

Solar Fuel for a sustainable Future

- Required for applications that need fuel (plane)
- Energy storage of sustainable **intermittent** energy

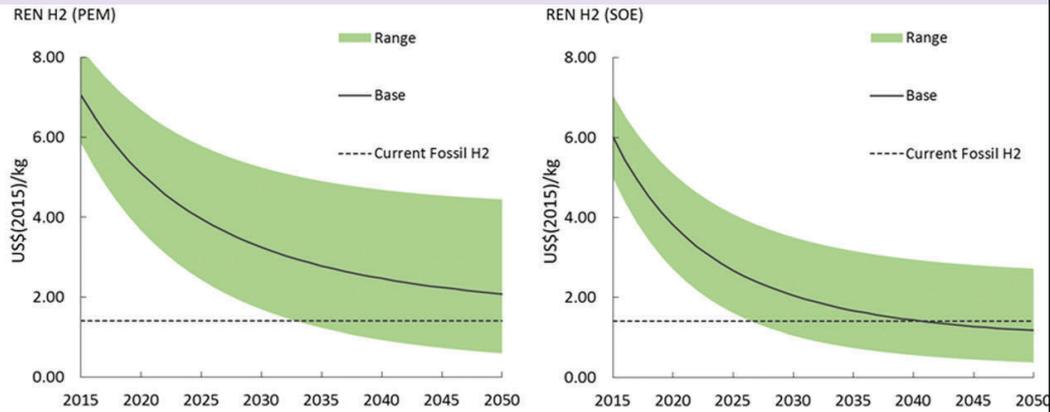
New opportunities:

Electrocatalytic processes for sustainable chemical applications



Solar Fuel: techno-economic analysis

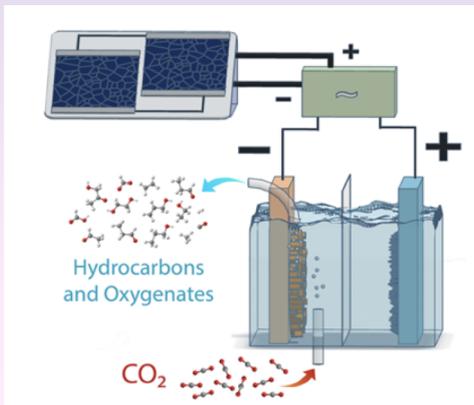
Economic competitive 2025-2040



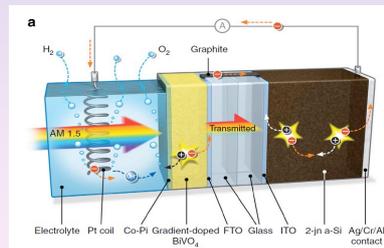
Detz, van der Zwaan, Reek *Energy Environ Sci.* **2018** in press ECN/TNO

Solar Fuel

■ PV-Electrolysis



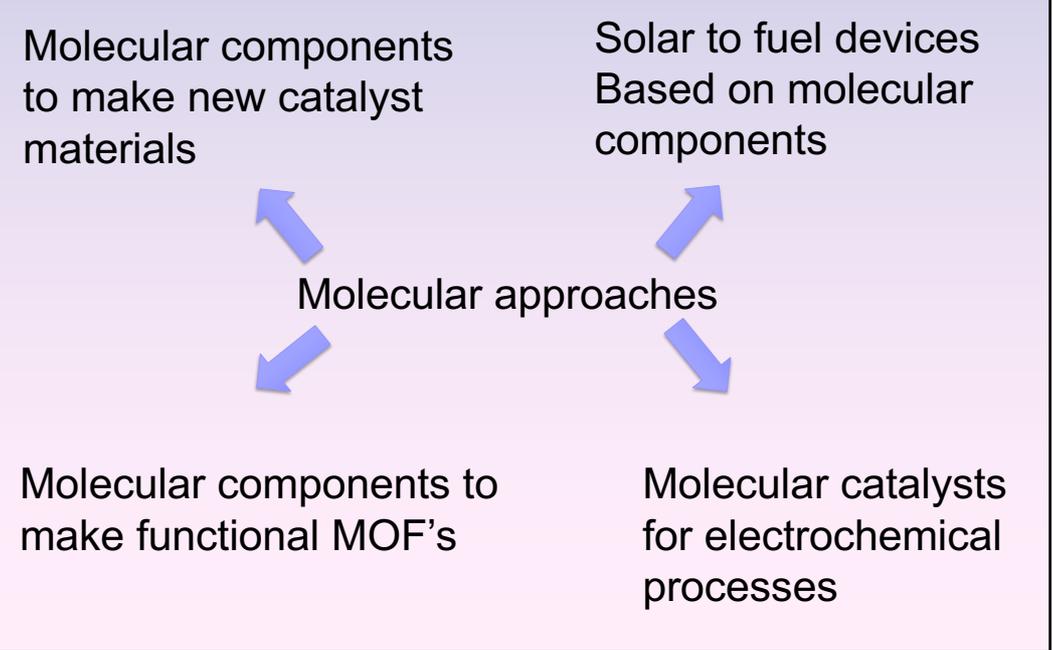
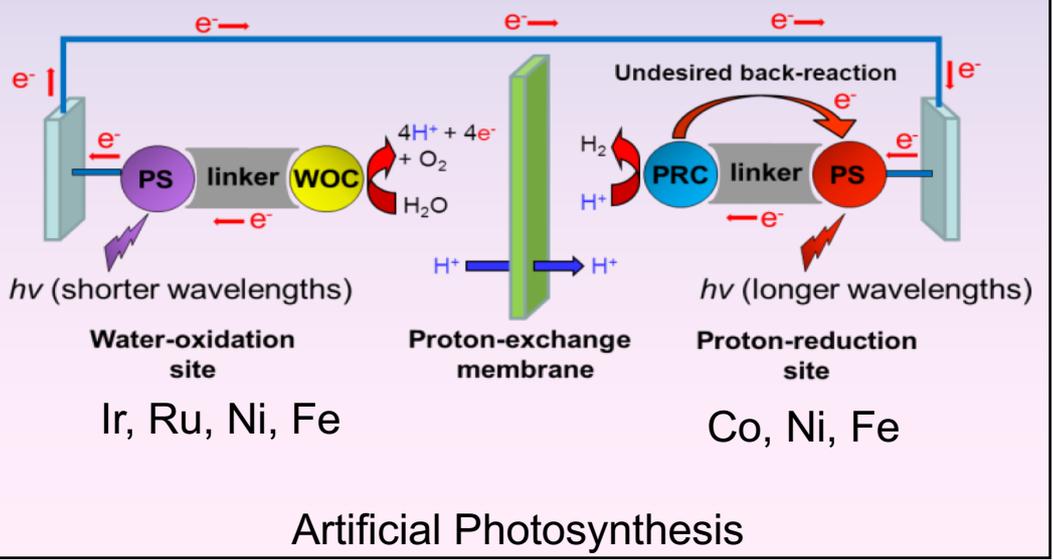
■ Integrated device



Dam, vd Krol et al. *Nat Commun* 2013

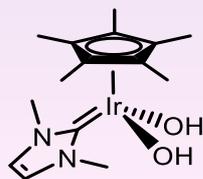
Catalysts may be the same!
Overpotential/rate crucial

Solar to fuel device based on molecular components



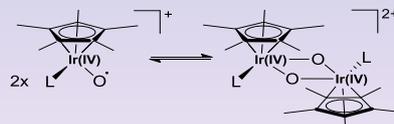
Example: Ir-NHC-WOC

- Highest activity with non-coordinating anions in the buffer at pH 3-4
- Onset overpotential is ca. 300 mV in ClO₄-media



With Hetterscheid/Koper
Diaz-Morales et al., JACS 2014, 10432-10439
Chem Commun 2011, Chem.Eur J 2014

Martin Koelewijn, ACS Catalysis, 2016, 3418-3427



In situ MS/Raman on gold electrode

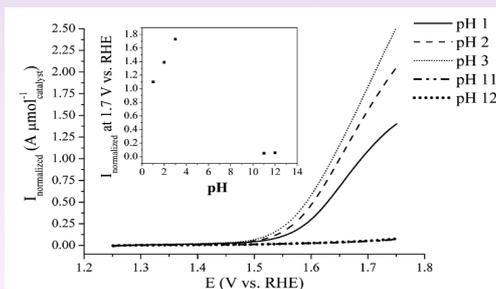
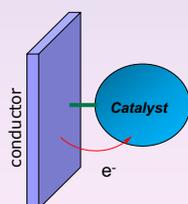


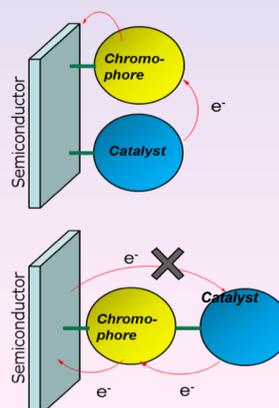
Figure 3. Current–potential profile for water oxidation catalyzed by iridium-N-dimethylimidazolin-2-ylidene immobilized on gold, obtained under hydrodynamic conditions at different pH's in perchlorate media. $\nu = 5 \text{ mV s}^{-1}$, $\omega = 1500 \text{ rpm}$. Insert: Current (activity) measured at 1.7 V vs RHE.

Anchoring water oxidation catalysts

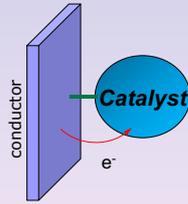
ELECTROCATALYSIS



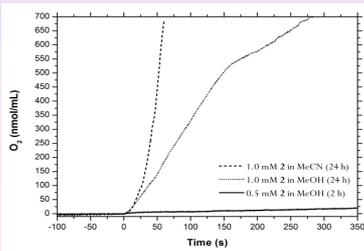
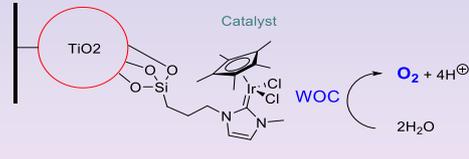
PHOTOCATALYSIS



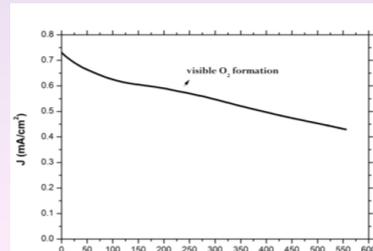
Electrode preparation



Electrode surface



Anode in Clark electrode with CAN



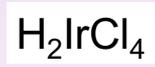
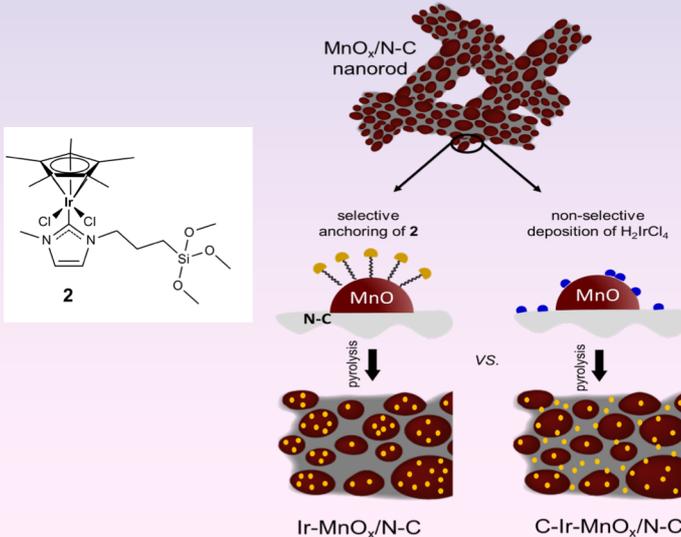
Electrocatalysis

1.5 V vs NHE

Electrode: glass/FTO/TiO₂ coated with Ir-NHC-catalyst



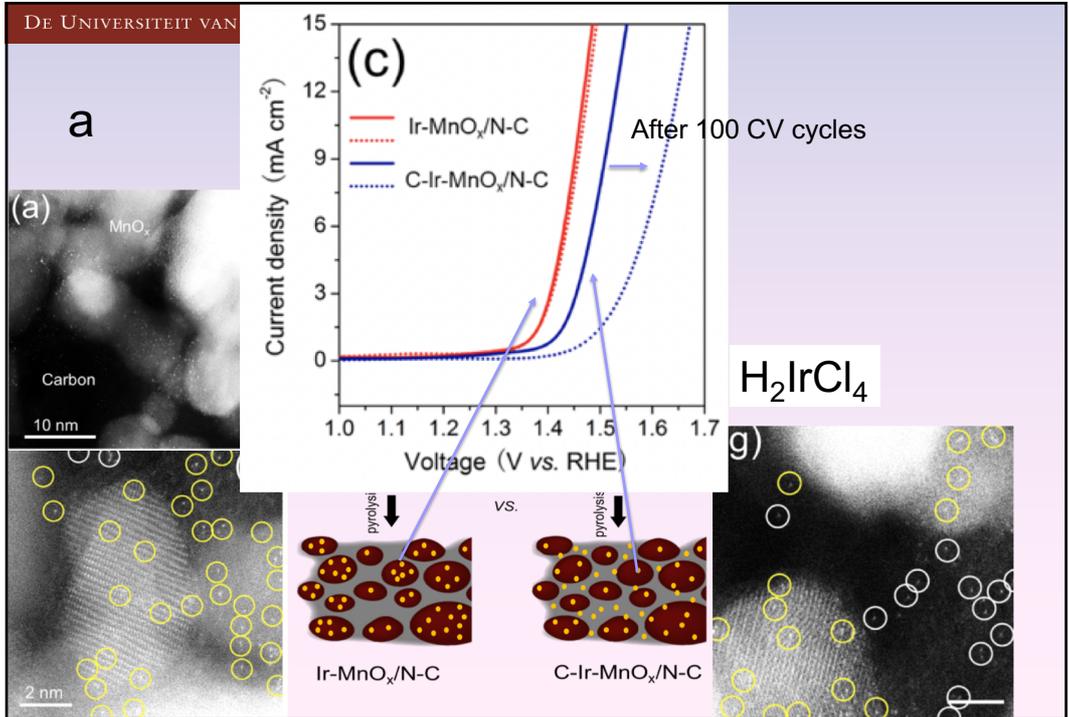
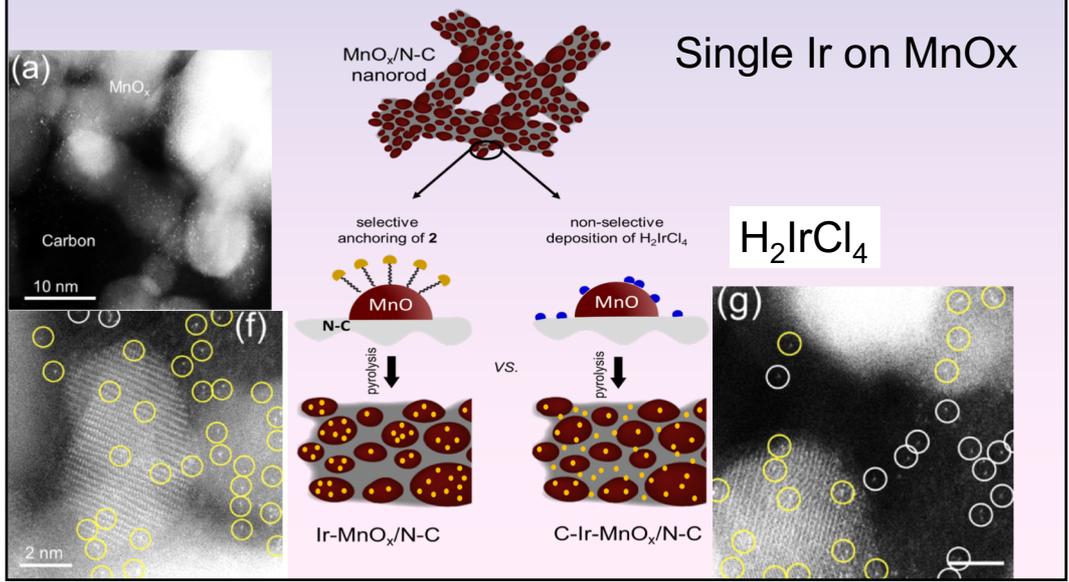
Molecular approach to make new catalyst materials

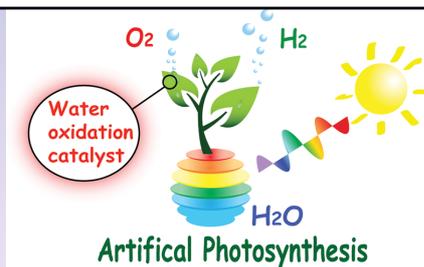


With dr Ning Yan
Suschem UvA

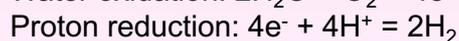
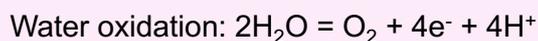
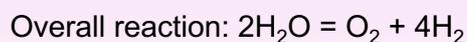
Molecular approach to make new catalyst materials

Single Ir on MnOx

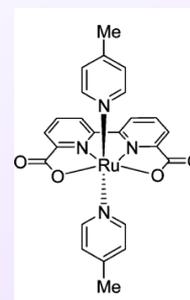
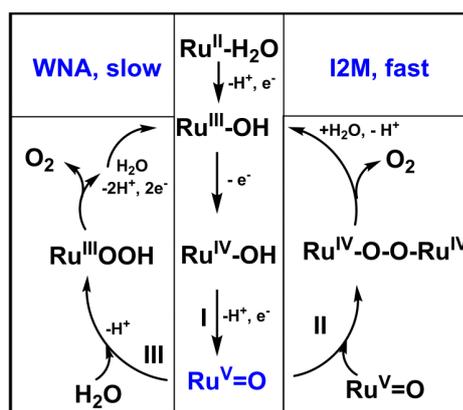
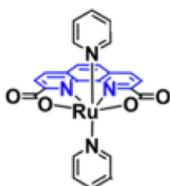




How to use supramolecular chemistry to promote redox catalysis for water splitting



Ruthenium catalysts for water oxidation

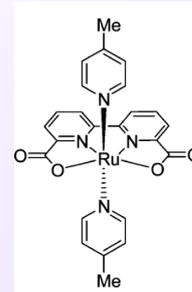
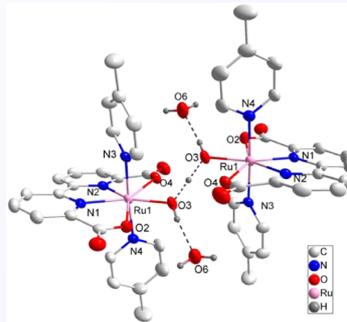
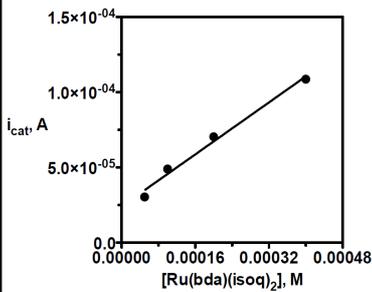


Dinuclear mech!

- L. Sun, et al., *Nat. Chem.* 4, 418–423 (2012).
 L. Sun, et al., *Angew. Chem. Int. Ed.* 2013, 52, 3398–3401.
 L. Sun, et al., *Chem. Commun.*, 2014, 50, 12947–12950.
 L. Sun, et al., *J. Am. Chem. Soc.*, 10397–10399 (2009)

- Conception et al., *Chem Soc Rev.*, 6170 (2017)
 Reek et al., *Chem Eur J.*, 16413 (2017)
 Meyer et al., *Chem Soc Rev.*, 6148 (2017)

Ruthenium catalysts for water oxidation



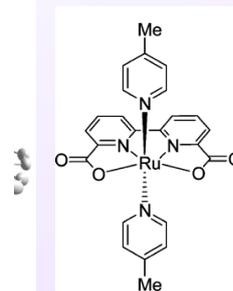
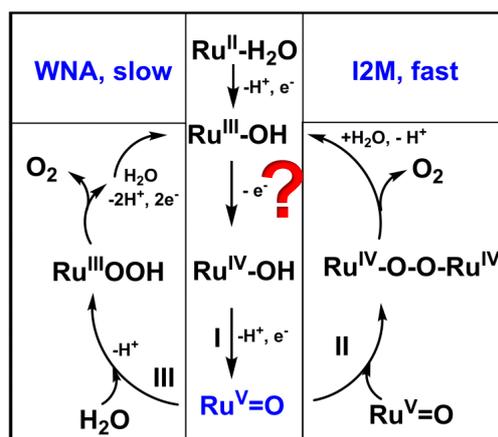
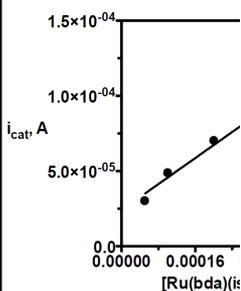
Electrochemical water oxidation
First order in catalyst;
 KIE: D₂O/H₂O around 2

T. J. Meyer, *et al.*, *Proc. Natl. Acad. Sci.* 112, 4935–4940 (2015).

Fastest catalyst with chemical oxidant
 Radical coupling; *second* order in catalyst.

L. Sun, *et al.*, *J. Am. Chem. Soc.*, 10397–10399 (2009)

Ruthenium catalysts for water oxidation



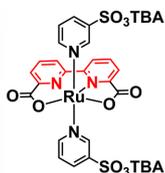
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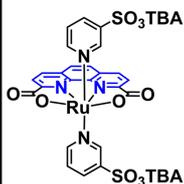
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Nanoconcentrator for water oxidation ?



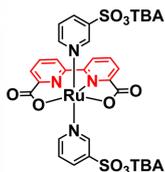
Complex 1



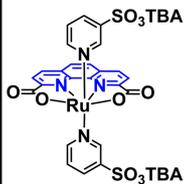
Complex 3

Fengshou Yu, submitted

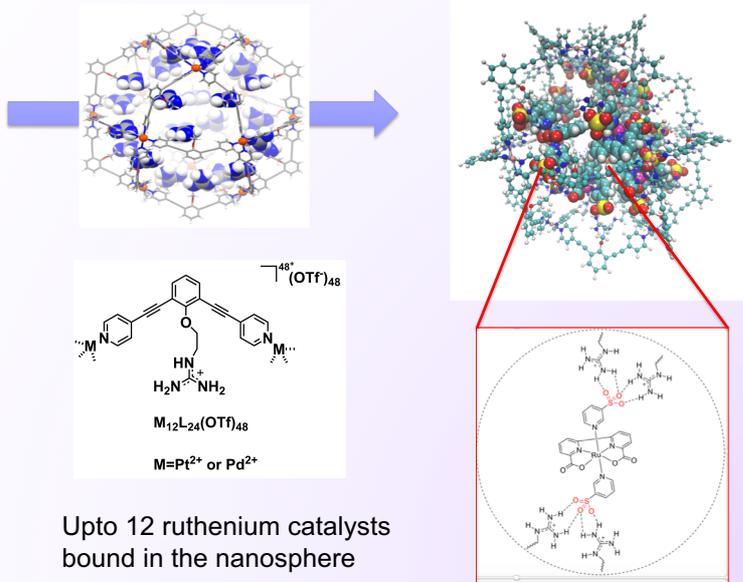
Nanoconcentrator for water oxidation ?



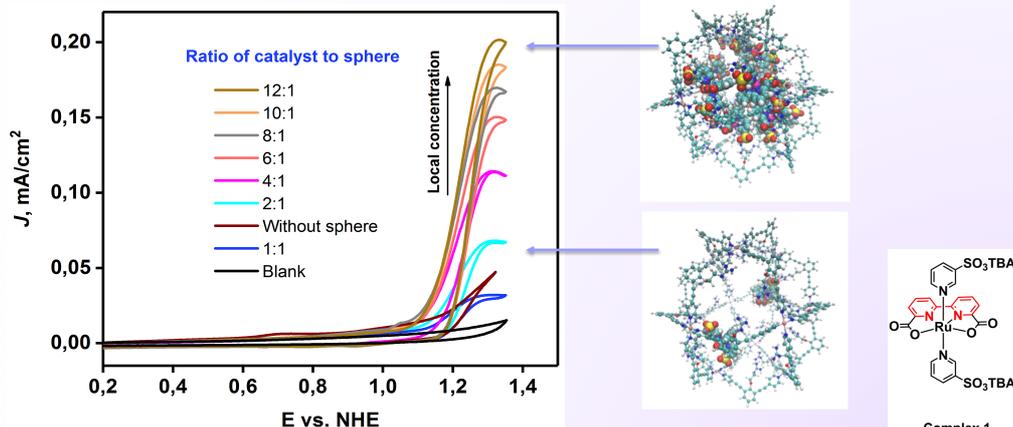
Complex 1



Complex 3

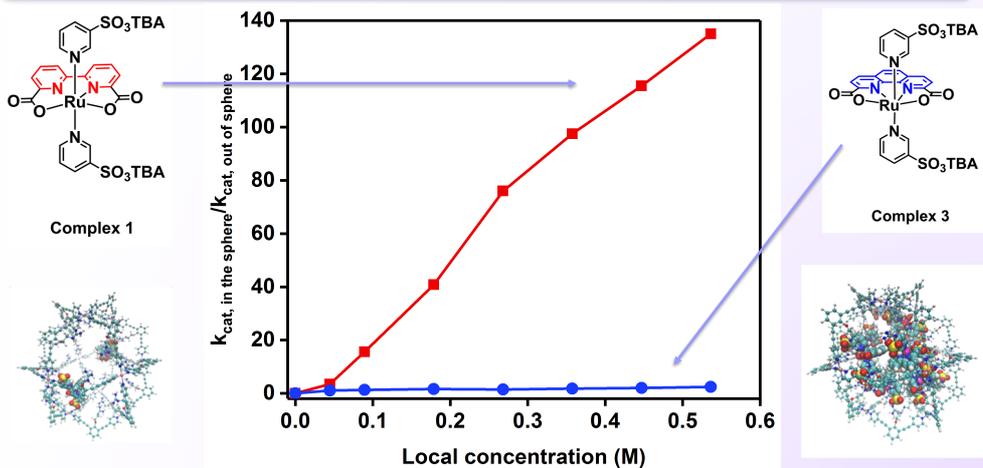


Electrochemical water oxidation: effect of local catalyst concentration



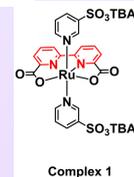
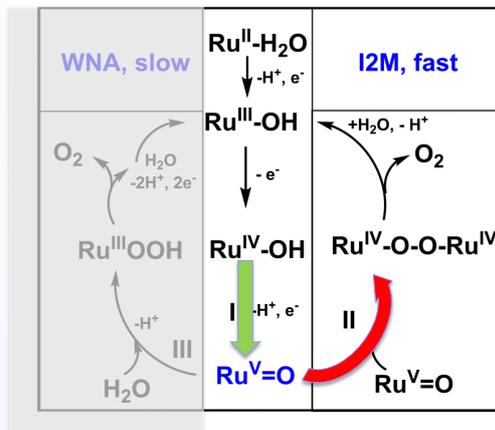
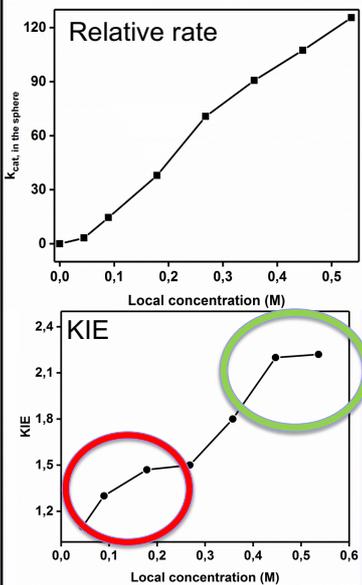
CV measurements with the ratios of complex 1 to sphere from 1 to 12 at scan rate of 10 mV s^{-1} . The overall catalyst concentration is $2.5 \cdot 10^{-5}$ for all samples.

Effect of local catalyst concentration on electrochemical water oxidation rate

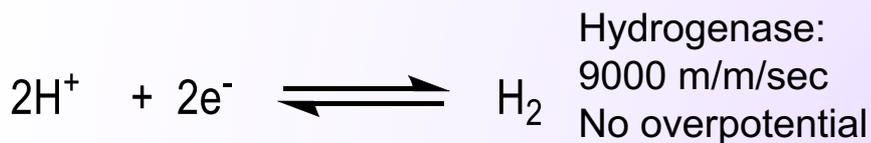
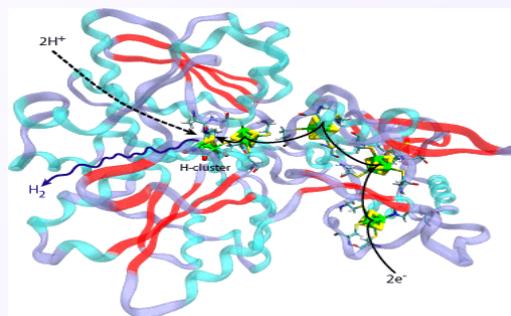
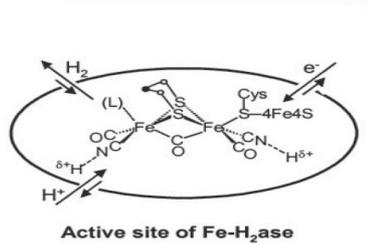


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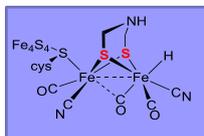
Rate determining step depends on local ruthenium concentration



Molecular cages to facilitate for proton reduction

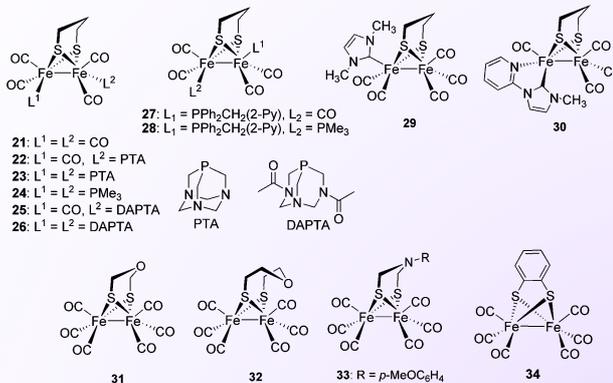


Hydrogenase mimics



Organic solvents
Instable

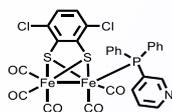
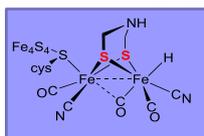
Overpotential
Lower activity
.....



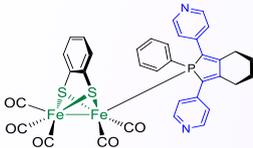
Players in the field: Raughfuss, Darensbourg, Gloaguen, Sun, Wu, Wang, Fontecave, Eisenberg, Nocera, Picket, Ott, Reek, Dubois

Recent Reviews: *Coord. Chem. Rev.* **2014**, p127; *Energy Environ Sci.* **2012**, 6763; *Energy Environ Sci.* **2012**, 6012; *Chem Soc. Rev.*, **2012**, 6763

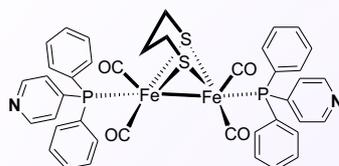
Hydrogenase mimics developed @ UvA



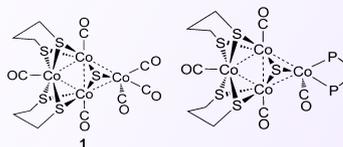
Van den Bosch



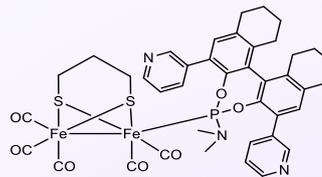
Rene Becker,
science adv. **2016** 2:e1501014



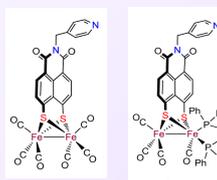
Kluwer PNAS **2009**



Ping Li, *Chem. Eur. J* **2015**

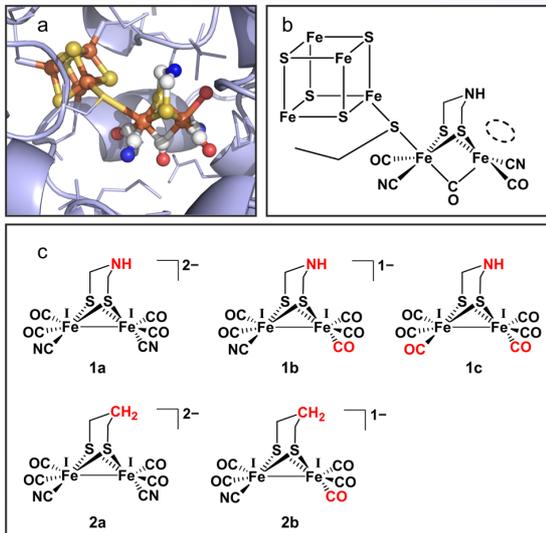


Becker, Dalton **2013**



Ping Li, *Inorg chem* **2014**

Hybride systems: importance of second coordination sphere

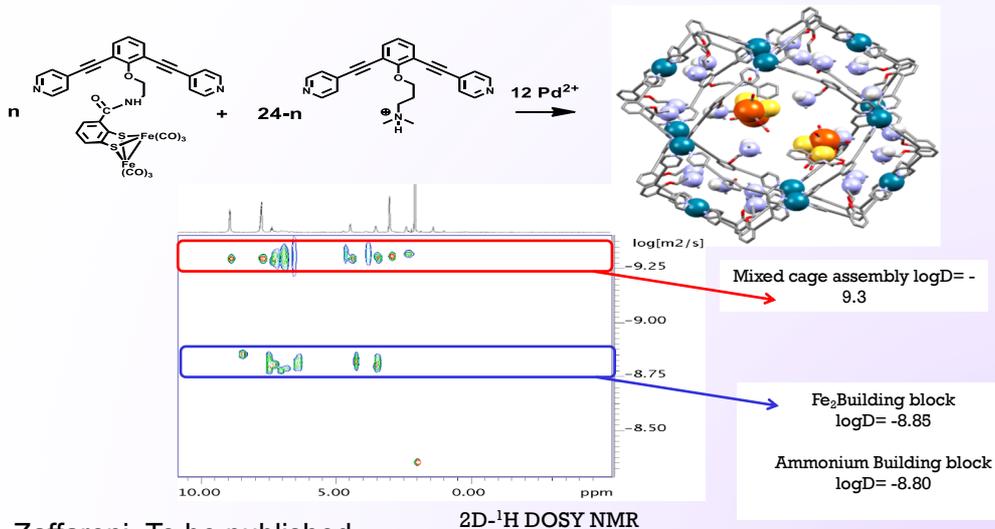


Full activity restored!

Lubitz and Reijerse
Biochemistry **2015**

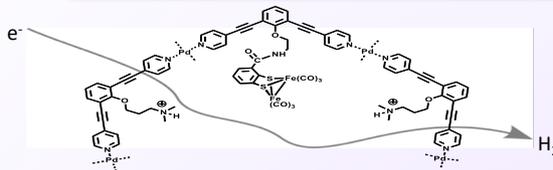
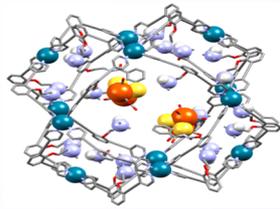
Lubitz and Reijerse
Fontecave
Nature **2013**

Caged Hydrogenase mimic

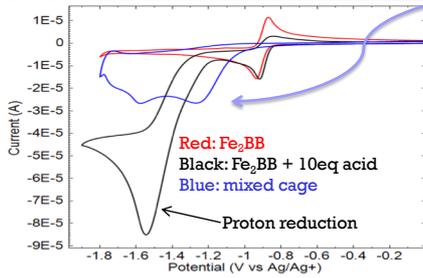


Zaffaroni, To be published

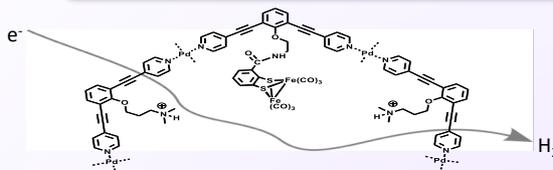
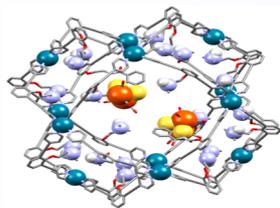
Caged Hydrogenase mimic



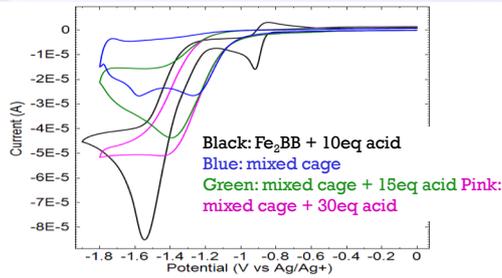
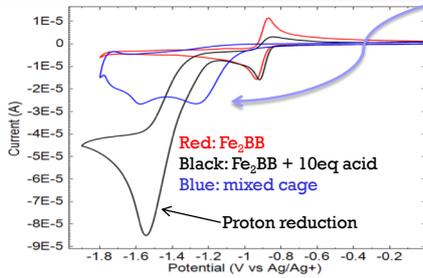
Catalysis at lower overpotential



Caged Hydrogenase mimic



Catalysis at lower overpotential



Conclusion

Molecular approaches can be very powerful
in electrocatalysis

Supramolecular approaches: ditto!

Acknowledgements

- Martin Koelewijn
- Hung-Cheng Chen
- Bart van den Bosch
- René Becker
- Riccardo Zaffaroni
- Esther Schippers
- Ping Li
- Sofia Derossi
- Joeri Hessels
- Fengshou Yu
- Simon Matthew
- **Dennis Hetterscheid**

- **Dr. Remko Detz**
- Prof B. de Bruin
- Dr. J.I. van der Vlugt

Collaborations

- Prof F. Brouwer
- Prof S. Woutersen
- Prof R. Orru
- Jeroen Rombouts (VU)
- Dr. Ning Yan



FOM
NWO
ERC

