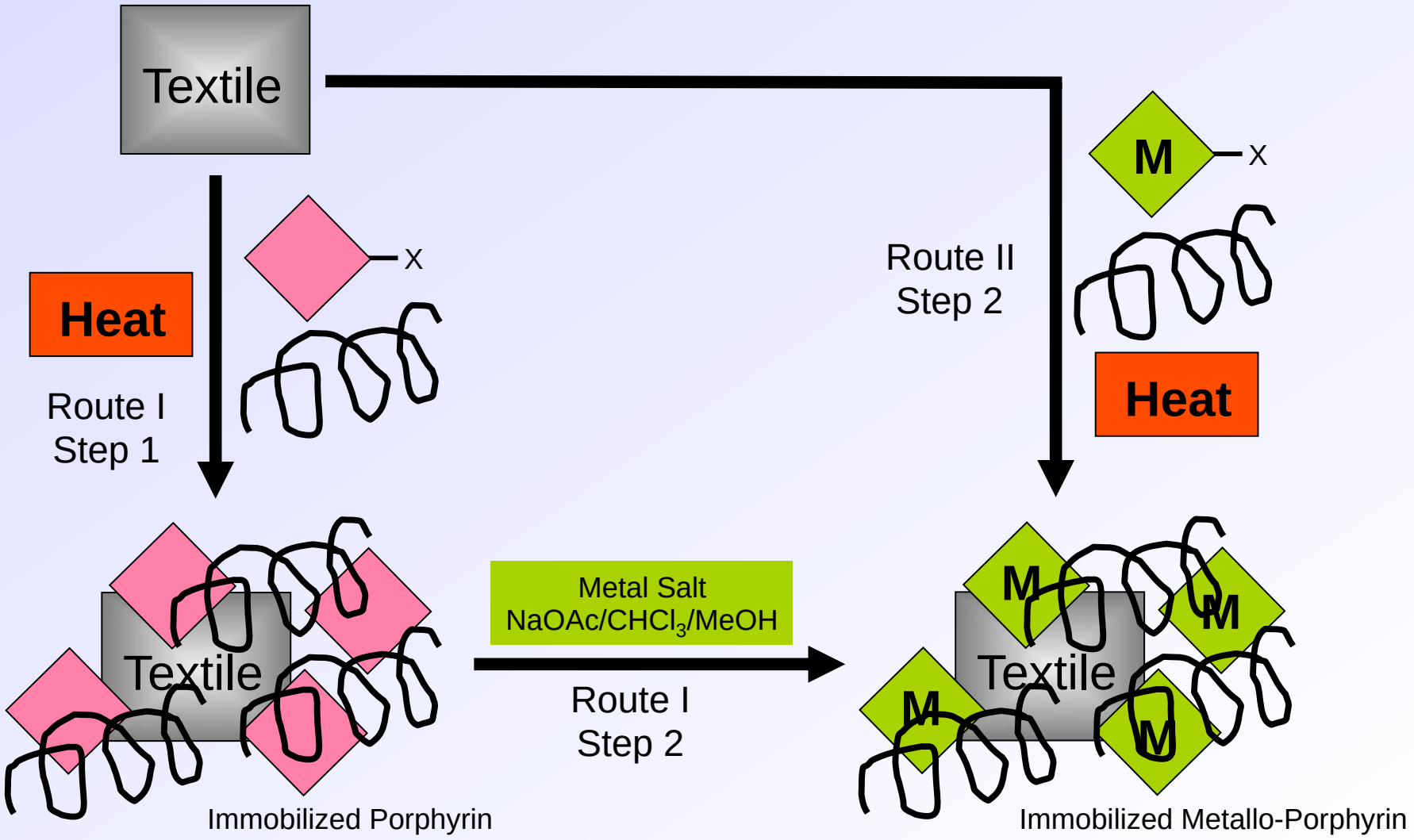
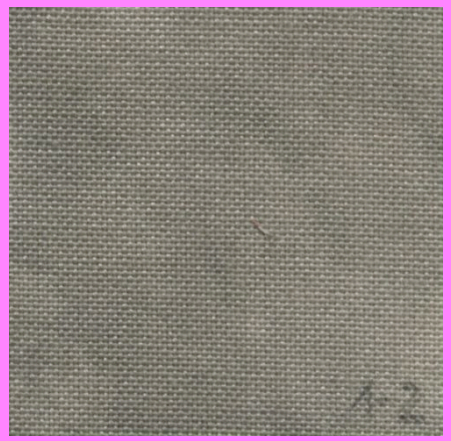
Thermal immobilization of modified porphyrins (cross-linker/heat)



Thermal immobilization of modified porphyrins

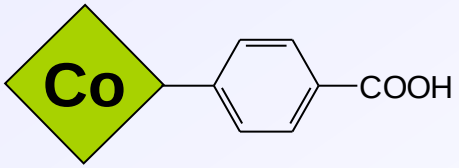
Photographs

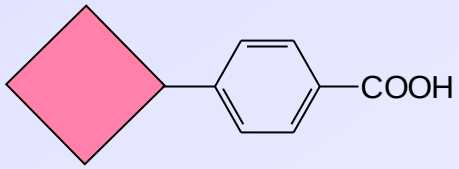


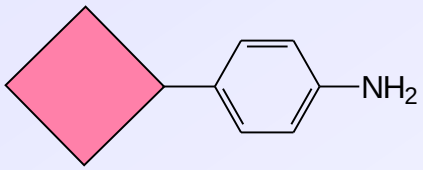
PET-Porphyrin

PET-Porphyrin

PET-Porphyrin-Co





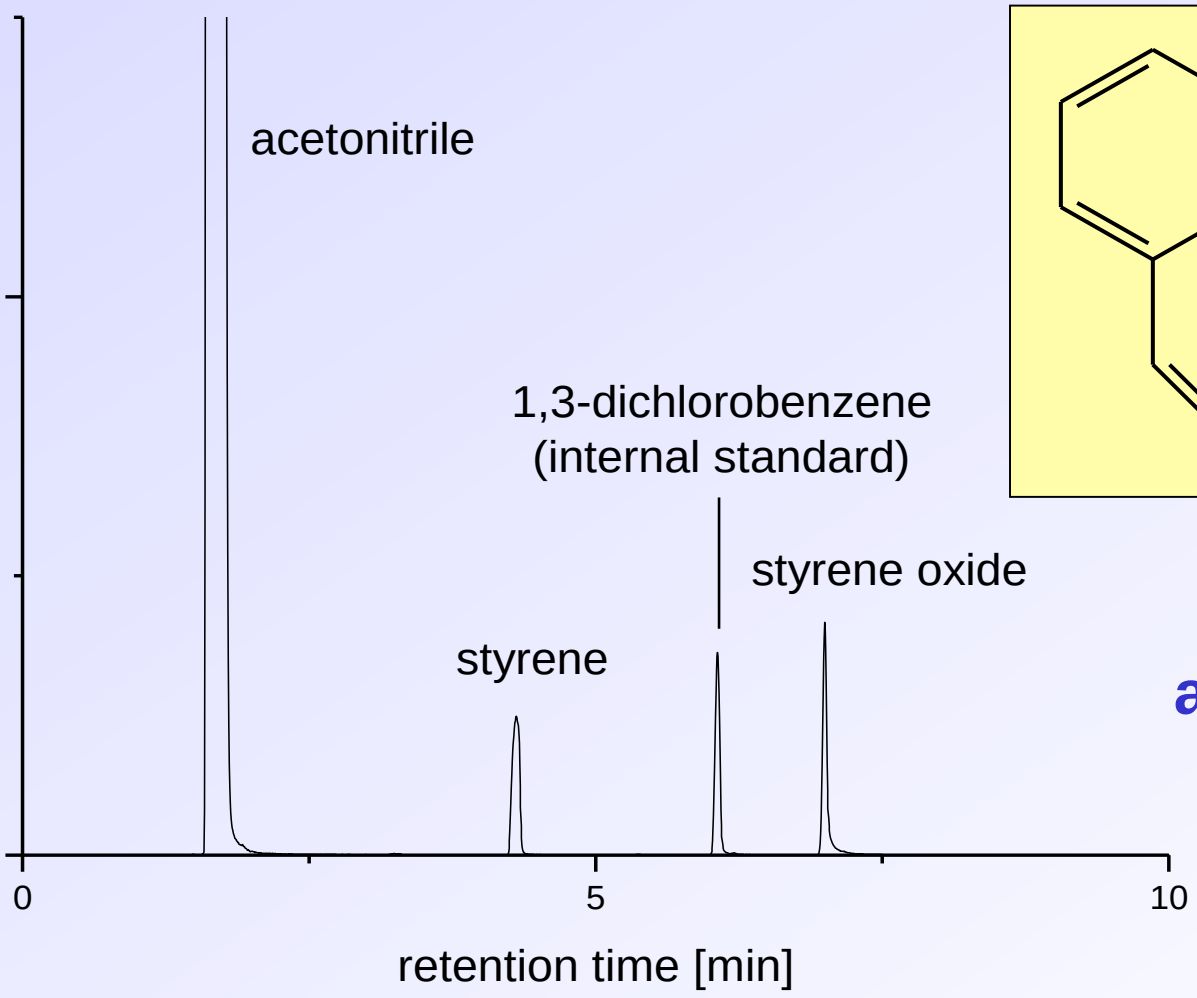


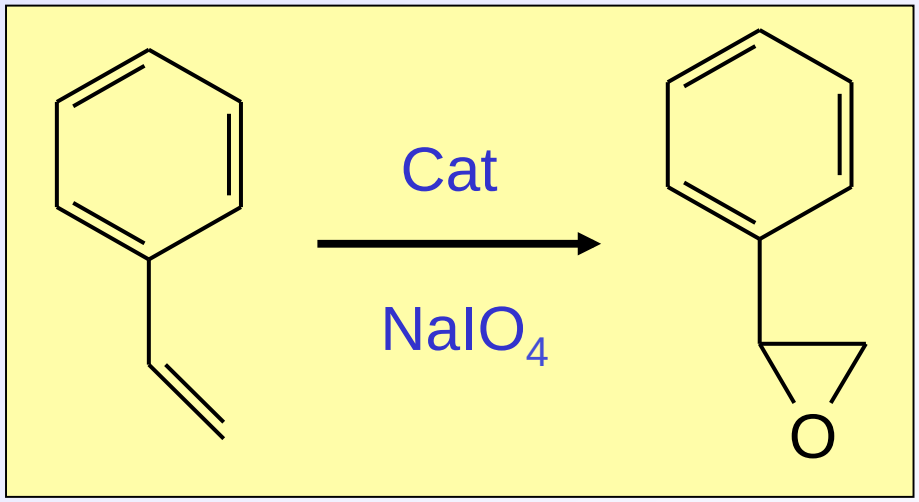
PA-Porphyrin-Co

Activity

Test Reaction

Epoxidation of Styrene with immobilized M-Porphyrin





analyzed via GC-MS

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Activity/Yield

Test Reaction

Epoxidation of Styrene with immobilized M-Porphyrin

	Fe	Mn
Homogeneous	66 %	50 %
Route I	54 %	52 %
Route II	65 %	52 %

Summary

- porphyrins and metallo-porphyrins can be fixed durably on various textile carrier materials
- different immobilization strategies are suitable
- immobilized metallo-porphyrins show catalytic activity

Outlook

- other organometallic catalysts
  (co-operation with MPI für Kohlenforschung, Mülheim)
- organo-catalysts, special textile constructions

→ development of ***Technical Textiles with Catalytic Properties***

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Thank you for your attention!

Acknowledgement

IGF No. 15691 N