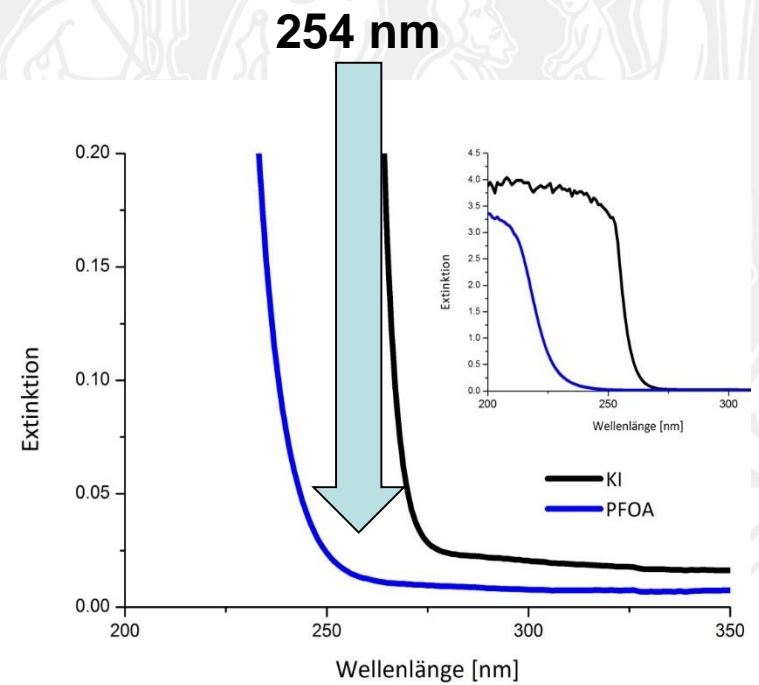
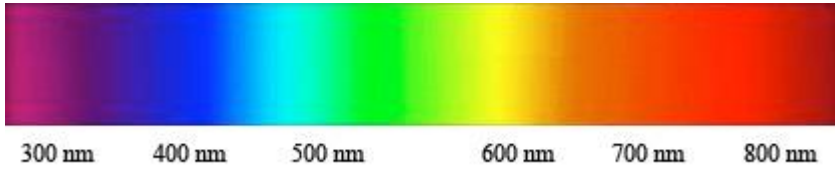
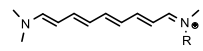
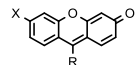
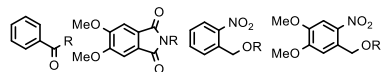
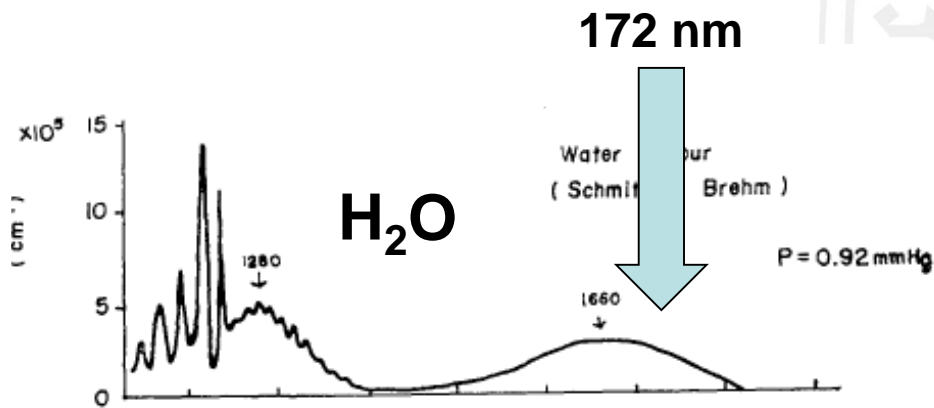


**Sichtbares Licht ist ~~nicht~~ energiereich
genug, um Abbaureaktionen in Wasser
zu initiieren.**

**Axel G. Griesbeck
Department of Chemistry
University of Cologne**

Fachforum Ressourcen-Wasser 30_11_2017

- Licht
- Pollutants (=Schadstoffe)
- Wasser



PFOA Perfluorooctanoic acid

Organic pollutants ?

At the **end** of a production process = side-products, undesired but unavoidable products, waste, catalysts (not recyclable), solvents

In the **middle** of a production process: condensation products, elimination or fragmentation products (reagent or substrate derived)

In the **beginning** of a production process: impurities in substrates, reagents, solvents, catalysts

How to degradate organic pollutants ?

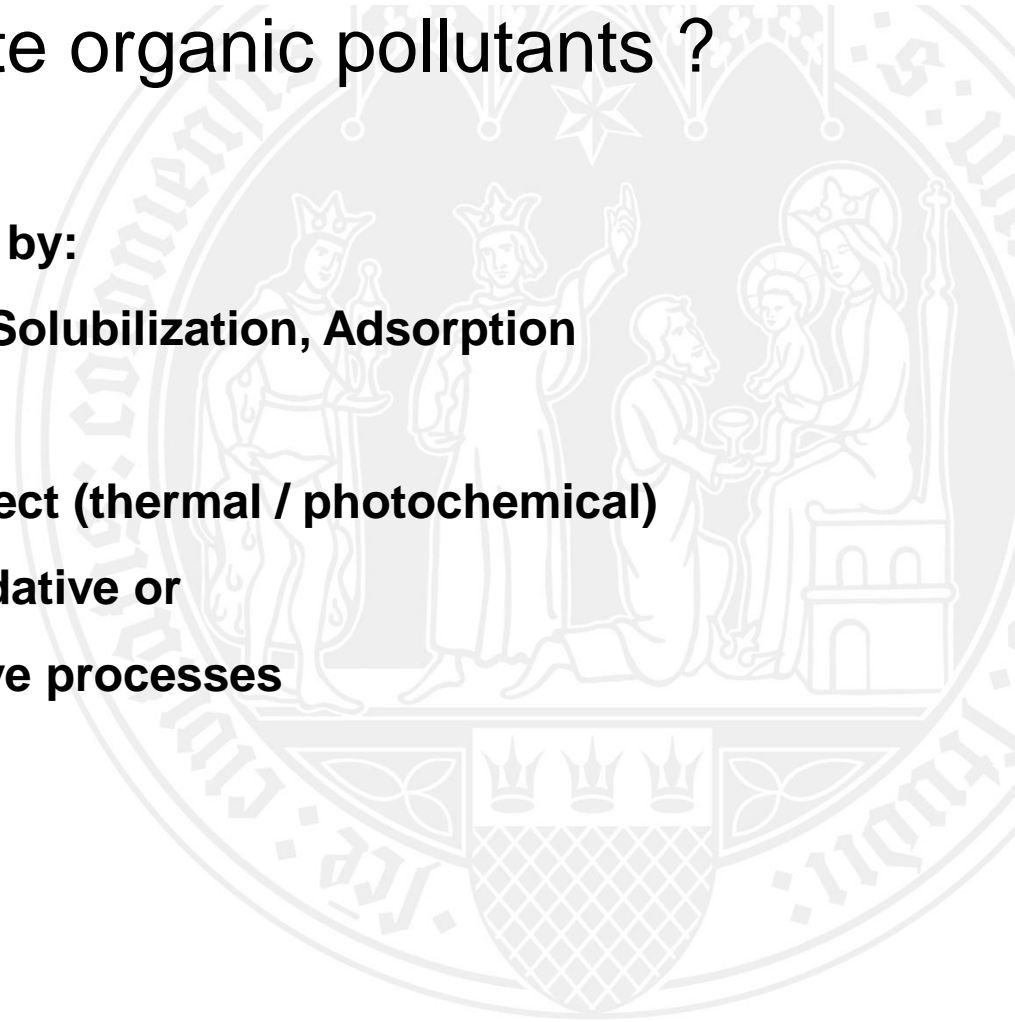
by:

Physical Processes: Solubilization, Adsorption

Chemical Processes: Direct (thermal / photochemical)

Oxidative or

Reductive processes



Oxidative approaches

“the normal path”

- with oxygen in catalytic processes or by combustion
- with chemical oxidants such as ozone, hydrogen peroxide, persulfate, etc.
- activated oxygen processes with ROS (reactive oxygen species) such as superoxide, singlet oxygen, OH radicals (from Fenton processes)
- photochemical oxidation / oxygenation: UV-Vis and oxygen, UV and ozone, UV and hydrogen peroxide (“photo-Fenton”)

Redox approaches

- **coupled reduction and oxidation processes, e.g. the gas Otto engine with controlled three-way catalytic converter**
- **separated oxidation and reduction steps, e.g. in the Diesel combustion converter with urea as a source for the reductant ammonia**



Reduction approaches

“the unusual path”

- with metals as (stoichiometric) reductants
- with catalytic metals and stoichiometric trivial reductants
- “trivial reductants”: hydrogen, ammonia, amines.....
- cathodic

Reduction approaches

The best solution?

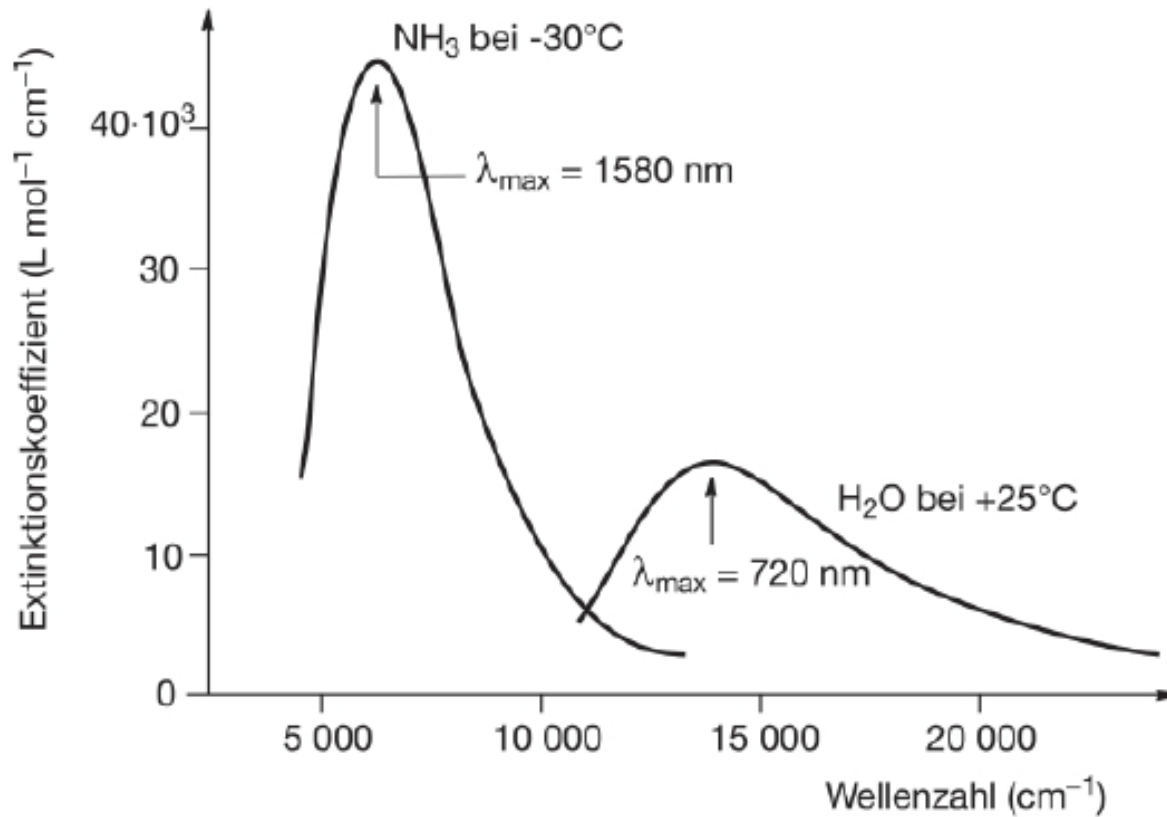
Take an electron!

In water, the reduction potential of an (hydrated, “wet”) electron is -2.7 V (-2 V in liquid ammonia).

„Organic Reducing Agent Sets New Record
Electron Donors: Bispyridinylidene has the highest
known redox potential (-1.7 V) for a neutral organic
Molecule rivaling alkali metals“
Murphy and Dyker, *Angew. Chem.* **2015**

Reduction approaches

Spectral properties



How to generate wet electrons?

Direct and indirect

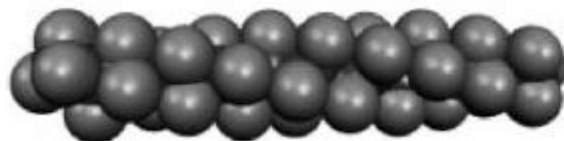
- **direct with ionizing radiation (not really useful)**
- **indirect with VUV (120-180 nm)**
- **indirect with UV (200-280 nm) and reagents**
- **indirect with Vis (400-600 nm) and two-photon reagents**

The incriminated class of compound: PFC (polyfluorinated compounds)

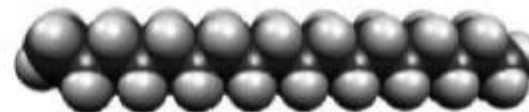
{earlier: PFT}

„Fluorine leaves nobody indifferent; it inflames emotions be that of affections or aversions. As a substituent, it is rarely boring, always good for a surprise, but often completely unpredictable.“ ^[23]

Schlosser, 1998



PF-octane



octane

Examples

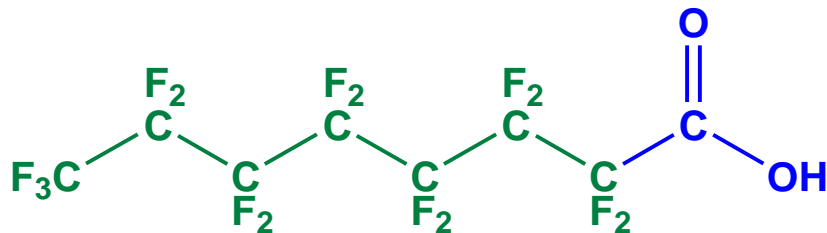
PFT **P**erfluortensides (about 800 known)

PFC **P**olyfluorinated **c**ompounds

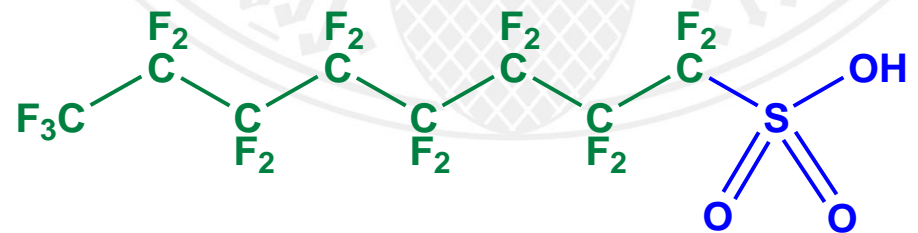
PFOA **P**erfluorooctanoic **a**cid

PFOS **P**erfluorooctane **s**ulfonic acid

PFOA



PFOS



PFTs are:

- **water soluble and surface active (amphiphilic)**
- chemically and thermally **very stable** (C-F bond energy 490 kJ/Mol; compare with 415 kJ/Mol for CH)
- anthropogenic = no enzymatic attacks

⇒ **numerous applications**

PFT and PFCs are used:

➤ PFT and derivatives: excellent impregnation compounds (for waterproofing applications)

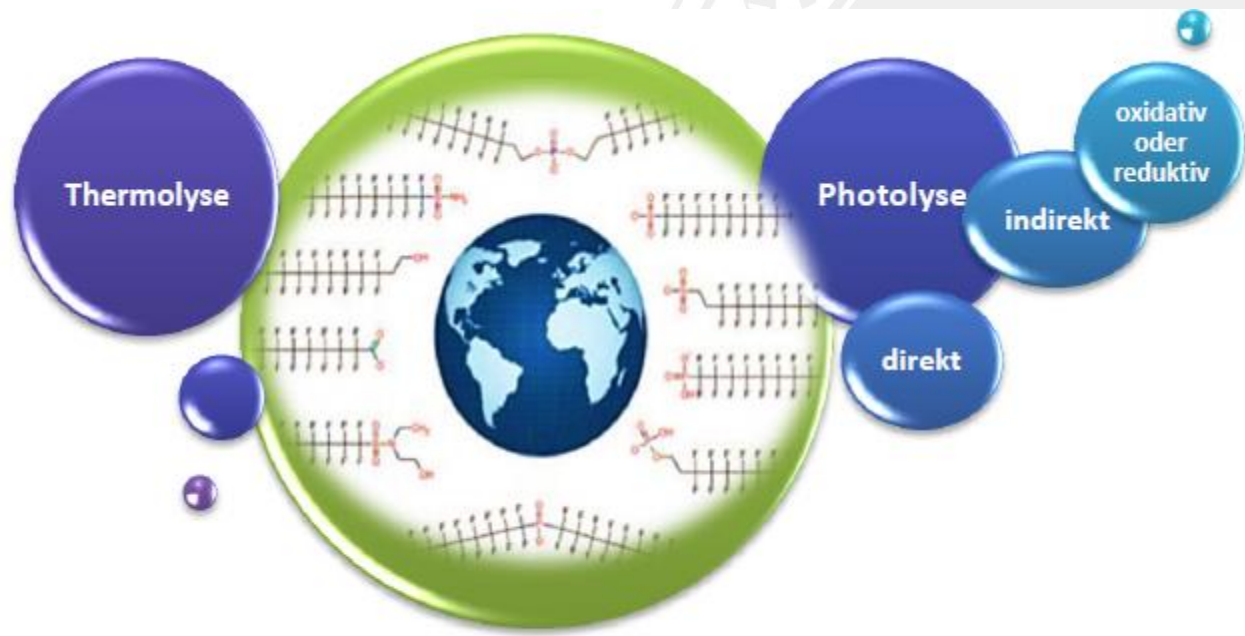
➤ PFT-applications: Surface modification and coating, fire extinguishing, electroplating...

➤ Products with PFC: numerous

products for industrial and household applications.....

textiles, paper, carpets, furs, leather, sprays, cleaning, membranes, packaging, cosmetics.....





Degrading PFC reductively (1)



172 nm photolysis:

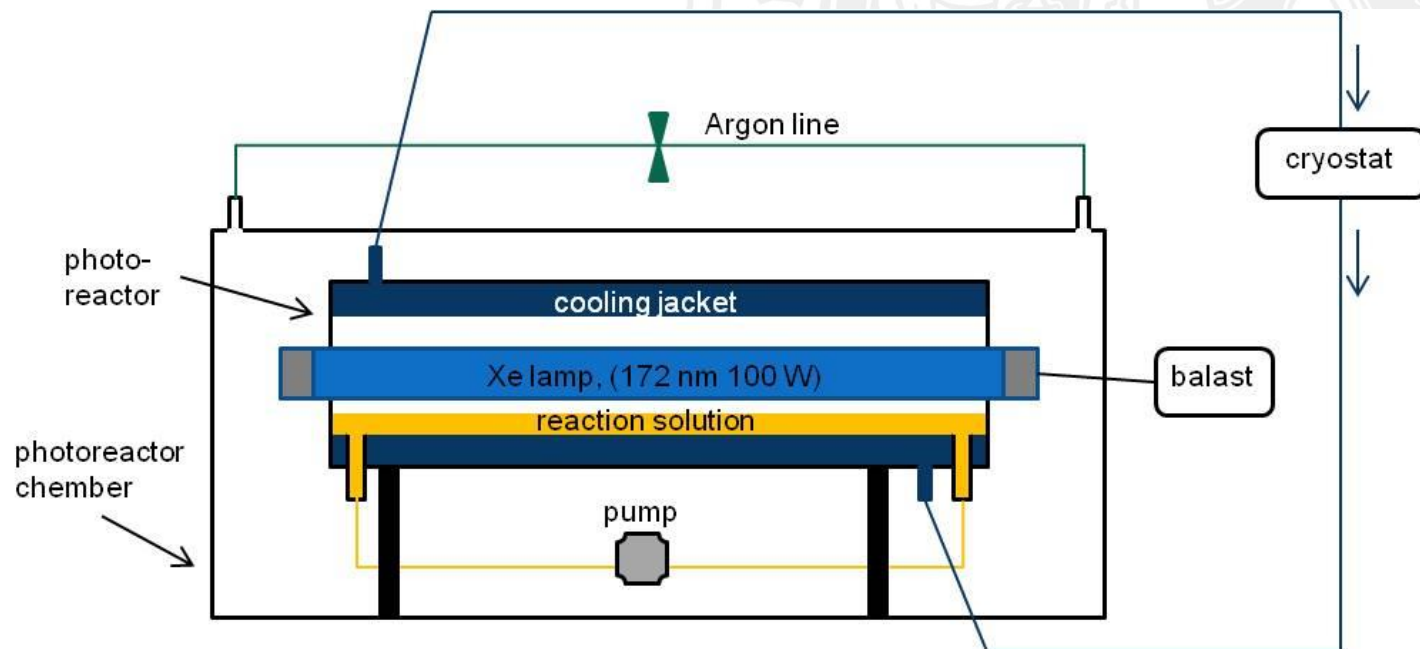
generates hydrogen atoms and OH radicals; hydrogen atoms are acidic (!!)
and generate wet electrons

Degrading PFC reductively (2)

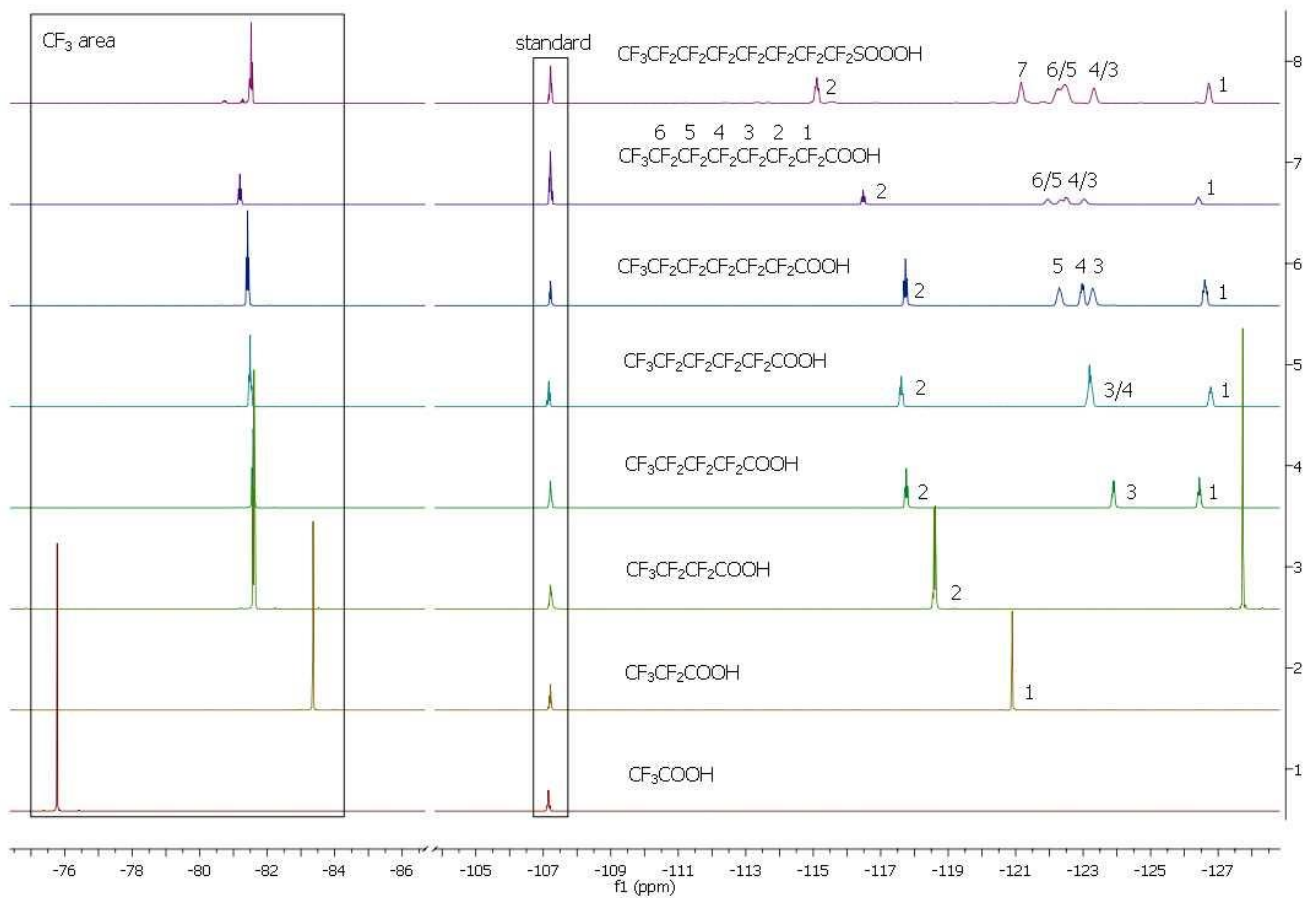


254 nm photolysis in water / iodine:
generates – from three iodines - two wet
electrons and – subsequently triiodine I_3^-

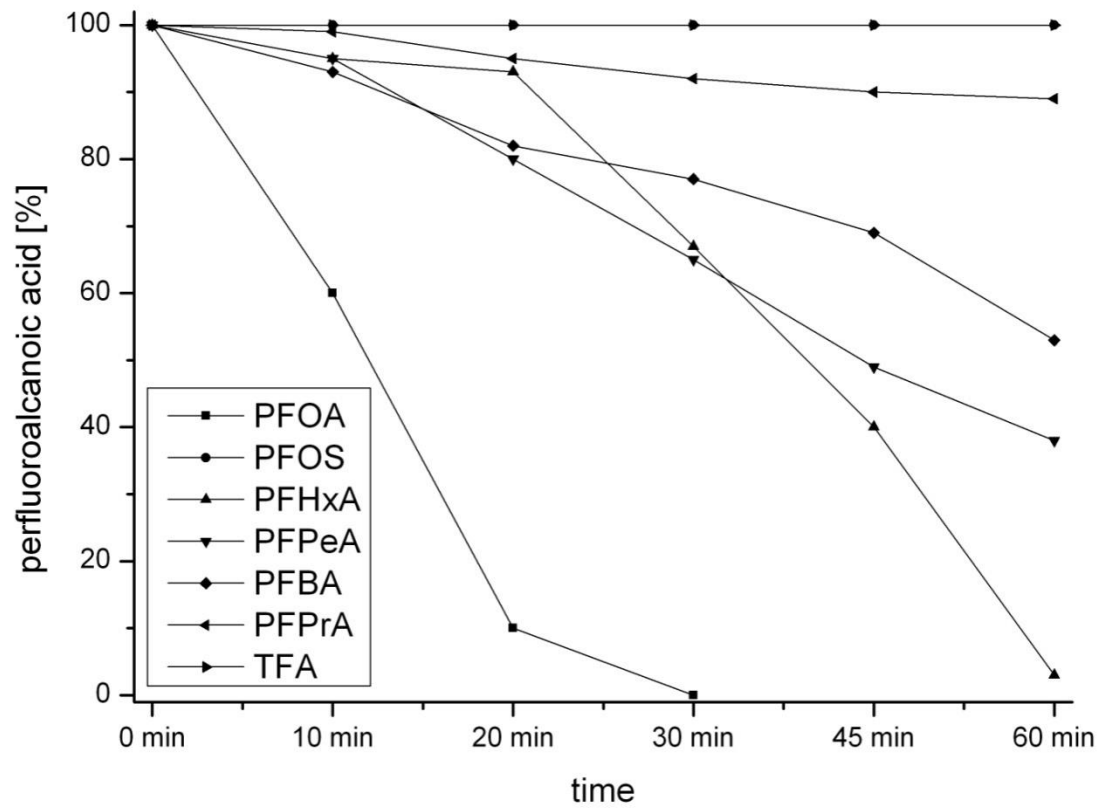
Method 1



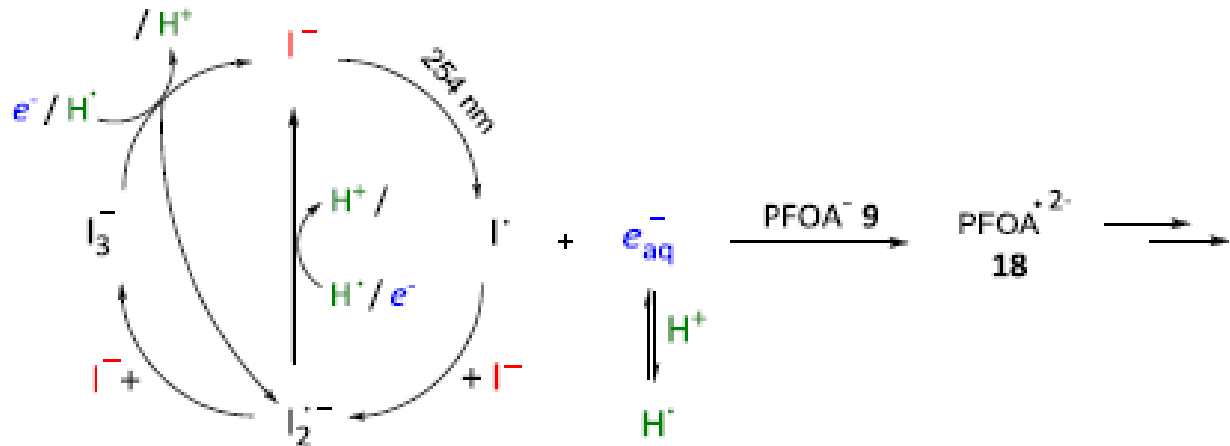
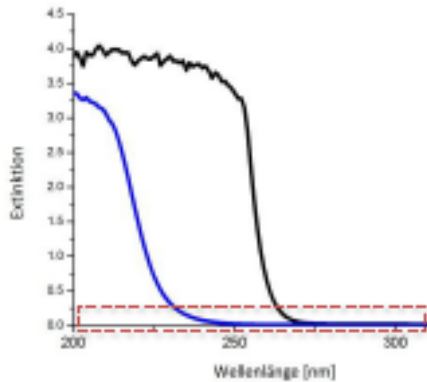
Method 1



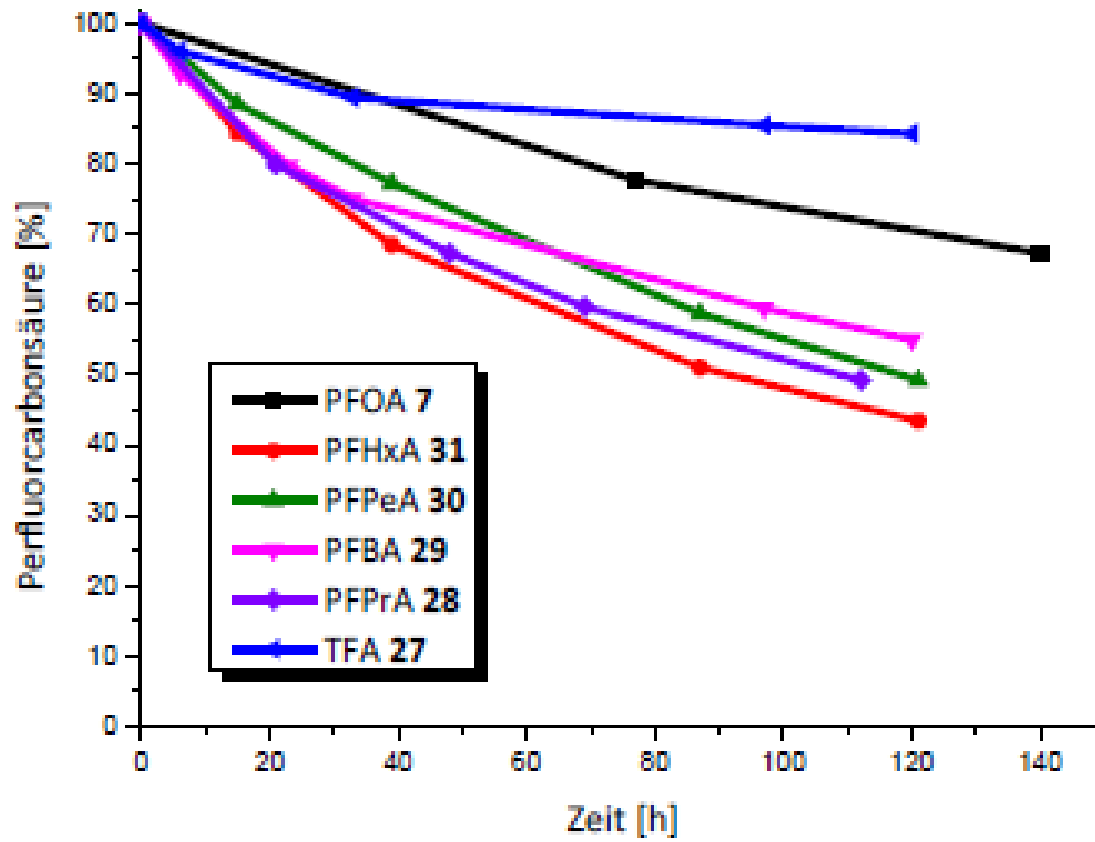
Method 1



Degrading PFC reductively (2)



Degrading PFC reductively (2)



Degrading PFC reductively: many open questions!

- methods are compatible, fluoride is formed, perfluoro alkanonic acids (i.e. the anions, pKs around 1) are “C1 or C2 shortened”
- the longer the chain the faster degraded
- C3 very slow and C2 (trifluoro acetic acid) is no longer reactive.

→→ *where is the electron accepted??*

(σ^*_{CF} or σ^*_{CC} ??)

→→ *LUMO-energies dependent on the chain lengths?*

Sichtbares Licht ist zu energiearm!!

Energie



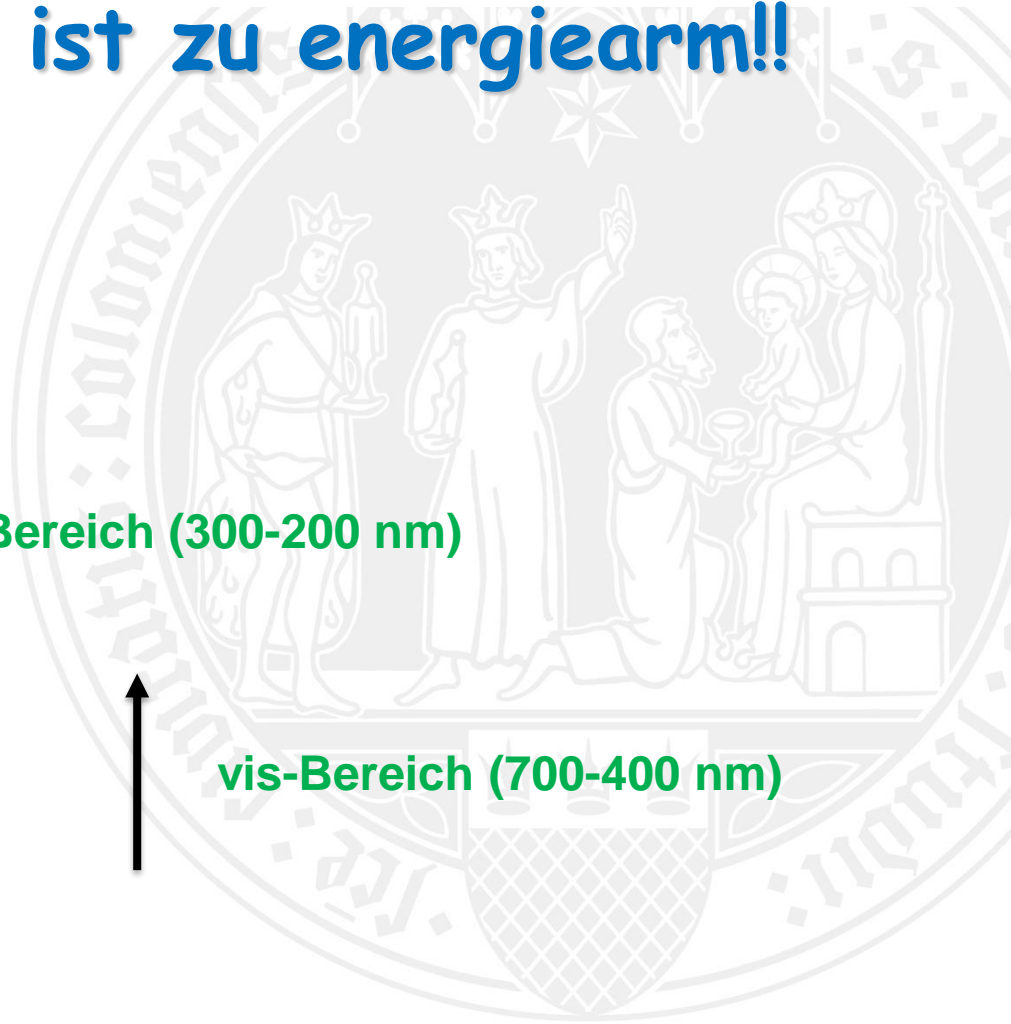
Aktivierung



UV-Bereich (300-200 nm)

vis-Bereich (700-400 nm)

Substrat



Sichtbares Licht kann verdoppelt werden!

Energie



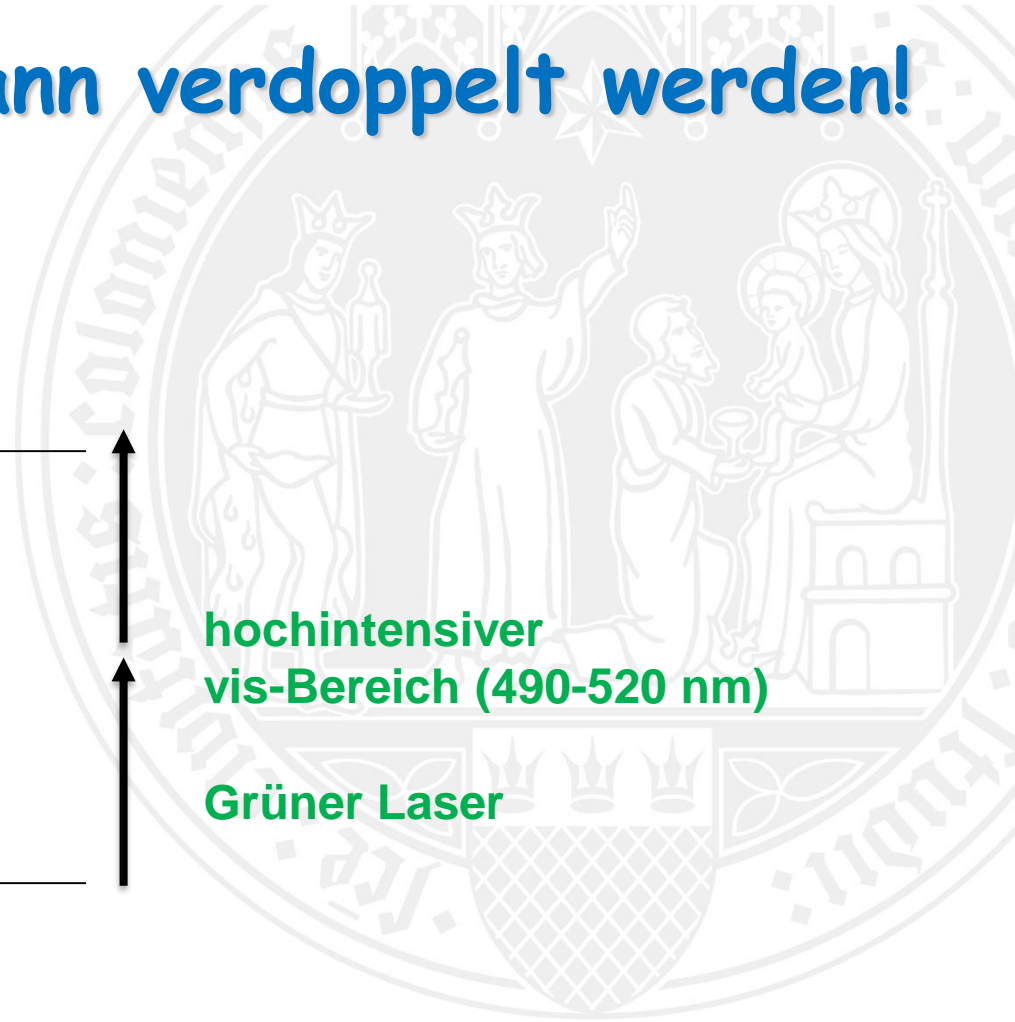
Aktivierung



hochintensiver
vis-Bereich (490-520 nm)

Grüner Laser

Substrat



Sichtbares Licht kann eingekoppelt werden!

Energie



Aktivierung



Zwischen-
verbindung

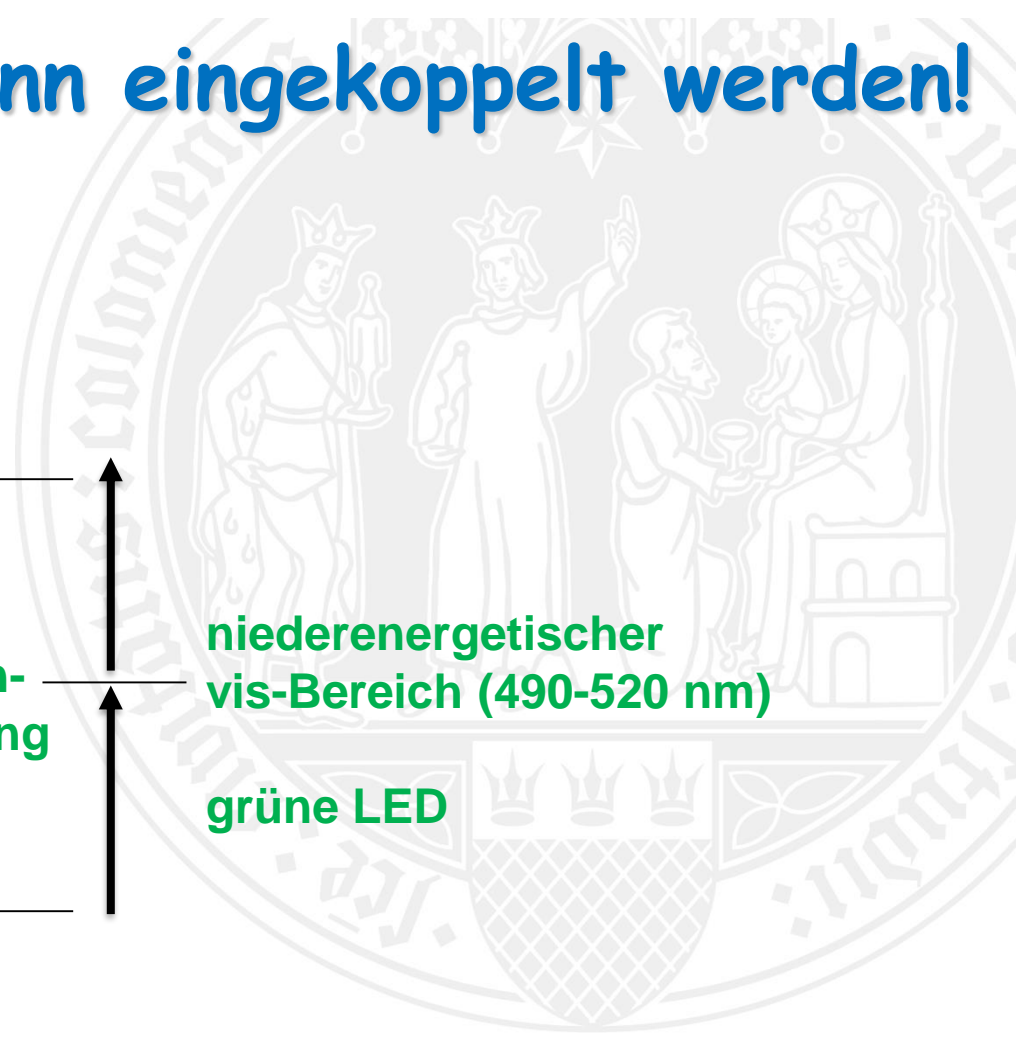


Substrat

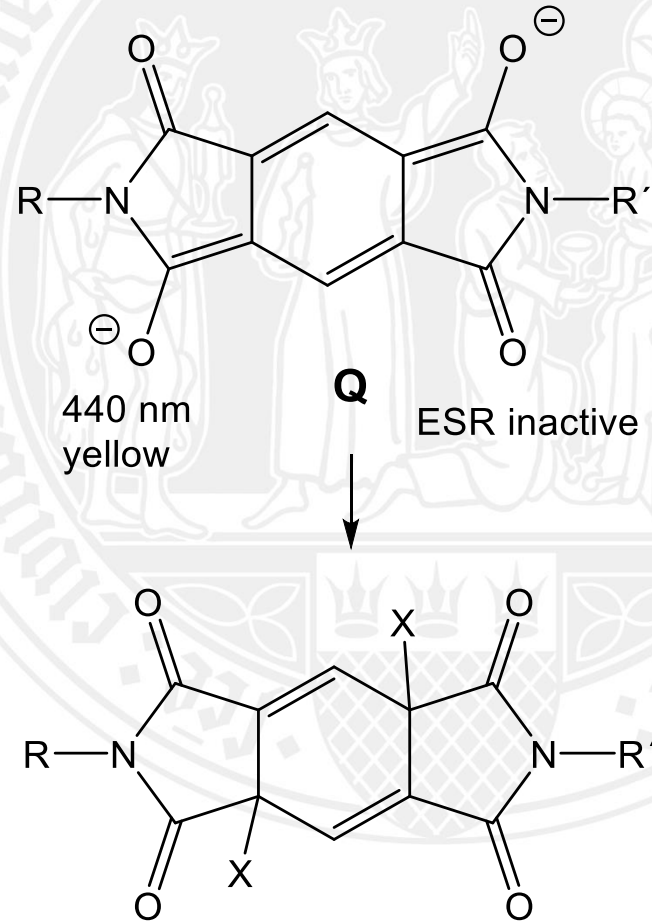
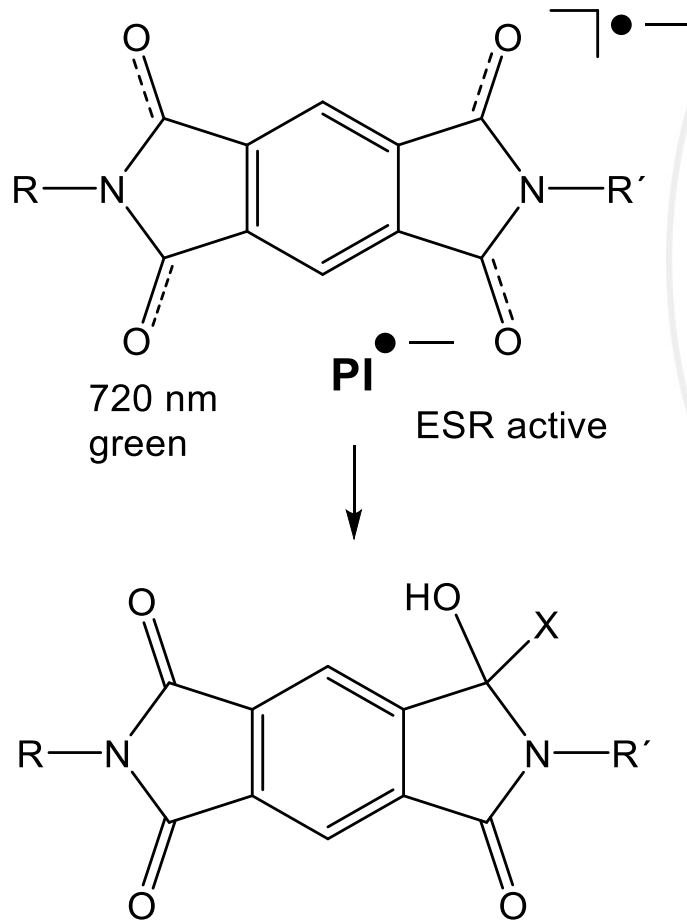


niederenergetischer
vis-Bereich (490-520 nm)

grüne LED



Sichtbares Licht kann eingekoppelt werden!



**Dr. Sabrina Molitor,
MSc, BSc**



METHOD 2: indirect vis

**PhD work on
photocatalysis**

**Dr. Nestor Nazarov,
Dipl.-Chem.**



METHOD 1: direct UV

**PhD from a collaborative project
funded by Rhein-Energie REW
between University Cologne
and FH Cologne (Prof. Rehorek)**