Réduire N_2 et CO_2 avec des matériaux à définition moléculaire pour aider la transition énergétique

25 mai 2021

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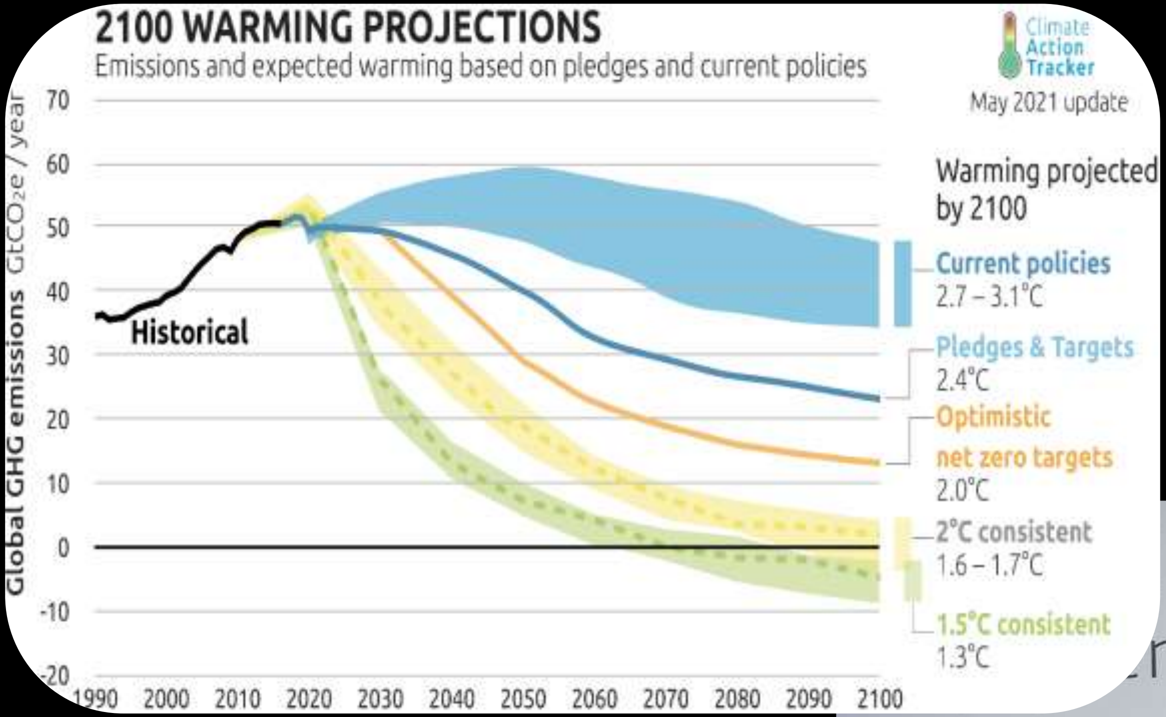
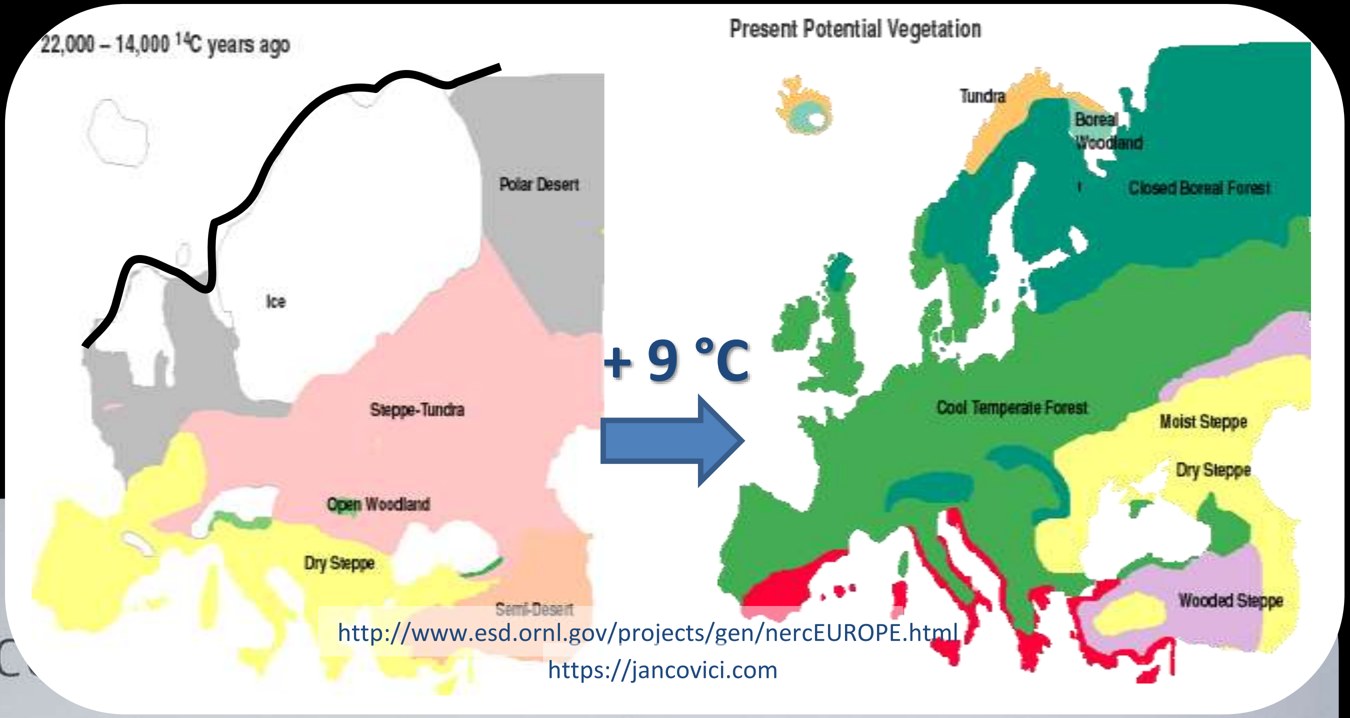
Université de Lyon,
Ircelyon (UMR 5256) et C2P2 (UMR5265)

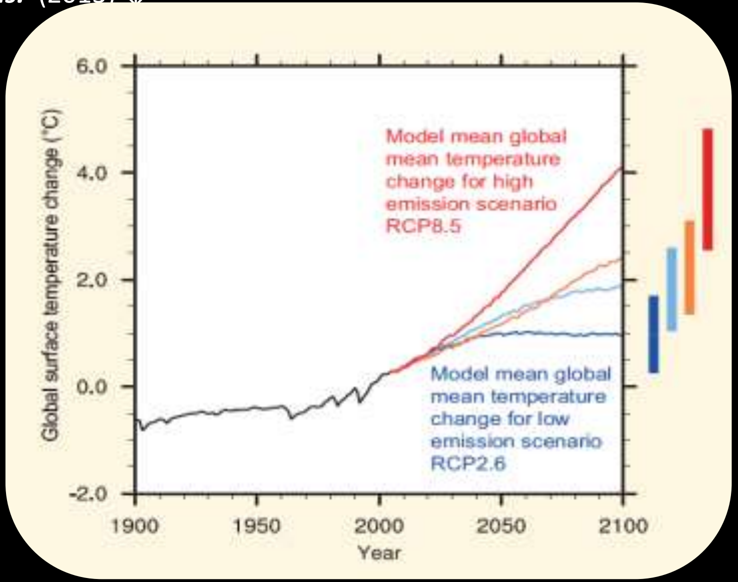
IRCELYON cnrs Lyon 1 CPE



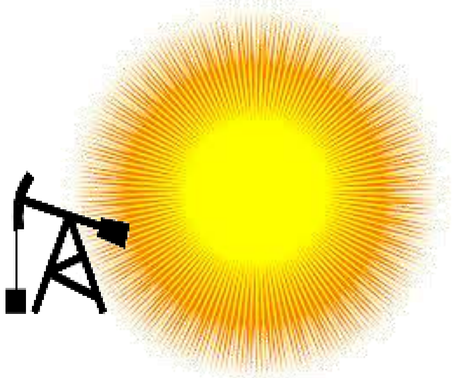


↑ . *Carbon tracker inititiative (2021)*↑ .

↓ 5th Asses. Report IPCollins *et al.* « *Long-term Climate Change: Projections, Commitments and Irreversibility.* » ***Climate Change 2013: The Physical Science Basis.*** (2013) ↓

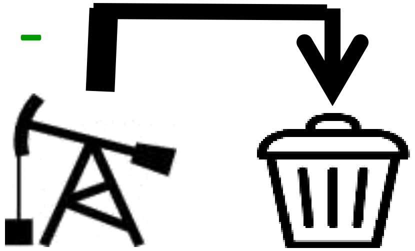


https://www.afd.fr © Arnaud Bouissou MEDDE / SG COP21



Circular -waste prevention-

Linear - Waste remediation -



I. FOSSIL FUEL AVOIDANCE

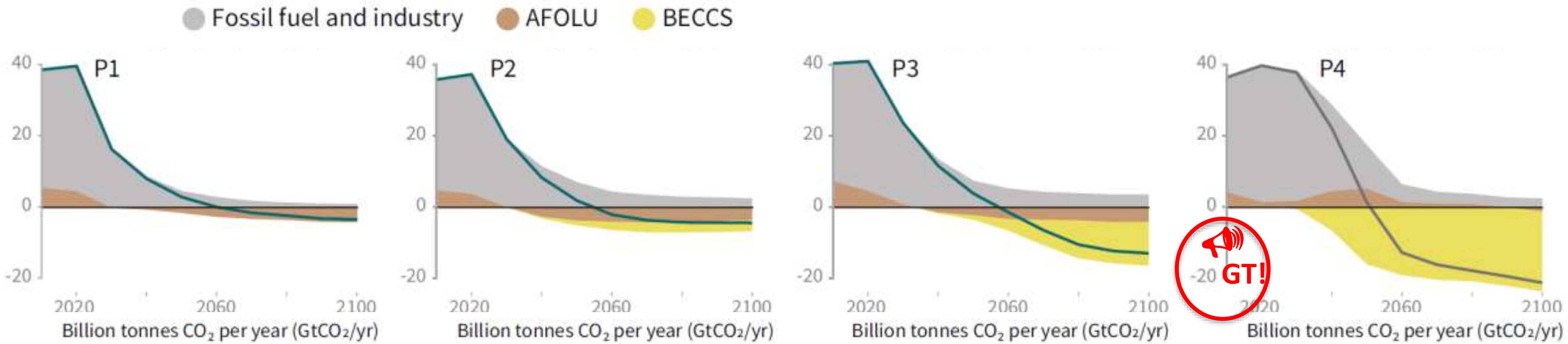
I-3 Replacement of feedstock of energetic fluids&solids

I-2 Increase Process (Energy) Efficiency

1-1 Reduce consumption

2 CO_2 – -mitigation related services

II. CO_2 SEQUESTRATION

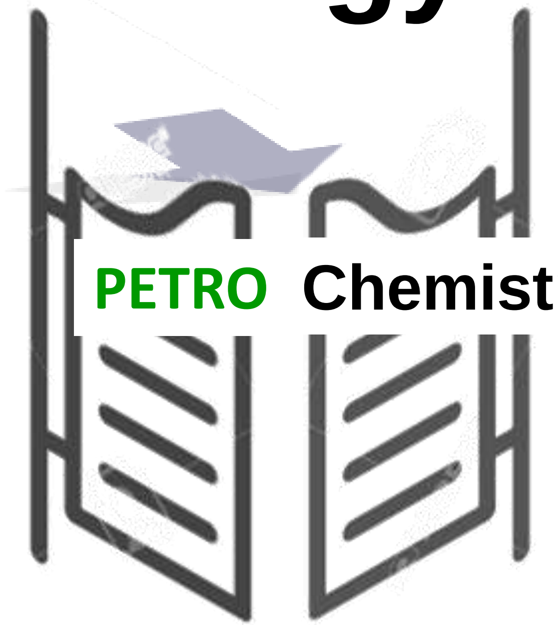


IPCC, 2018: Summary for Policymakers. In: Global warming of 1.5°C.

Same Atmospheric CO_2 emissions.
Very different futures

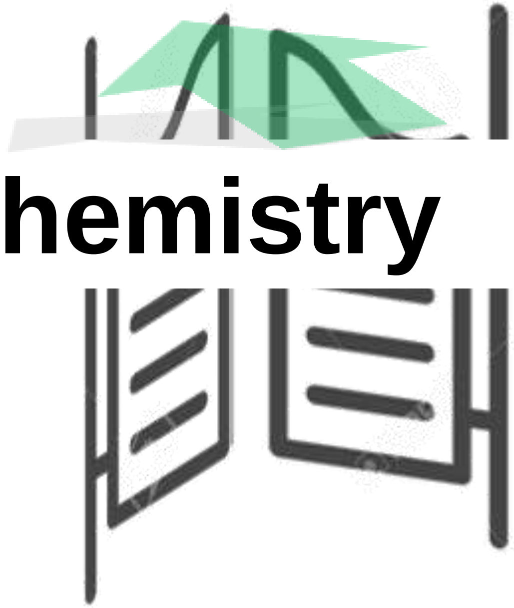
2-way Door

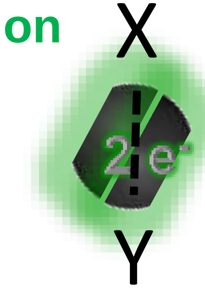
FOSSIL
Energy



PETRO Chemistry

RENEWABLE
Energy **Storage, distribution**

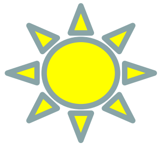




Chemistry

Energy consumption (mostly fossil fuel) to fuel energy-intesive (mostly thermic) Chemical industry

Chemistry to make « solar » fuels (that is fuels containing electrons produced form renewable resources)

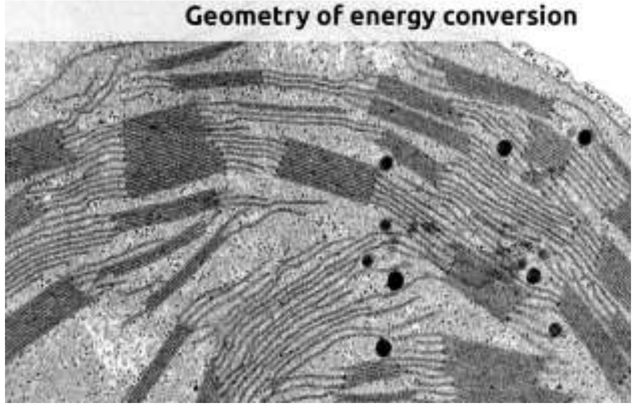


Principle GC Energy : +effciency & -Usage

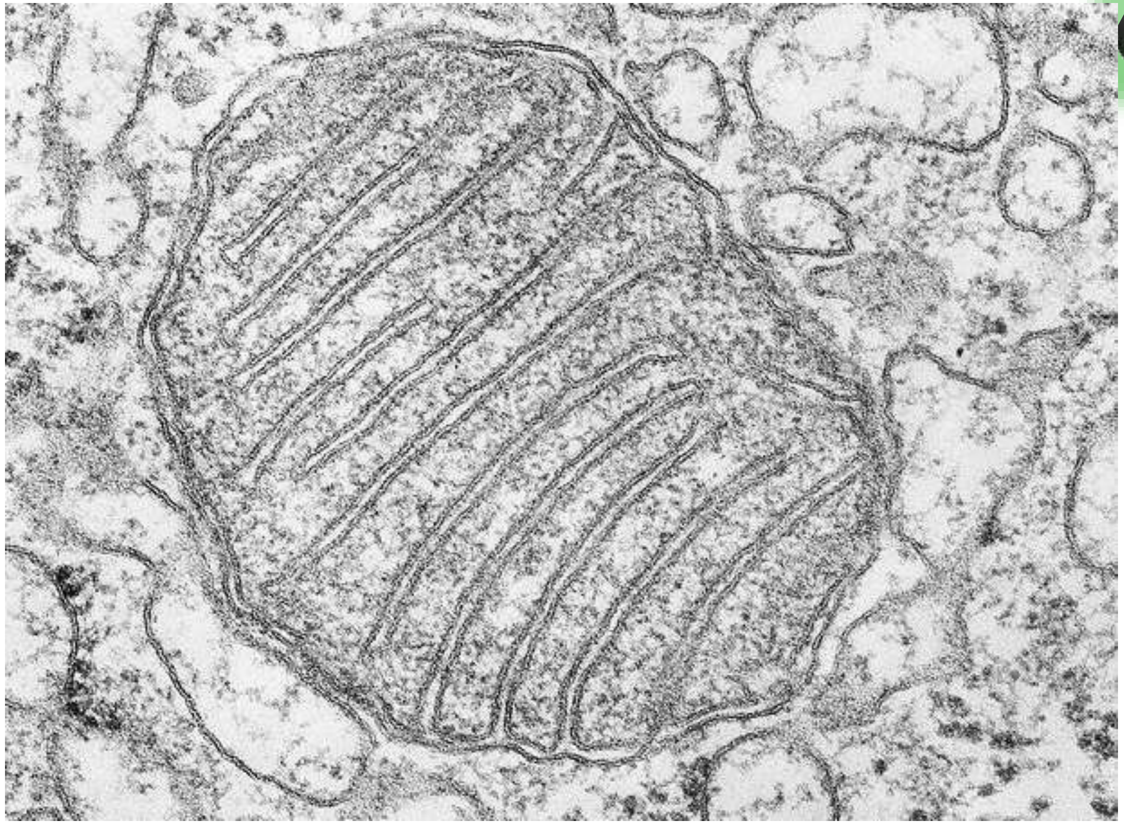
[2] P. T. Anastas, J. C. Warner *"Green Chemistry: Theory and Practice"*; Oxford University Press: Oxford, U.K., 1998.

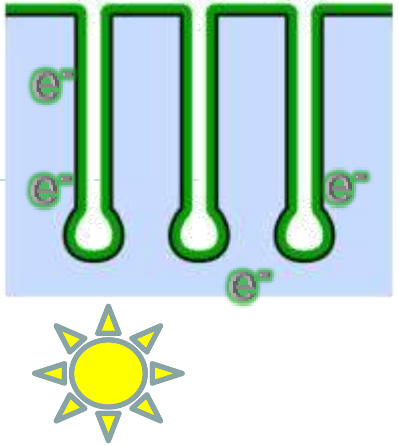
AQ Green Chem., **2016, 18, 328**

Nanostructured substrates for energy conversion and transport

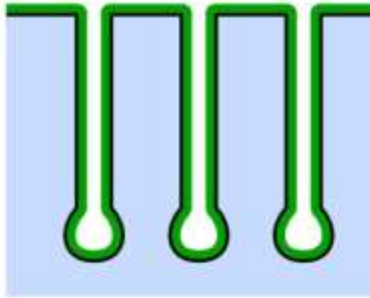


Elongated structures, scale 10 – 100 nm:
Balance large interface area and short transport paths
Enable for a systematic optimization
of energy conversion devices





…in nanostructured supports….

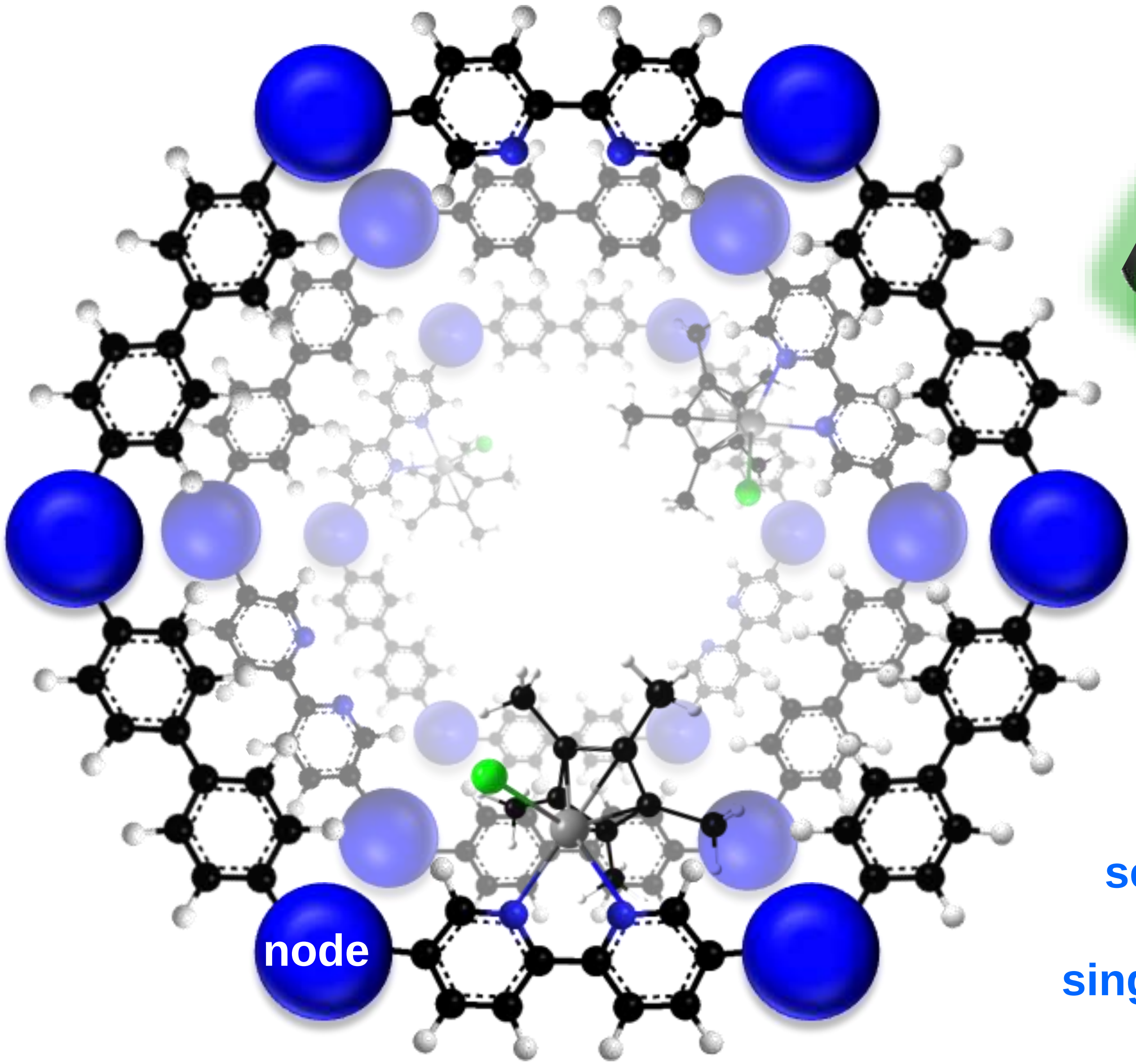


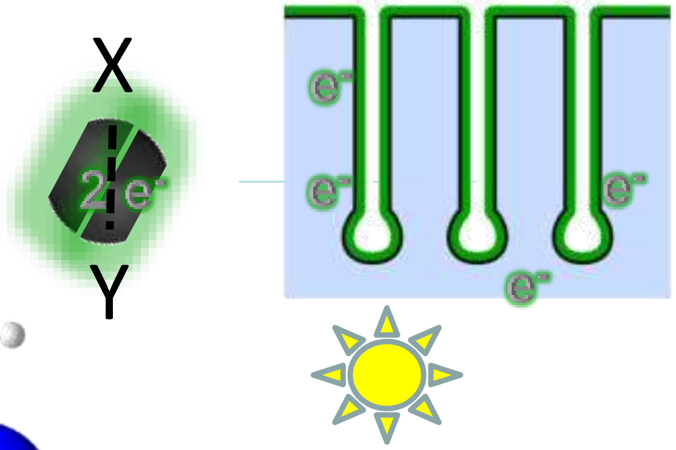
J. Bachmann, *Beilstein J. Nanotechnol.* **2014,** *5,* 245–248
Q. Liu et al. J. Nanopart. Res. 15:1–7.

from molecules

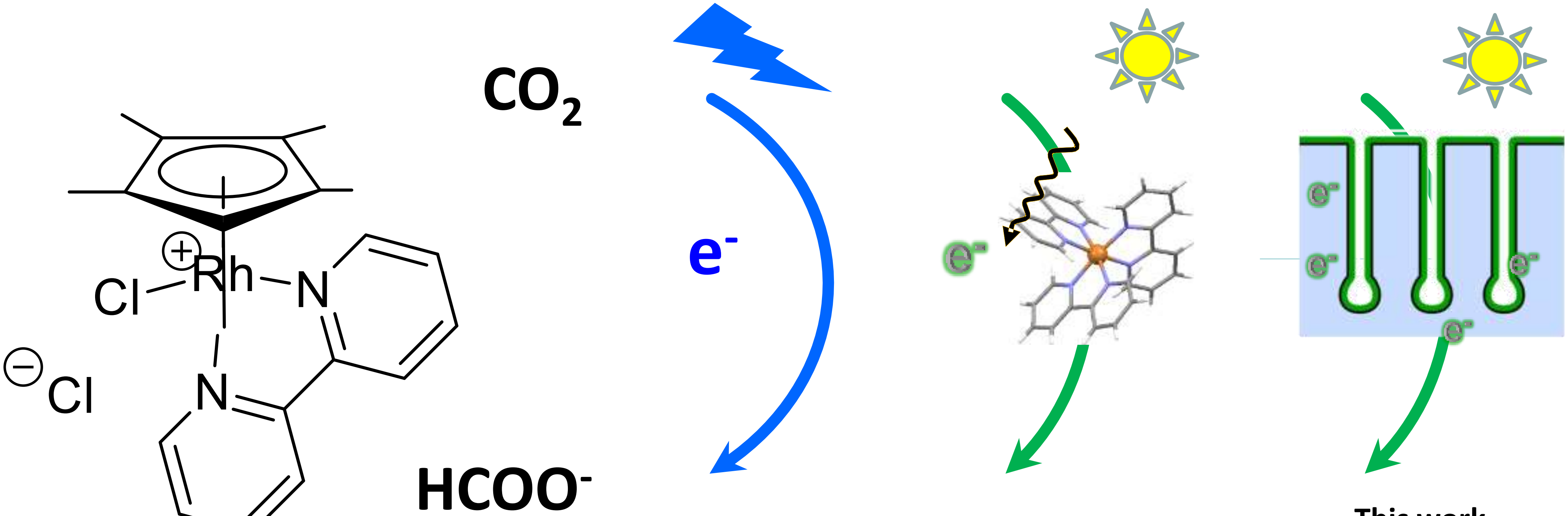
macromolecules

to solids





self-supported
porous
single site catalyst



S. Chardon-Noblat, A. Deronzier,
J. *Electroanal. Chem*. **1997**, 434, 163-170.

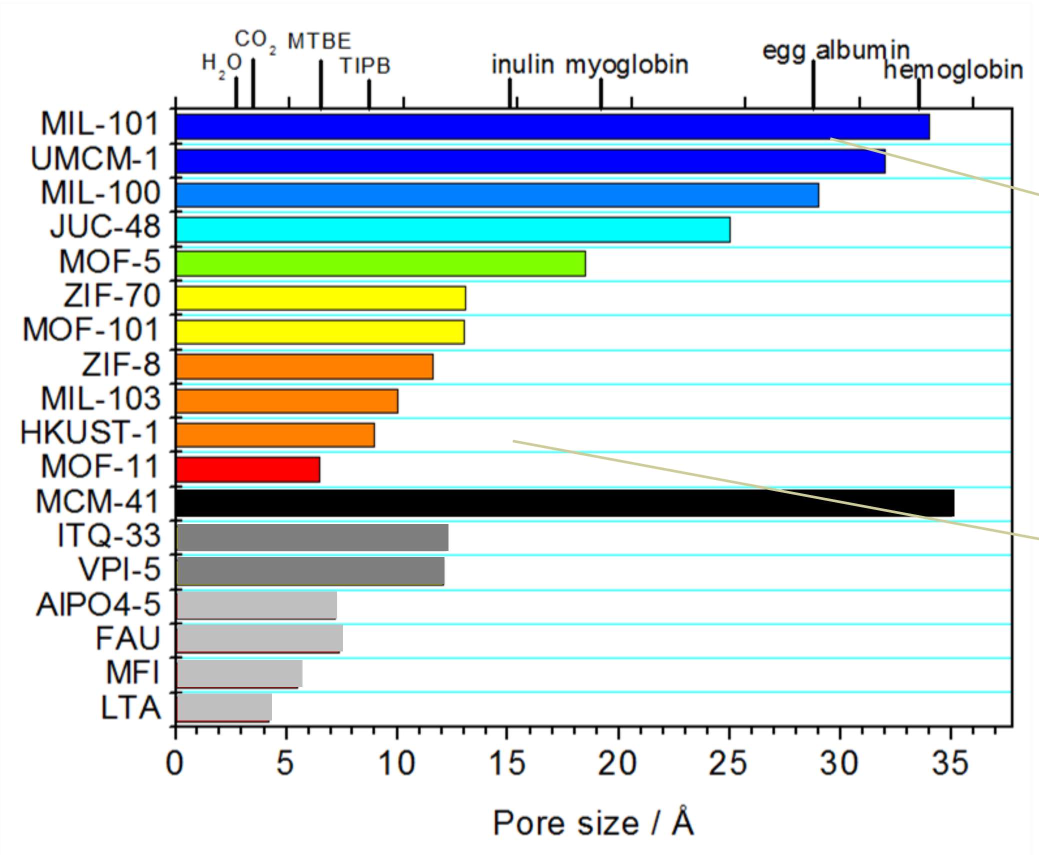
Marc Fontecave Caroline Mellot-Draznieks, Collège de France
Pers. Comm. ca. **2013**

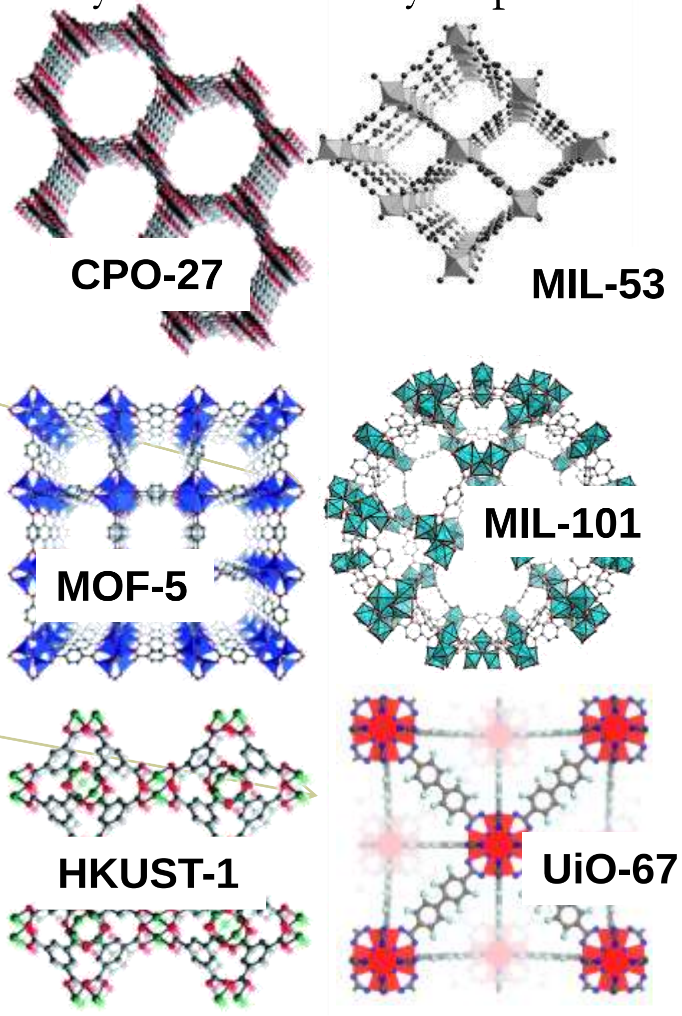
This work

Metal-Organic Frameworks

- Porous Coordination Polymers
- Organic-inorganic hybrids
- Stable

Numerous topologies:
Large variety dimensionality & pore size





J. CANIVET
IRCELYON

D. FARRUSSENG
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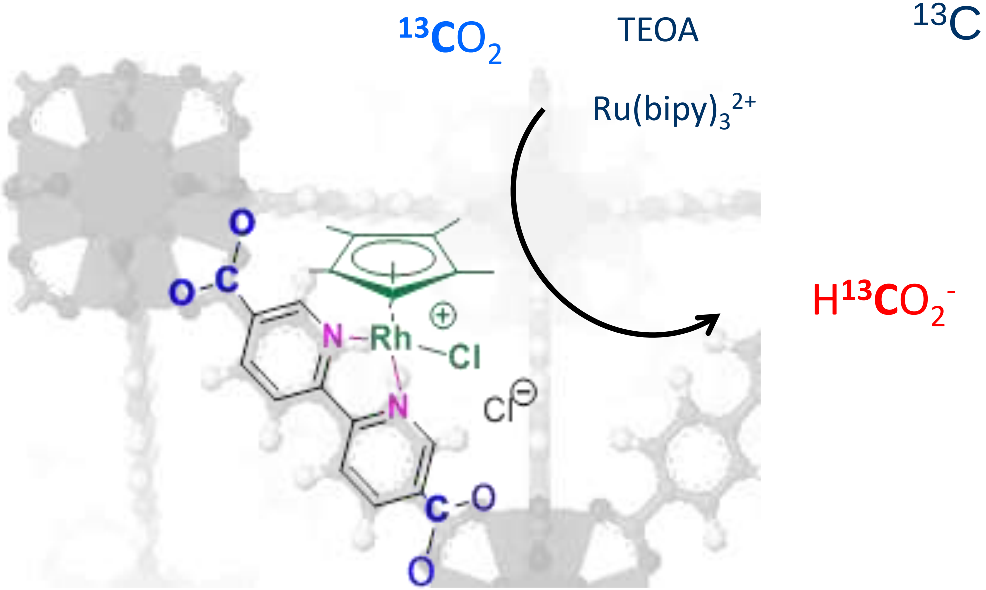
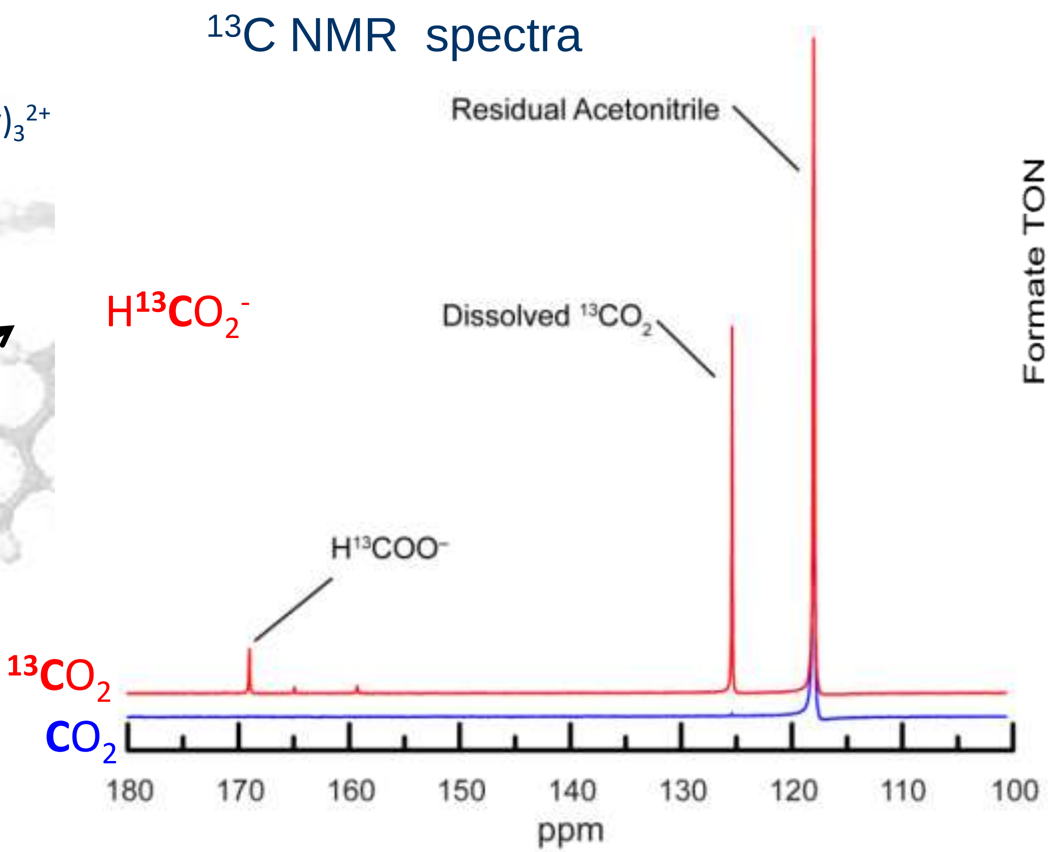
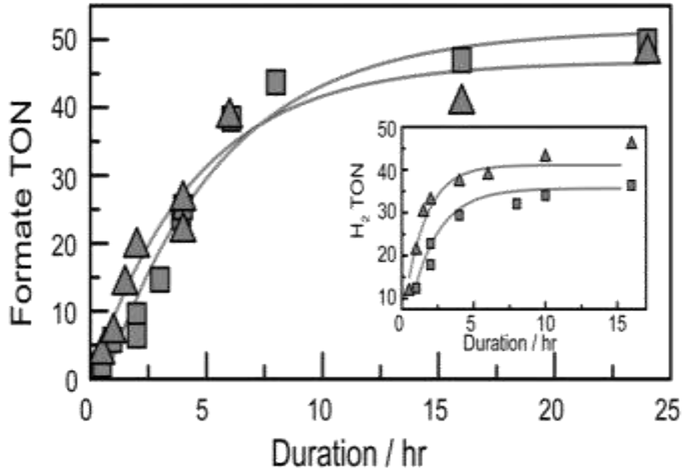


1.0m [Ru] ACN:TEOA (5: 1 vol:vol)
CO_2 saturated , 300 W Xe arc (415 nm), 20° C.





- □ -1.4 mg of 10%-Cp*Rh@UiO-67
- Δ - 0.1 mM of Rhodium complex

1.0mM $Ru(bpy)_3Cl_2$, ACN:TEOA (5: 1 vol:vol) , CO_2 saturated , 300 W Xe arc (415 nm), 20° C.

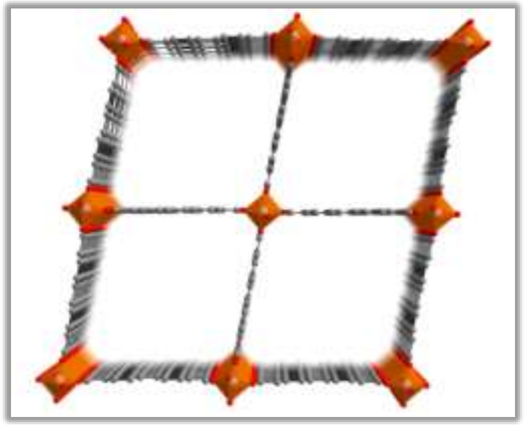
N. Elgrishi, M. B. Chambers, X. Wang, C.H. Hendon, A.Walsh, J.Bonnefoy, J. Canivet, E. A. Quadrelli, D. Farrusseng, C. Mellot-Draznieks M. Fontecave,* **ChemSusChem** , 8, 603 (2015)

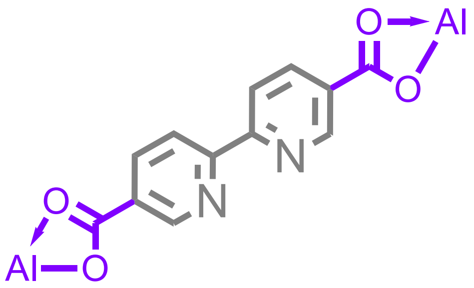
The Principle of Microporous Macroligands

F. WISSER
REGENSBURG

Host structures

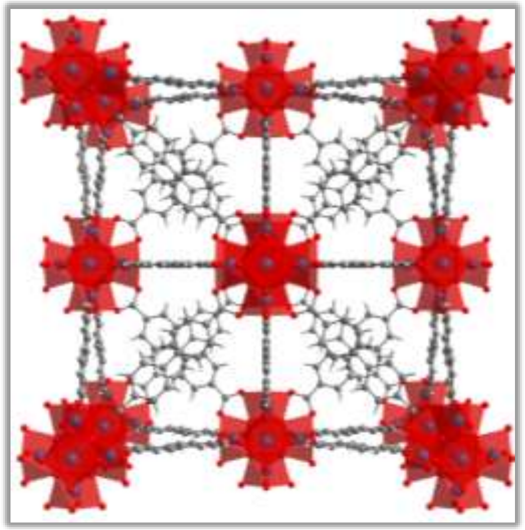
MOF-253 / DUT-5

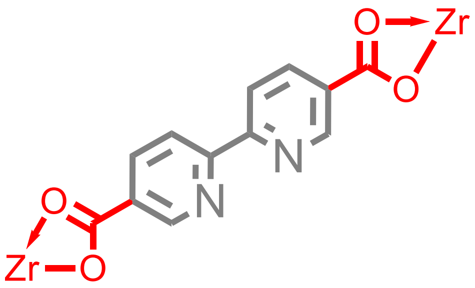




- 1D channels
- Pore size: 1.1 nm

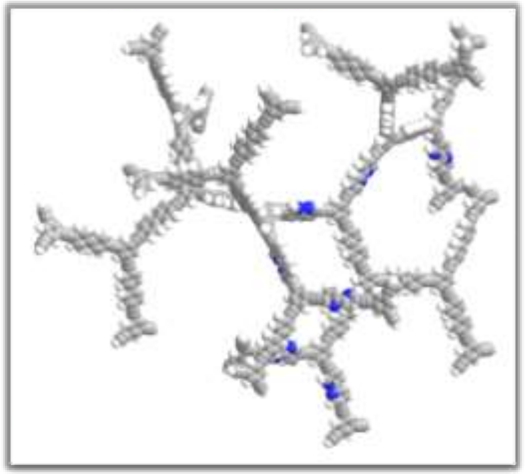
UiO-67

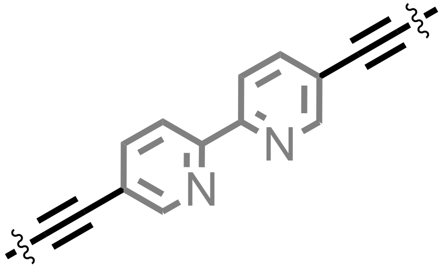




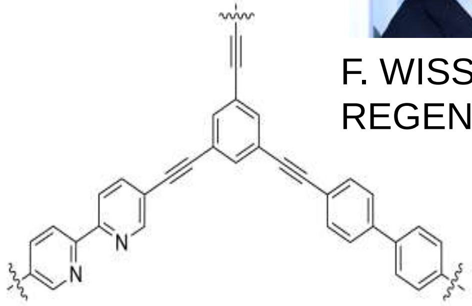
- 3D pore network
- Pore opening: 0.65 nm

BpyMP-1/-2

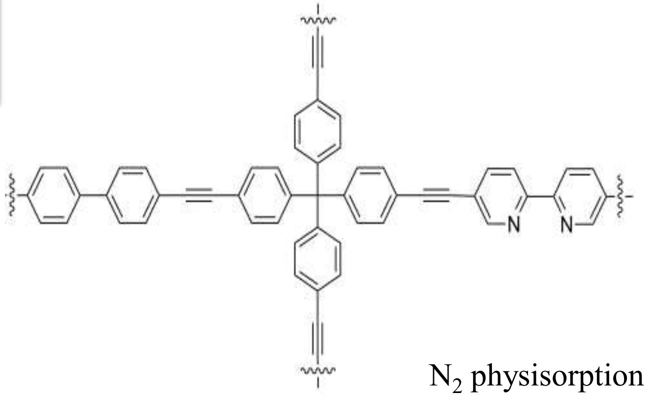




- 3D pore network
- PSD: 0.6 – 1.6 nm



BpyMP-1



BpyMP-2

N_2 physisorption isotherms

Elemental composition

XPS (N1S, Rh3d, C)

DNP SENS CP MAS spectra

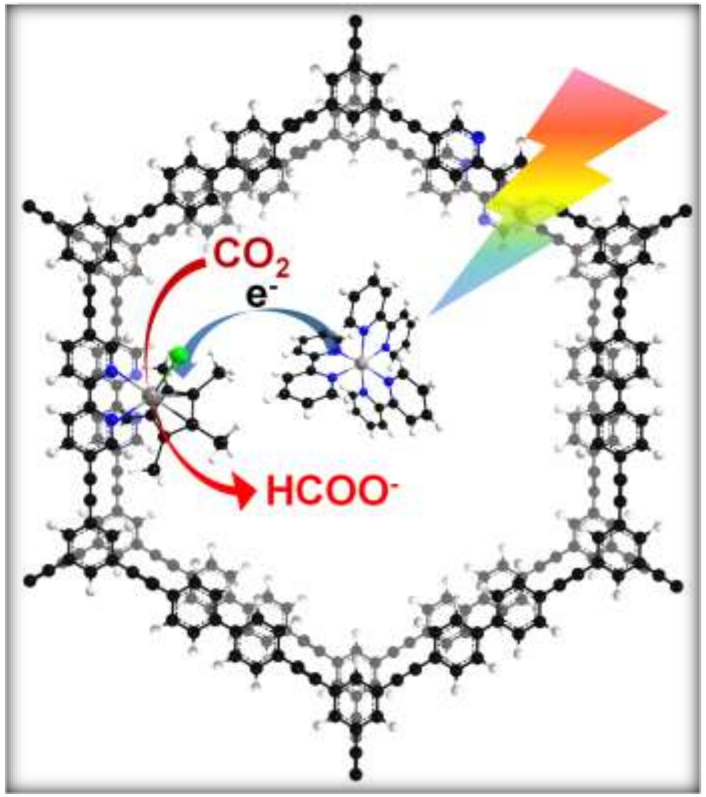
^{1}H-^{13}C HETCOR, ^{13}C

IR

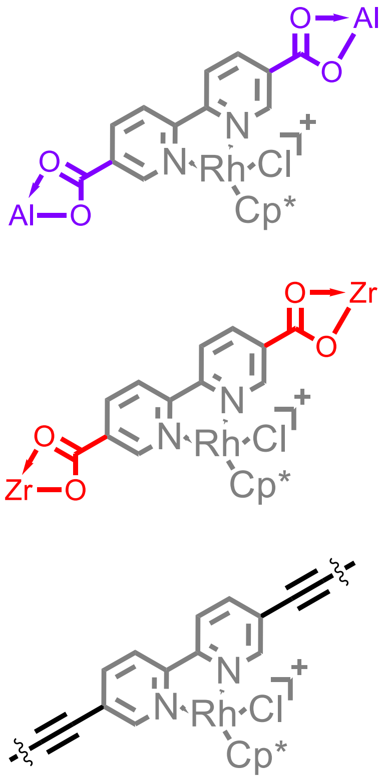
UV Vis

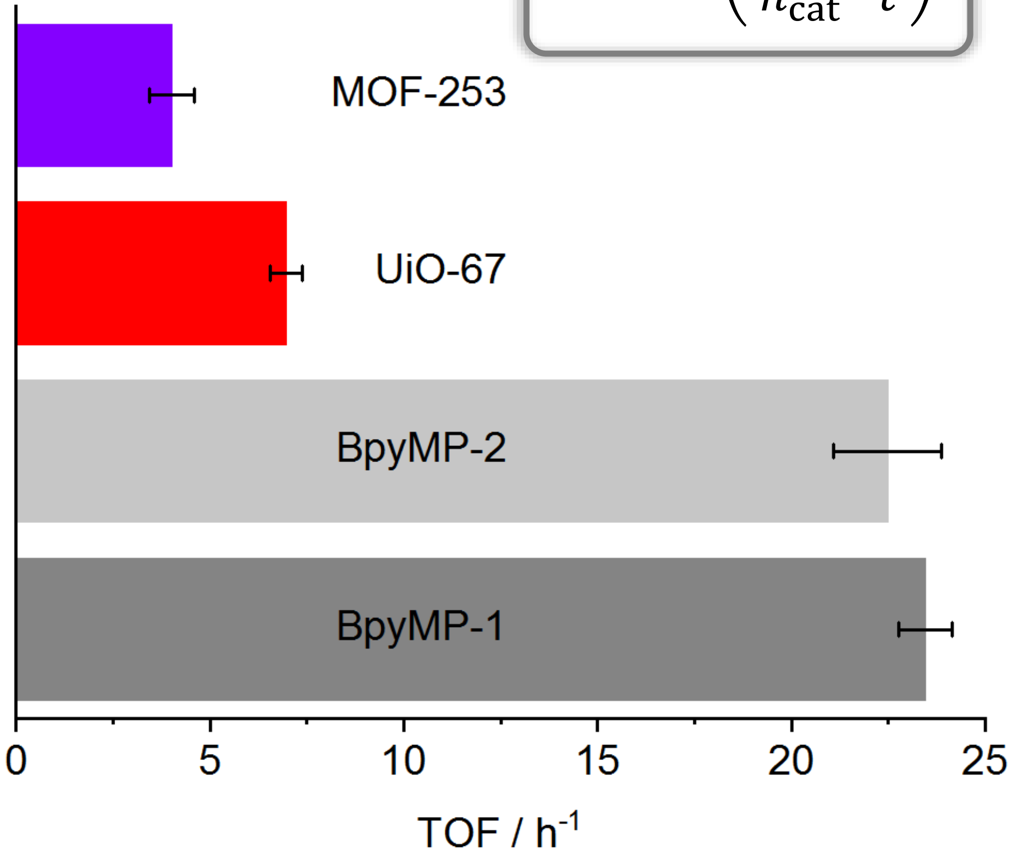
Photocatalytic CO_2 reduction

$$TOF = \left(\frac{n_{HCOO-}}{n_{cat} \cdot t}\right)$$



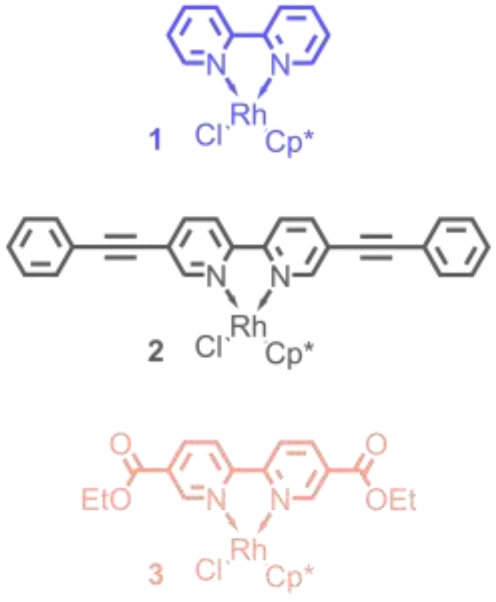
2.2 ml 1 mM $Ru(bpy)_3Cl_2$ in ACN : TEOA
1 mg catalyst (~ 0,15 µmol)
200 W Hg lamp, 420 – 800 nm

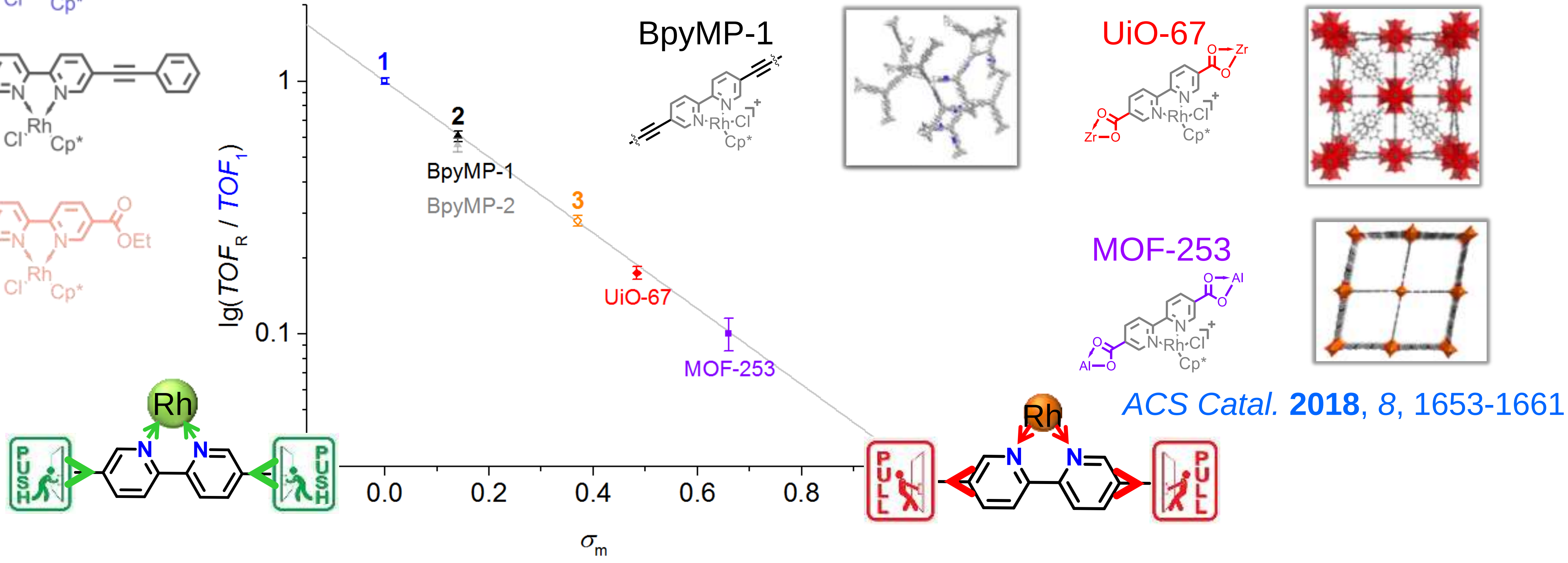




- highest *TOF* for formate production (24 h^{-1})

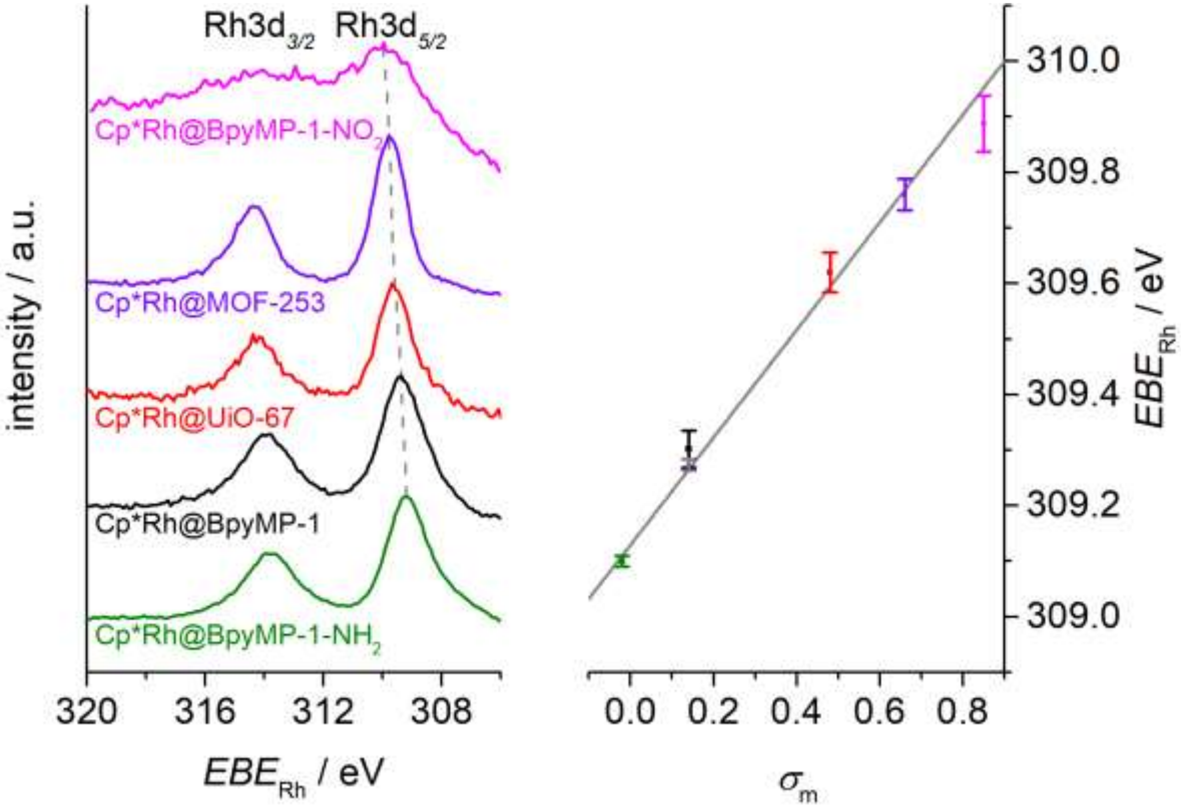
Hammett principle valid for heterogeneous molecular catalyses
Common **descriptor** for homogeneous and heterogeneous catalyses

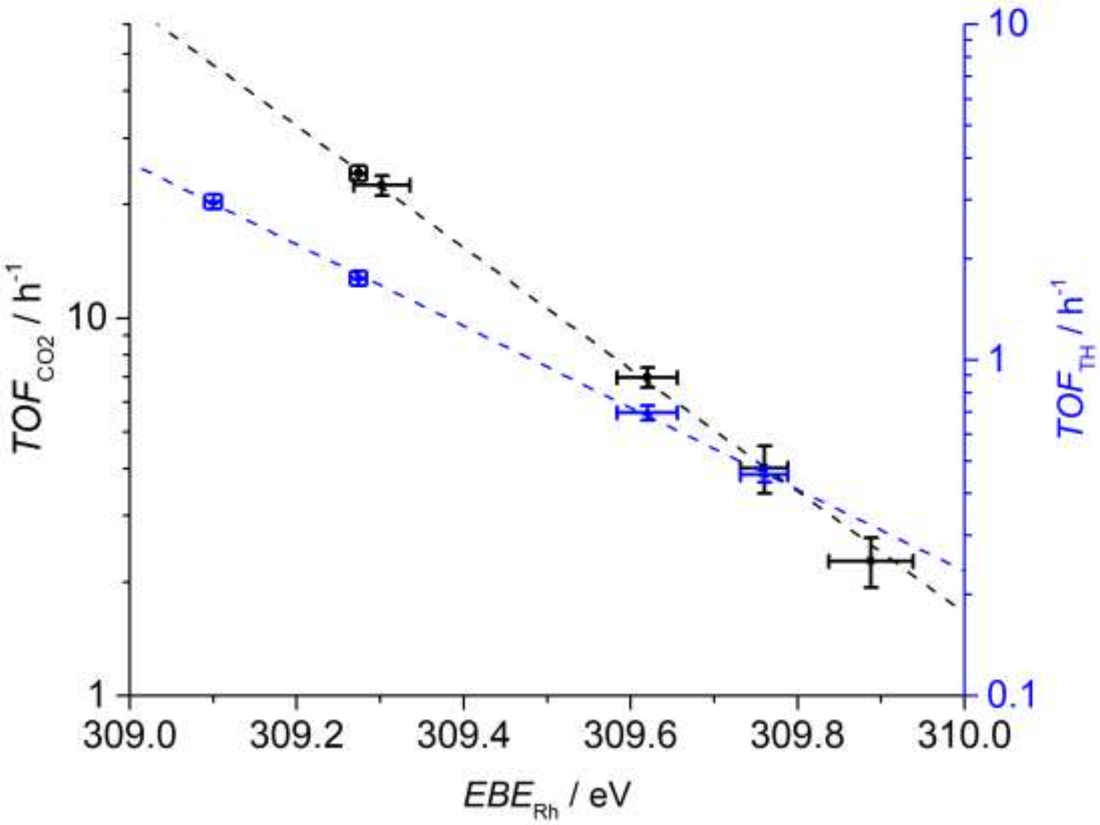




- ✓ **Linearity** σ_m vs. *TOF*
- ✓ **Hammett equation is valid for photocatalysis**

- ➢ BpyMP-1, BpyMP-2, MOF-253 und UiO-67
  - ✓ Performance is driven by **electronic effects** of the host
  - ✓ **No diffusion limitation**

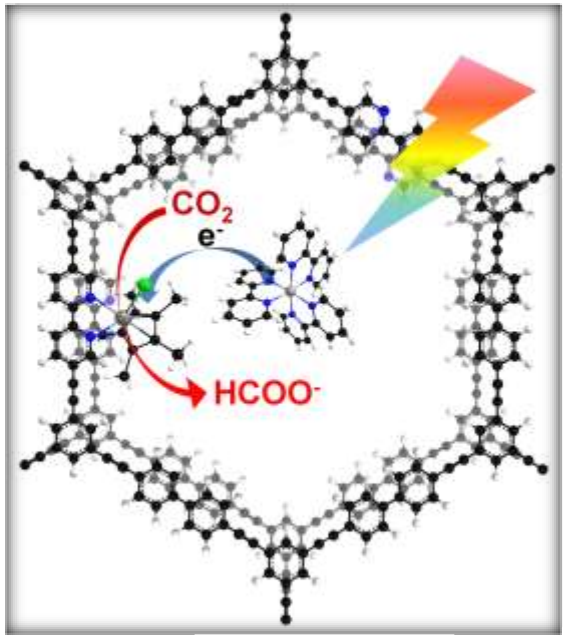


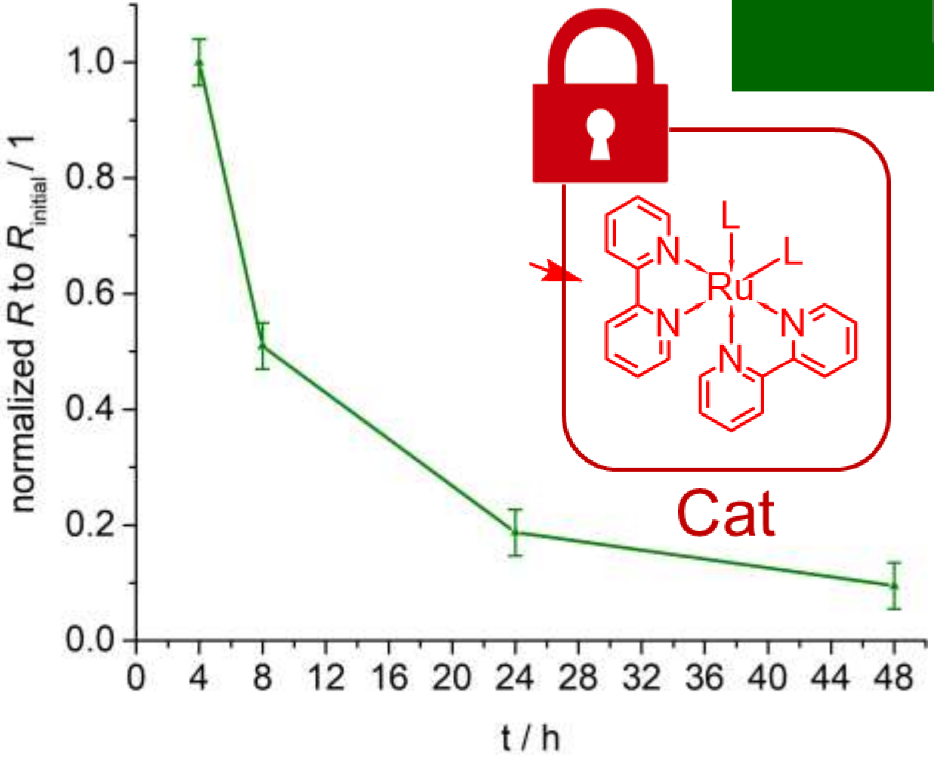


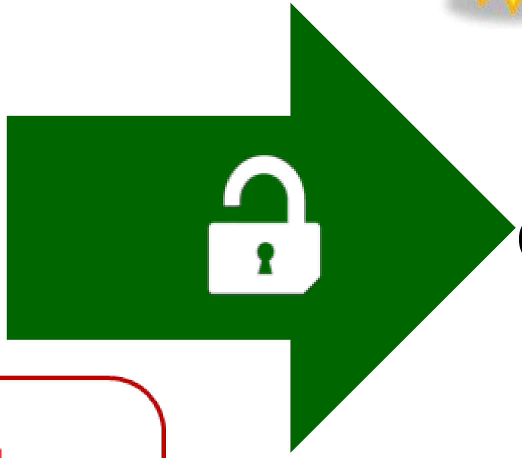
- $\boldsymbol{\sigma_m}$ proportional to ***EBE***
- ***TOF*** proportional to ***EBE***

ACS Catal. **2018**, *8*, 1653-1661

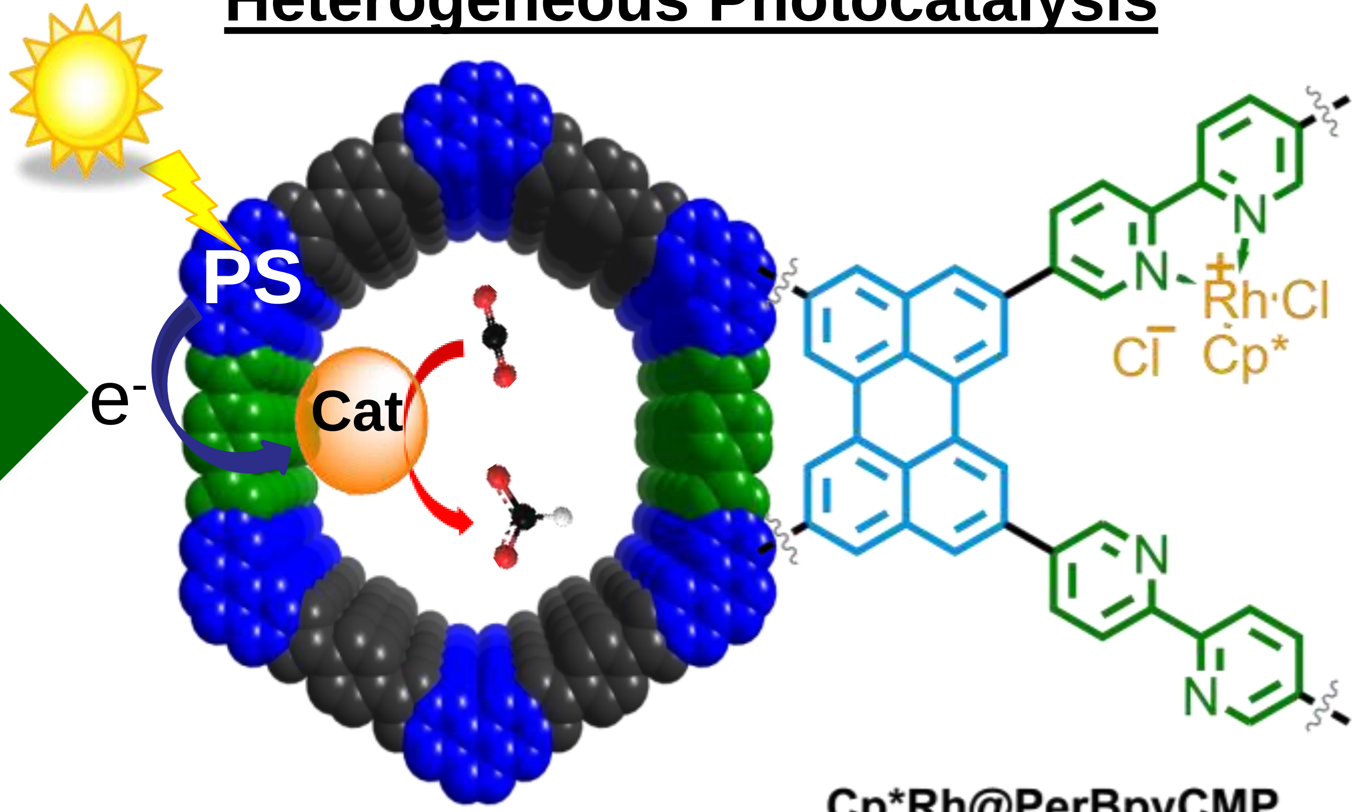
ChemCatChem **2018**, *10*, 1778-1782.







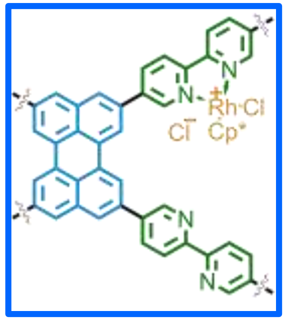
Heterogeneous Photocatalysis



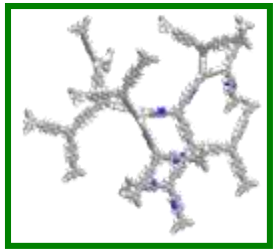
Cp*Rh@PerBpyCMP

single material
all in one photosystem
100 % working atoms

New completely heterogeneous catalysts – catalytic activity –



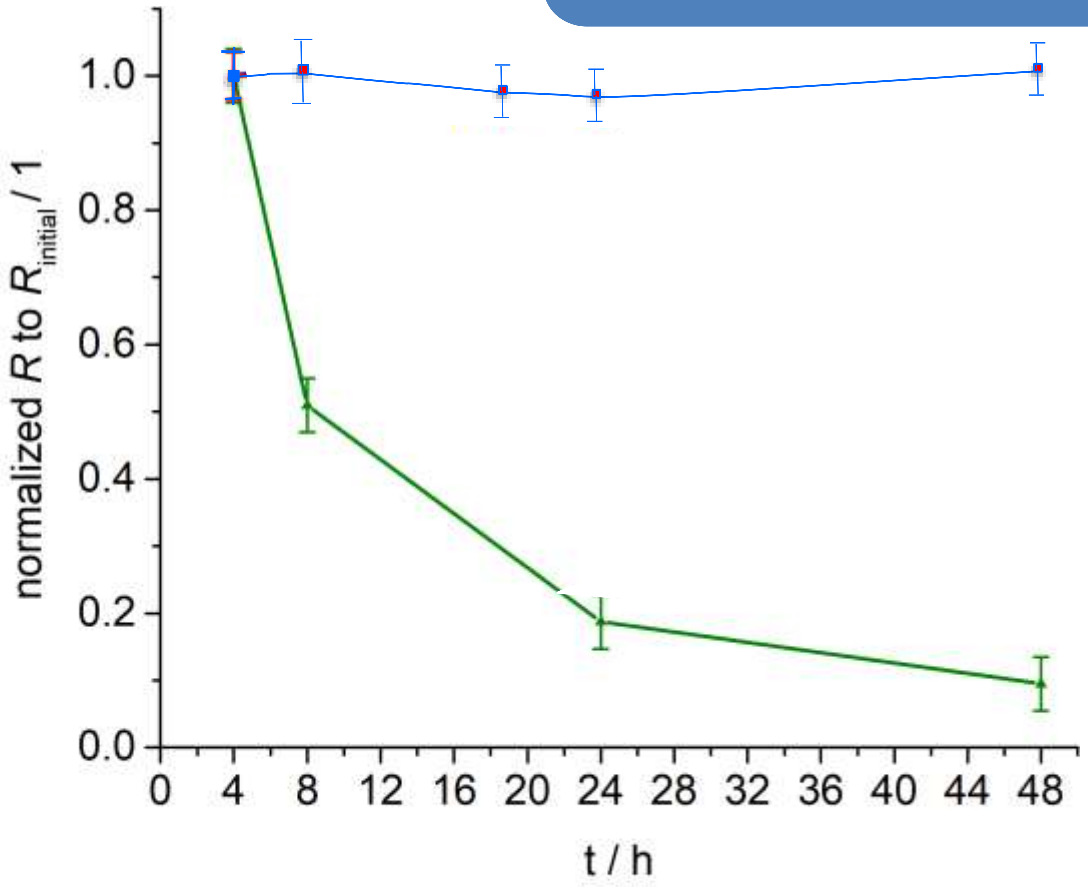
perylene



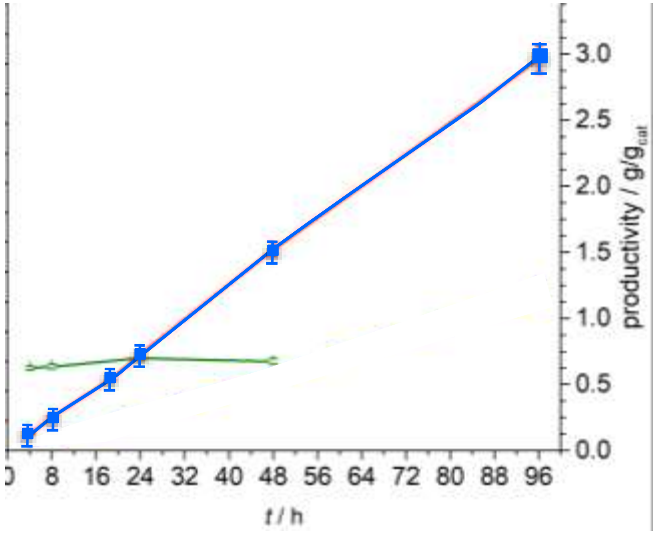
(external photo-Sensitizer)

BpyMP-1

$Ru(bpy)_3Cl_2$



$$R = \left(\frac{n_{HCOO-}}{m_{cat} \cdot t}\right)$$



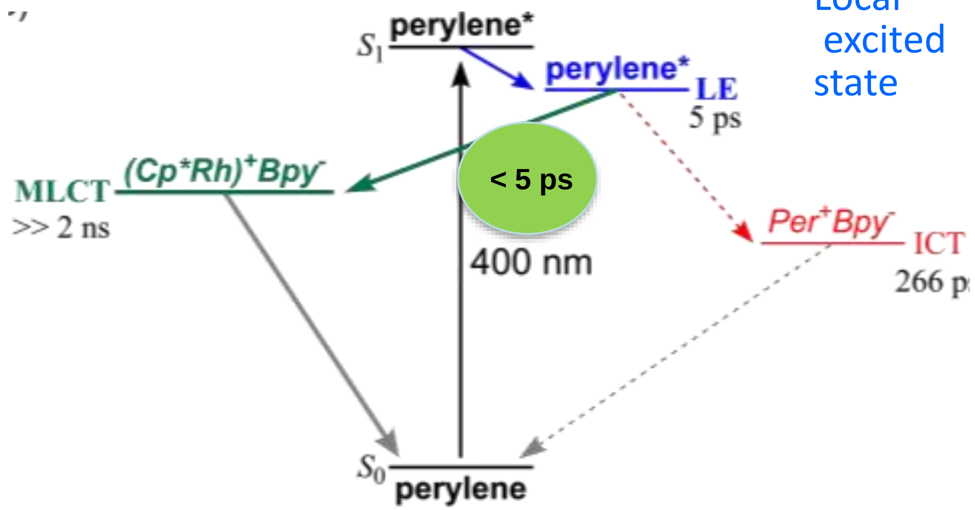
- ✓ time independent production rate
- ✓ higher overall production after 24 / 50 h
- ✓ Pyrene and Perylene based photosystems still active after 96 h

Wisser, ANGEW CHEM IEE

Inisight on activity through Excited state photodynamic & DFT

time-correlated single photon counting (TCSPC) and femto-second transient adsorption (TA) spectroscopy :
Quentin Perrinet, Vincent de Waele, U. Lille

« Metal-to-Ligand » like Charge Transfer state



Local excited state

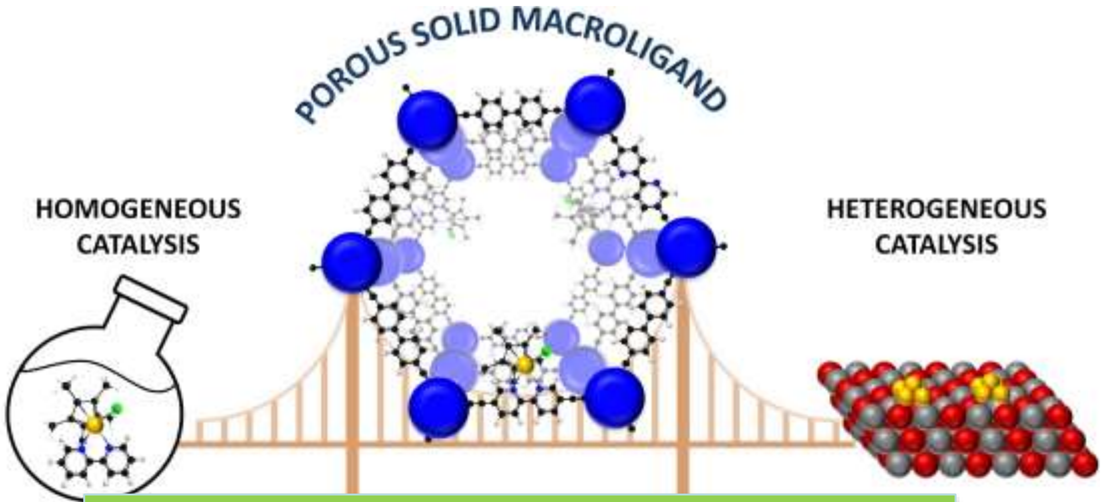
Internal Charge Tranfer state

HOMO LUMO by DFT(B3LYP/6-311++g(d,p) level of theory and at B3LYP/6-311++g(d,p)/LanL2DZ level of theory)
Caroline Mellot-Drazniek, Collège de France

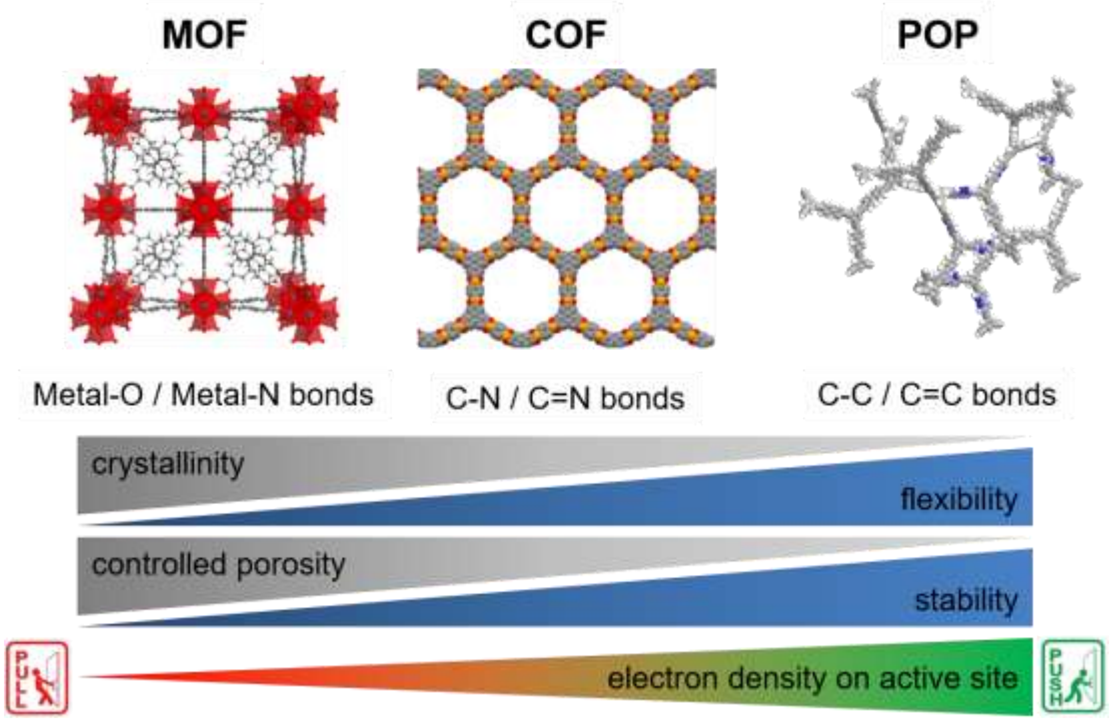
Florian M. Wisser, et al.* ***Angew.Chem.Int. Ed.*** *2020, 59,5116 –5122*

The Principle of Microporous Macroligands – conclusion –

From homogeneous to heterogeneous catalysis: Different systems but one rule

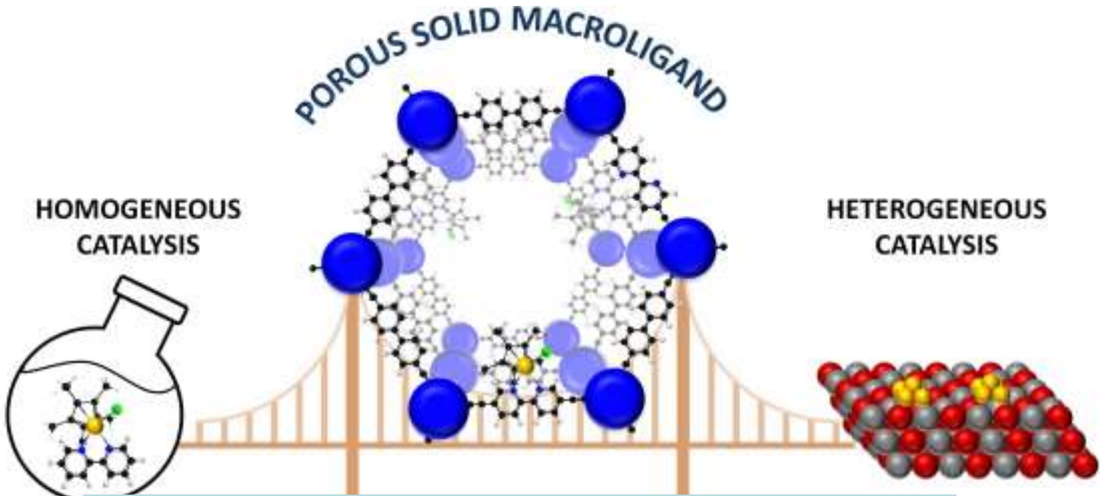


Molecular concept portability



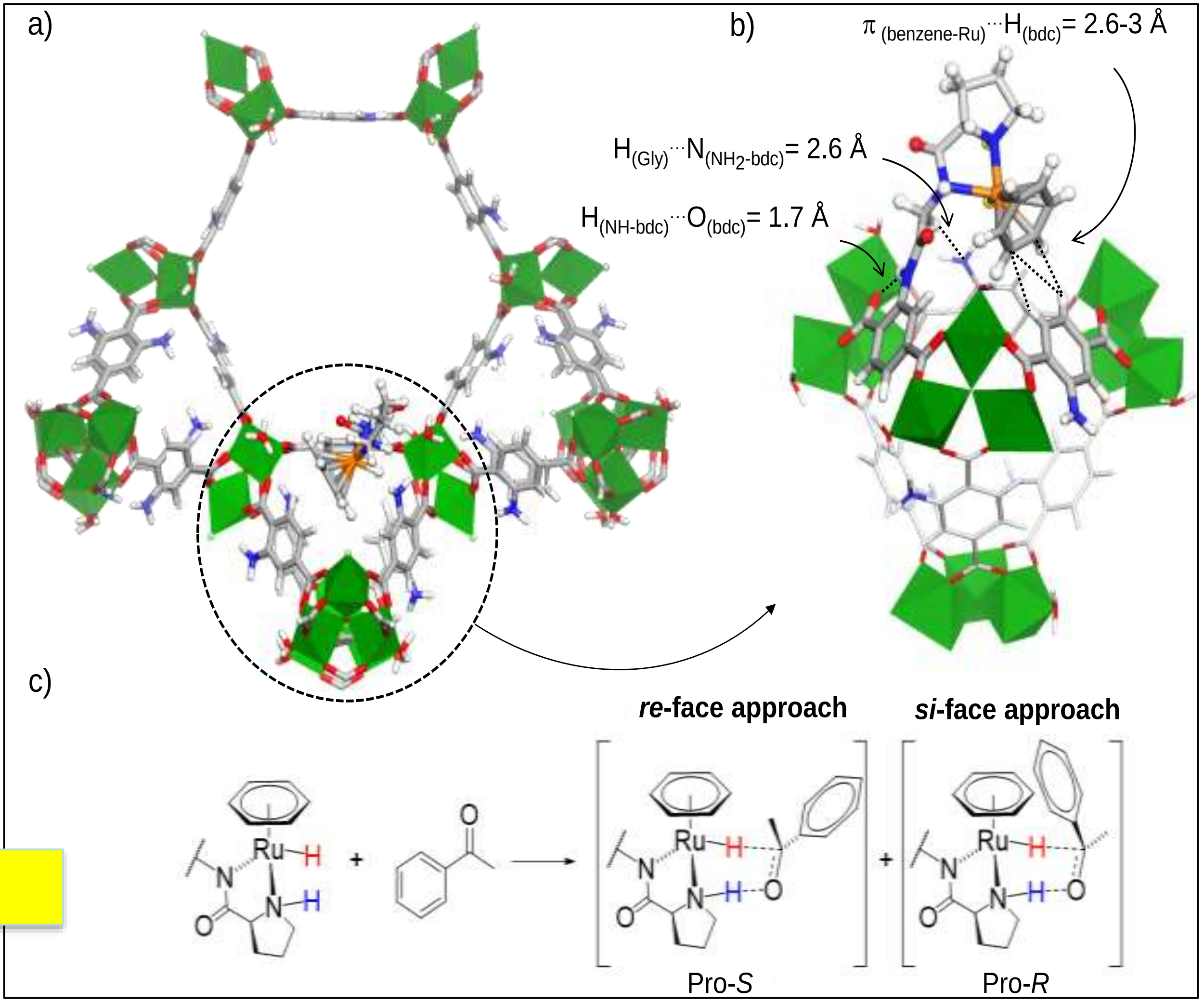
The Principle of Microporous Macroligands – conclusion –

From homogeneous to heterogeneous

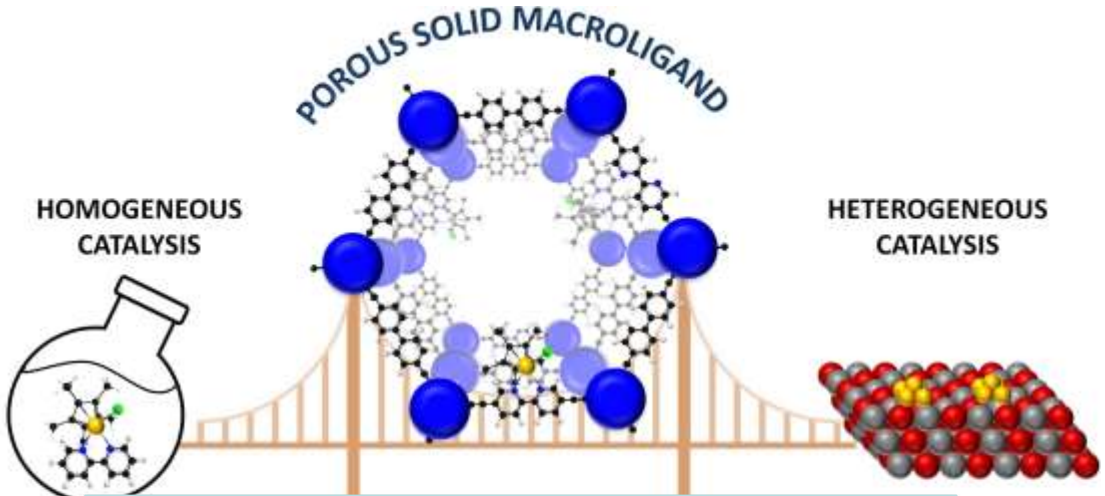


Molecular concept portability

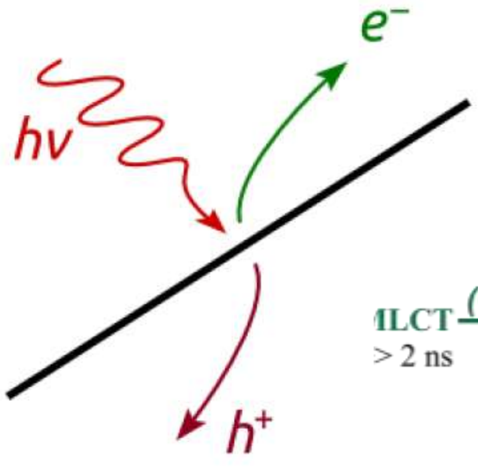
Control Beyond the 1st coord. sphere

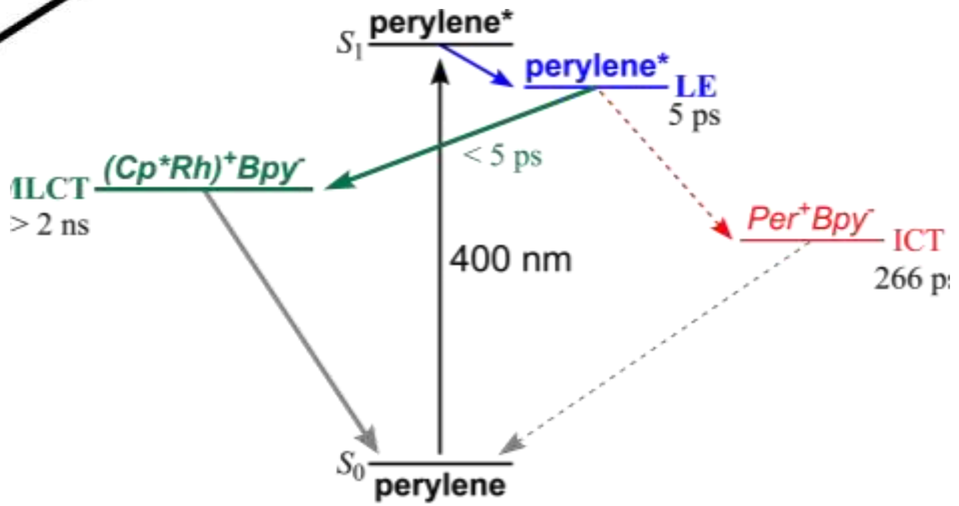


Canivet*, Mellot-Drazniek* et al. Chem Science, 2020, 11, 8800-8808



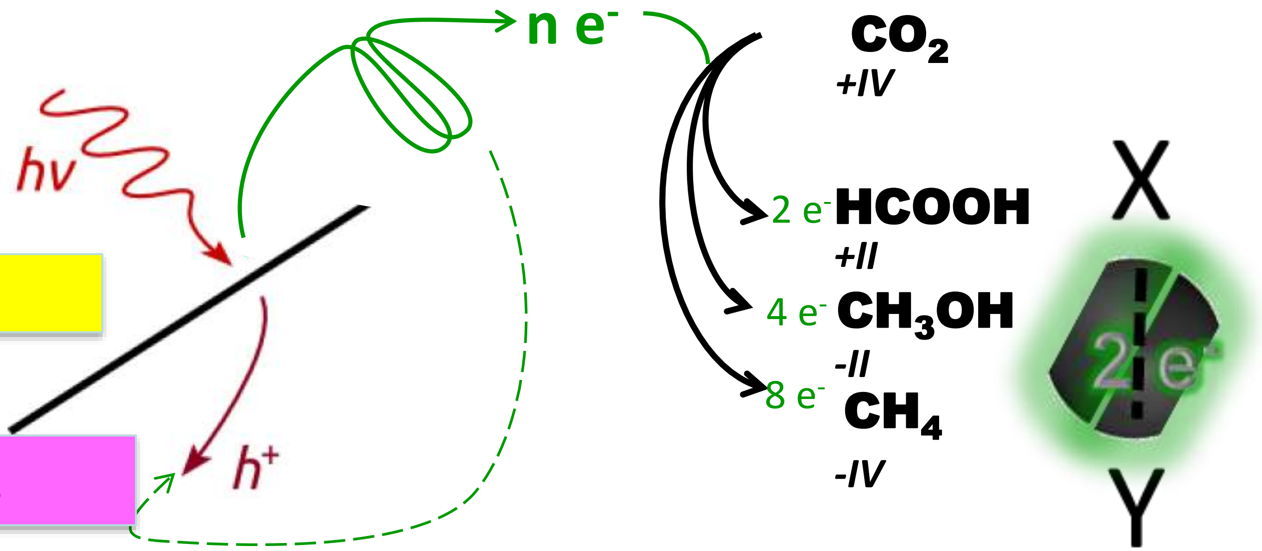
Molecular concept portability



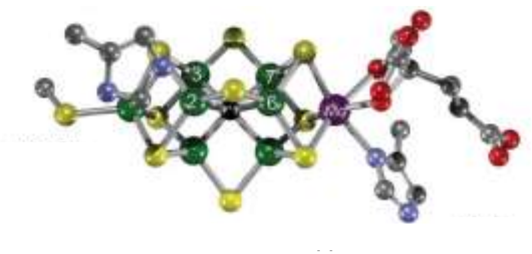


Control Beyond the 1st coord. sphere

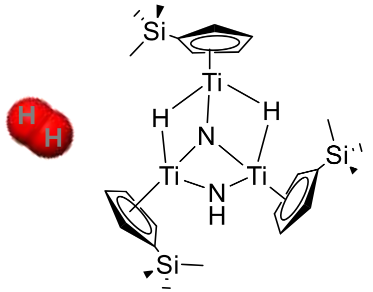
Spatially Engineer e- buffering systems



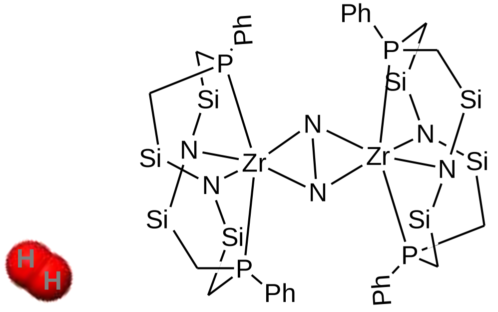
N_2 Cleavage: Different Mechanisms at hand



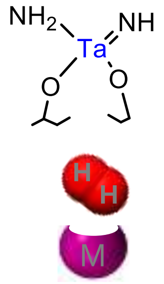
Henderson *et al.* ***Chem. Rev.*** 2005



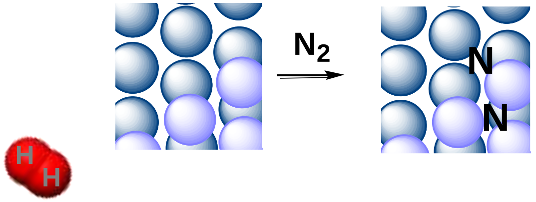
Hou *et al.* ***Science*** 2013



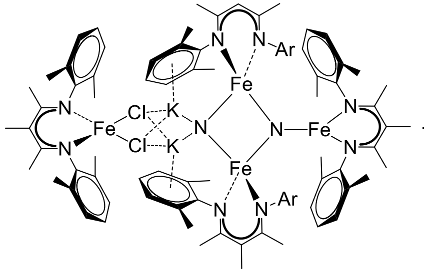
Fryzuk *et al*. ***Science***, *97* 1997



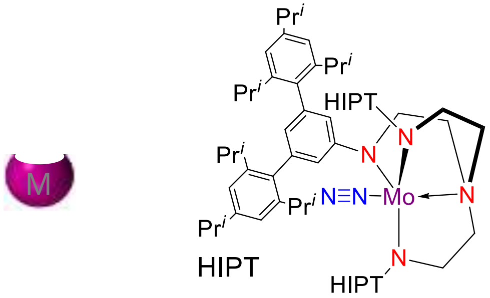
Science 317, 1056-1060 (2007).



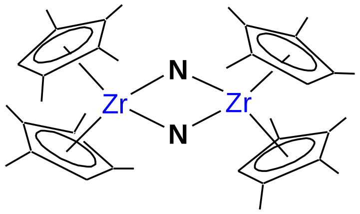
Ertl ***Angew Chem.*** 2008



Holland ***Science***, 2011



Schrock & Yandulov ***Science*** 2003



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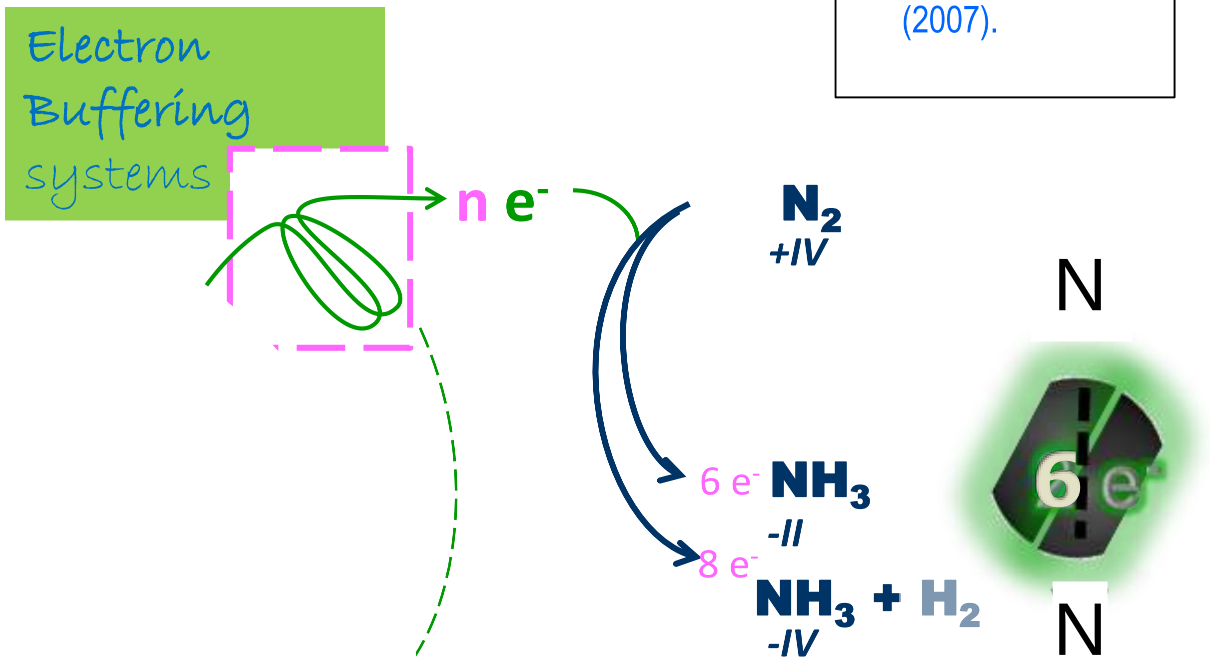
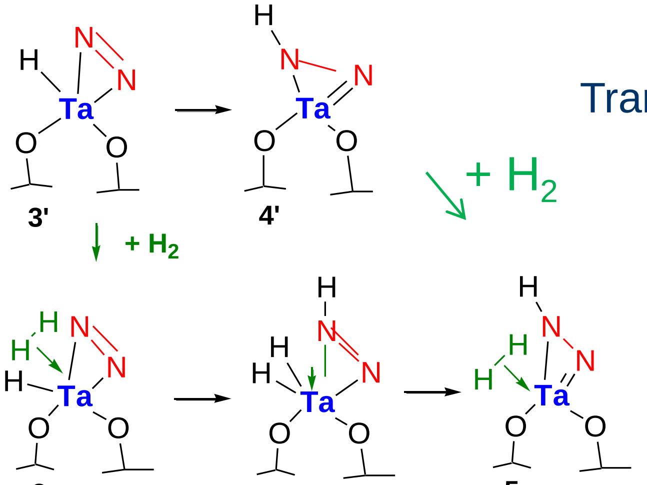


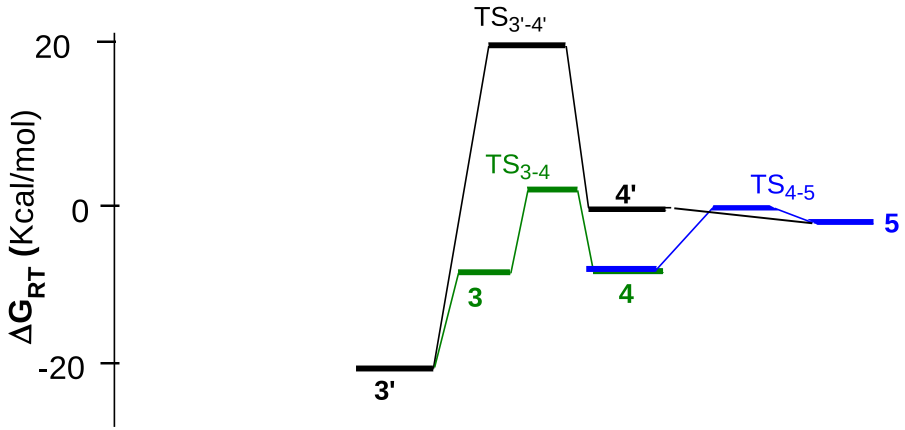
Role of isolated metal in proposed mechanism

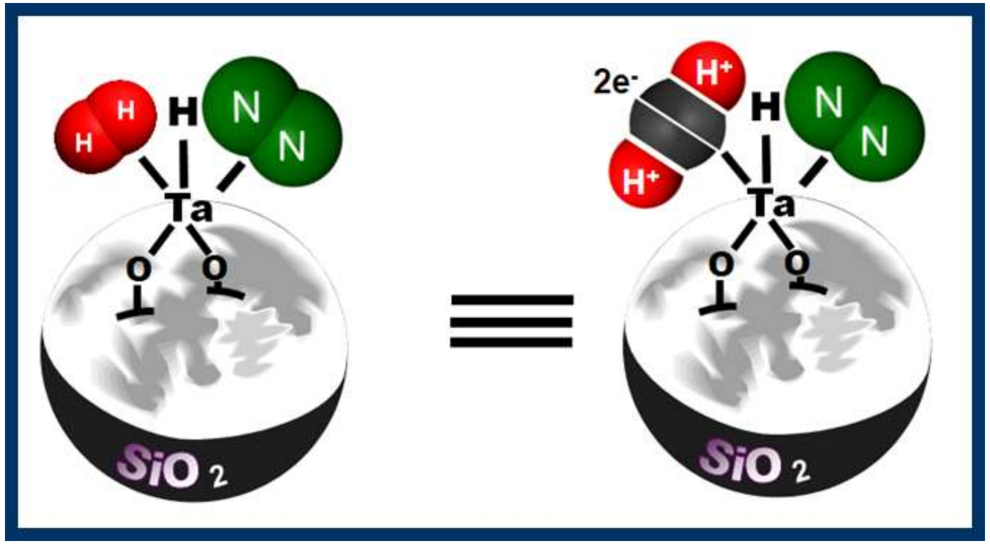


Transfer  aided by **Ta$_1$(η2-H$_2$)**

H_2 as '  ' source

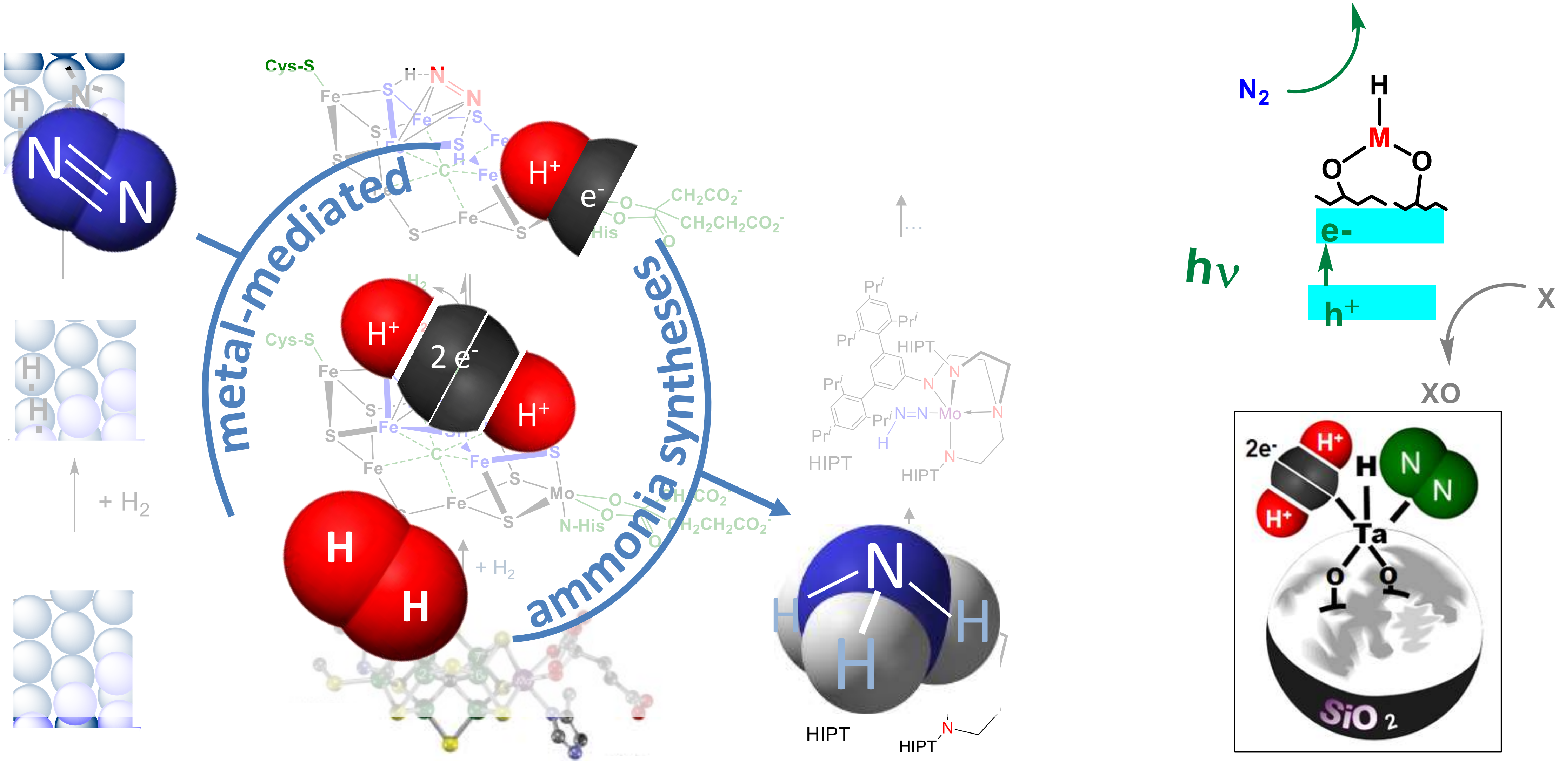
H_2 in '  ' transfer





X. Solans-Monfort,* C. Chow, E. Gouré, Y. Kaya, M. Taoufik, J.-M. Basset,* E.A.Q* and O. Eisenstein* ***Inorg. Chem.*, 7237 (2012)**

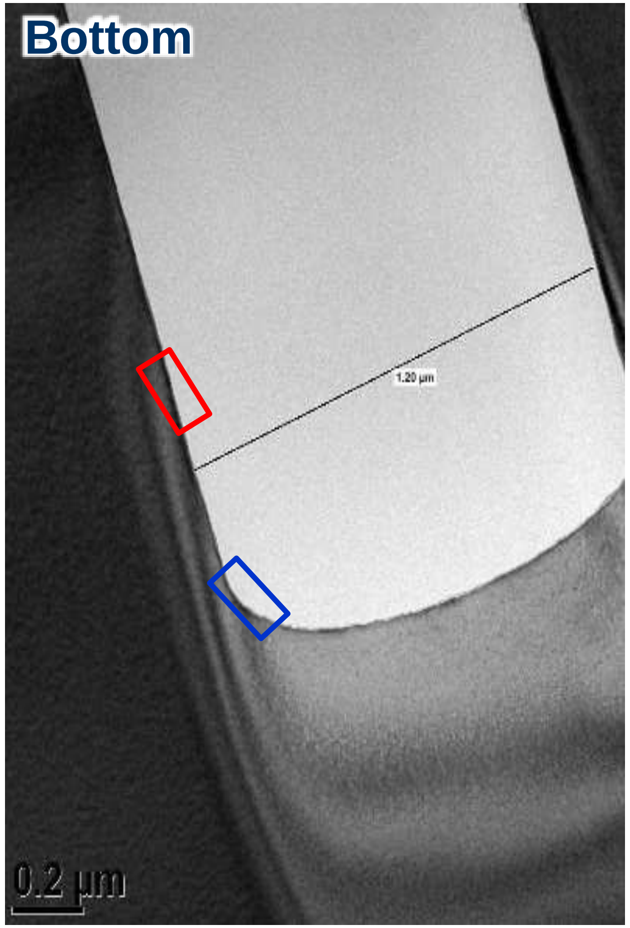
Mechanistic comparison of catalysts

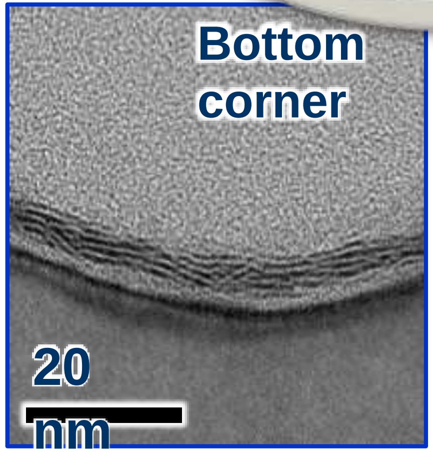


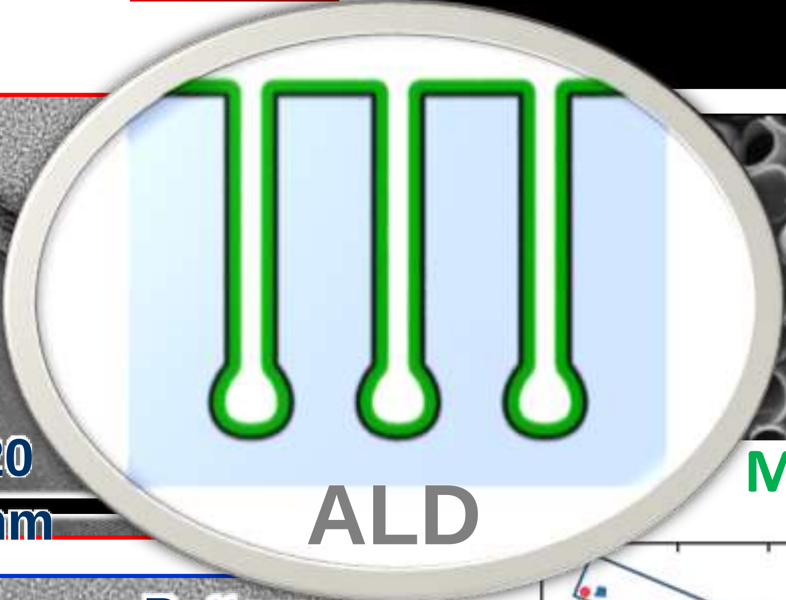
H.-P. Jia and E. A. Quadrelli **Chem. Soc. Rev.** *43 247* (2014)

ML MoS_2 on ALD tool

Uniform MoS_2 deposit in a 1 µm-wide TSV







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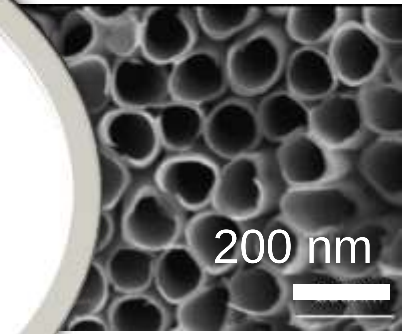
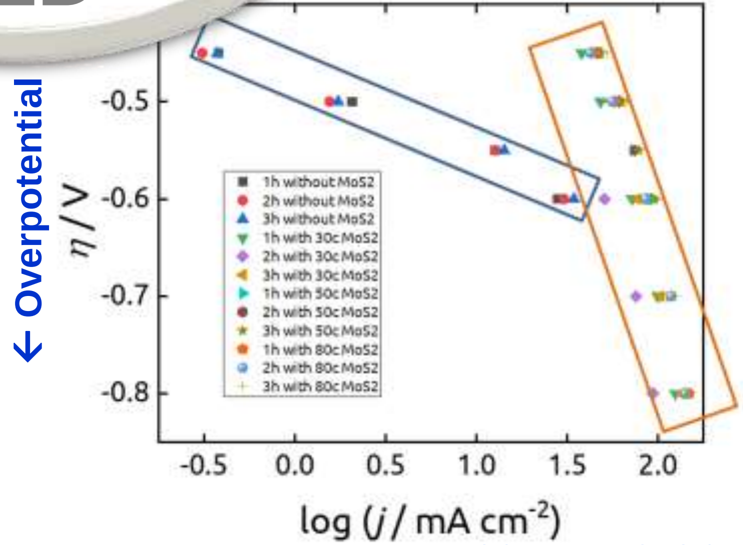
MoS_2@TiO_2 for HER

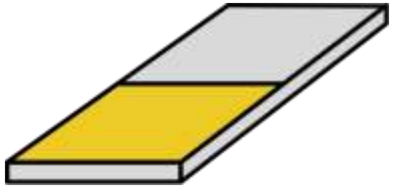


MoS_2@TiO_2

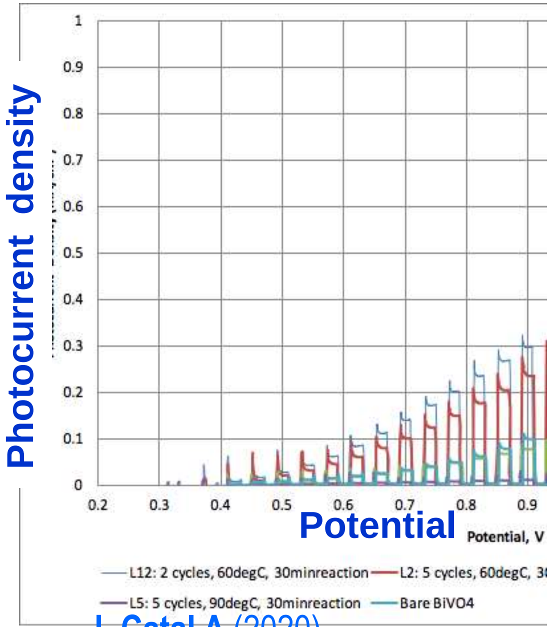


ACS OMEGA (2019) RSC ADVANCES (2021)

Al_2O_3@$BiVO_4$ for Photo



$BiVO_4$ thin film



J. Catal A (2020)

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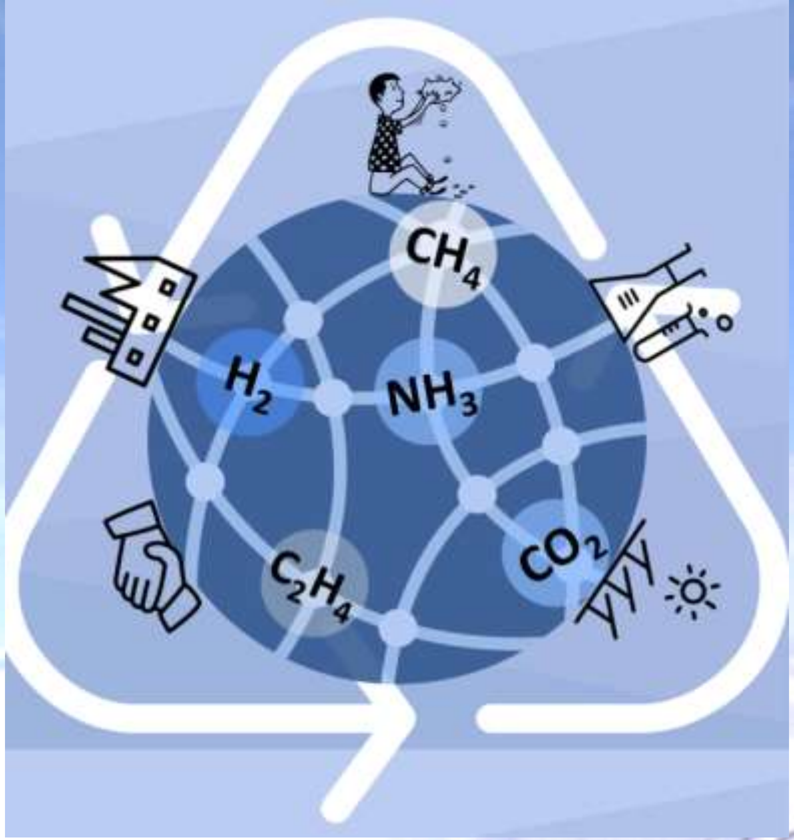

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