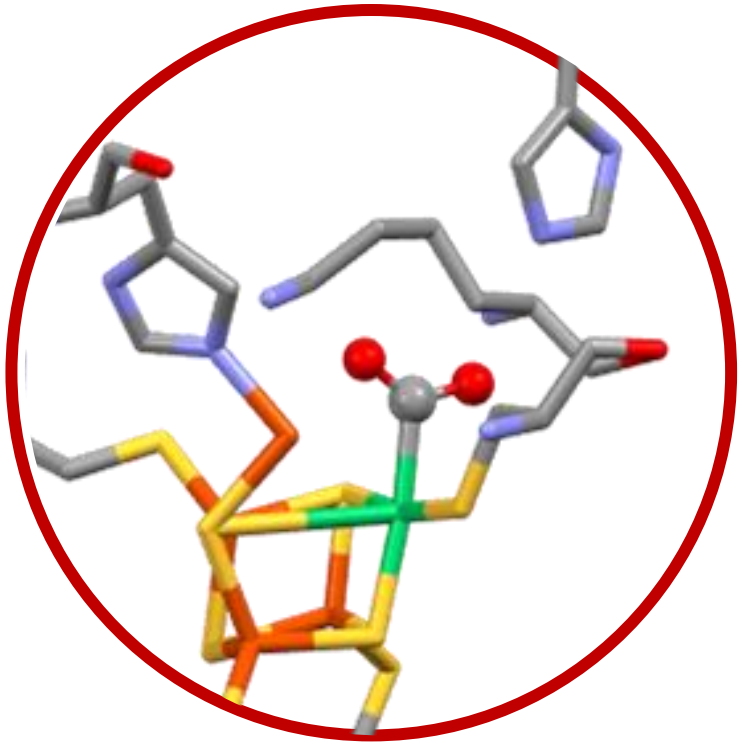
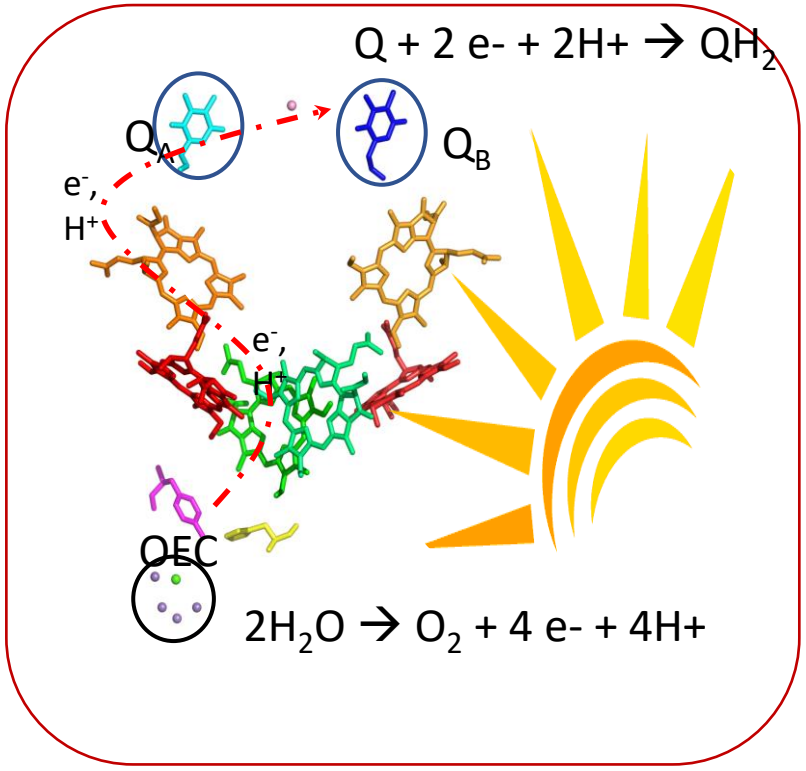
Catalyse bioinspirée pour l'électrocatalyse de la réduction du CO_2.

Maison de la Chimie
Rencontres Académie-Industrie
CO2 Déchet ou matière première: Etat de l'art et perspectives
5 Décembre 2025

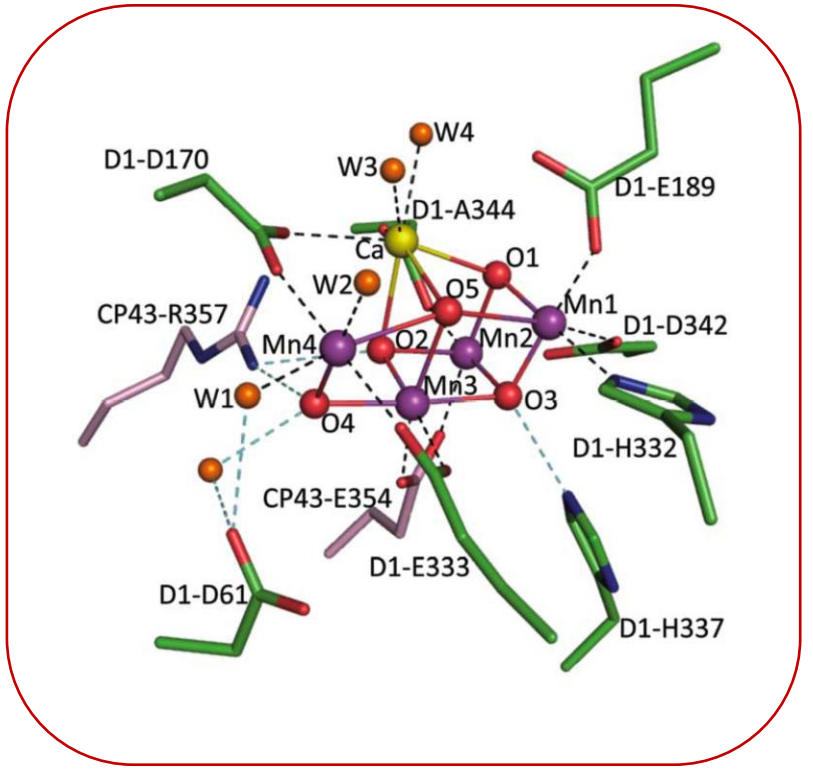
Ally.aukauloo@universite-paris-saclay.fr



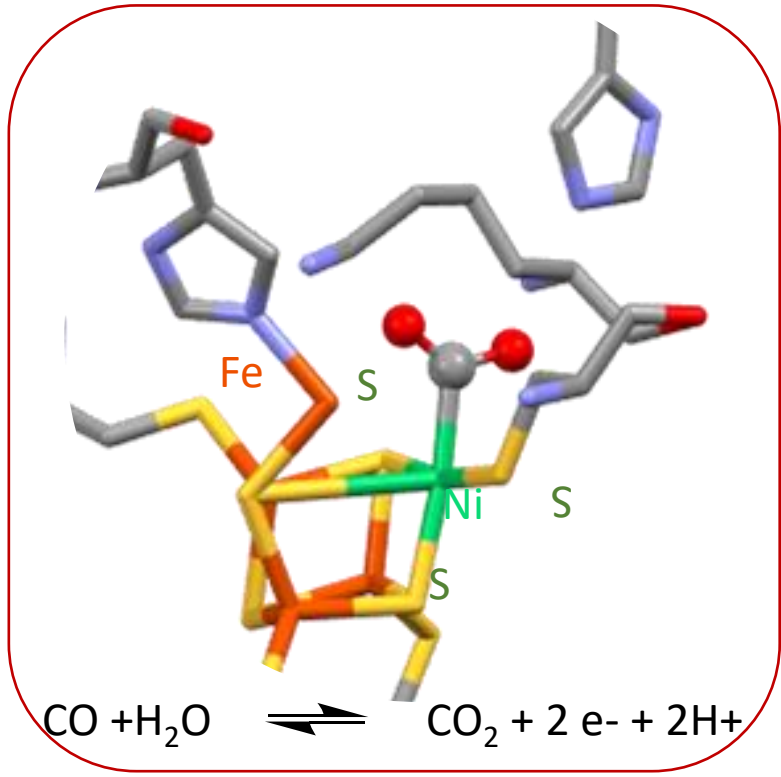
Nature's complexed machineries!



Map of co-factors of PSII

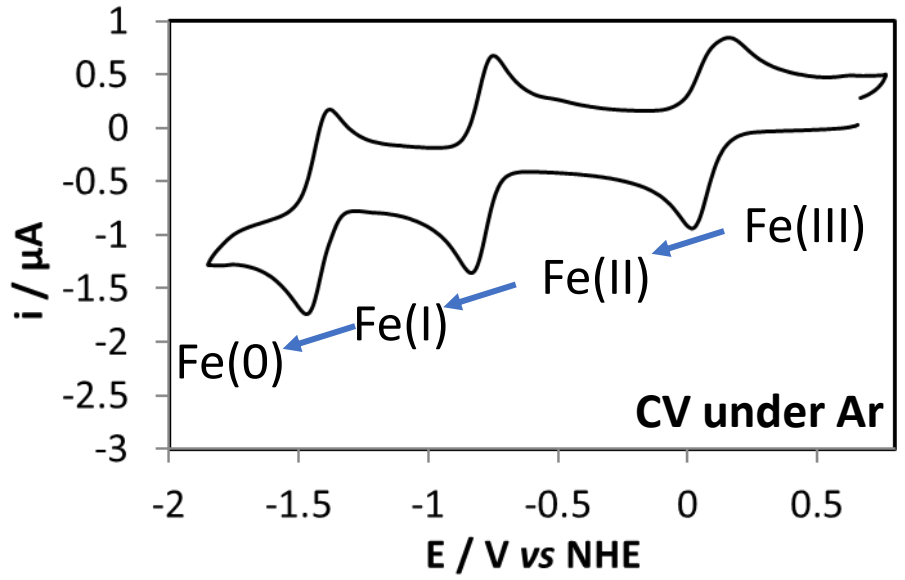


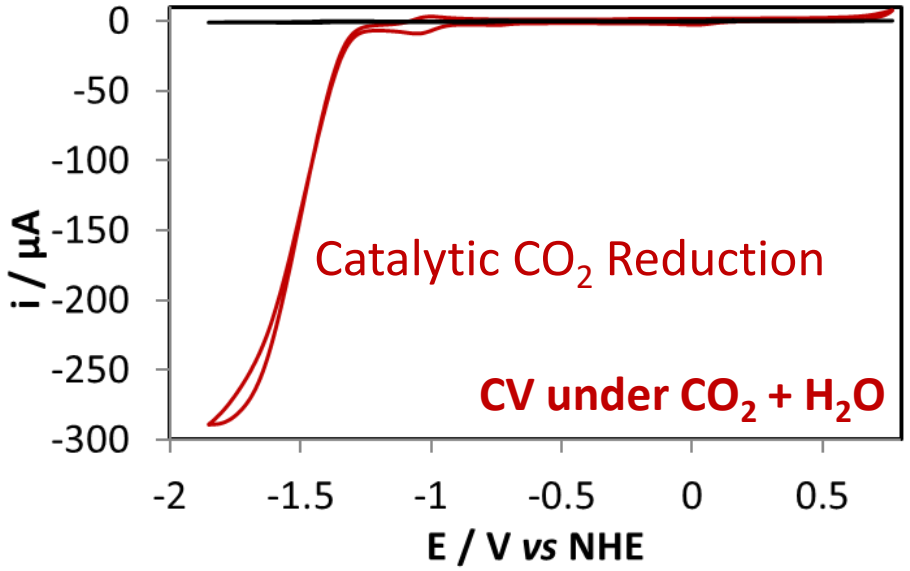
OEC



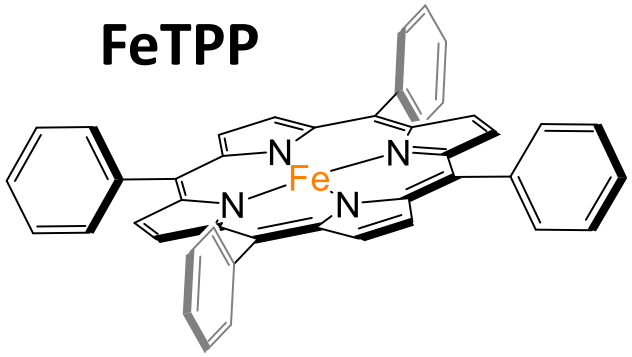
CODH

Iron porphyrin as catalysts



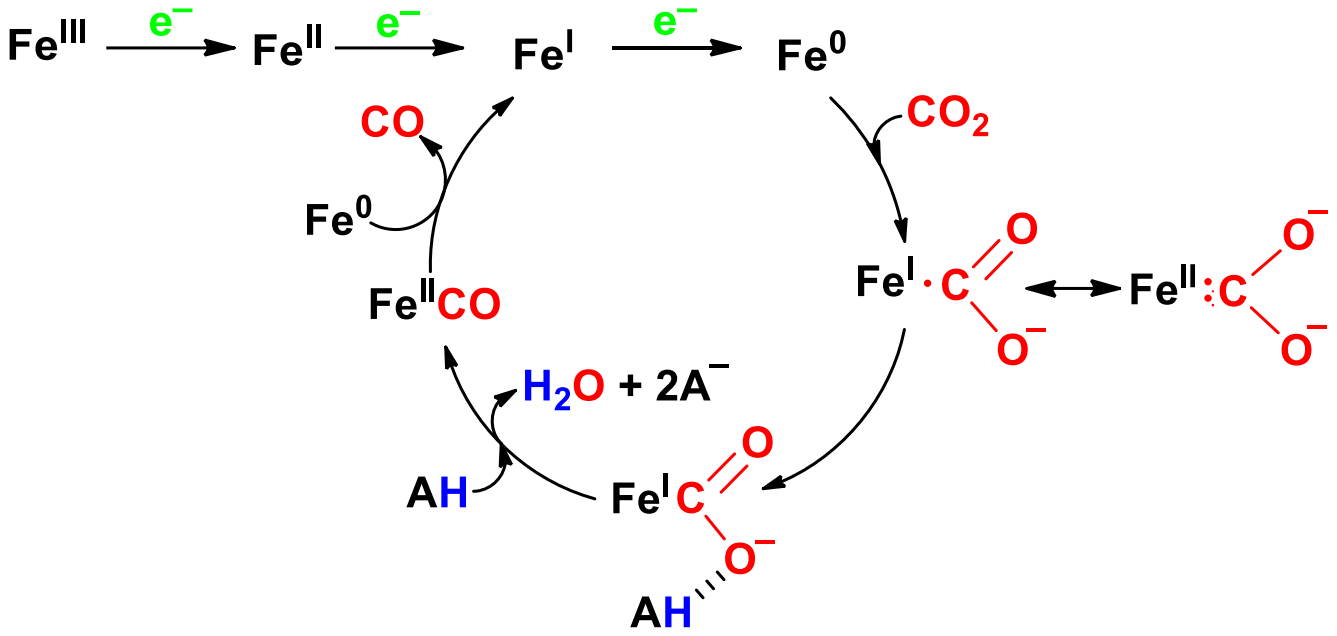


FeTPP



High Turnover Frequency
TOF = 10 700 s^{-1}

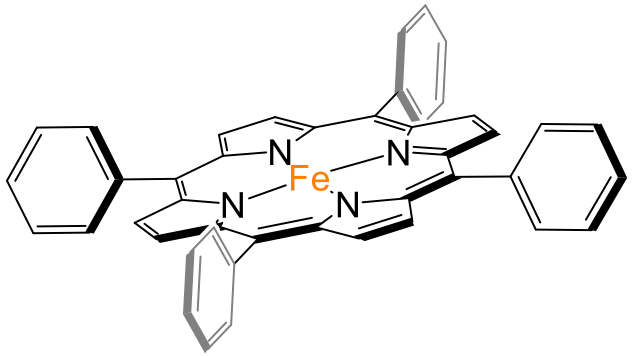
High Overpotential
η = 730 mV



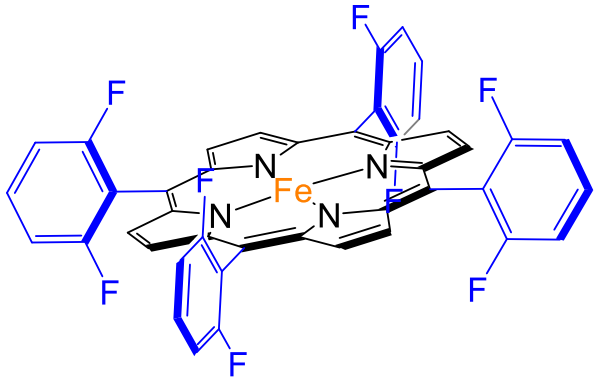
I. Bughun et al. J. Am. Chem. Soc. 1996, 118, 1769-1776

Manipulating the electroctalytic activity of Iron porphyrin

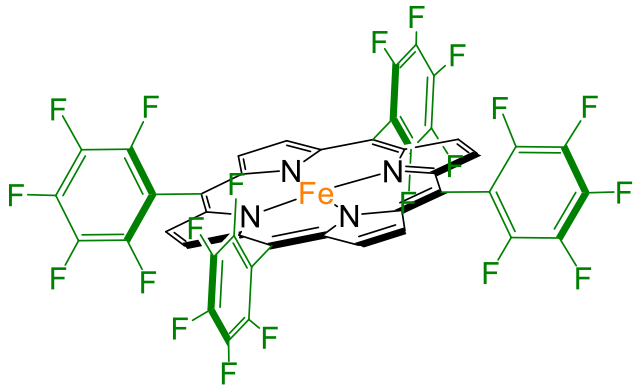
How can the overpotential be lowered?



FeTPP

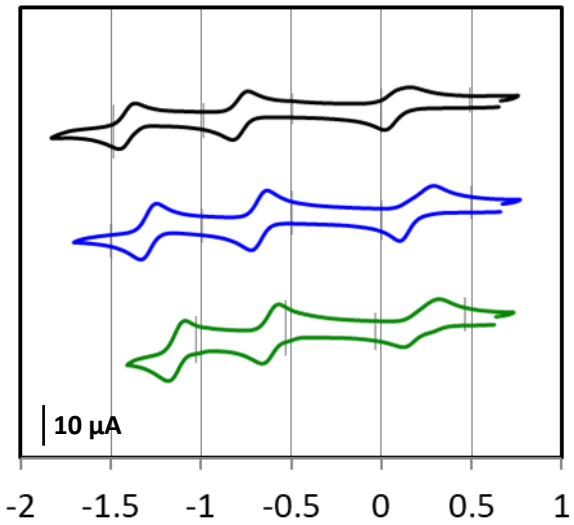


FeTPP-F8

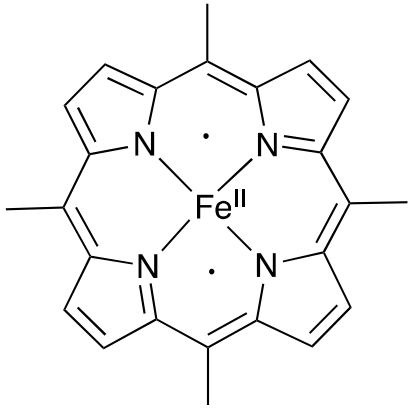


FeTPP-F20

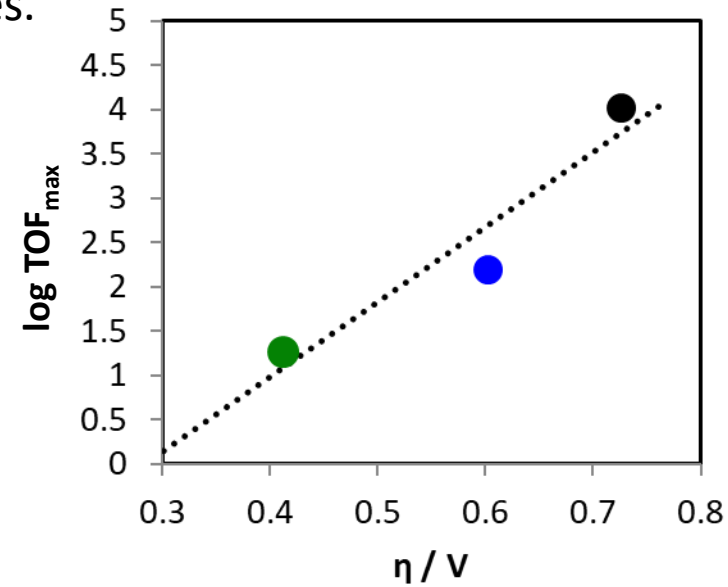
Electrochemical performance of complexes.



CV under Ar

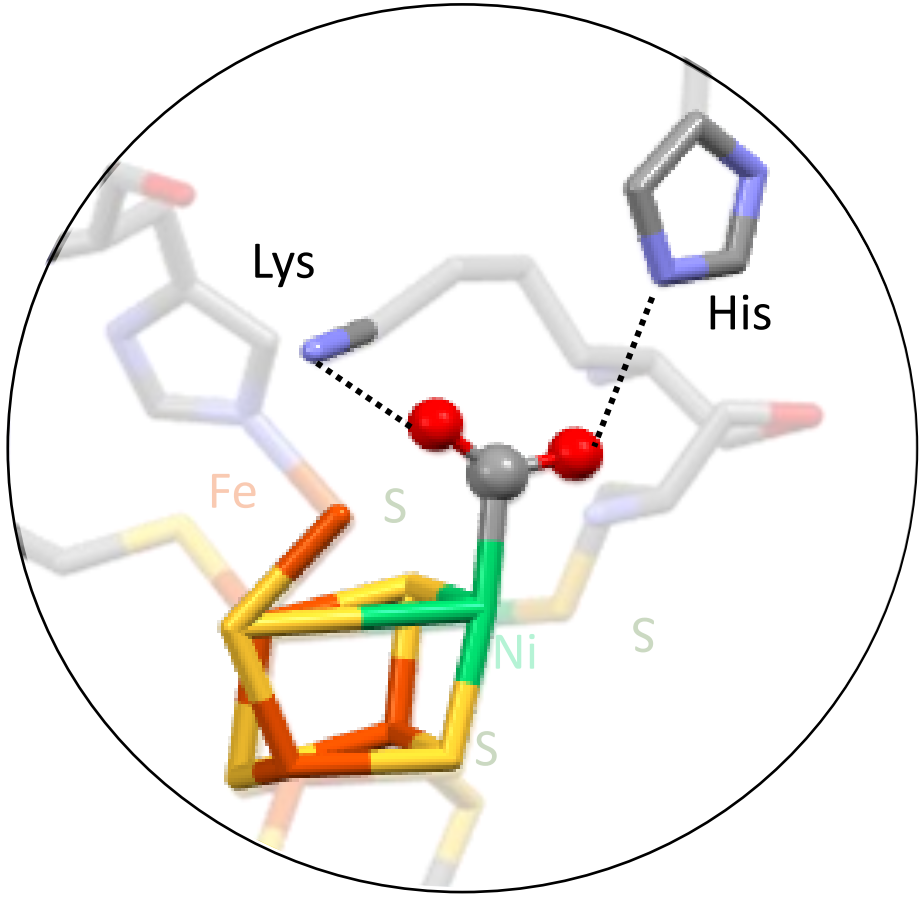


Fe^{II}-Bisradical

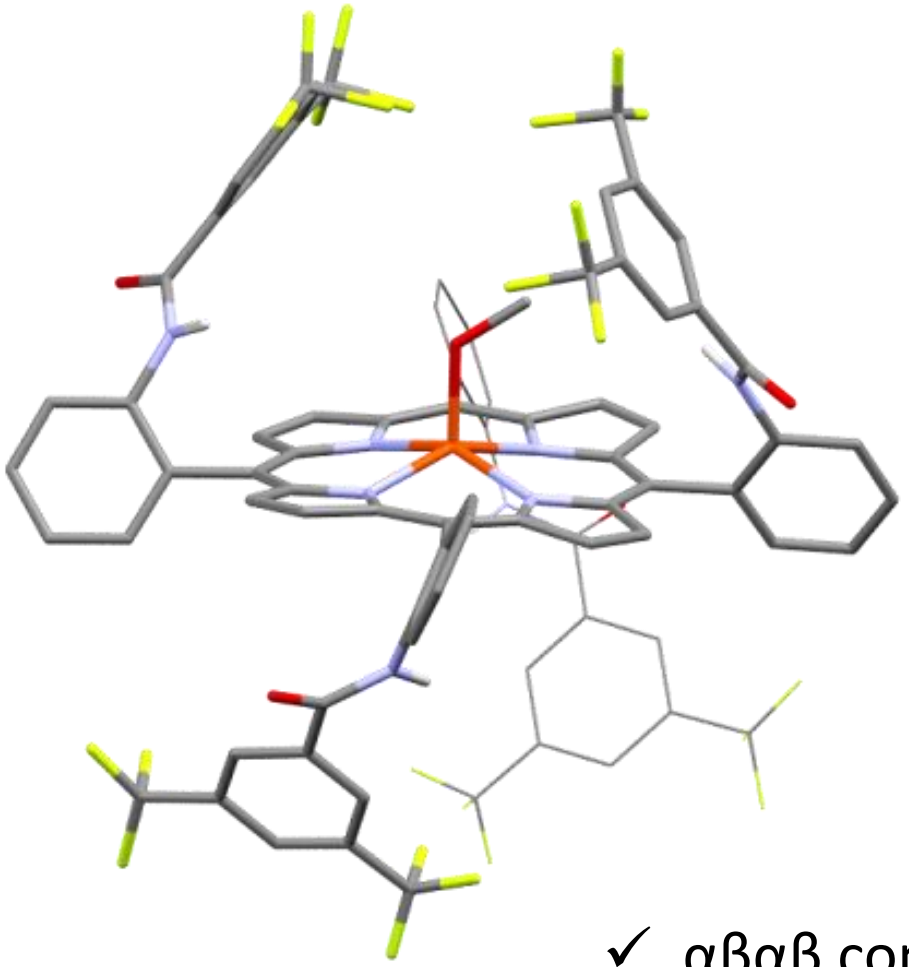


Leveraging Nature's Secrets

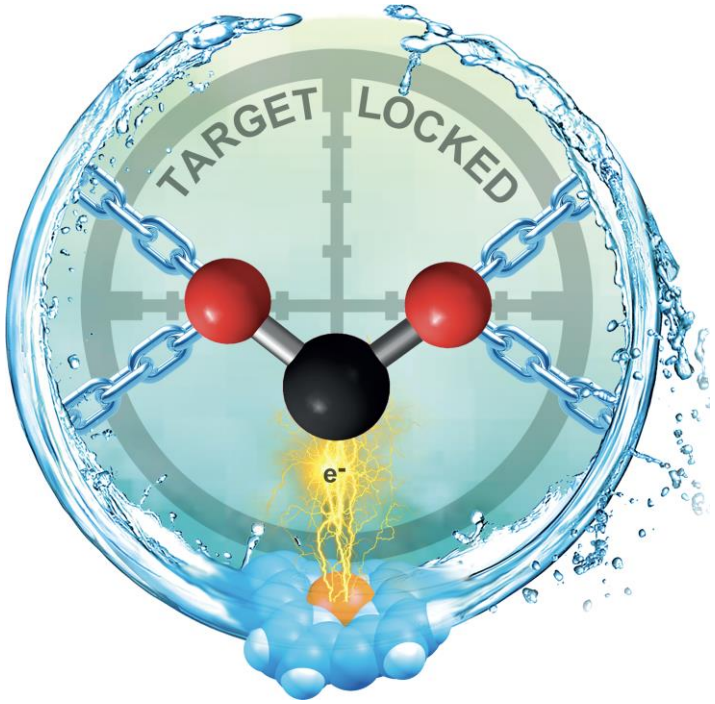
- Multi-hydrogen bonding scheme
- Bimetallic cooperativity
- Electrostatic interactions
- Proton relays
- Entatic states
- Structural dynamics

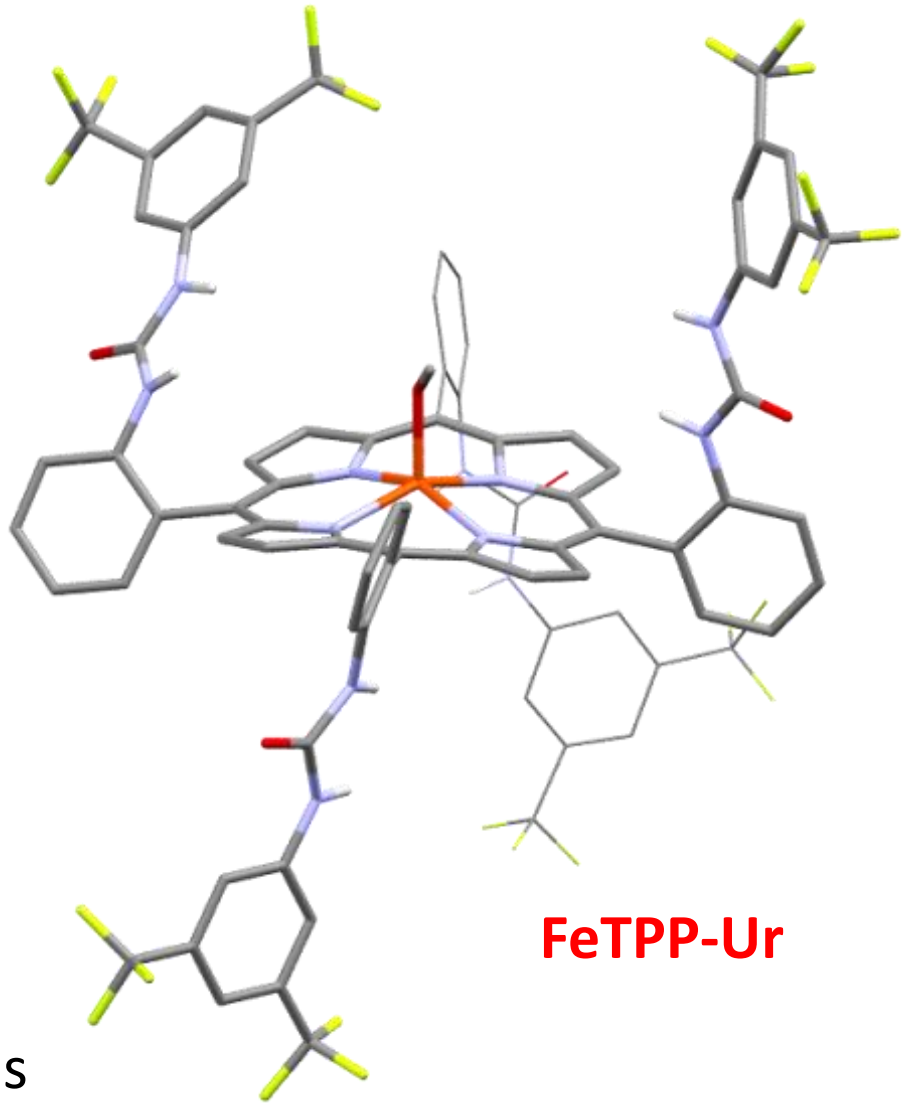


Hydrogen Bonding



FeTPP-Am



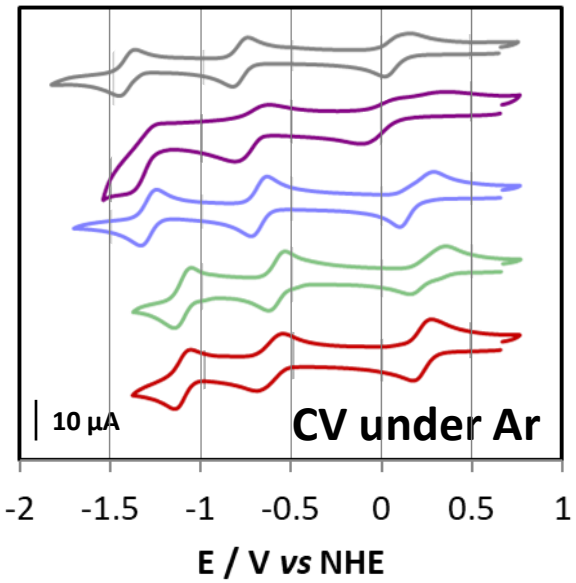


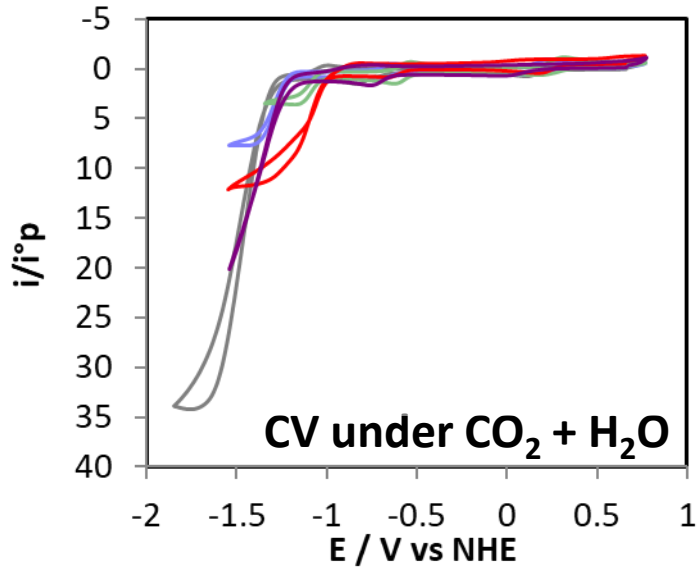
FeTPP-Ur

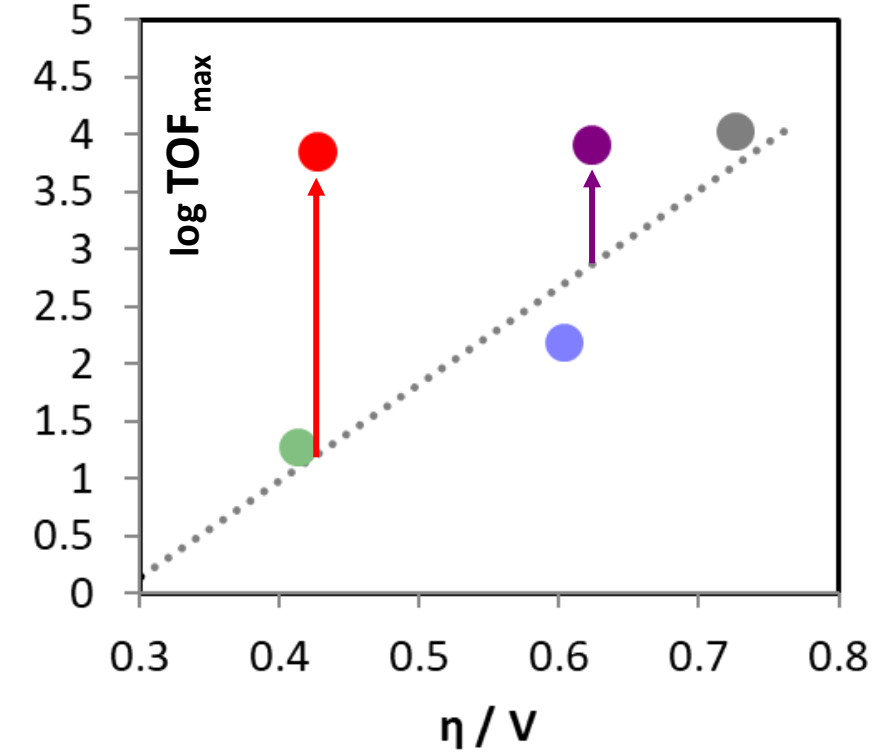
- ✓ αβαβ configuration
- ✓ Proper orientation of hydrogen atoms
- ✓ Fe···H distance of 4.8 - 5.8 Å

Electrochemical performance of complexes.

Complex	E_{cat} / V *vs* NHE	η / mV	TOF_{max} / s^{-1}
FeTPP	-1.420	730	10 700
FeTPP-Am	-1.315	630	7 100
FeTPP-F8	-1.296	610	160
FeTPP-F20	-1.106	420	20
FeTPP-Ur	-1.118	430	6 800

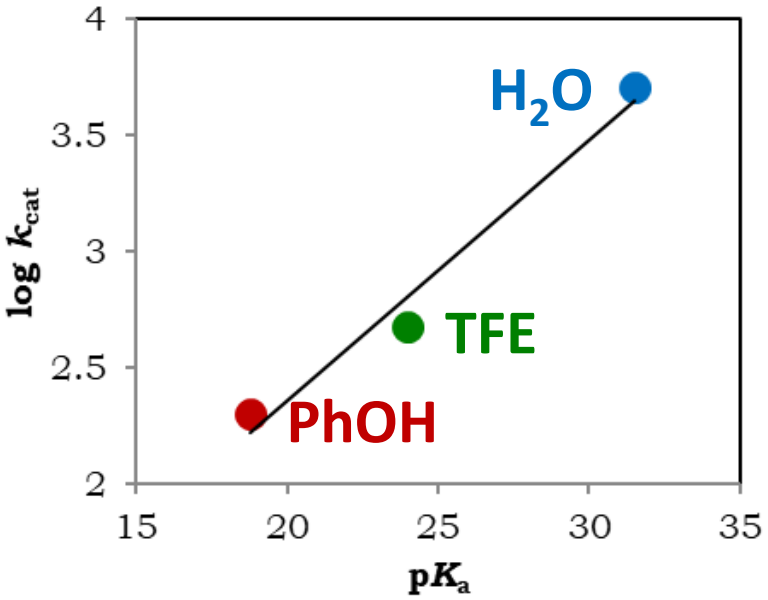






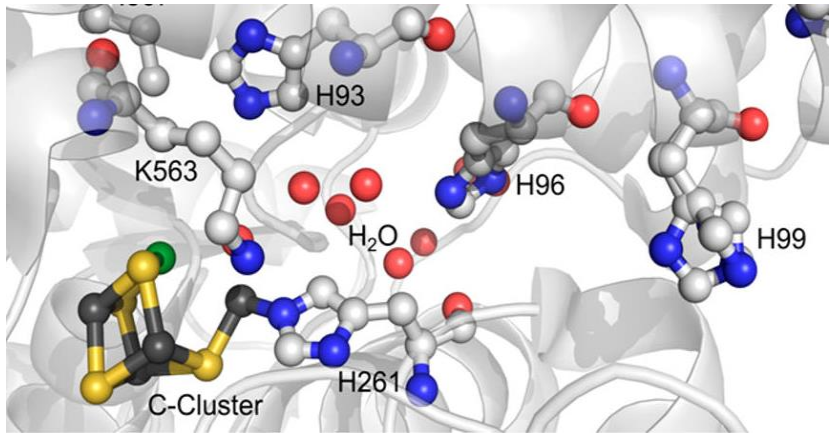
P. Gotico et al Angew. Chem. Int. Ed, 2019, *58*, 4504-4509

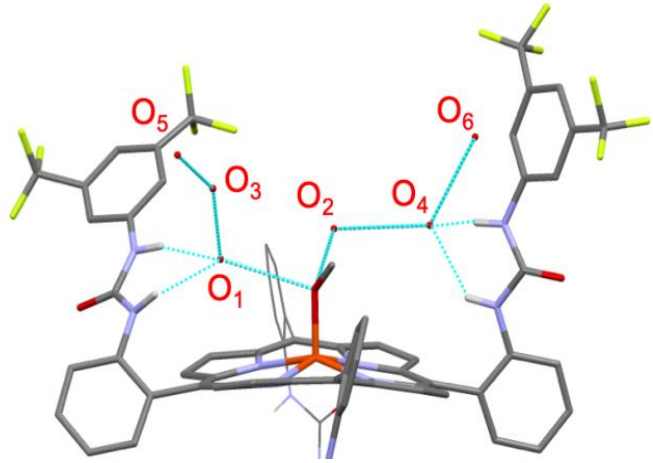
Effect of Proton Source



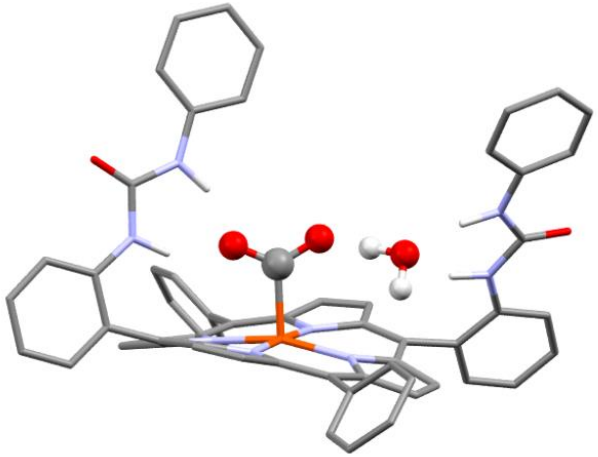
Kinetic Isotope Effect

***H/D*$_{ave}$ = 5.77**





*X-ray structure of **FeTPP-Ur** w/ H_2O*



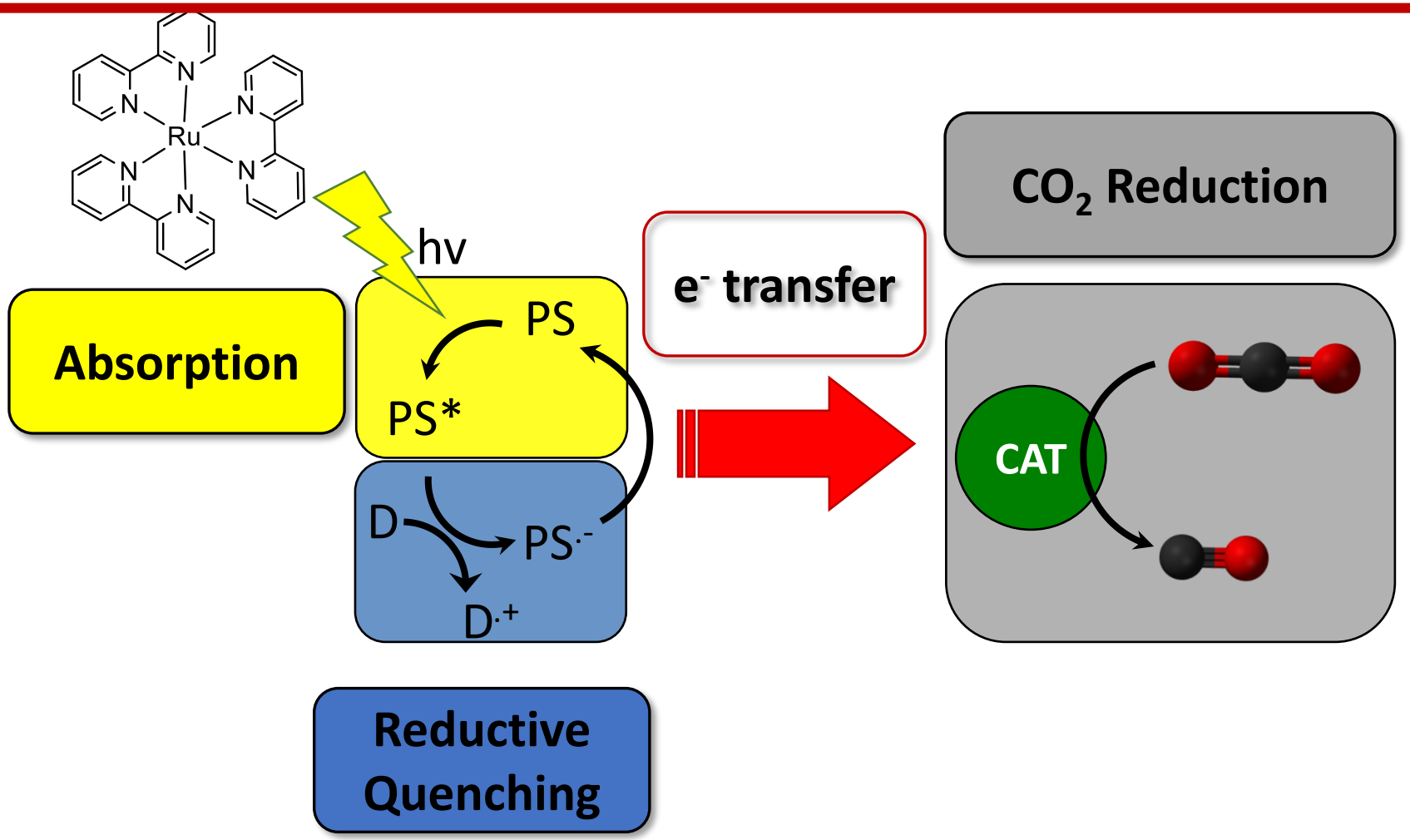
DFT-optimized CO2-H2O adduct

- **Proton transfer is involved in rate-determining step**
- **Water network in the vicinity of the catalytic site is presumed to play a critical role**

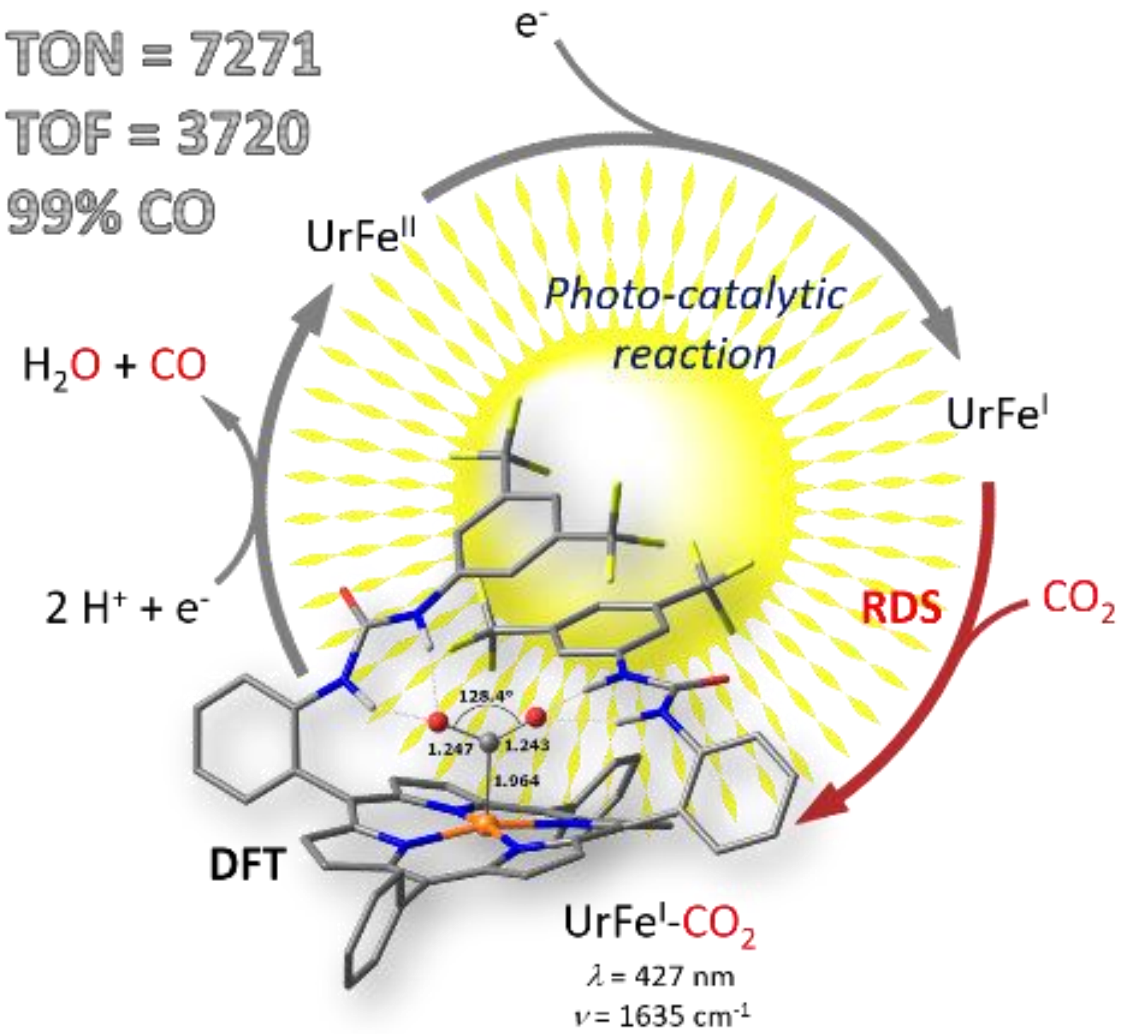
P. Gotico et al Angew. Chem. Int. Ed, 2019, *58*, 4504-4509

Two-Electron Two-proton Photocatalysis

CO_2 Reduction

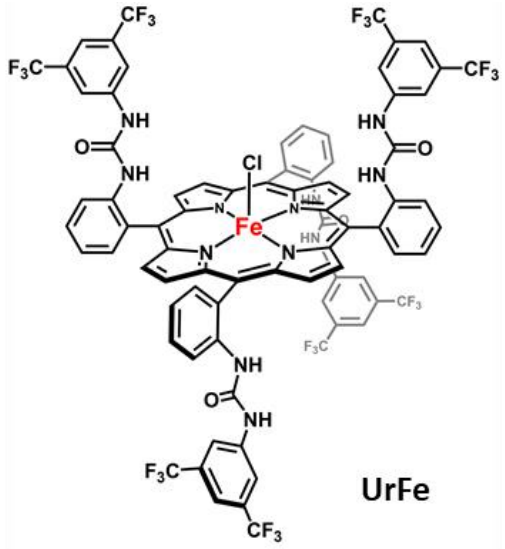


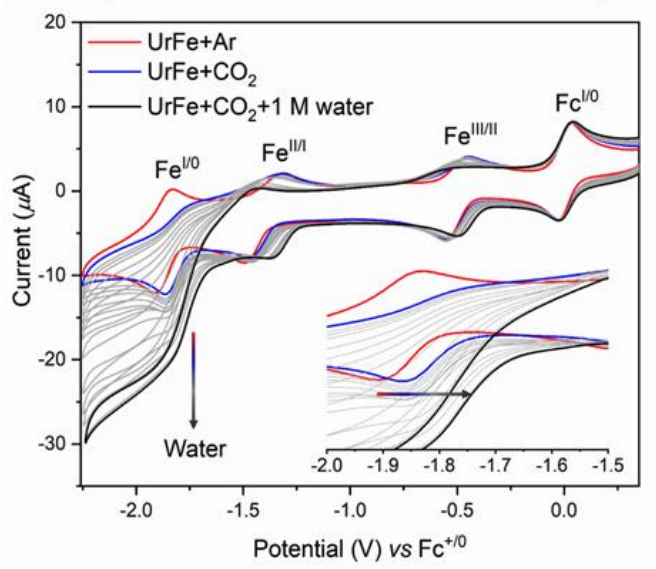
Photocatalytic CO_2 reduction

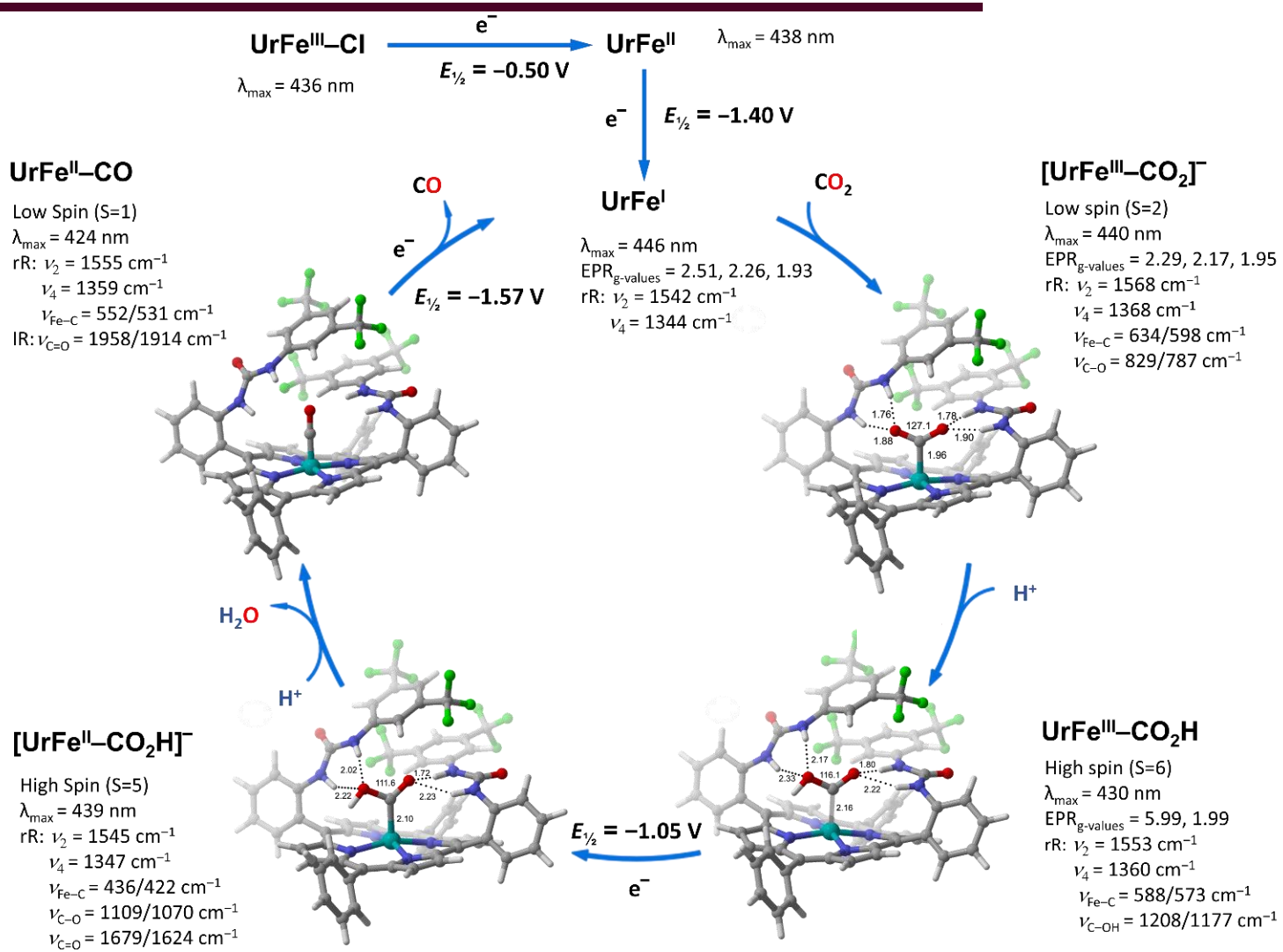


E. Pugliese et al, *Angew. Chem. Int. Ed. Engl.* **2022**, *61*, e202117530

Second Coordination Sphere Effect Shifts CO_2 to CO Reduction by Iron Porphyrin from Fe^0 to Fe^I

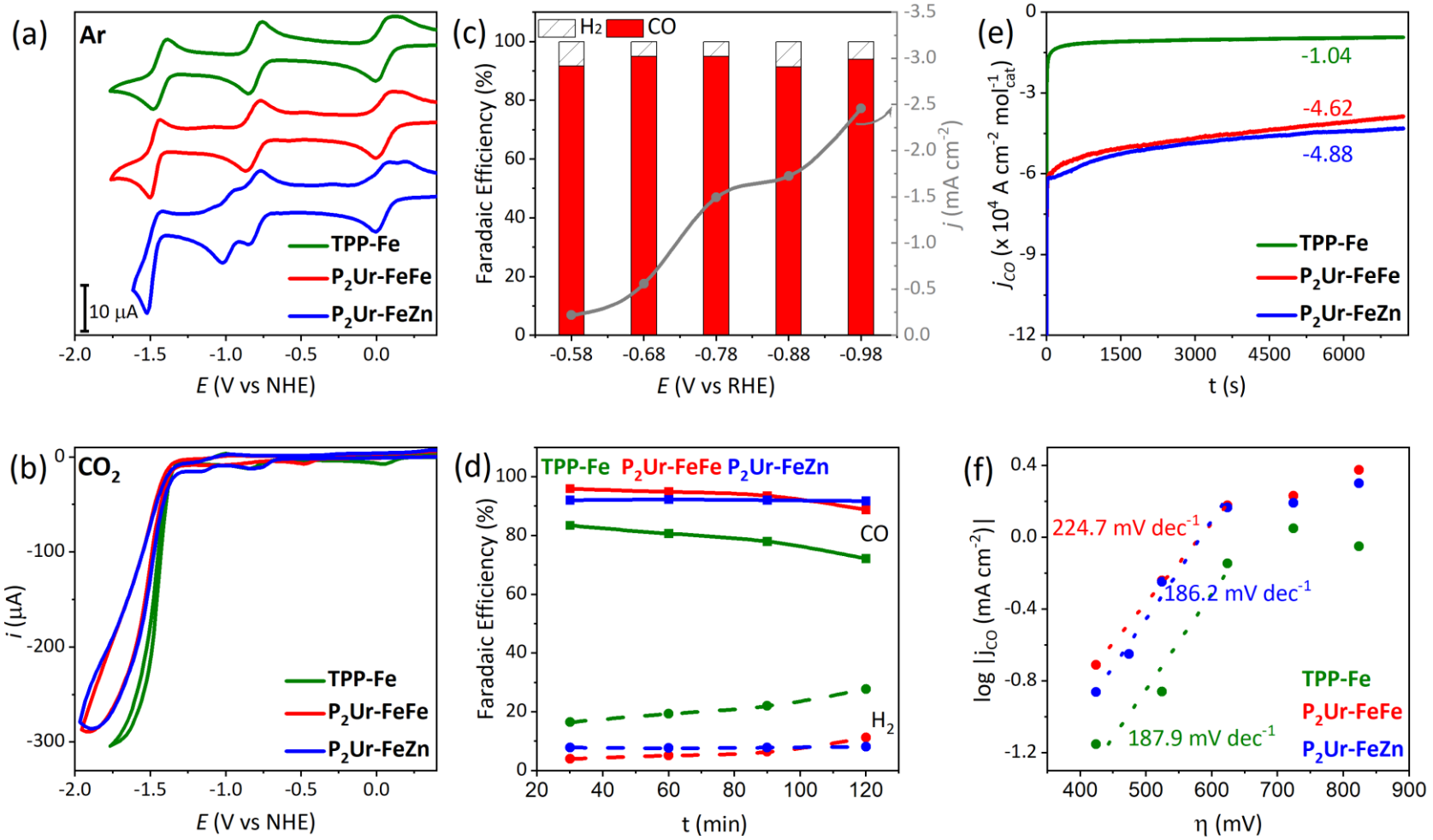


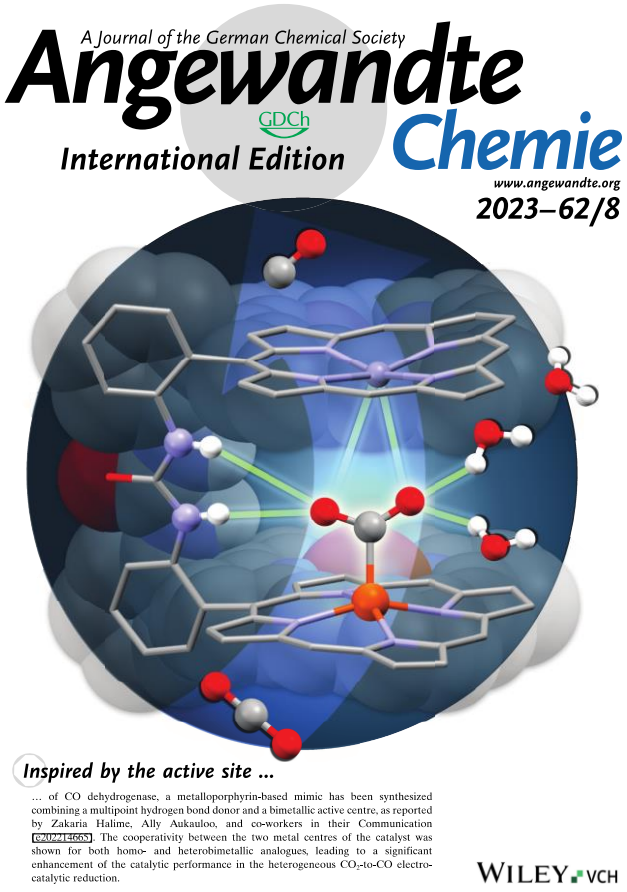




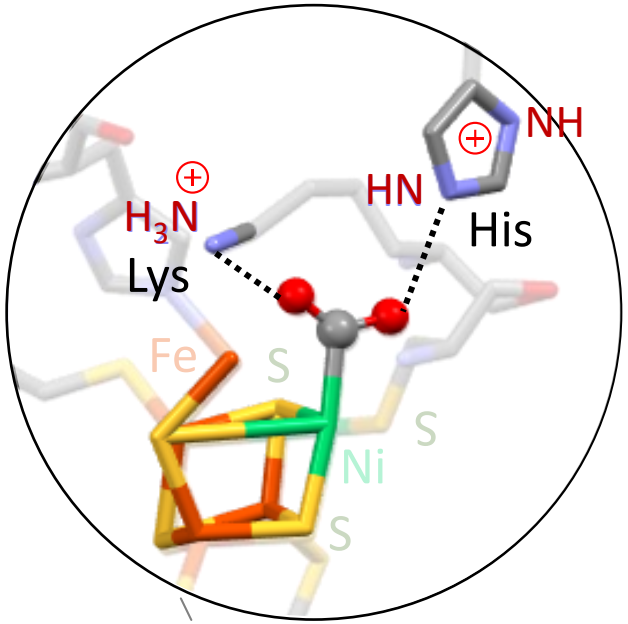
Amanullah Sk et al, *Angew. Chem. Int. Ed. Engl.* **2023**, *61*, e202117530

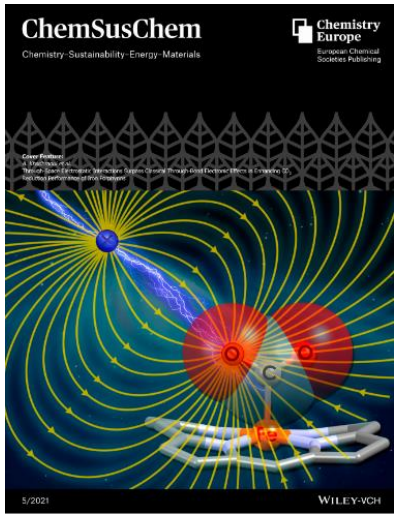
Bimetallic heterogeneous catalysis



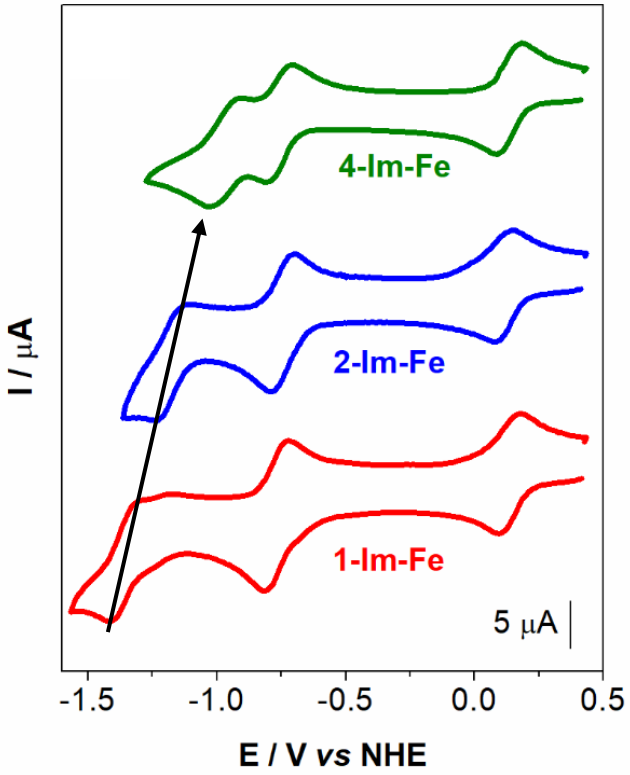


Electrostatic assisted catalysis

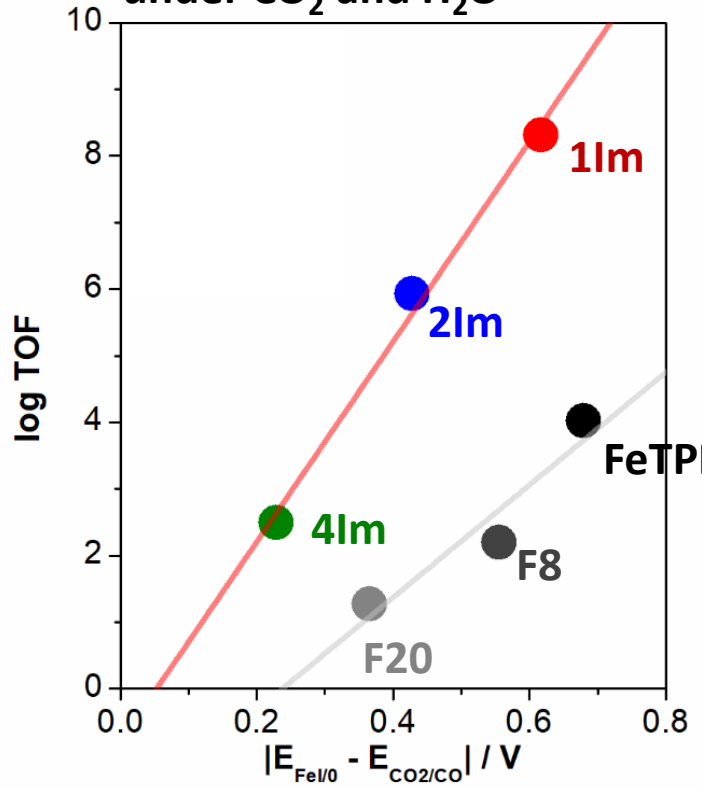


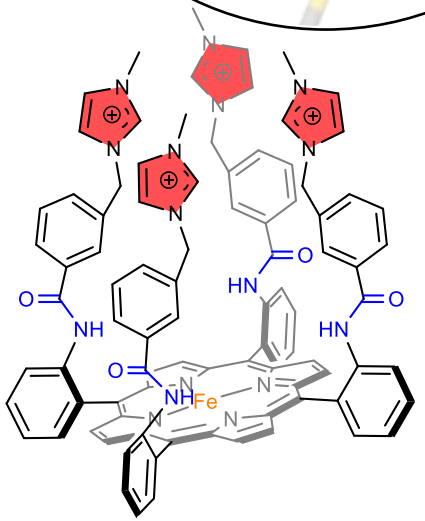


CVs under Ar

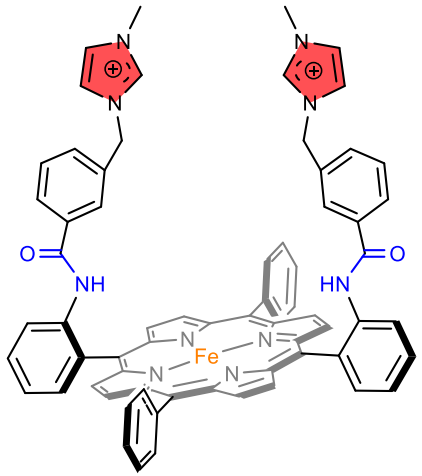


under CO_2 and H_2O

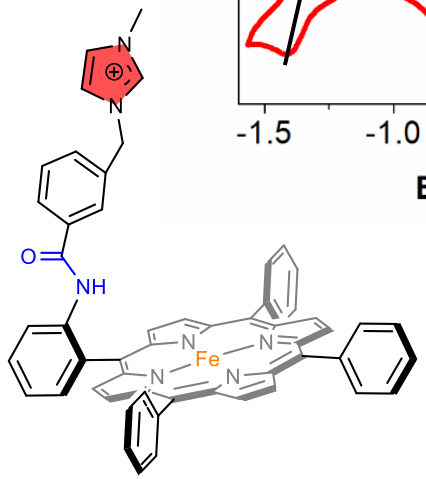




αααα-4Im-FeTPP



αα-2Im-FeTPP

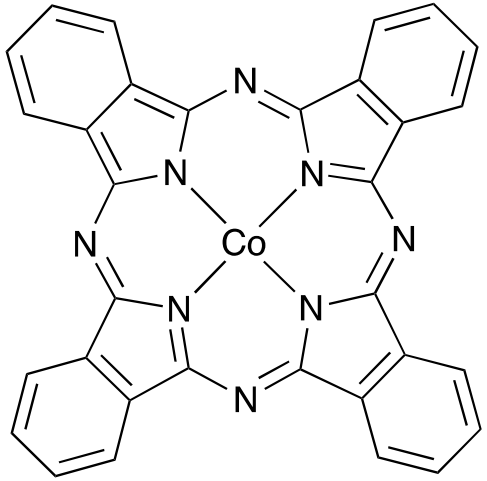


o-1Im-FeTPP

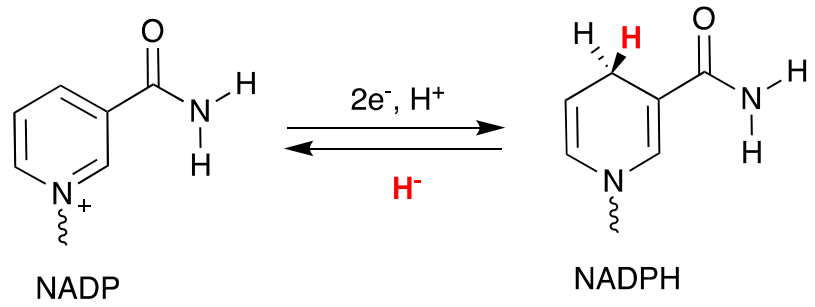
- **Overpotential as a function of the number of imidazolium groups**
- **Through-space electrostatic effect > Through-bond electronic effect**

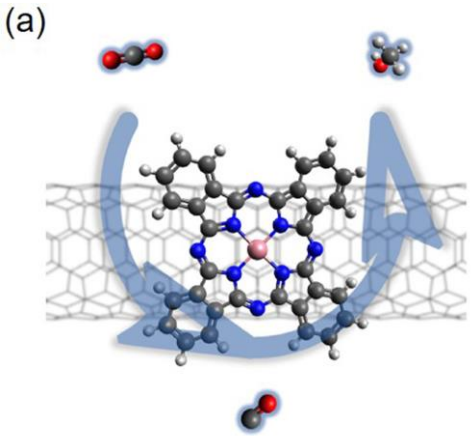
Chem. Commun. **2018**, *54*, 11630–11633. *ChemSusChem* **2021**, *14*, 1308-1315.

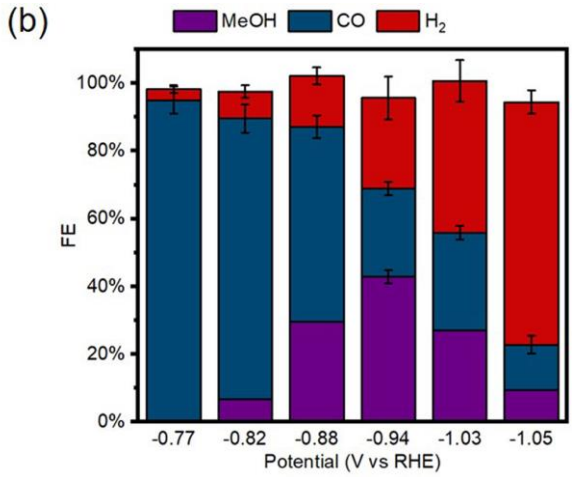
Cobalt Phthalocyanine for CO2 Reduction: Hydride transfer?

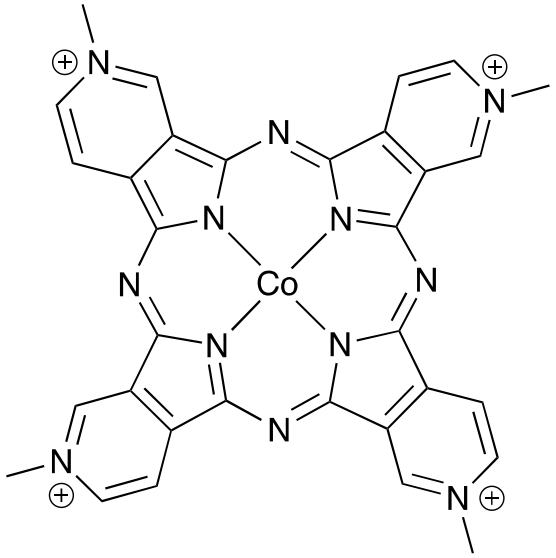


Introducing a potential center for organic hydride formation



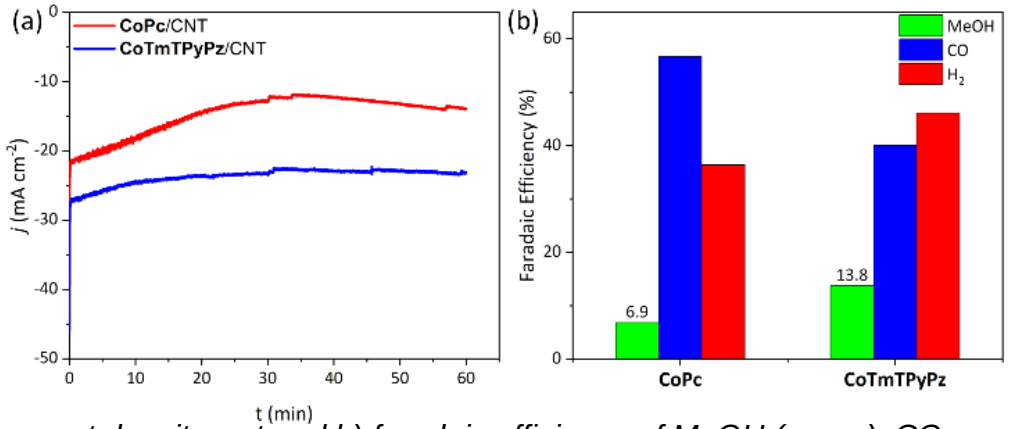




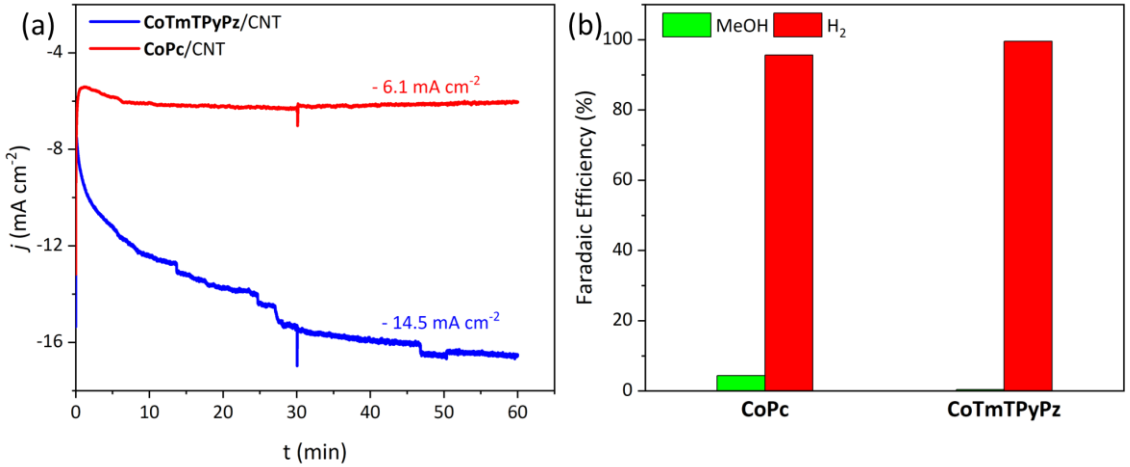


H. Wang and coll.Acc. Chem. Res. 2021, 54, 3149−3159

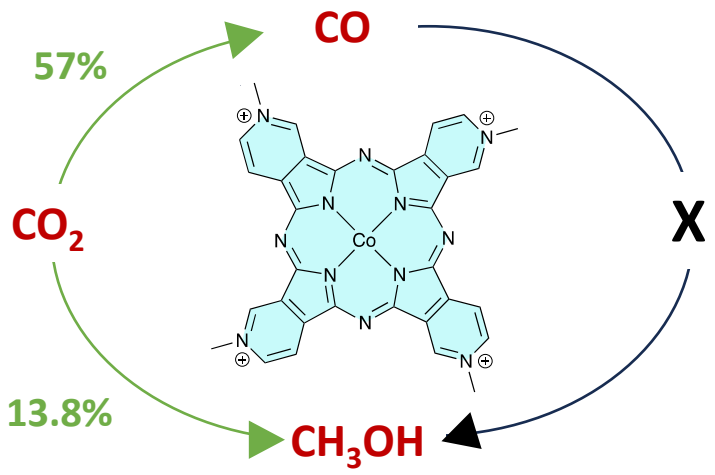
Cobalt Phthalocyanine for CO2 Reduction

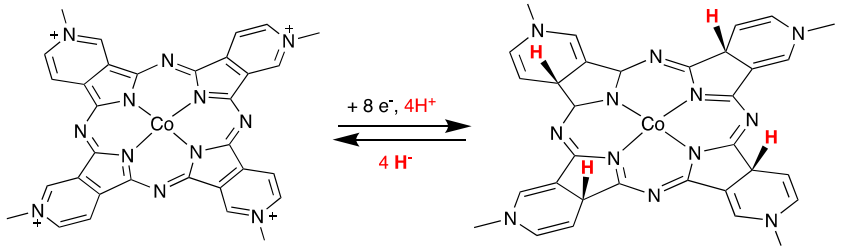


a) current density vs t and b) faradaic efficiency of MeOH (green), CO (blue) and H2 (red) of 1 hour electrolysis of CoTmTPyPz/CNT/CP (blue) and CoPc/CNT/CP (red) in CO2-saturated 0.5 M KHCO3 aqueous solution (pH = 7.3) at -1.0 V vs RHE.



(a) j vs t, (b) Faradaic efficiency of methanol (green) and H2 (red) for the controlled potential electrolysis of CoPc/CNT/CP (red) and CoTmTPyPz/CNT/CP (blue) electrodes in CO-saturated 0.5 M KCl aqueous solution (catholyte) and 0.5 M KHCO3 aqueous solution was used for the anolyte



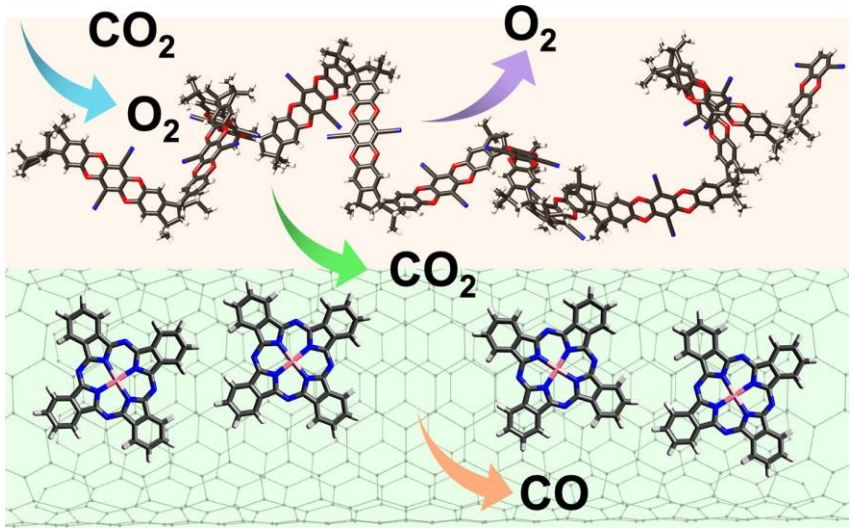


Collaboration with VITO, Belgium

Angewandte Chemie Int Ed. 2024, 10.1002/anie.202411967

Reducing CO2 in presence of O2

O_2 reduction is thermodynamically favored over that of CO_2.
5% O_2 in CO_2 near catalyst surface is sufficient to completely inhibit the CO_2 reduction reaction

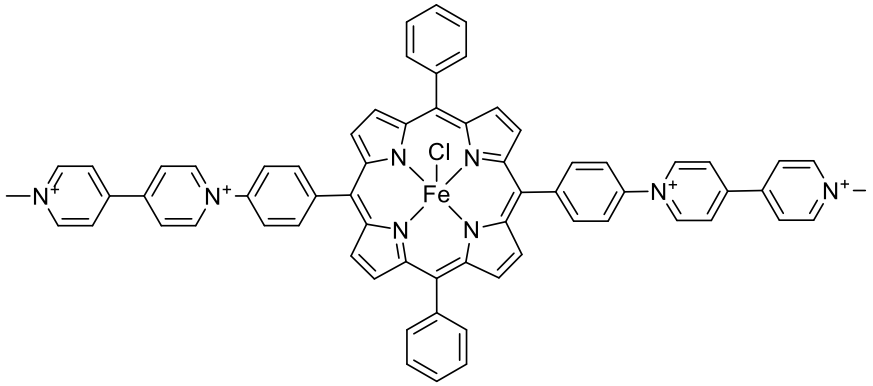


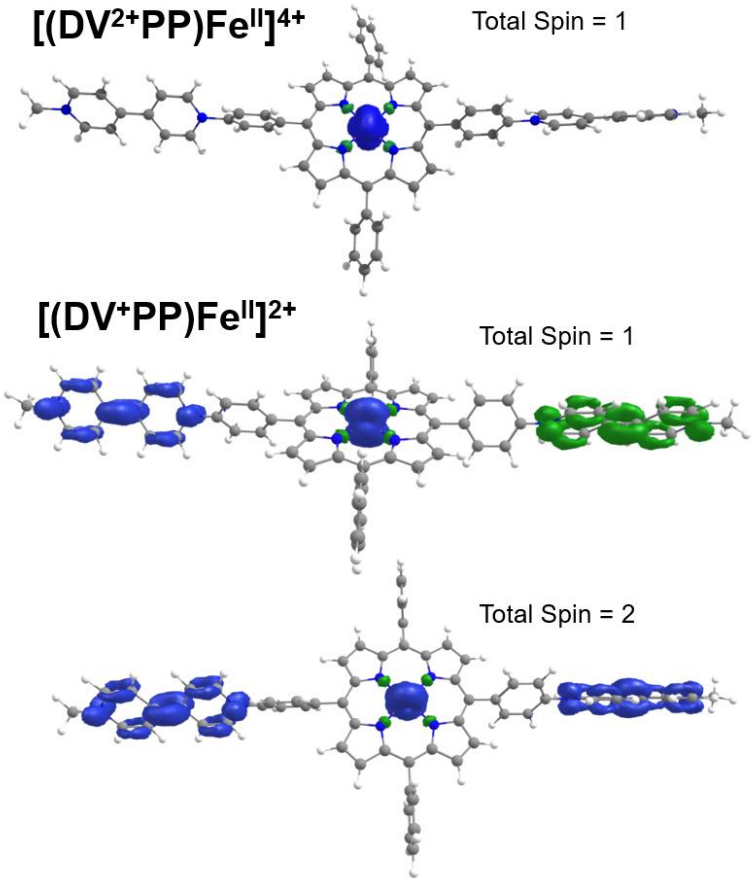
FE_{CO}=75.9%
O_2 =5%

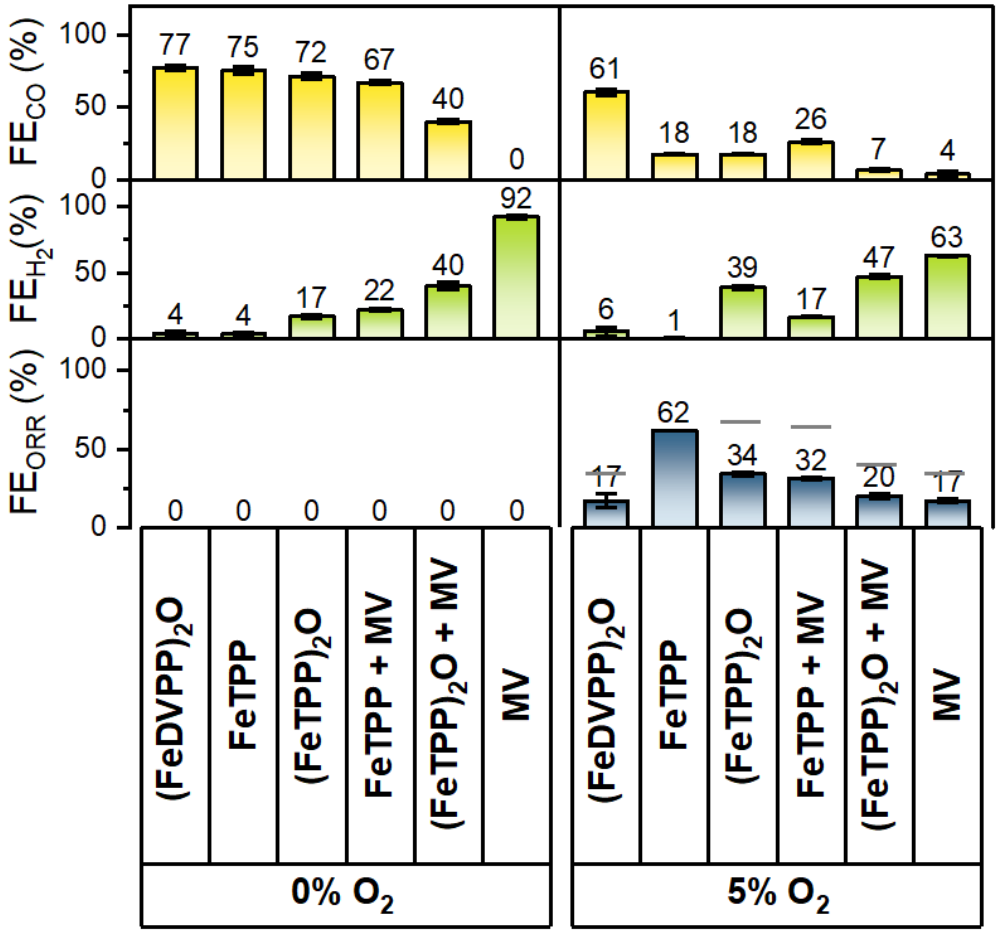
Schematic diagram of the PIM-CoPc/CNT hybrid electrode for O_2-tolerant catalytic CO_2 reduction.

H. Wang and collScience bulletin. 2019, 64, 1890–1895

CV and Heterogeneous electrocatalysis







Faradaic efficiencies (FE) of **$(FeDVPP)_2O$** in comparison to various controls [FeTPP, $(FeTPP)_2O$, FeTPP + MV, $(FeTPP)_2O$ + MV, MV] after 30 min electrolysis at –0.8 V vs RHE at 0 % and 5 % O_2 Volume fraction. Proper stoichiometries are maintained for accurate comparison of controls relative to **$(FeDVPP)_2O$**.

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Perspectives

Réduire le CO_2 directement de l'air à des faibles concentrations

i) Introduction d'un module pour le captage du CO_2

ii) Développement de catalyseurs

iii) Réalisation de réduction du CO_2 en présence de O_2

iv) Développement de la catalyse hétérogène

Projet AUDACE

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