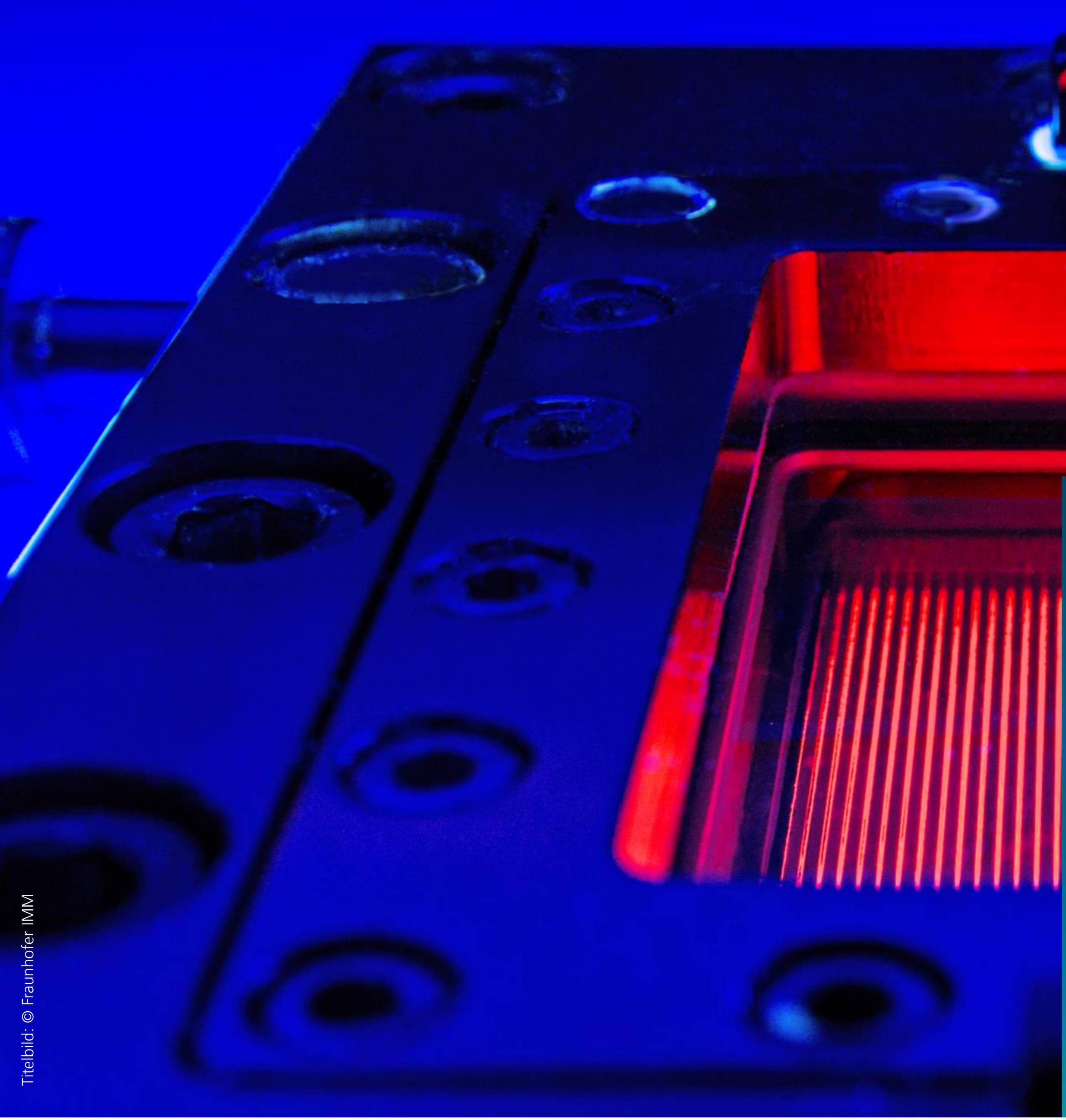


Photochemistry in flow as tool for sustainable syntheses

Enlightening chemical processes

with Dr. Thomas H. Rehm

Fraunhofer IMM

Flow Photochemistry – Take the best of both worlds!

Flow Chemistry

- Microreactor technology
- Excellent phase contacting
- Catalyst immobilization
- Novel process windows (p, T, hν)
- Excellent process control
- LED technology (defined λ, architecture)

Engineer your technology!

Photochemical Catalysis

- From UV to visible light
- Mild reaction conditions
- Broad tolerance to many functional groups
- Catalyst development
  - Metal complexes
  - Dyes
  - Dual catalysis

Engineer your chemistry!

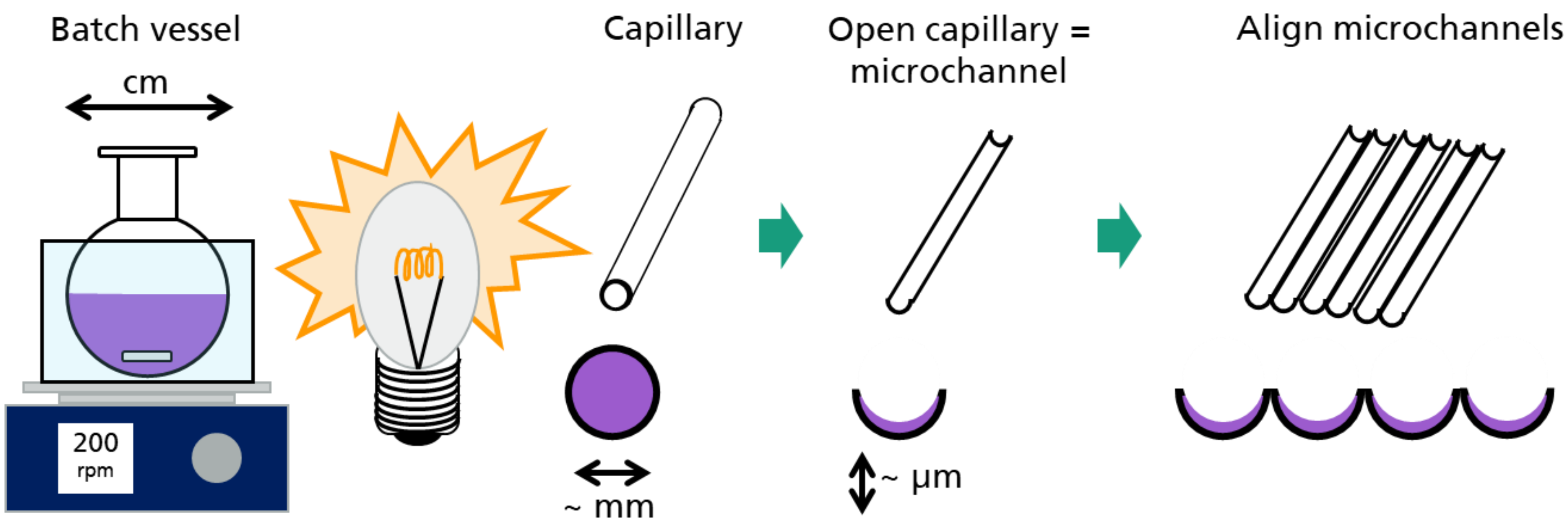
Toolbox for manufacturing complex molecules with light!

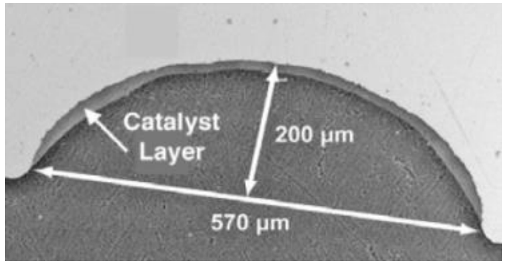
Our examples and Your take home messages for photochemistry in flow

These advantages	translated into	Your benefit
Mild reaction conditions with (visible) light	maximize	your product quality by less degradation
Different reactivity of photochemistry *vs.* thermal chemistry	allows	novel synthesis routes and products for your portfolio
High compatibility of photochemistry to other types of catalysis	allows	straight forward integration into your existing processes
Clever reactor design	achieves	better process control
Process intensification	avoids	needless waste
Intrinsic scale-up of flow reactors	results in	cost reduction for your processes

Safe TIME, MONEY & ENERGY by going to photoflow !

Advancing photochemistry with thin films



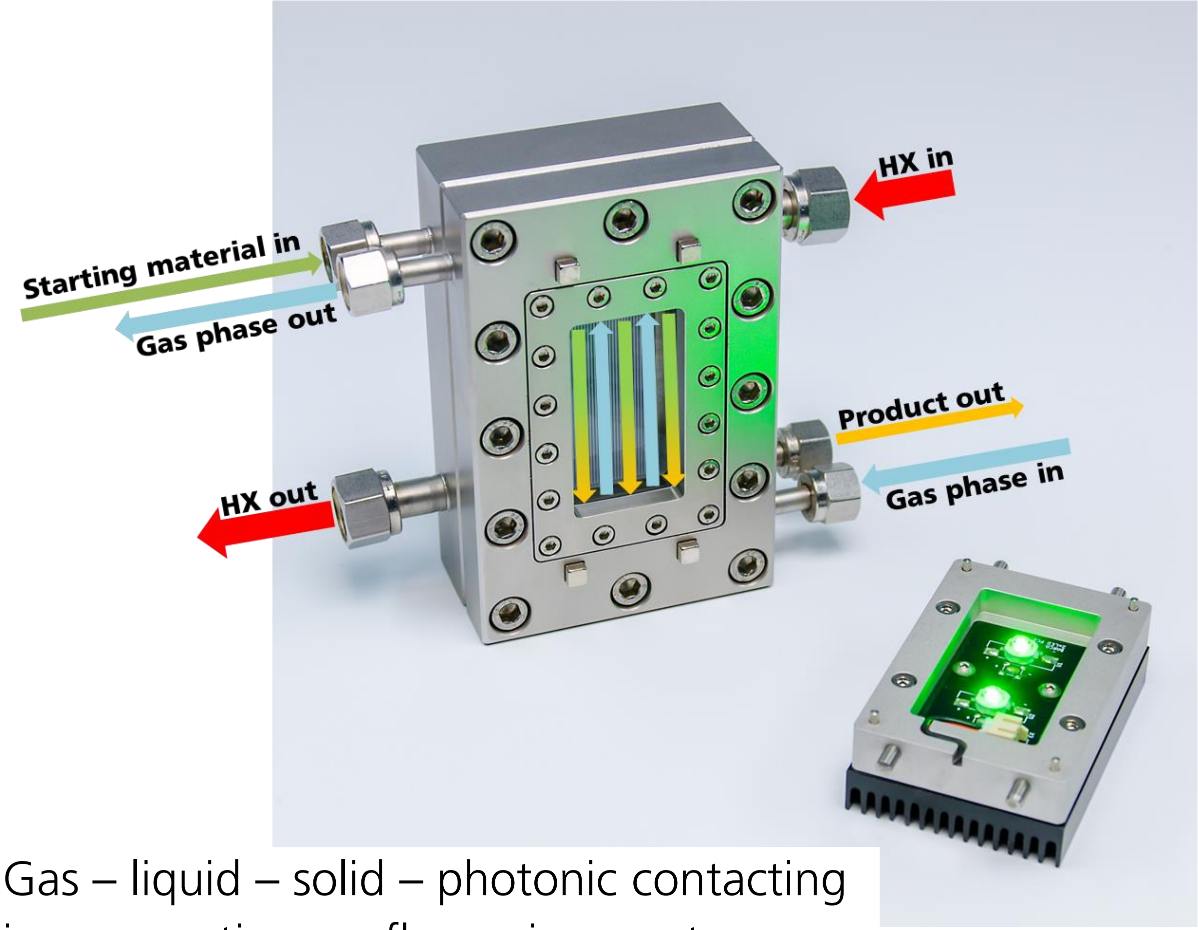


- Thin film formation (full irradiation)
- Very efficient gas - liquid contacting or release
- Catalyst immobilization on channel wall

- Defined channel length
- Flow rate defines irradiation time
- High concentrations possible

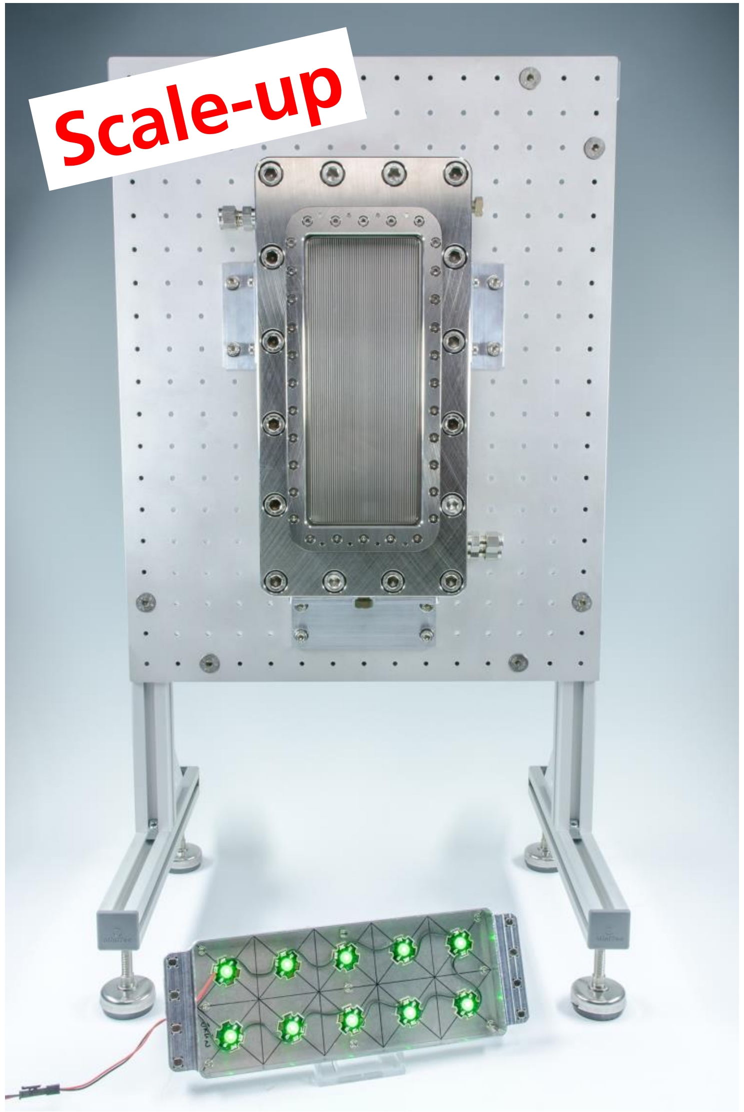
Chem. Eng. J., **2013**, *227*, 182-190.

Falling film microreactor for flow photochemistry



Gas – liquid – solid – photonic contacting
in one continuous flow microreactor

10 x



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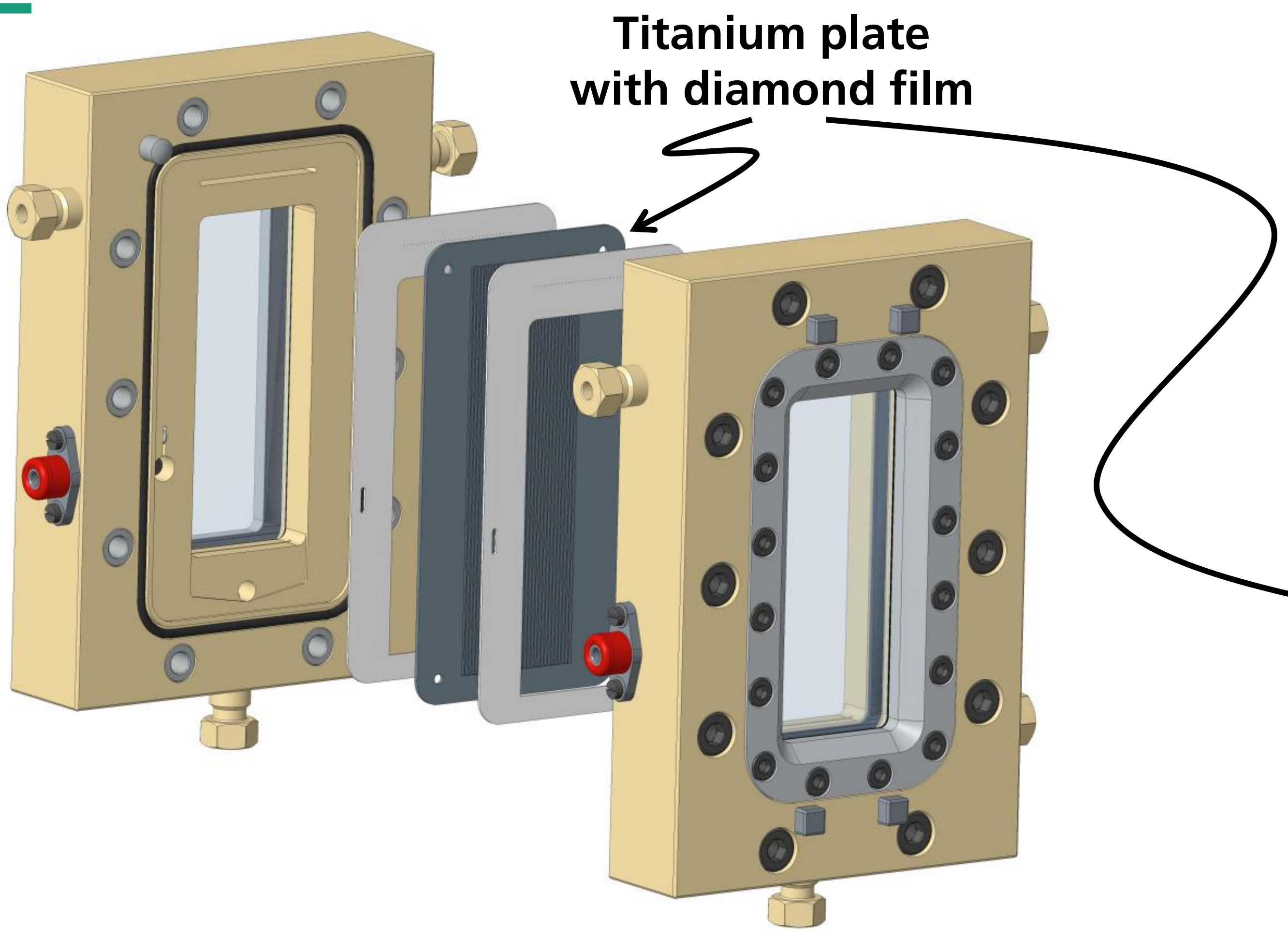
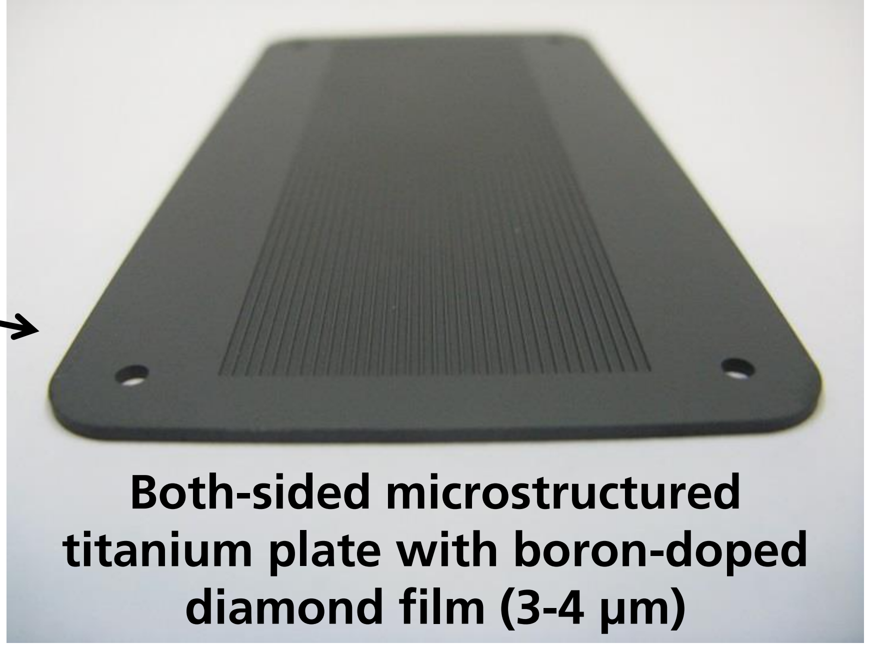
Novel catalyst – Diamond in a microreactor

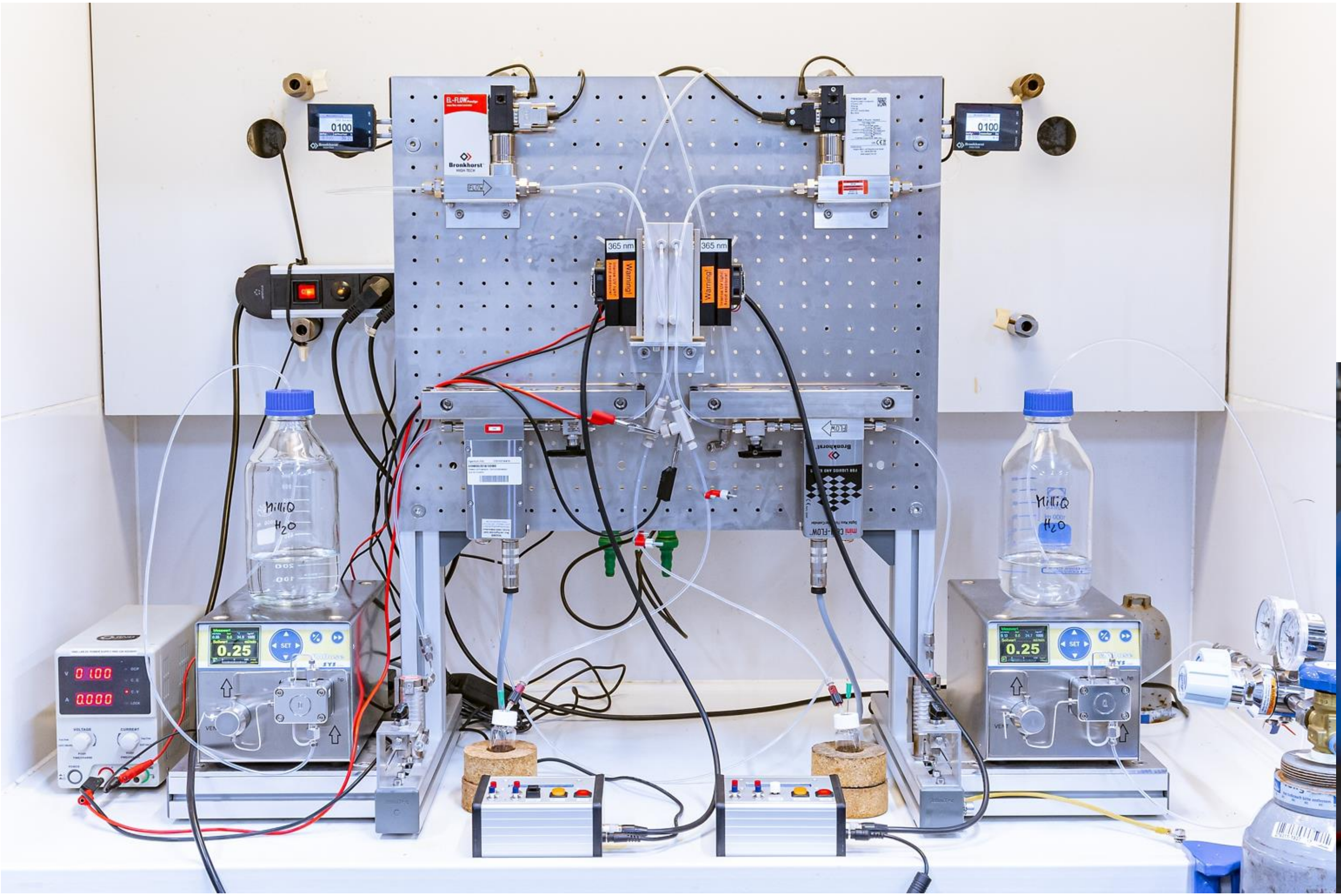


- Symmetric reactor module
- Doubled reaction area
- Both-sided irradiation
- Up to 10 bar system pressure

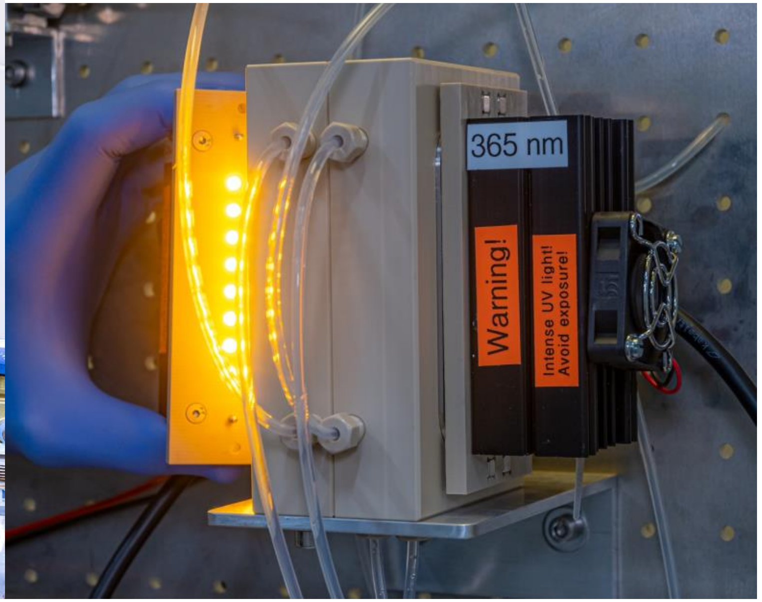


Joint project CarbonCat with Prof. Anke Krüger (University of Stuttgart) and Sahlmann Photochemical Solutions GmbH, sponsored by BMBF, Grant number: 033RC009A

Plant development for CO_2 conversion to C_1 building blocks



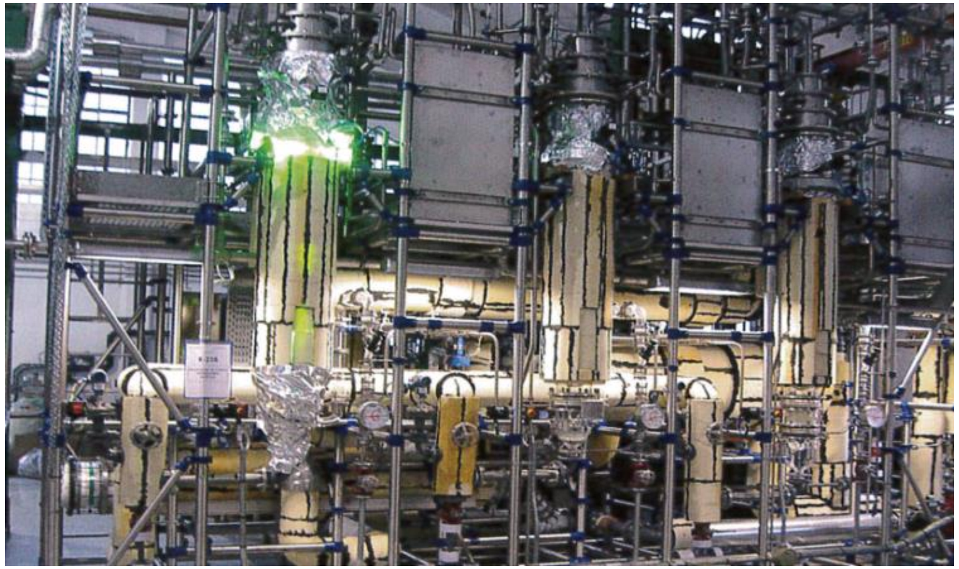
- Gas → CO_2
- Liquid → water
- Solid → Boron-doped diamond
- Photons → light energy



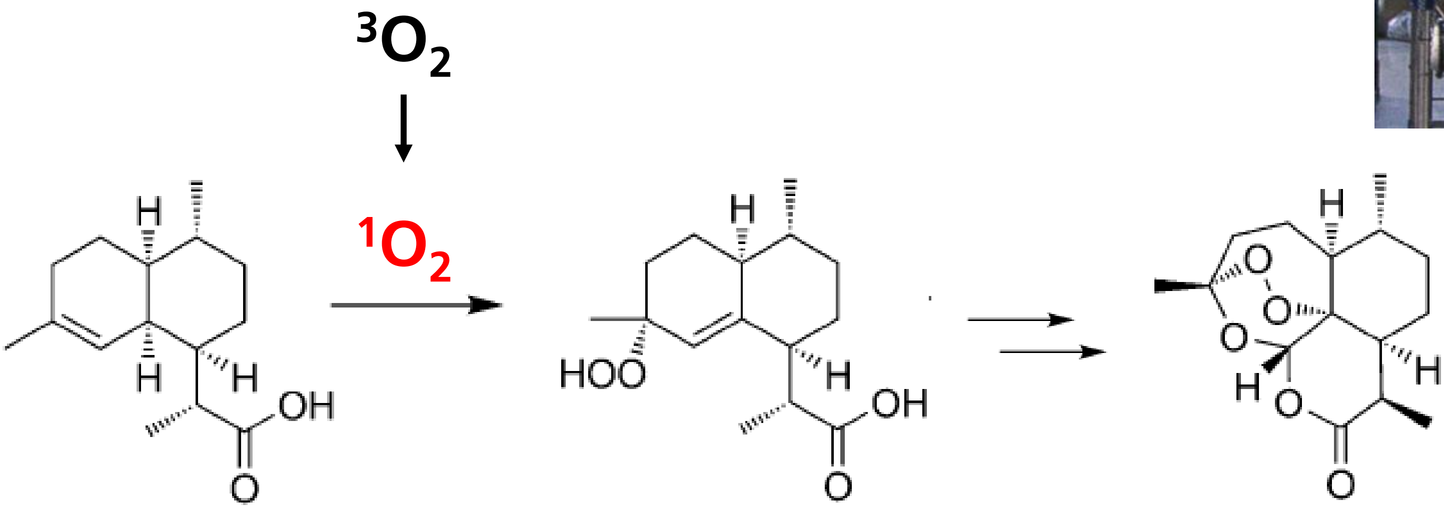
Joint project CarbonCat with Prof. Anke Krüger (University of Stuttgart) and Sahlmann Photochemical Solutions GmbH, sponsored by BMBF, Grant number: 033RC009A

Singlet oxygen – Industrial & pharmaceutical relevance

- Synthesis of Artemisinin – natural product for anti-malaria treatment
- Photochemical approach to produce singlet oxygen with visible light

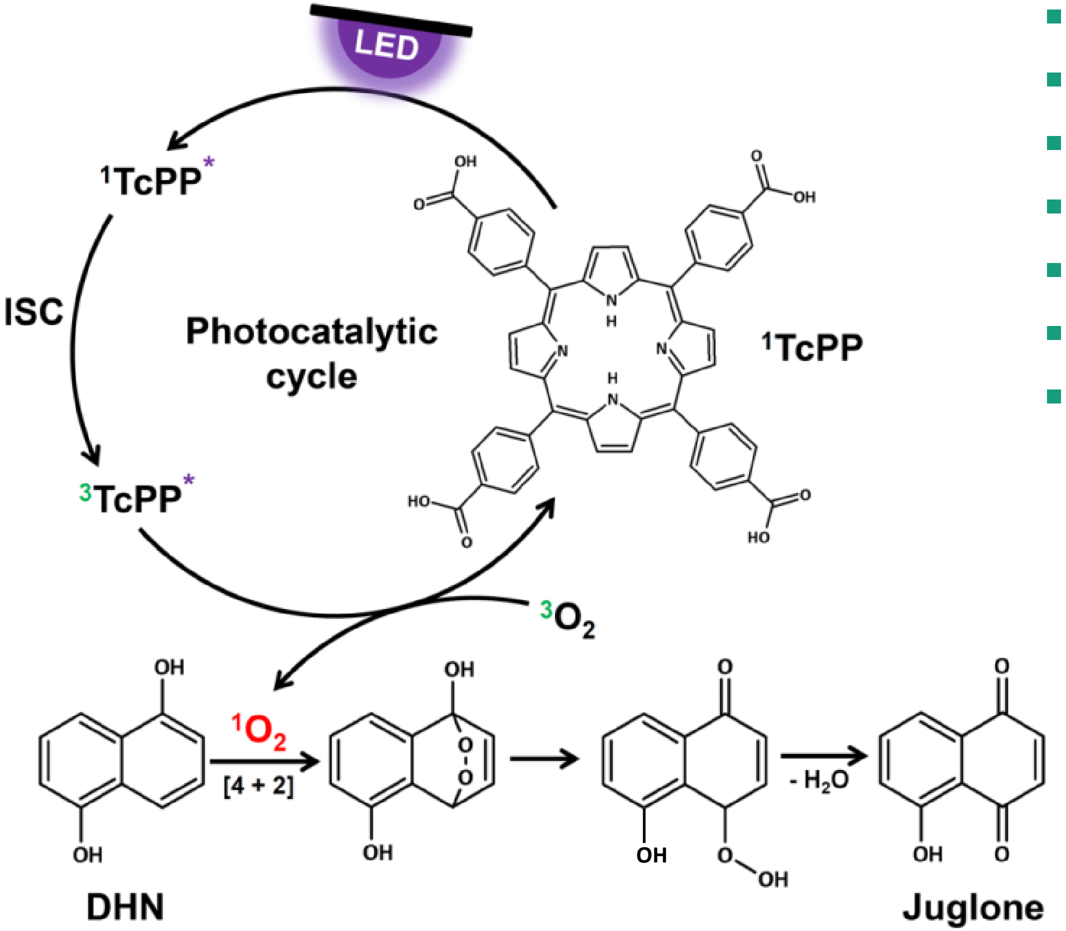


Org. Process Res. Dev., 2014, 18, 417.

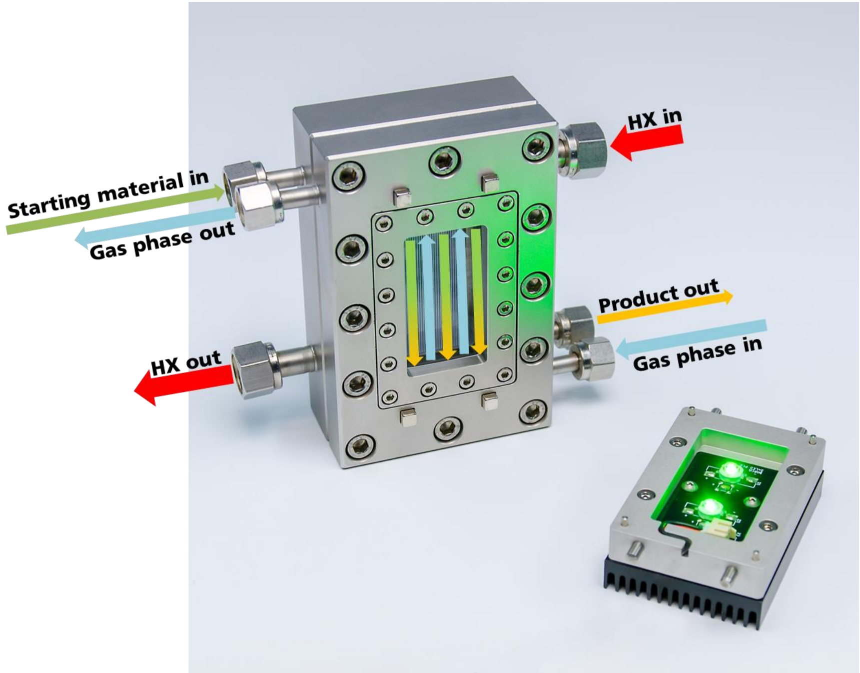


a) *Angew. Chem. Int. Ed.* **2012**, 51, 1706; b) *Chem. Eur. J.* **2013**, *19*, 5450.

Fine chemicals synthesis – Singlet oxygen for safe photooxygenations



- 5 mol% sensitizer
- 10 mM 1,5-dihydroxynaphthalene
- Solvent: 2-propanol
- f_{gas} = 2 mL min-1
- f_{liquid} = 0.16 mL min^{-1}
- T = 20 °C
- τ = 19 s



Rehm *et al.*, *React. Chem. Eng.*, **2016**, *1*, 636.

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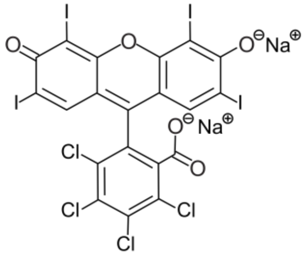
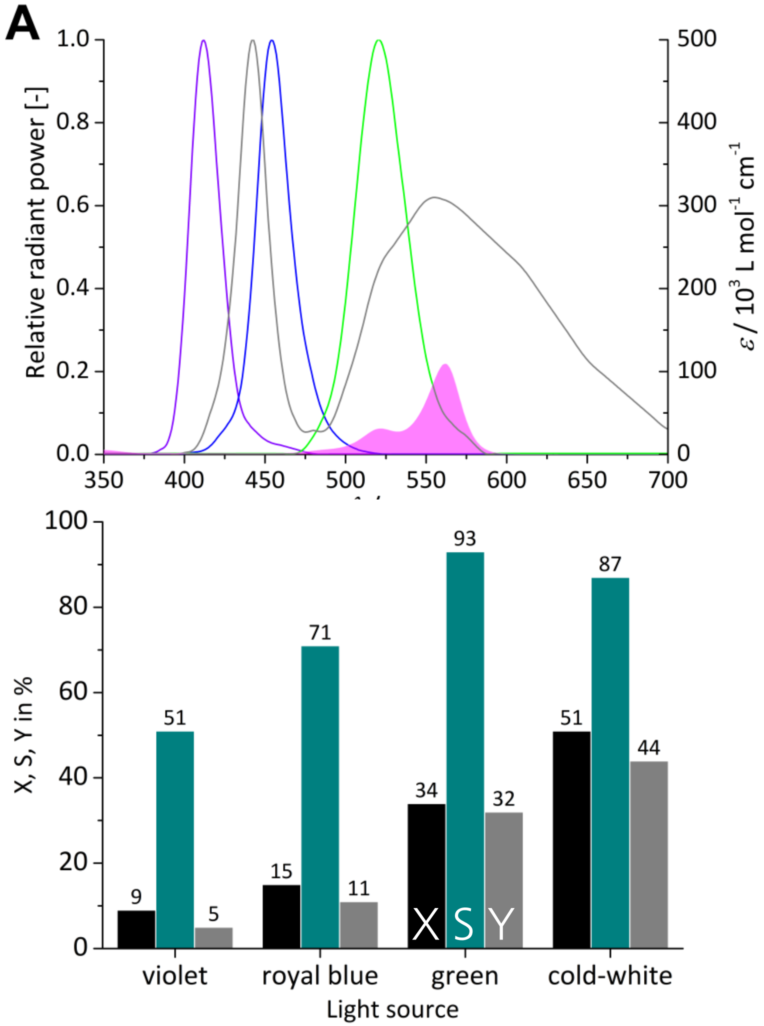
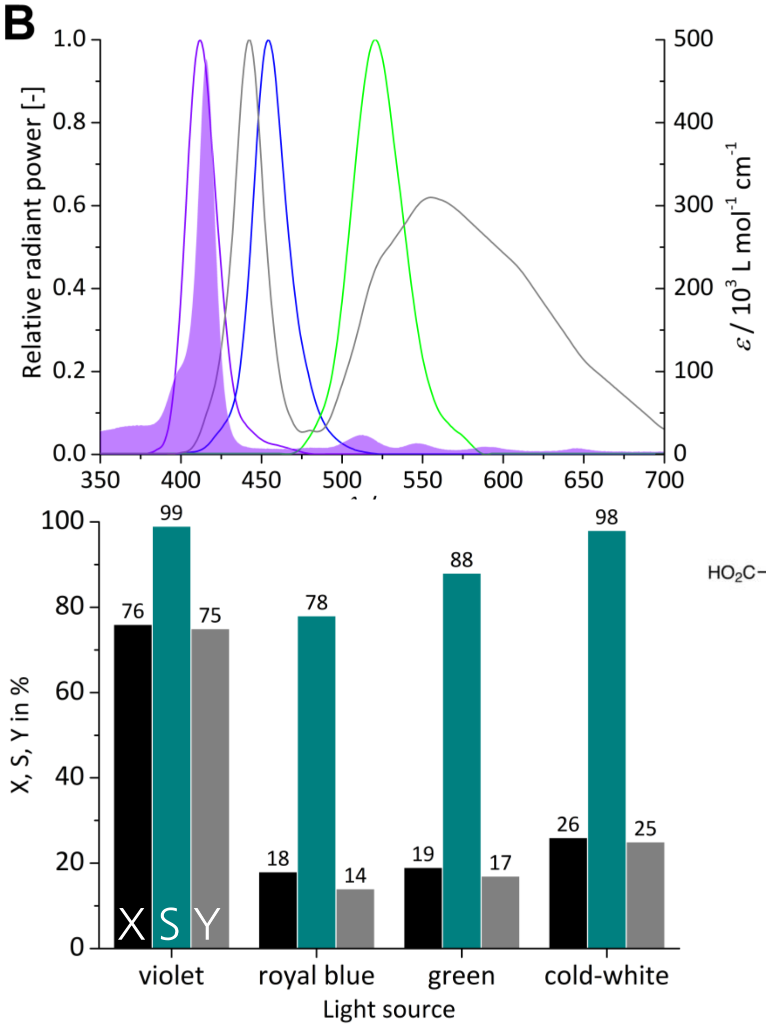
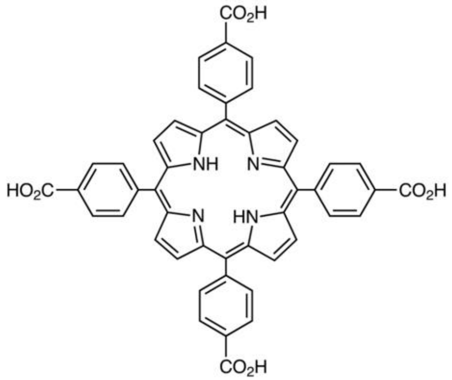
Sensitizer – light source combination for efficient singlet oxygen formation





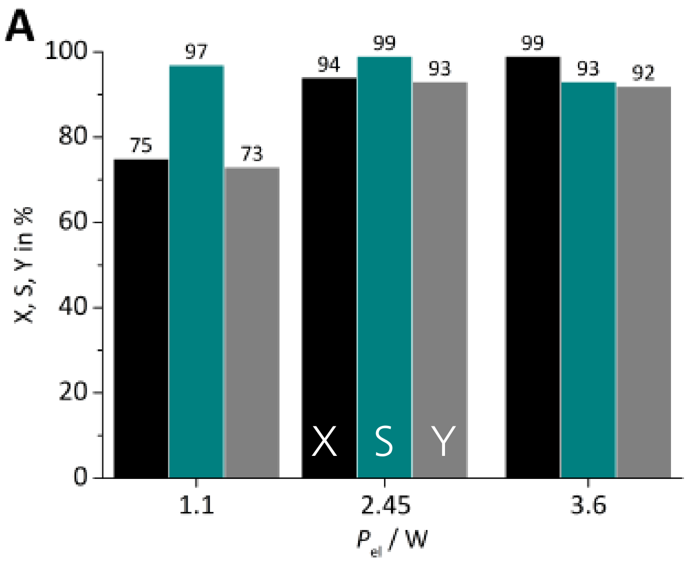
O_2



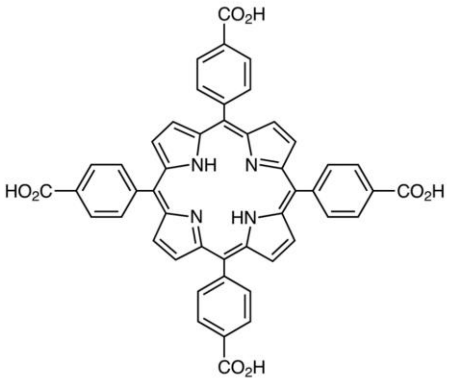


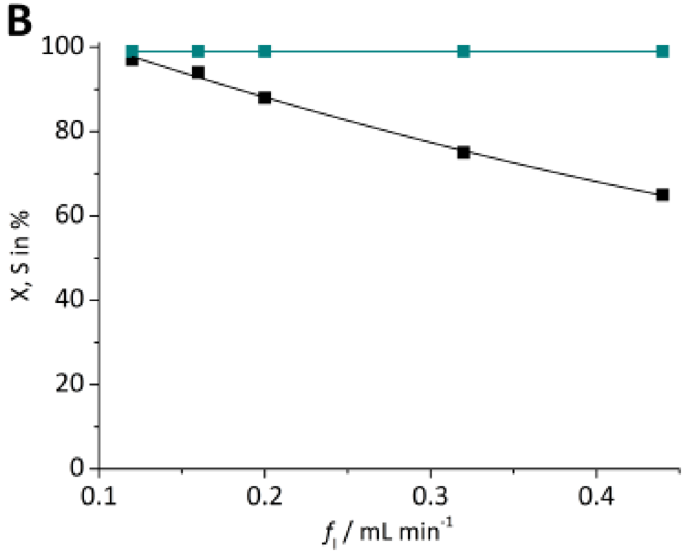
Rehm *et al.*, *React. Chem. Eng.*, **2016**, *1*, 636.

Optimization of reactor and process parameters



O_2





- Available radiant power in reactor: 0.76 W
- Irrad. area in channels: 1037 mm^2
- Film thickness: 50 µm
- Residence time: 19 s
- Energy efficiency: 13%
- Quantum efficiency: 1.4%

Rehm *et al.*, *React. Chem. Eng.*, **2016**, *1*, 636.

  - **PUBLIC** -

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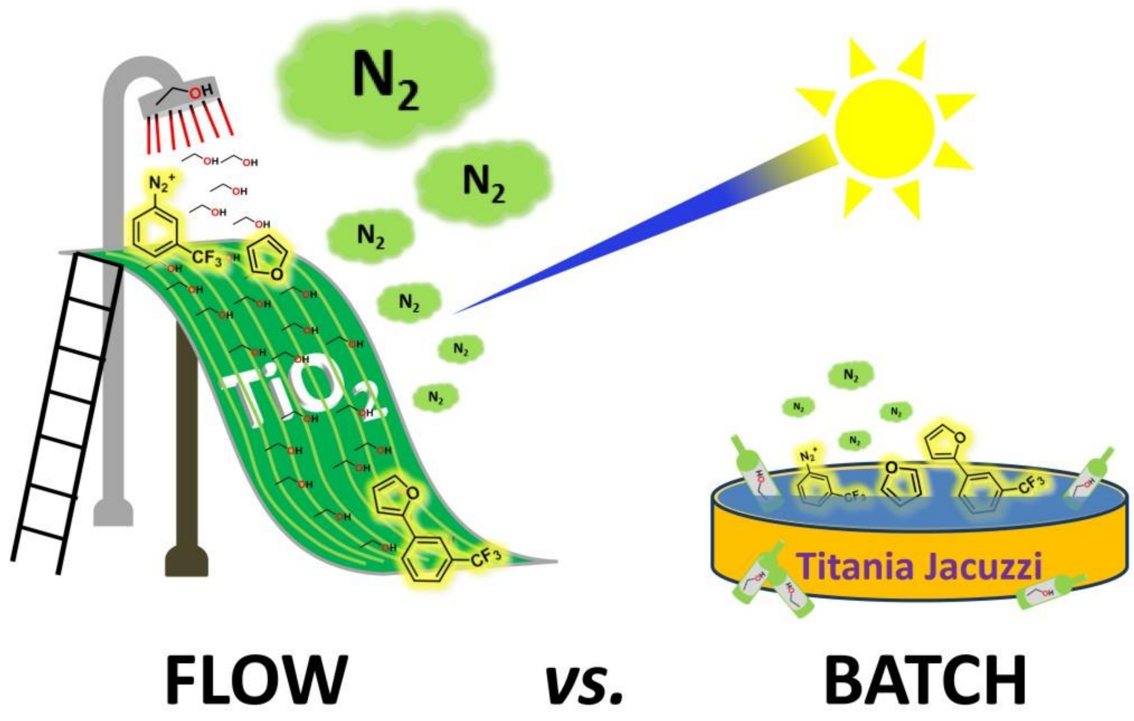
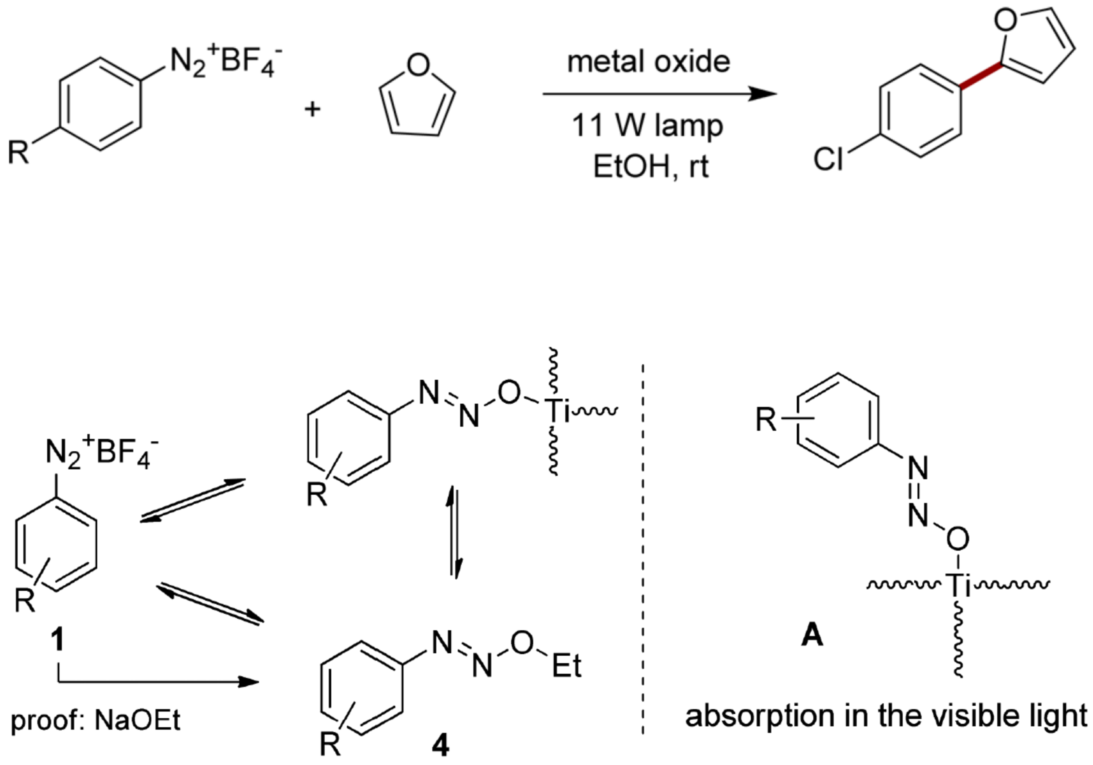
Blue light mediated C-H arylation of arenes with diazonium salts in a falling film microreactor



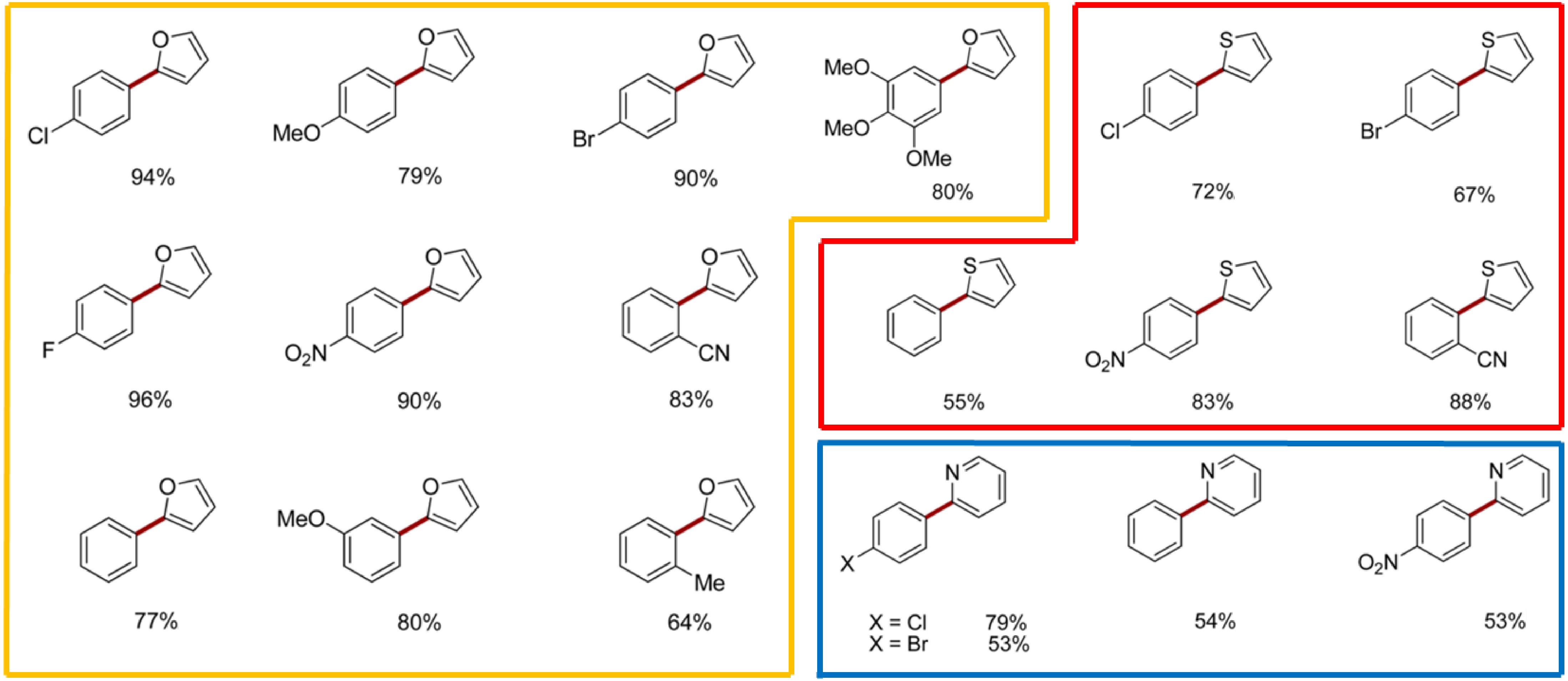


Rueping, Rehm *et al.*, *Green Chem.*, **2017**, *19*, 1911.

Rueping *et al.*, *ACS Catal.*, **2015**, *5*, 3900.

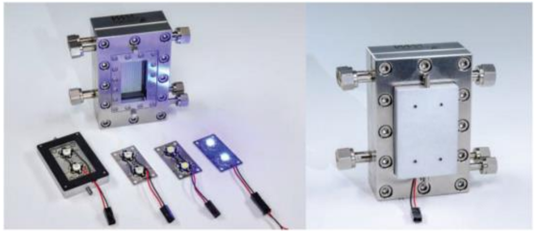
Fraunhofer IMM

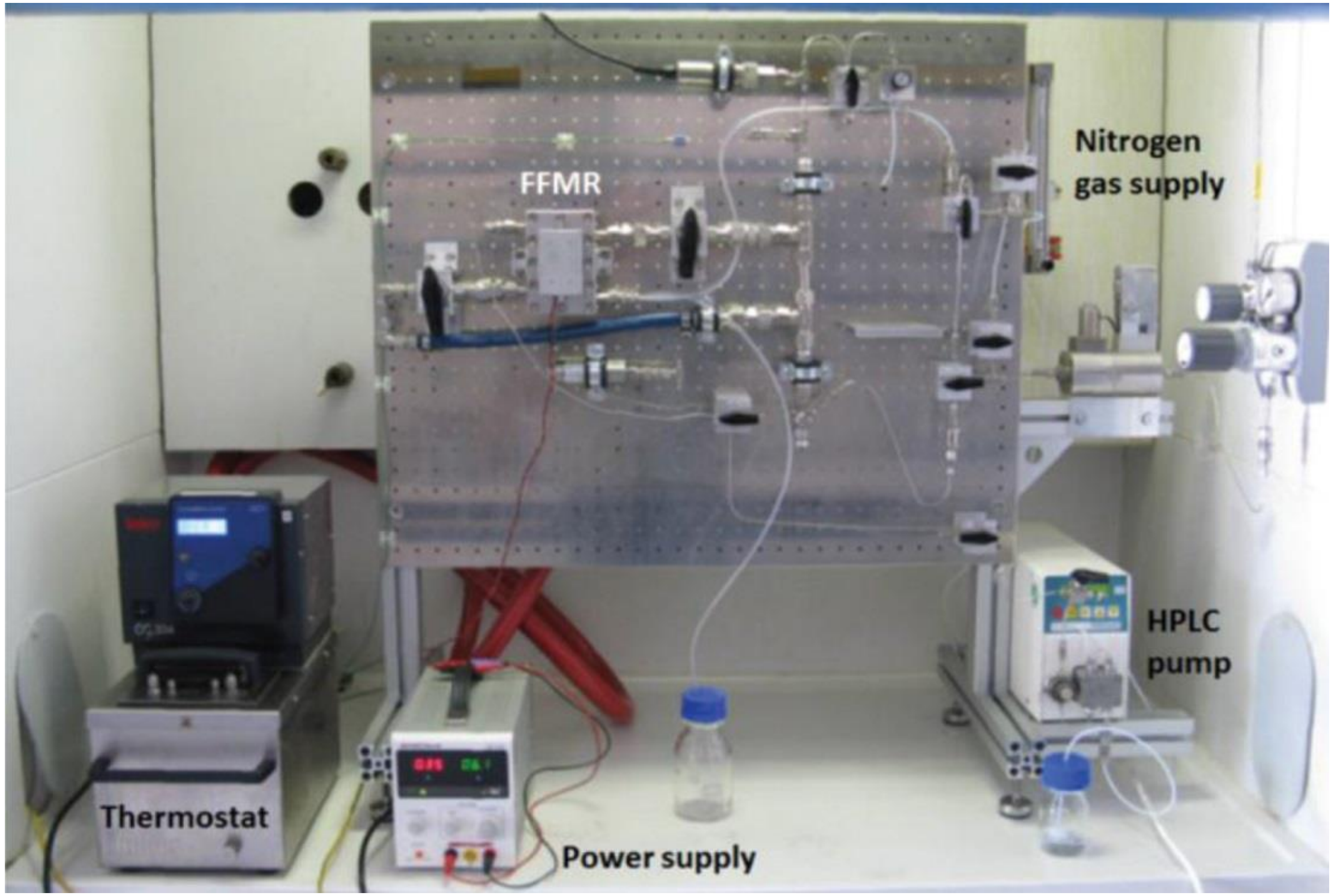
Scope of photochemical catalyzed C-C coupling in BATCH



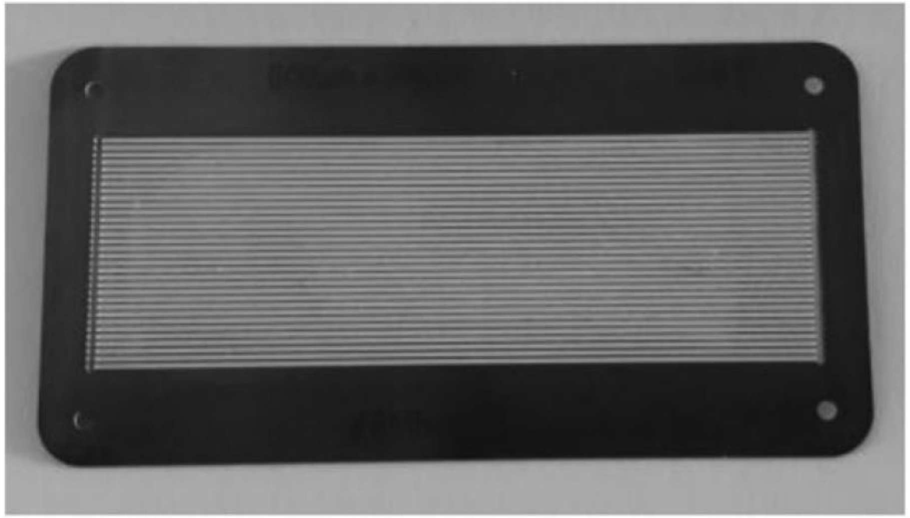
Rueping *et al.*, *ACS Catal.*, **2015**, *5*, 3900.

Transfer from batch to FLOW

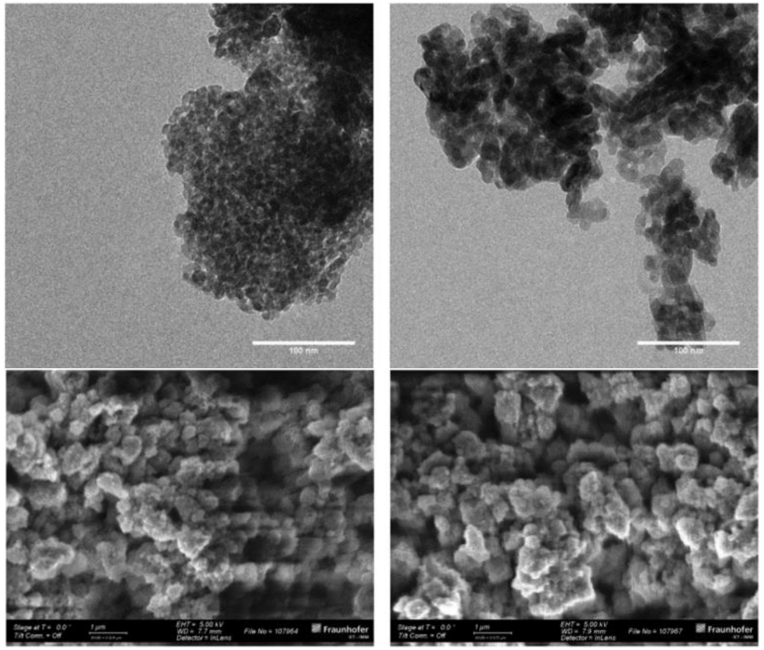




Rueping, Rehm *et al.*, *Green Chem.*, **2017**, *19*, 1911.



TiO_2



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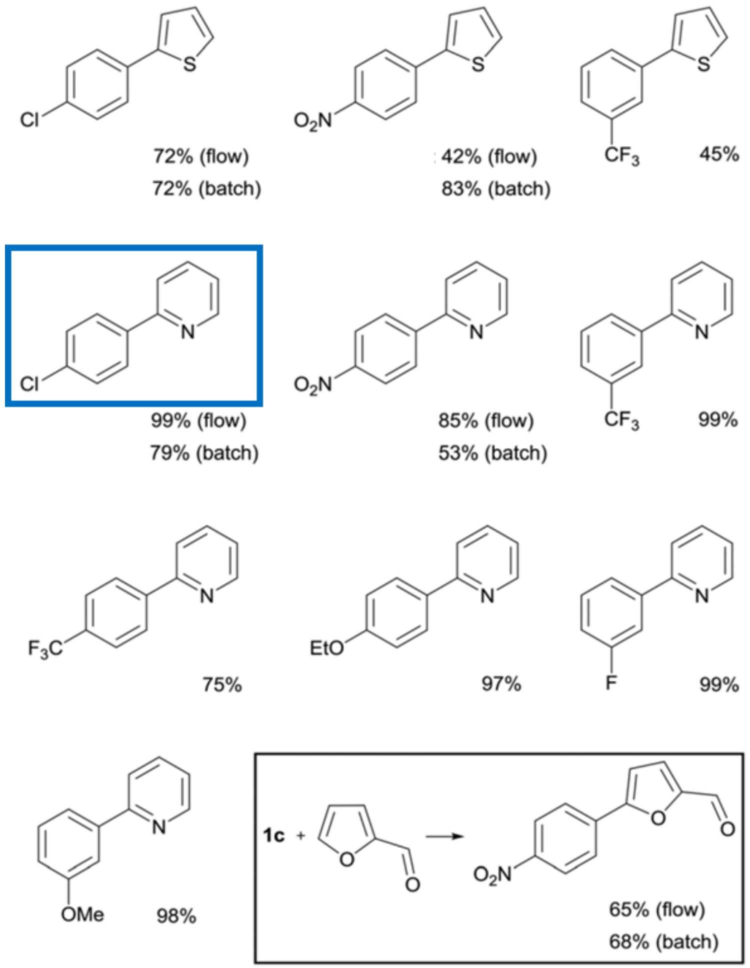
Batch *versus* flow



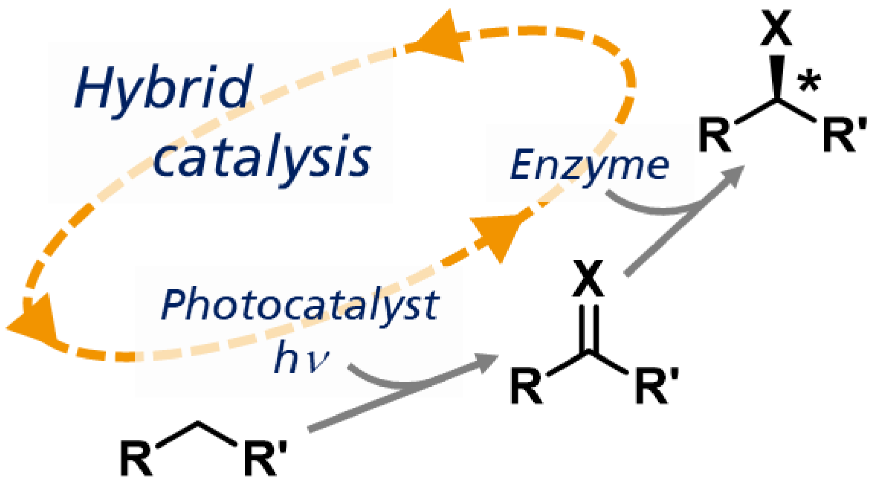
Rueping, Rehm *et al.*, *Green Chem.*, **2017**, *19*, 1911.

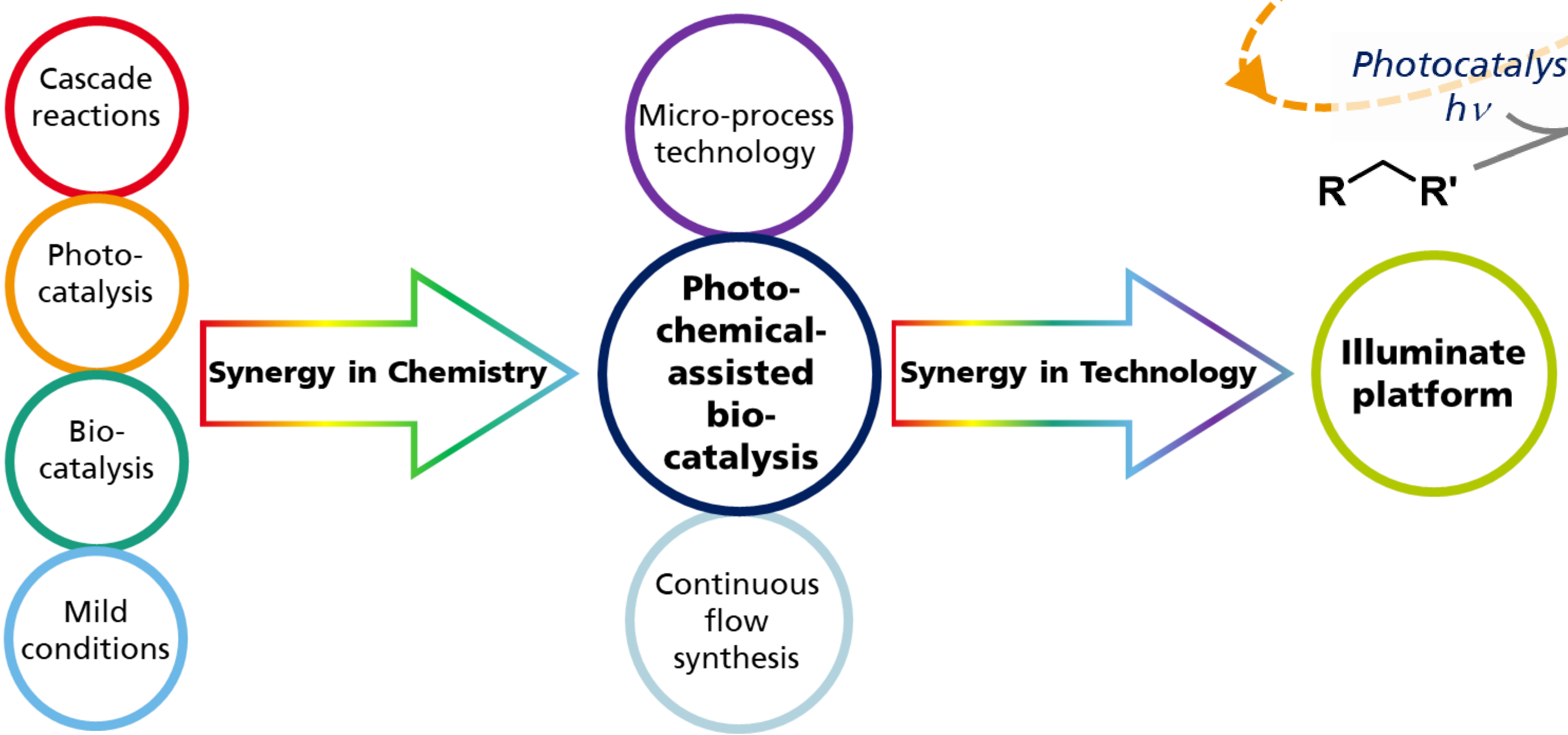
	Batch[a]	Flow	Unit
Molar concentration $c_{\text{starting material}}$	0.05	0.05	mol L^{-1}
Yield Y_{product}	79%	99%	—
Number N of microchannels	—	32	—
Microchannel width, W	—	600	µm
Channel length, L	—	78[c]	mm
Gravitational constant, g	—	9.81	m s^{-2}
Liquid flow rate, f_{liq}	—	0.5	mL min^{-1}
Dynamic viscosity, μ	—	0.8839[d]	g mL^{-1}
Density, ρ	—	0.8910[d]	mPa s
Reaction time, t_R	720	—	min
Dead time, t_D	15[b]	—	min
Liquid thin film thickness, δ	—	50.9	µm
Residence time, τ	—	9.1	s
Specific reactor performance, L	5.4×10^{-5}	0.32	mol L^{-1} min^{-1}

6000 x

Strong
process intensification

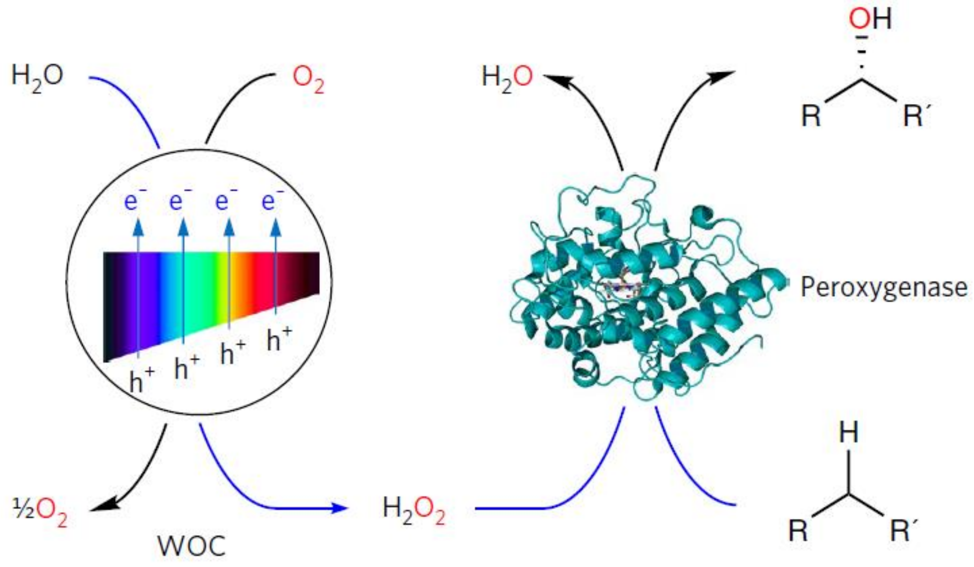
Trend to photochemical assisted biocatalysis

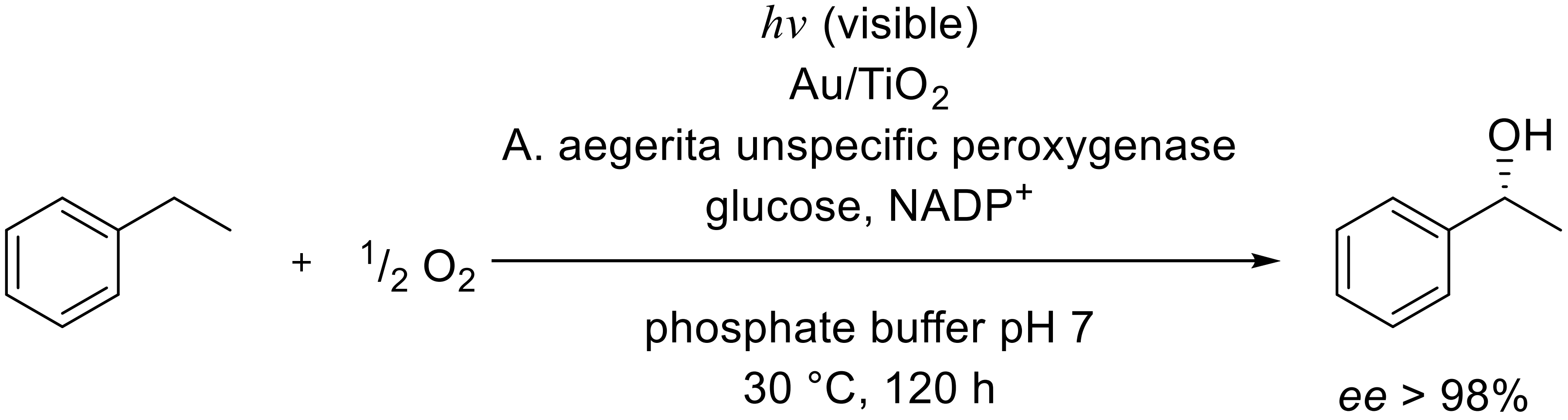




Joint project ILLUMINATE with Fraunhofer IGB, IME, IMM and ISC, sponsored by BMBF, Grant number: 031B1121

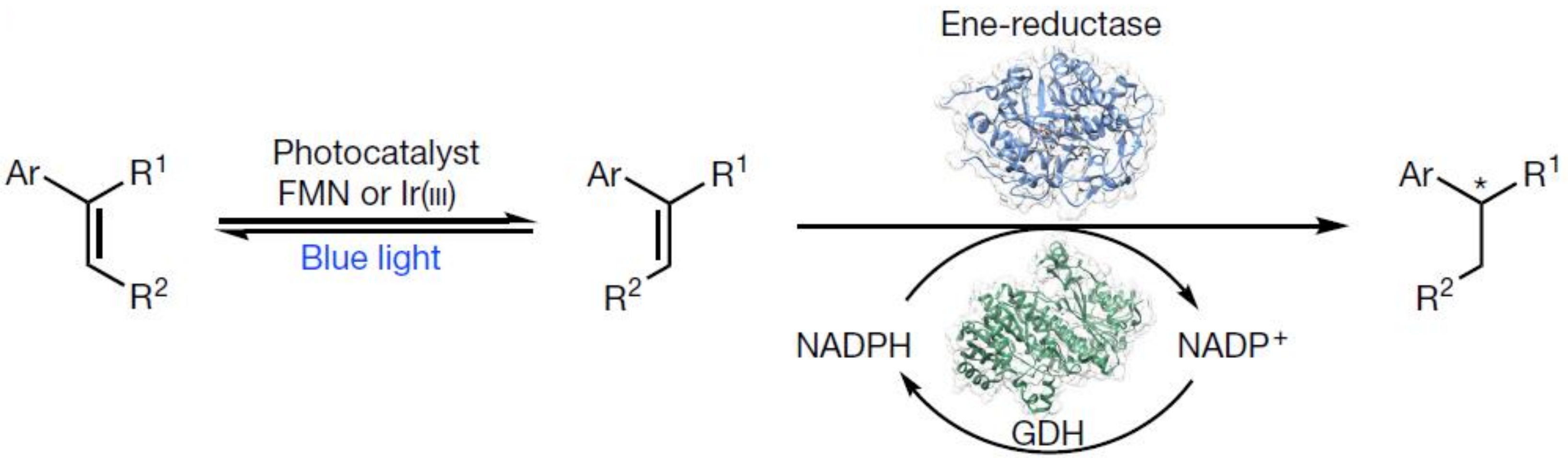
Cascade reaction to chiral phenyl ethanol

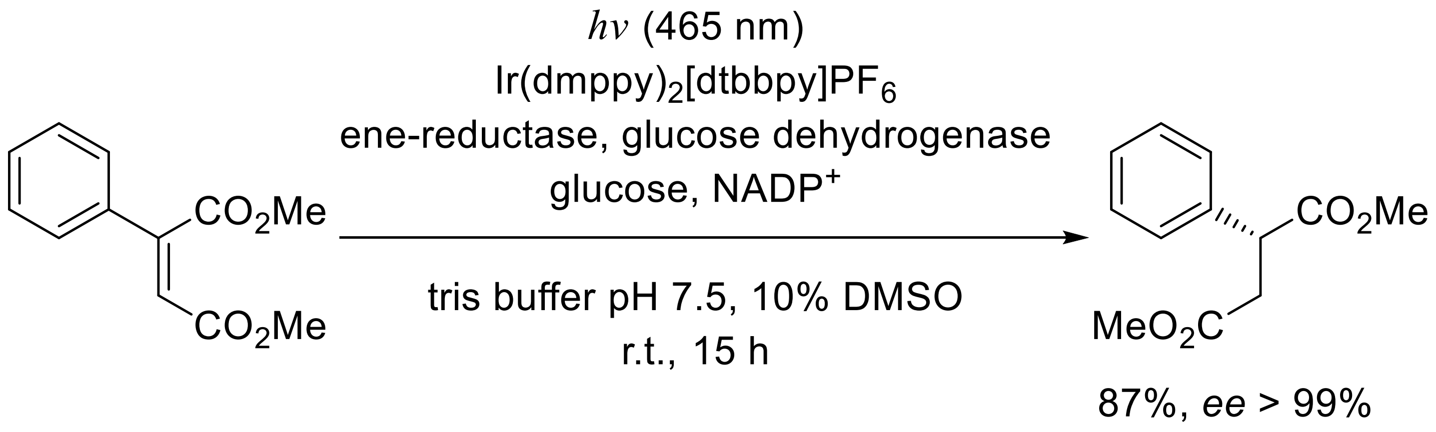




Hollmann *et al.*, *Nat. Catal.*, **2018**, *1*, 55.

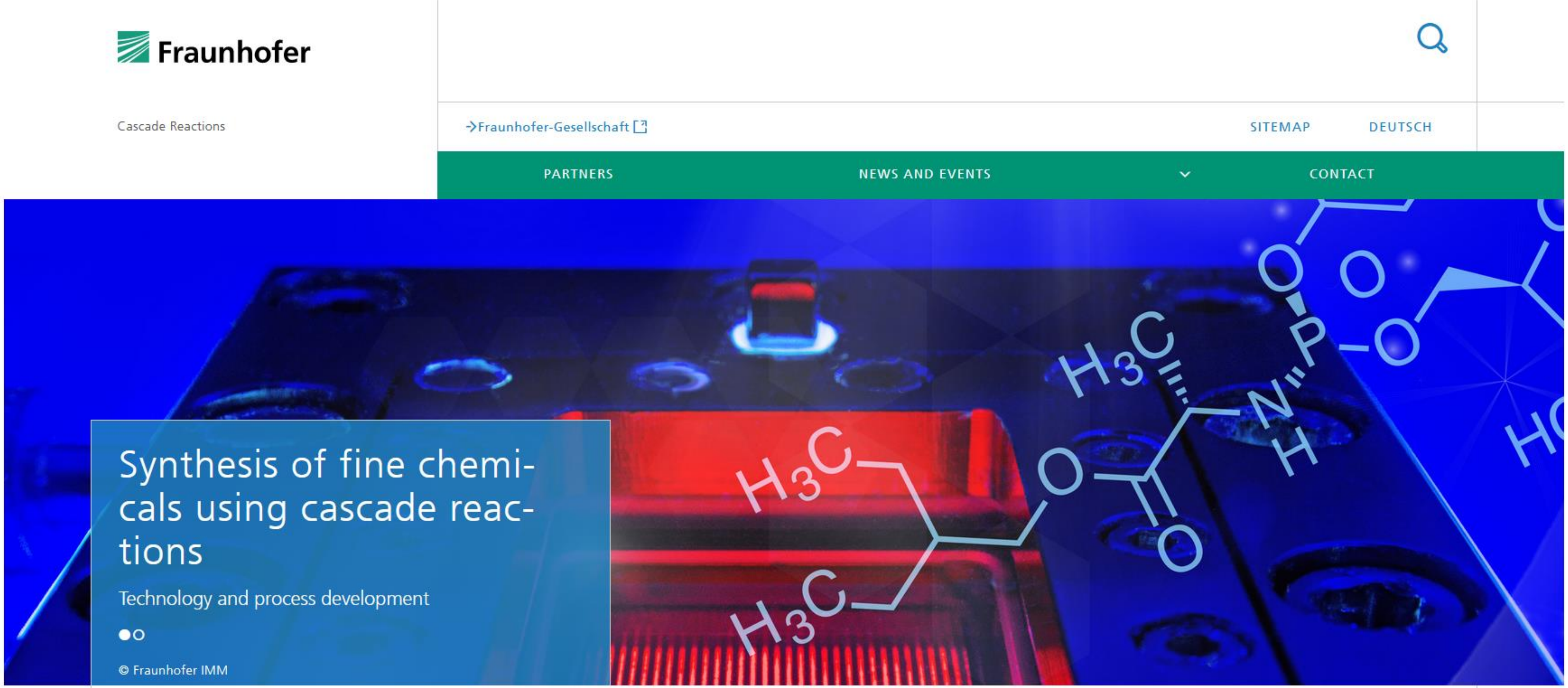
Cascade reaction with isomerization and chiral reduction





Hartwig *et al., Nature,* **2018**, *560*, 355.

Website https://www.cascade-reactions.de/



Summary – Why photochemistry?

Why visible light?

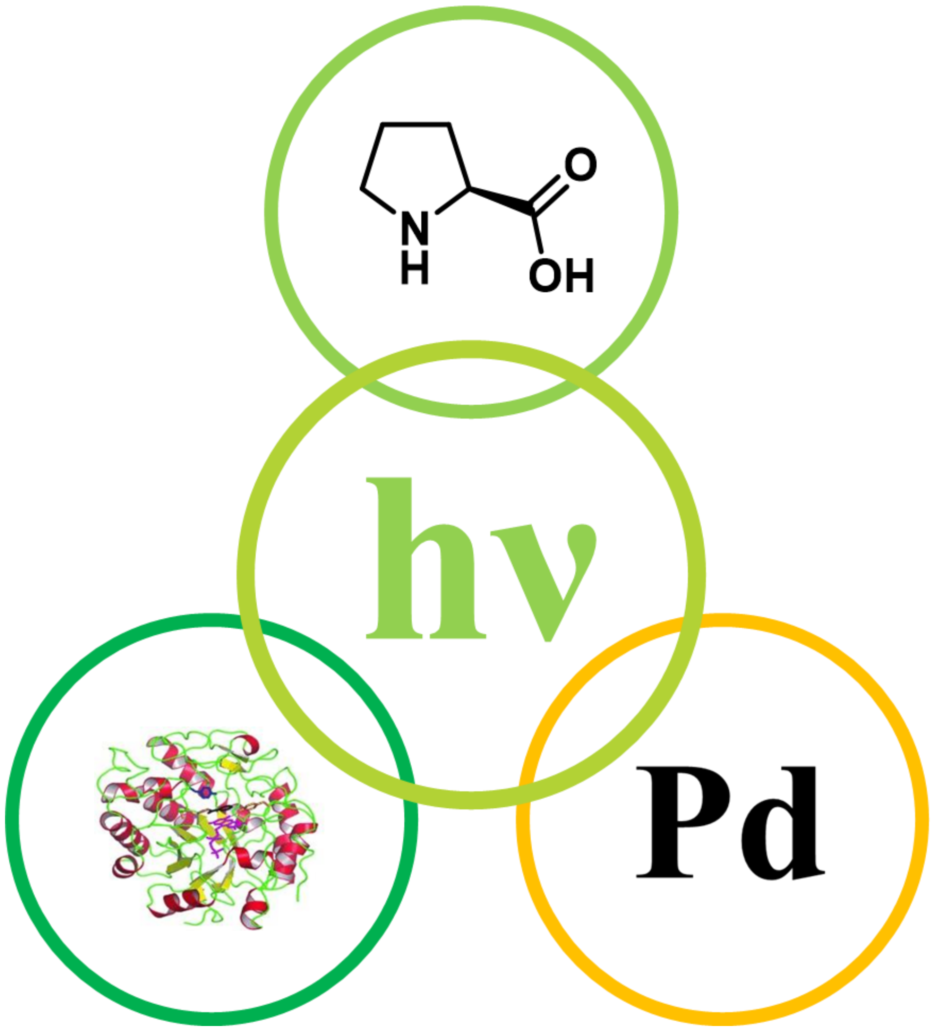
- Photons are

  traceless reagents.
- Mild reaction conditions

  with visible light.
- Different reactivity to thermal chemistry

  allows novel synthesis routes.
- High compatibility

  to other types of catalysis.



Enlightening chemical processes
With smart and small flow reactors

- Better process controll

  by clever reactor design.

- Less waste

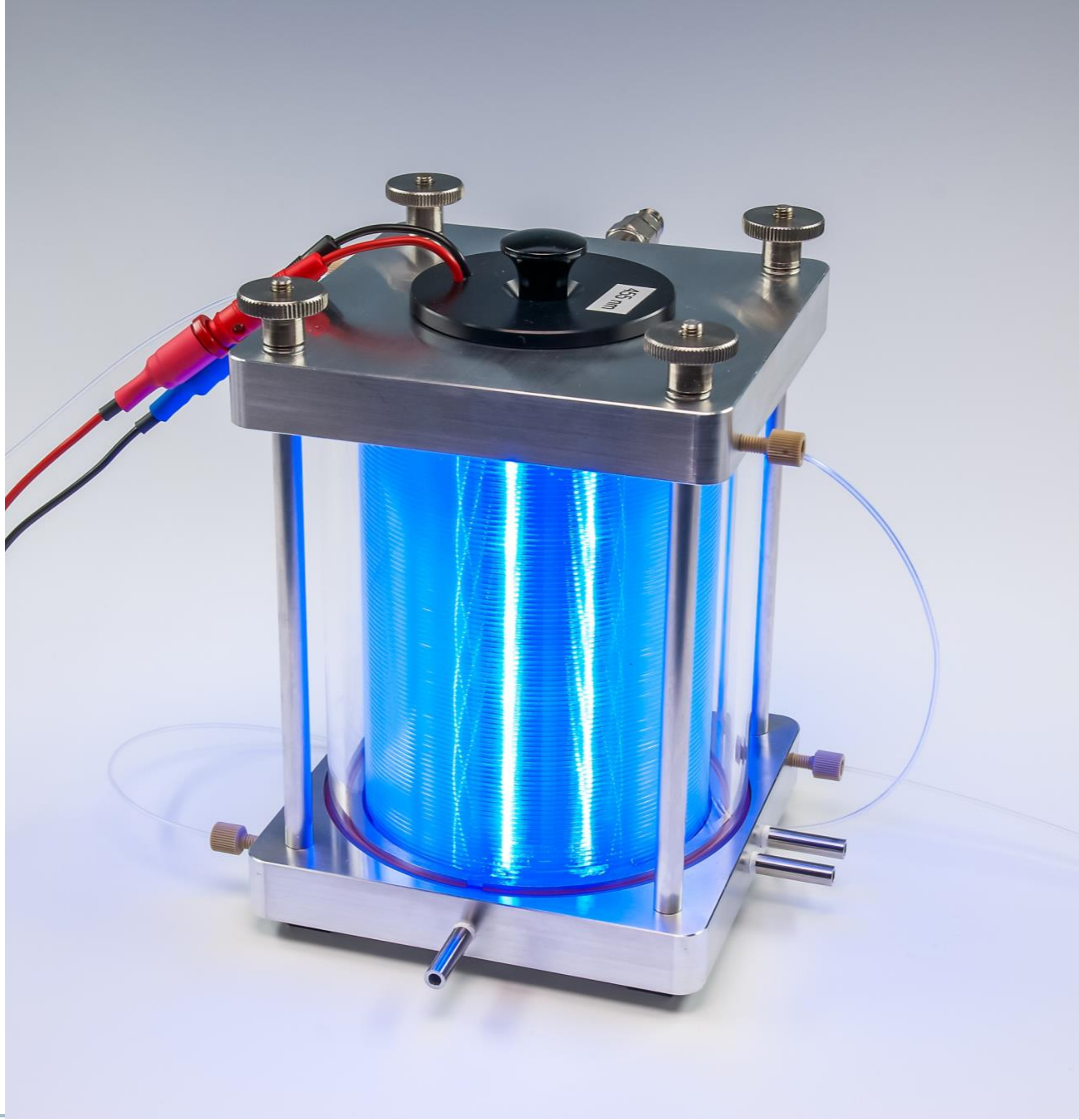
  by process intensification.

- Reliable production

  by high stability of flow plants.

- Cost reduction

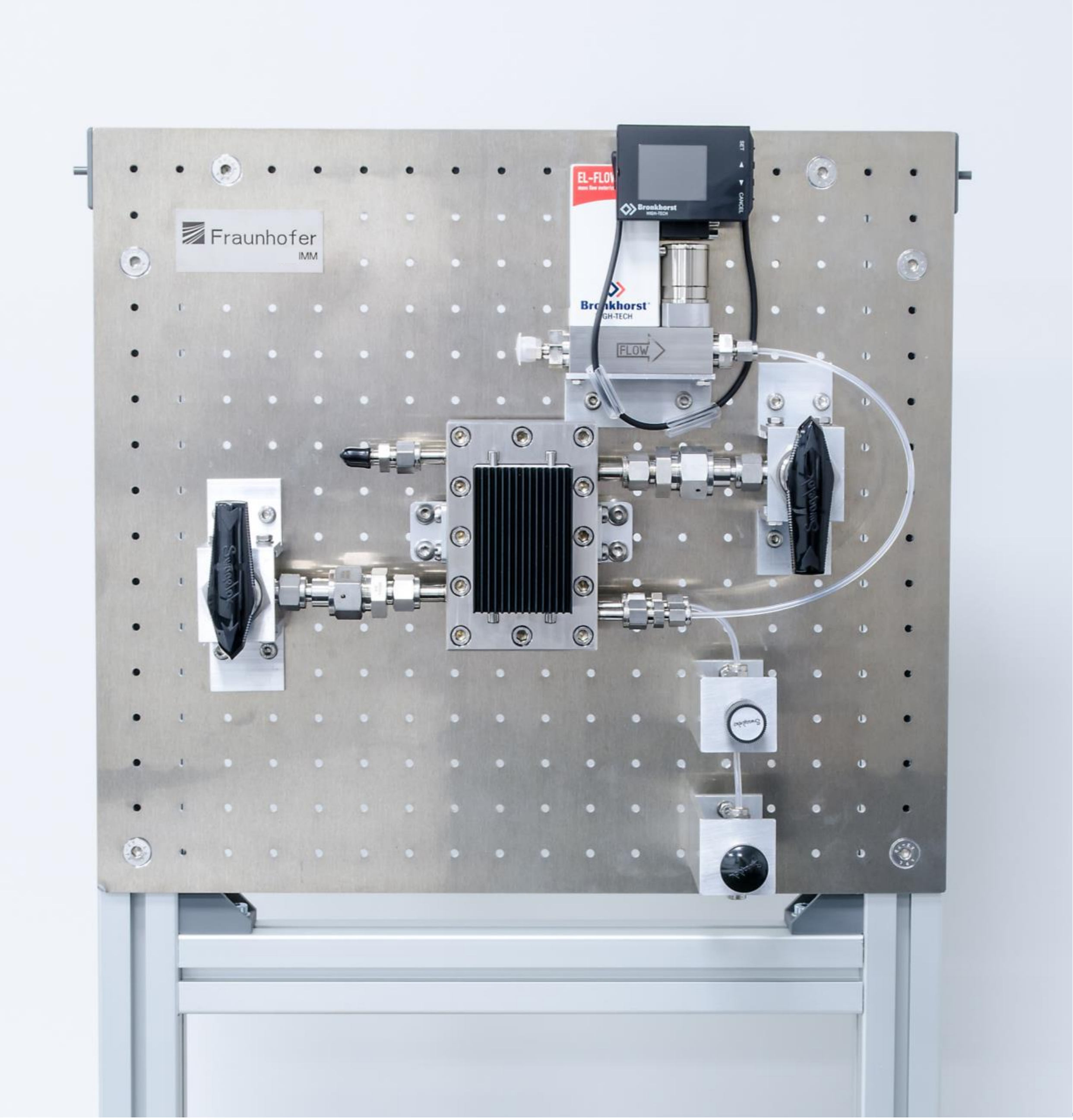
  by intrinsic scale-up of flow reactors.



What can we do for you?

And for your chemical process?

- Feasibility studies
  to understand your needs.
- Transfer of your batch process
  to continuous flow.
- Your unique flow reactor
  for your needs.
- Dedicated plant development
  as blue print for your future process.



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