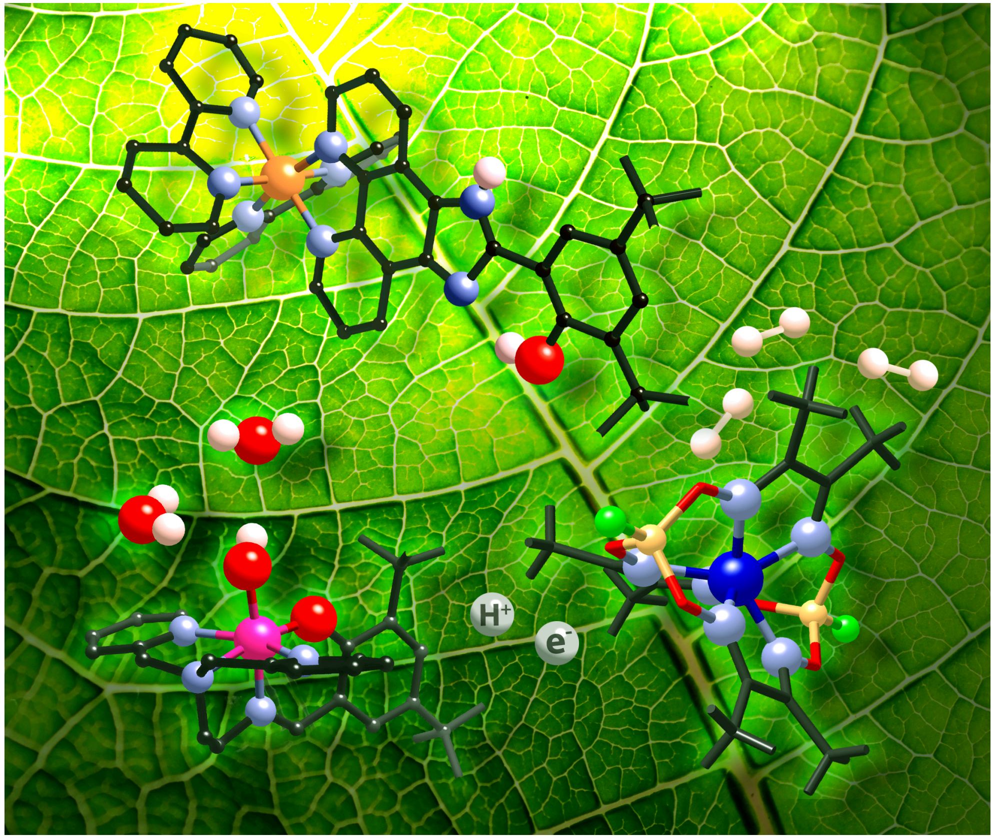
Photosynthèse Naturelle : source d'inspiration pour les chimistes



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Innovation Bioinspirée, Iledescience

16/04/2019

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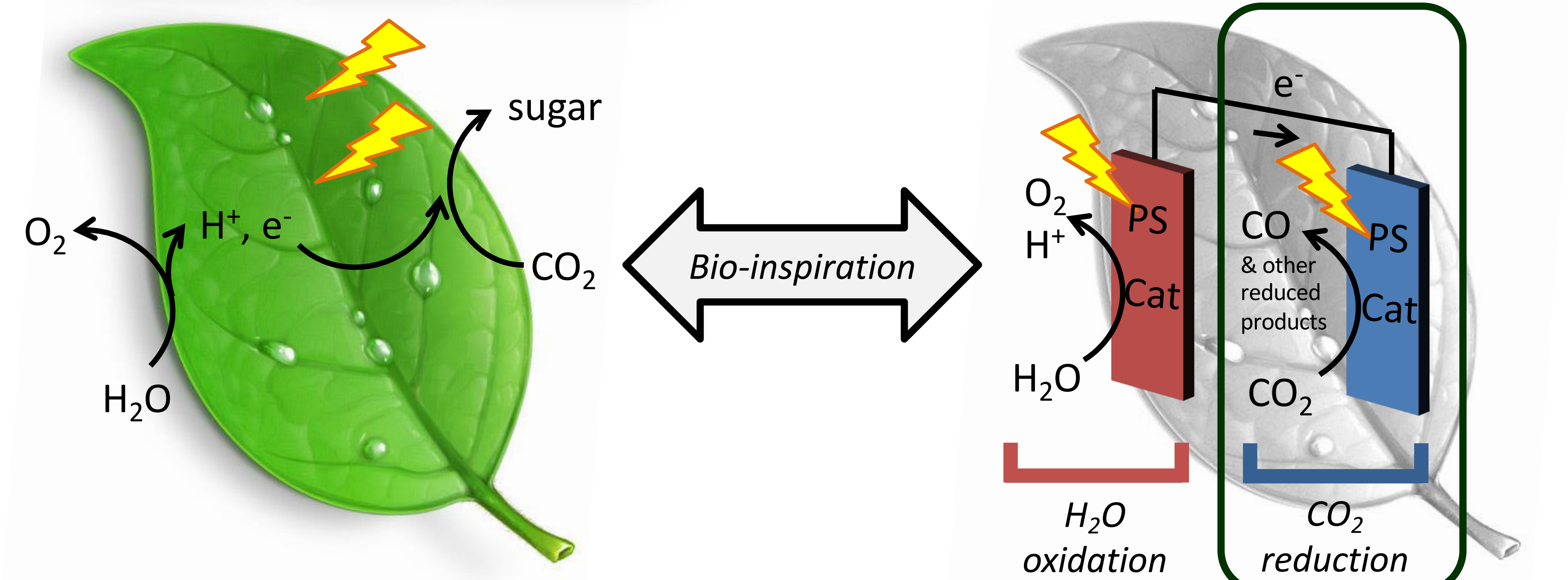
Photosynthèse Artificielle

The Great Concern

Carbon Dioxide Reduction + **Renewable Energy Source**



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Carbone dans tous états…

Half-electrochemical reactions	Potential (V vs. SHE)
$CO_2 + e^- \rightarrow CO_2^{\bullet -}$	−1.90
$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	−0.53
$CO_2 + 2H^+ + 2e^- \rightarrow HCO_2H$	−0.61
$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O$	−0.48
$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	−0.38
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + H_2O$	−0.24
$2H^+ + 2e^- \rightarrow H_2$	−0.41

Table 1 Known pathways of CO_2 fixation by microbes

Pathway name	CO_2-fixing enzymes	Examples of Microbes	O_2 sensitivity
Calvin-Benson-Bassham Cycle	RubisCO	Aerobic autotrophic bacteria (cyano-bacteria, purple sulfur bacteria…*etc.*)	Tolerant
Reductive tricarboxylic acid cycle	2-oxoglutarate synthase, isocitrate dehydrogenase, pyruvate synthase, PEP carboxylase	Bacteria such as *Chlorobium* sp. and *Desulfobacter* sp.	Sensitive
Reductive acetyl-CoA pathway	Acetyl-CoA synthase, formate dehydrogenase	Methanogenic archaea and acetogenic bacteria	Sensitive
3-Hydroxypropionate/ malyl-CoA cycle	Acetyl-CoA carboxylase, Propionyl-CoA carboxylase	Phototrophic bacterium, *Chloroflexus aurantiacus*	Sensitive
3-Hydroxypropionate/ 4-hydroxybutyrate cycle	Acetyl-CoA carboxylase, Propionyl-CoA carboxylase	Autotrophic Crenarchaeota, Sulfolobales, *Metallosphaera sedula*	Microaerobic conditions
Dicarboxylate/ 4-hydroxybutyrate cycle	Pyruvate synthase, Phosphoenol pyruvate carboxylase	Archaea such as *Ignicoccus hospitalis*, *Thermoproteus neutrophilus*	Sensitive

La nature n'est pas pressée...

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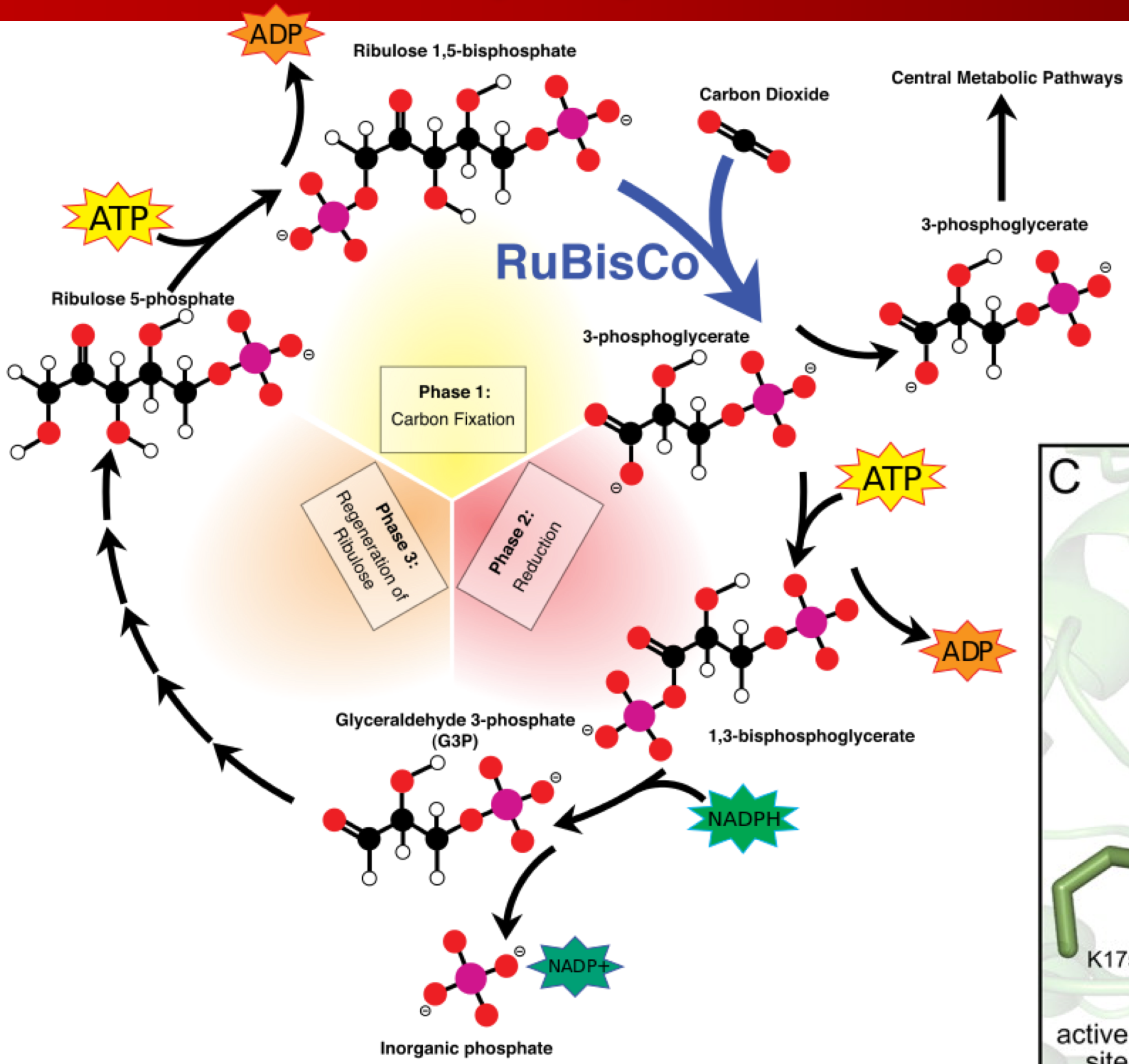
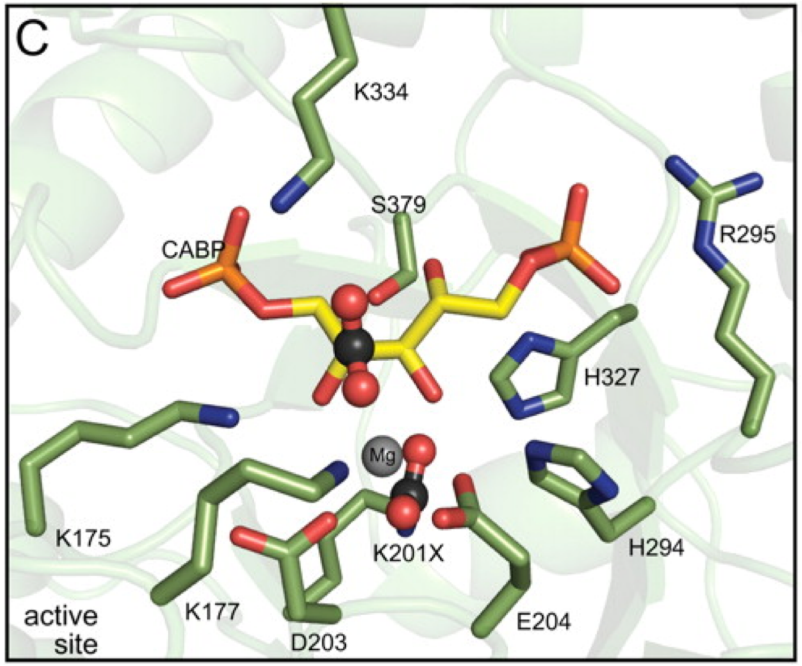
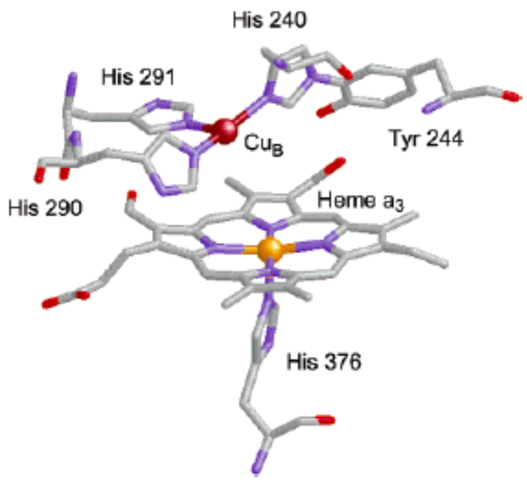


Ribulose-1,5-bisphosphate carboxylase/oxygenase (RuBisCO)

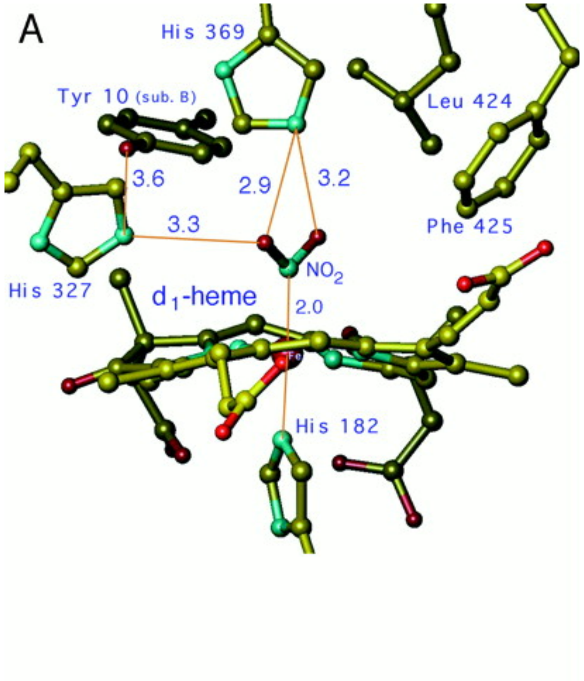


$$3\ CO_2 + 9\ ATP + 6\ NADPH + 6\ H^+ \rightarrow C_3H_6O_3\text{-phosphate} + 9\ ADP + 8\ P_i + 6\ NADP^+ + 3\ H_2O$$

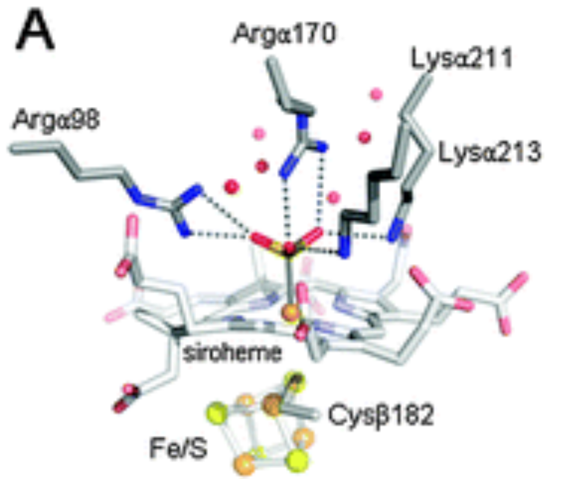
Leçons de la nature: Réduction de O_2, NO_2^-, SO_3^{2-}



Cytochrome c Oxidase



Nitrite reductase



Sulfite reductase

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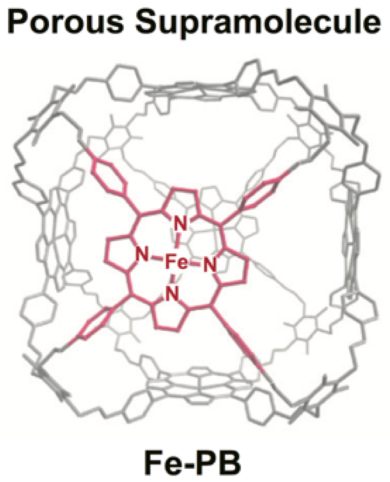
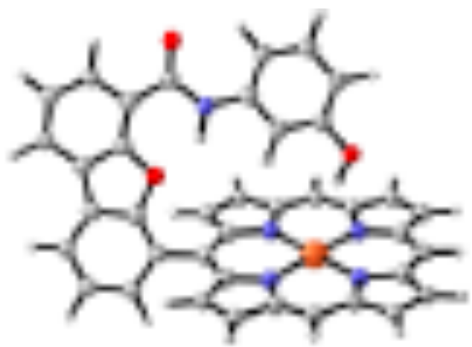
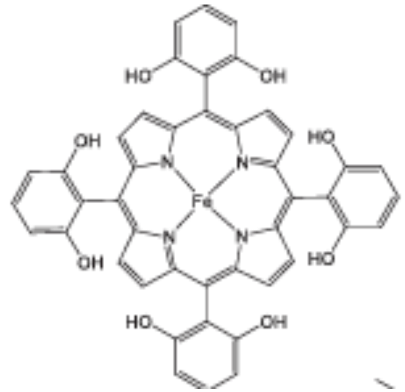
Complexes porphyriniques pour la réduction du CO_2…



Chang Angew. Chem. 2019



Nocera Organometallics 2018



Robert PNAS 16

$$CO_2 + 2\,e^- + 2H^+ \rightarrow CO + H_2O$$

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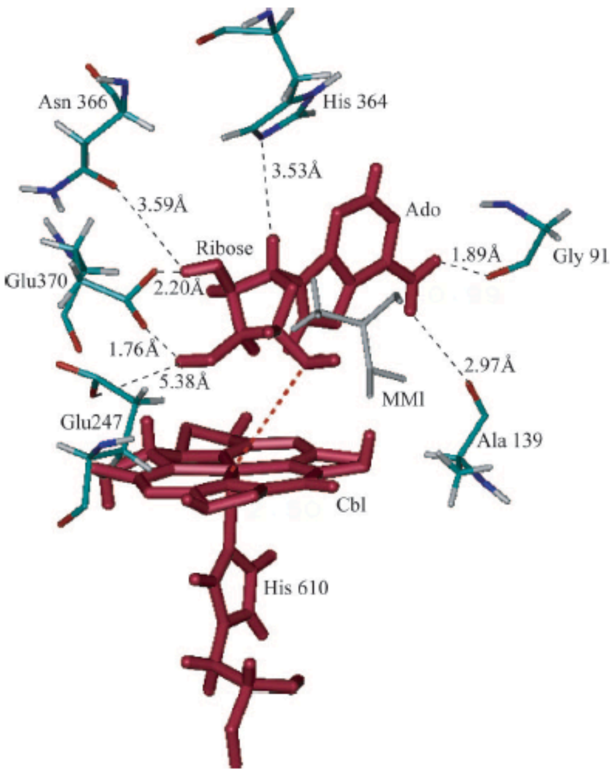
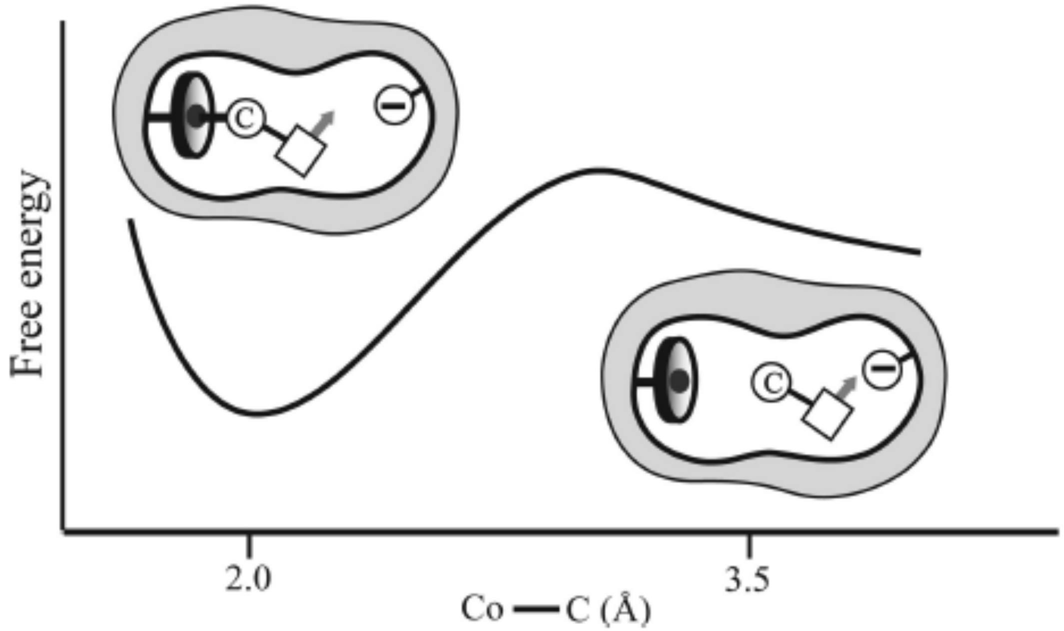
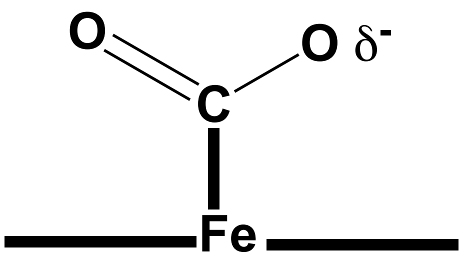
Stabilisation par voie électrostatique

Arieh Warshel Nobel Prize 2013







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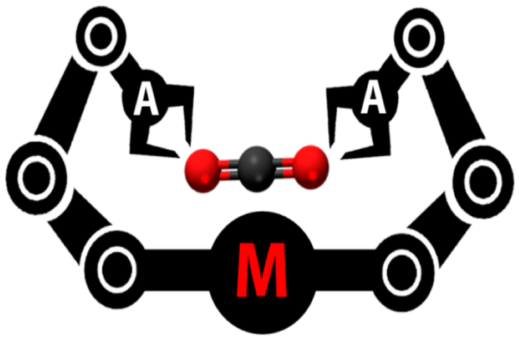
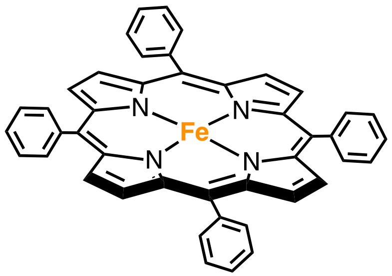
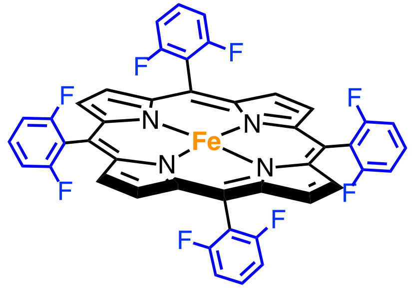
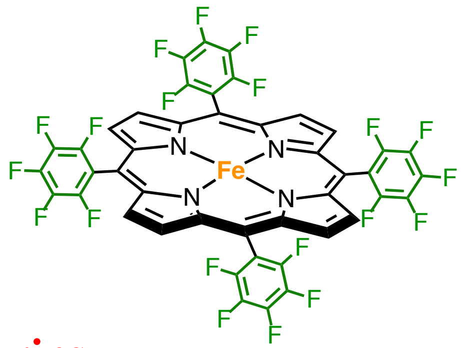


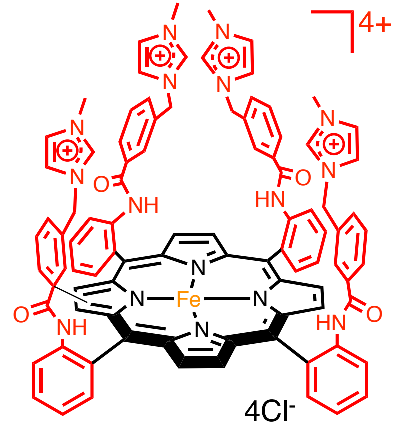
Porphyrins with embarked Ionic liquids

Ière Stratégie: Effet électrostatique



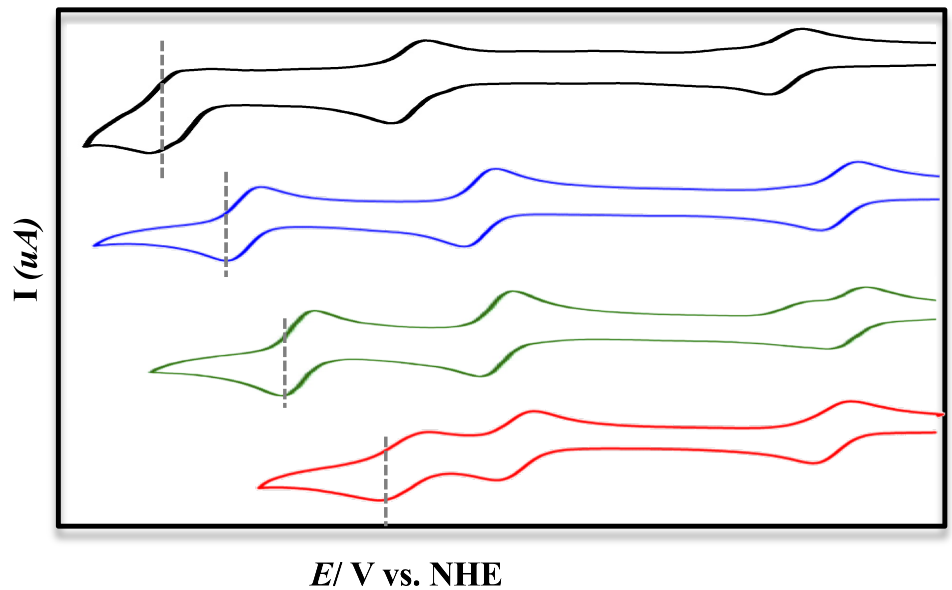




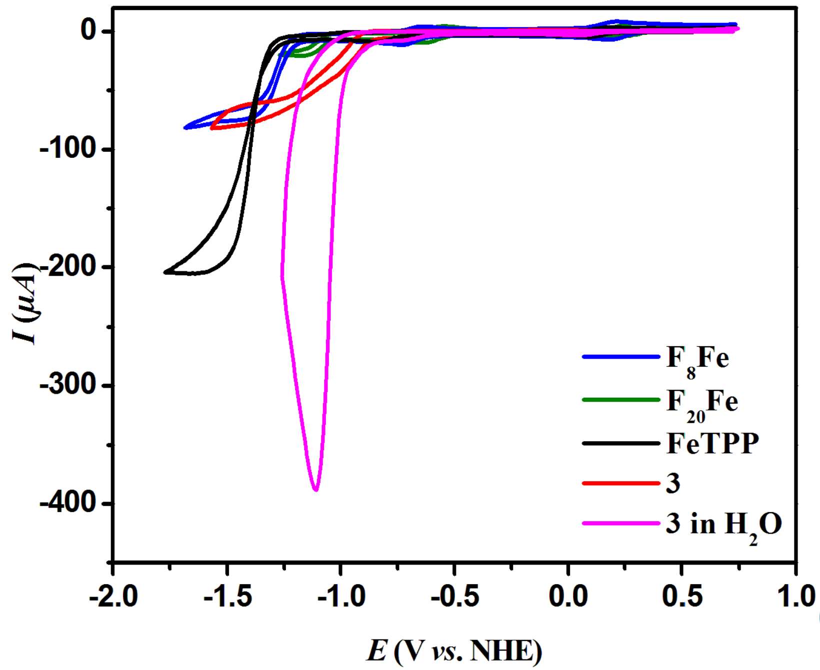


Cyclic Voltammetry of modified iron porphyrins

(a)



(b)



$\eta = 366mV\ (IL)$

Cyclic voltammogram of 1mM FeTPP; 1mM FeTPPF$_8$, 1mM FeTPPF$_{20}$; in 9:1 DMF:H_2O
(a) under Ar, (b) under CO_2

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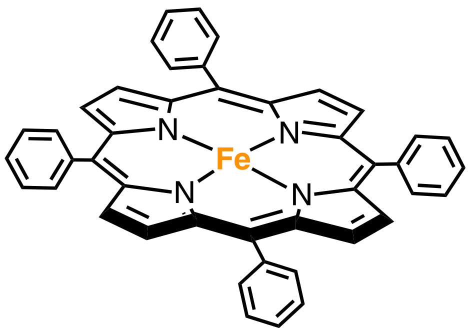
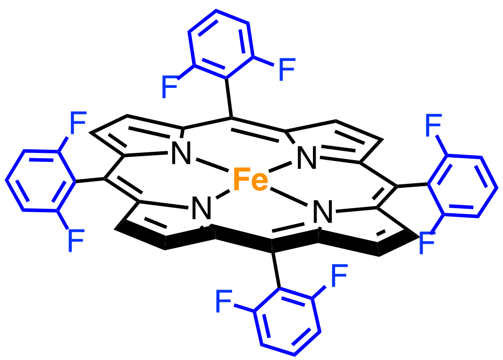
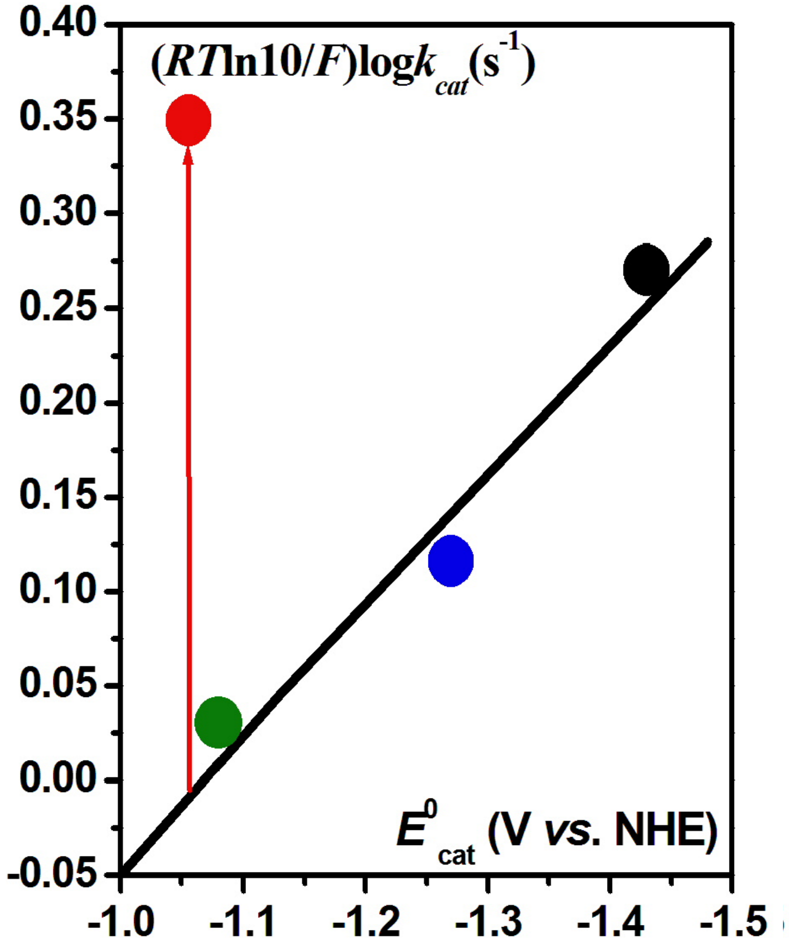
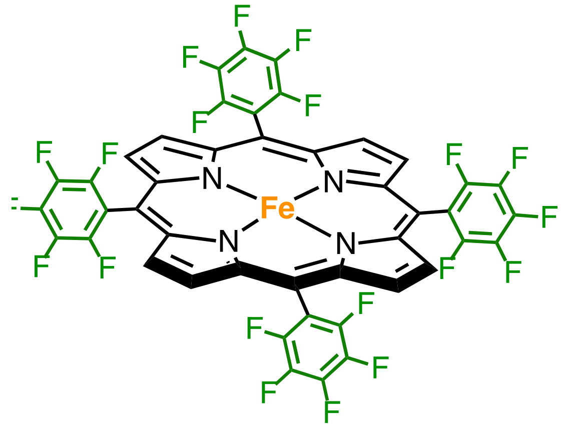
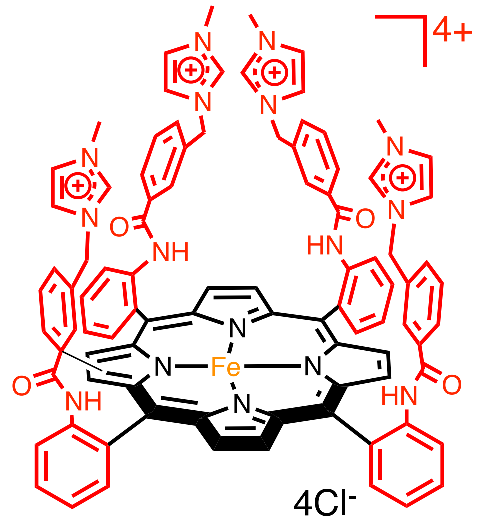
Propriétés électrocatalytiques





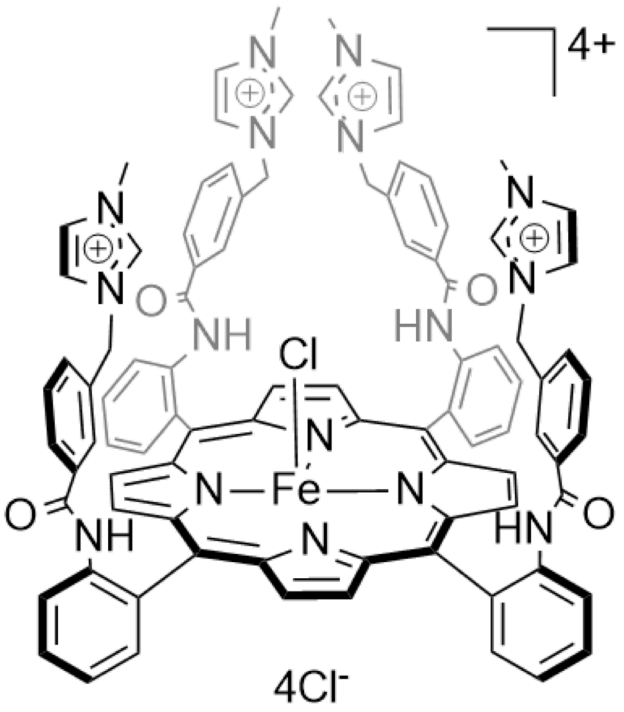


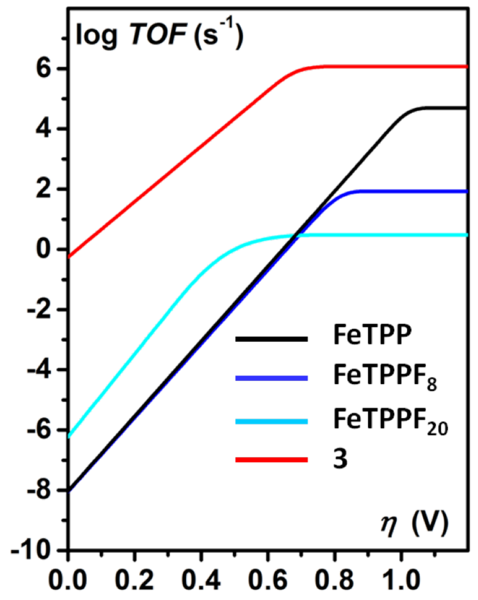


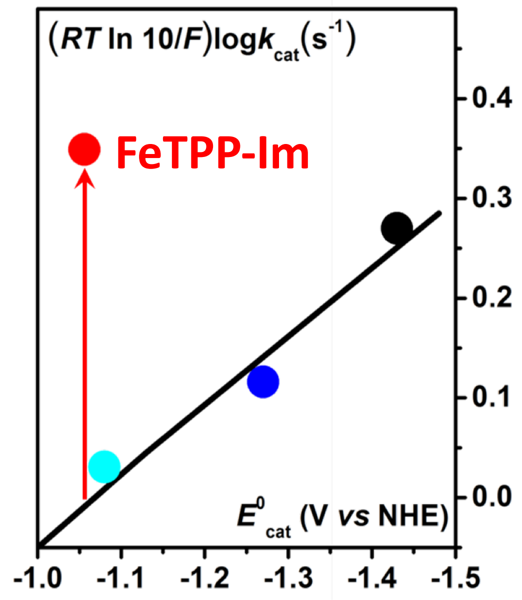


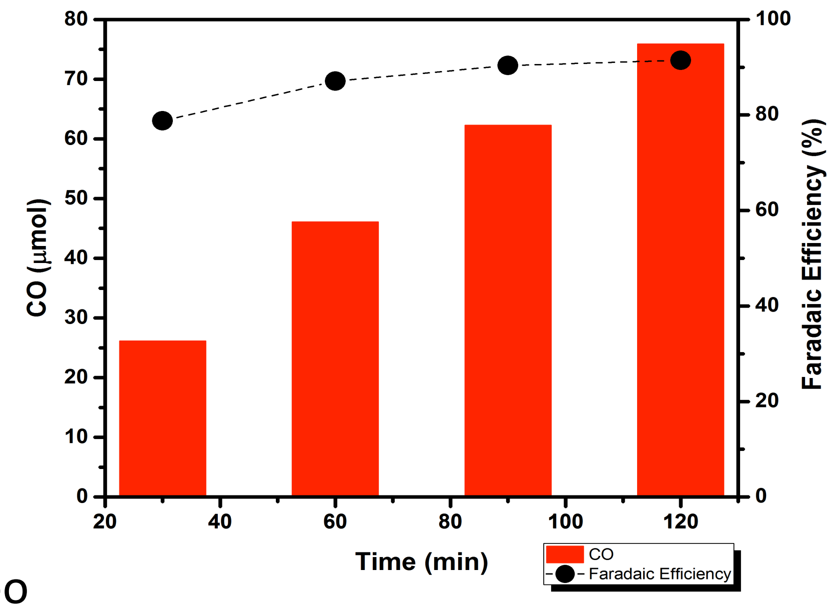
Asma Khadhraoui et al. Chem Comm 2018

Performance électrocatalytique éxaltée!









- ❑ Electrocatalytic CO_2 reduction to CO in water
- ❑ No need of external proton source
- ❑ Overpotential of 420 mV
- ❑ TOF of 240 000 s^{-1}

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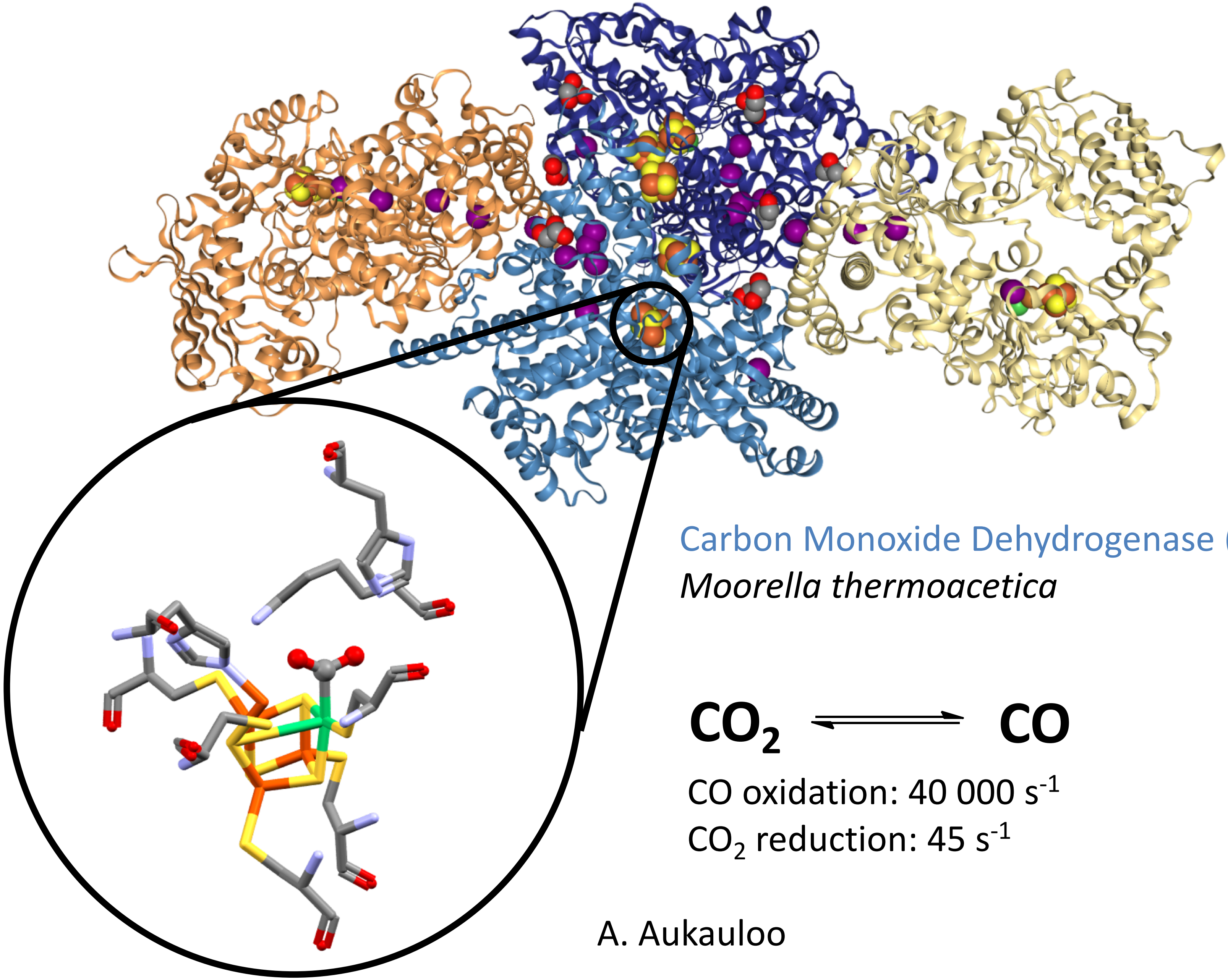
2ème stratégie. Liaisons Hydrogène



Carbon Monoxide Dehydrogenase (CODH)

Moorella thermoacetica

$$CO_2 \rightleftharpoons CO$$

CO oxidation: 40 000 s^{-1}

CO_2 reduction: 45 s^{-1}

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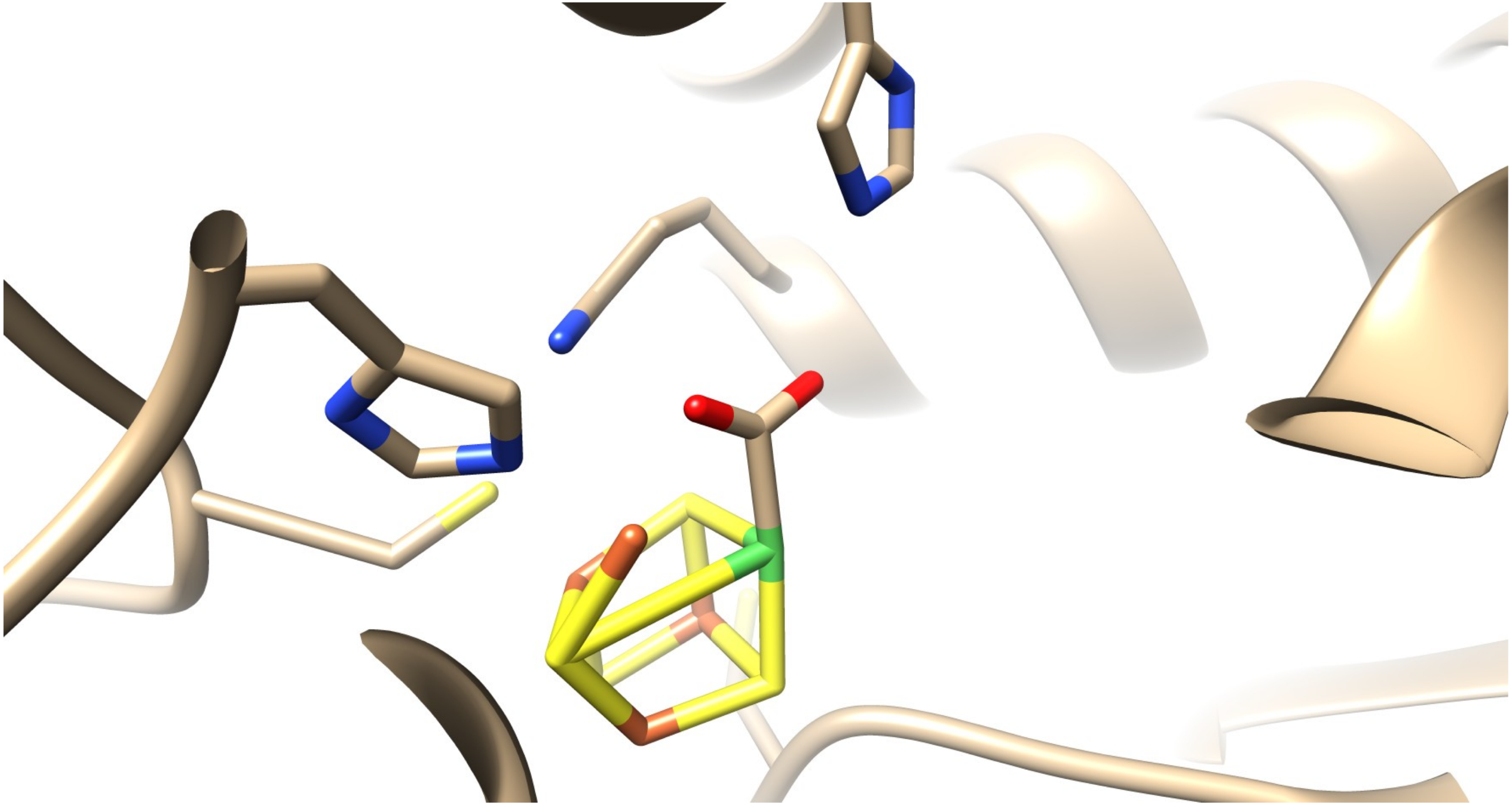
2ème stratégie. Modèle biomimétique de la CODH



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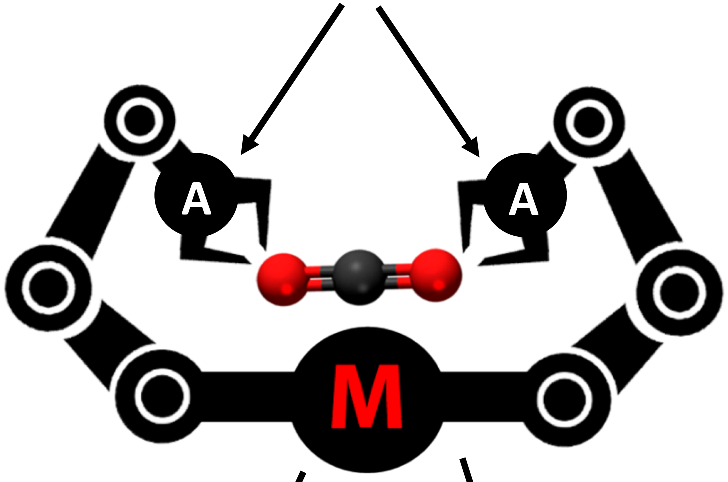
Manipulation de la seconde sphère de coordination

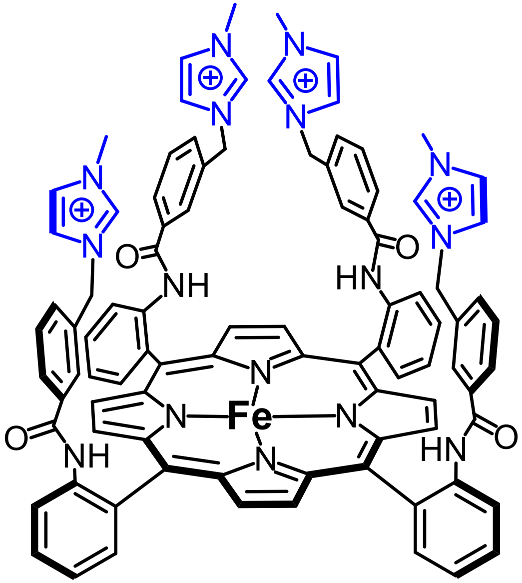
Substrate activation



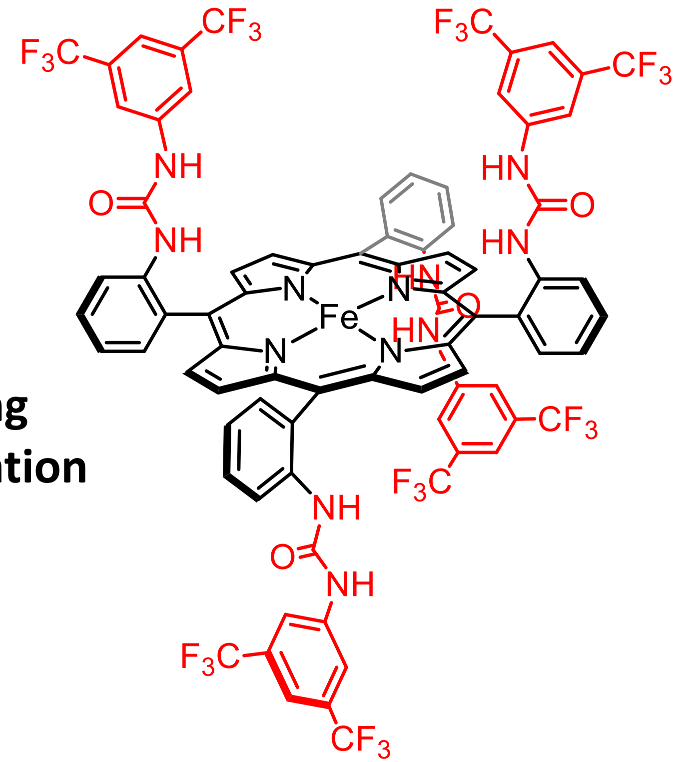
Substrate capture and binding

Ligand supporting charge accumulation

✓ **Electrostatics**



✓ **Hydrogen bonding**



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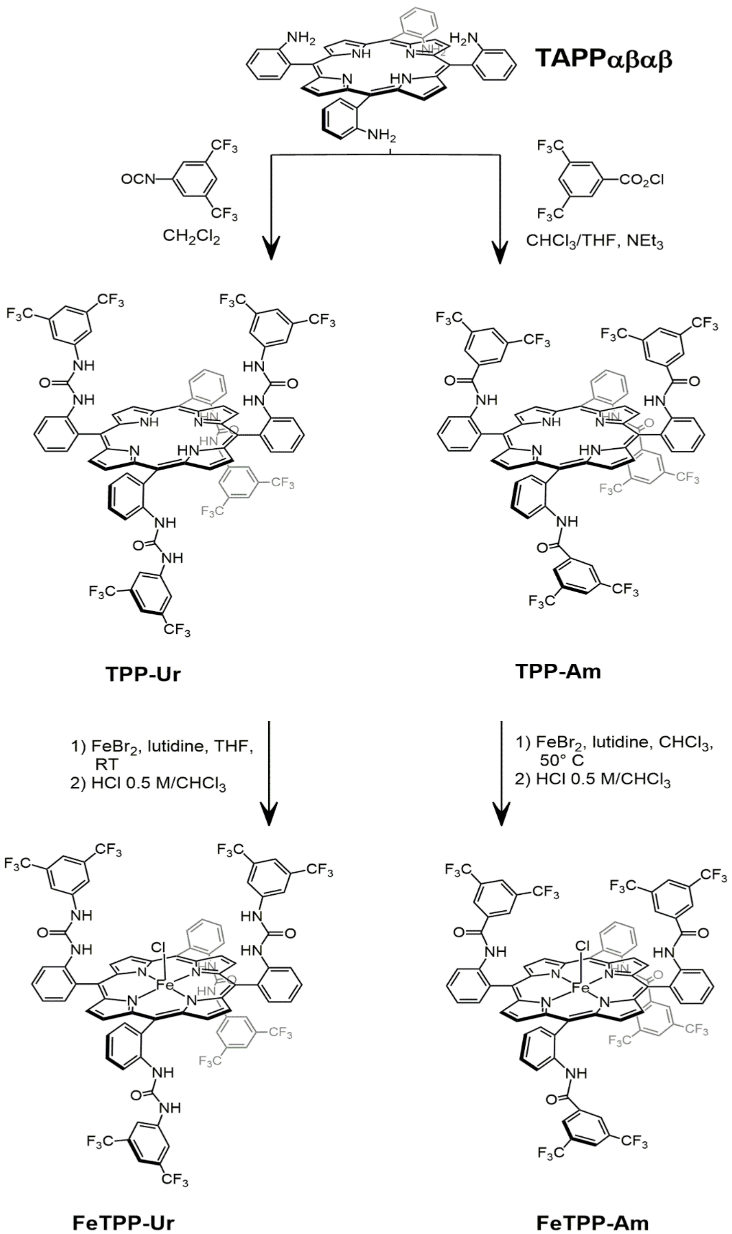
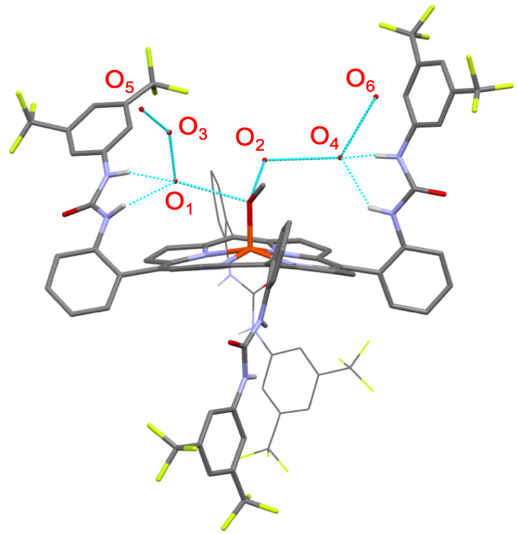
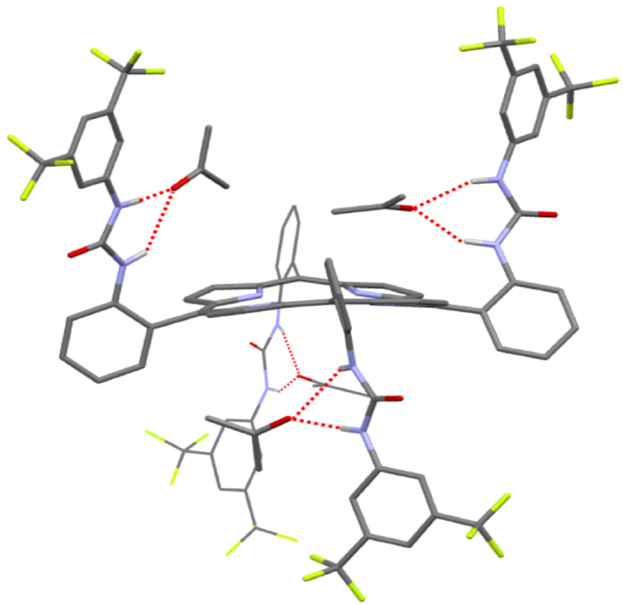
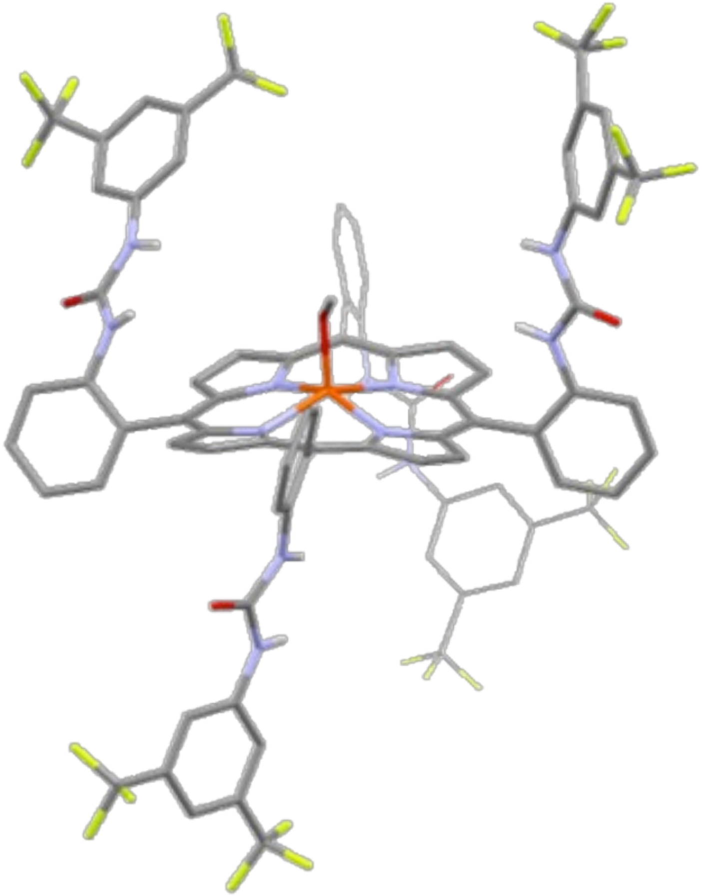
Synthèse et caractérisation

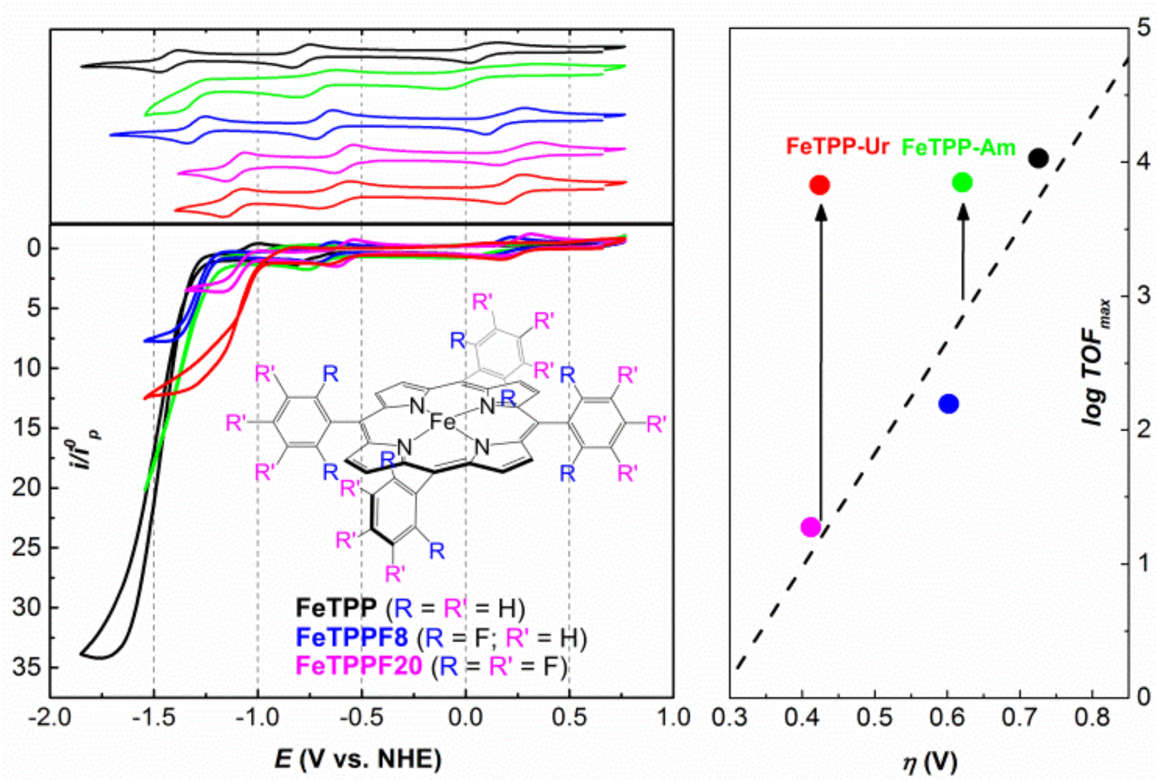


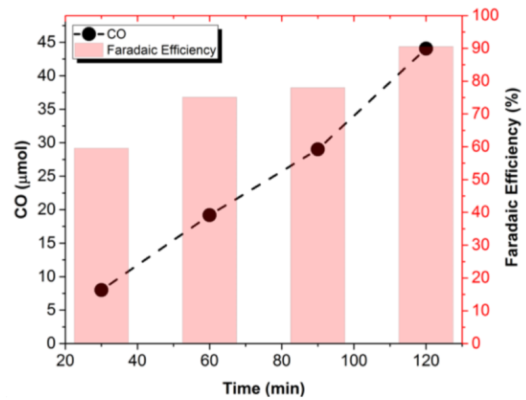




Propriétés électrocatalytiques







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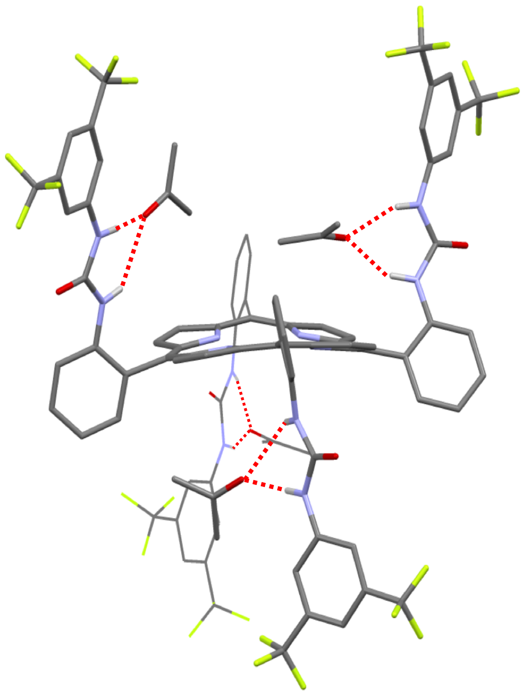
Captage du CO_2..

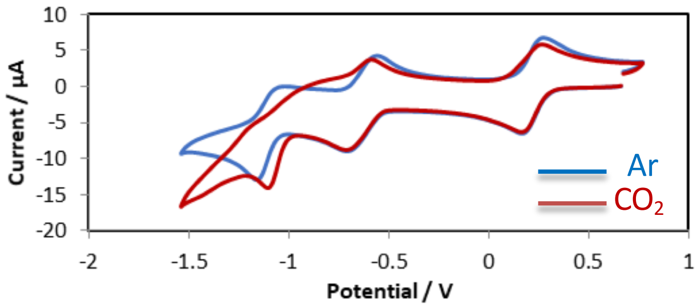
$$Fe^{I} + 1e^{-} \rightleftharpoons Fe^{0}$$

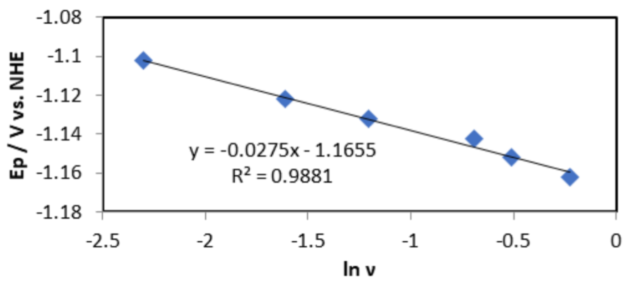
$$Fe^{0} + CO_2 \longrightarrow Fe^{I} - CO_2^{-} \qquad k_{CO_2}$$

$$E_p = E^0 - 0.78\frac{RT}{F} + \left(\frac{RT}{2F}\right)\ln\frac{RTk[CO_2]}{Fv}$$



In absence of proton





	k_{CO_2} (M^{-1} s^{-1})
FeTPPUr	58.0
FeTPPAm	7.6
FeTPP	6.8

Enhanced binding constant

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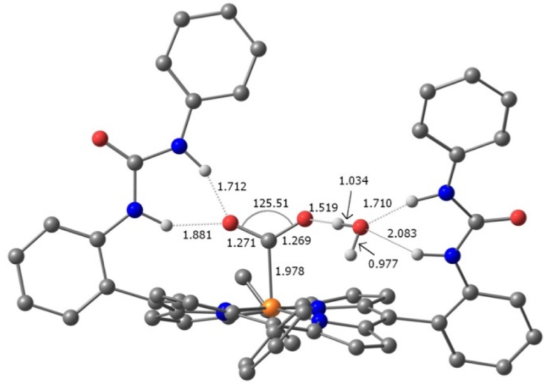
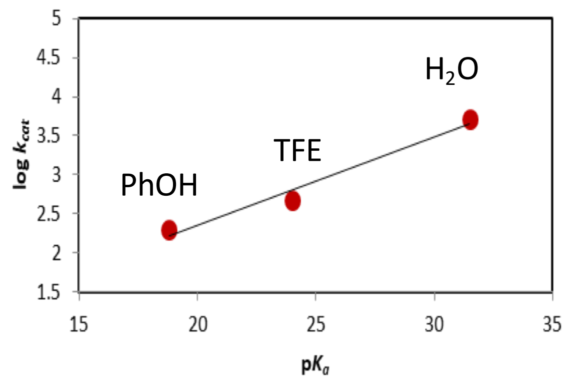
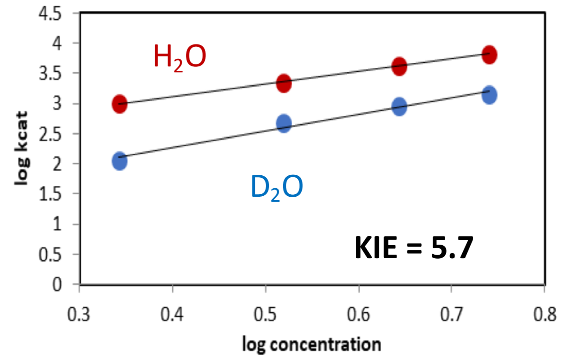
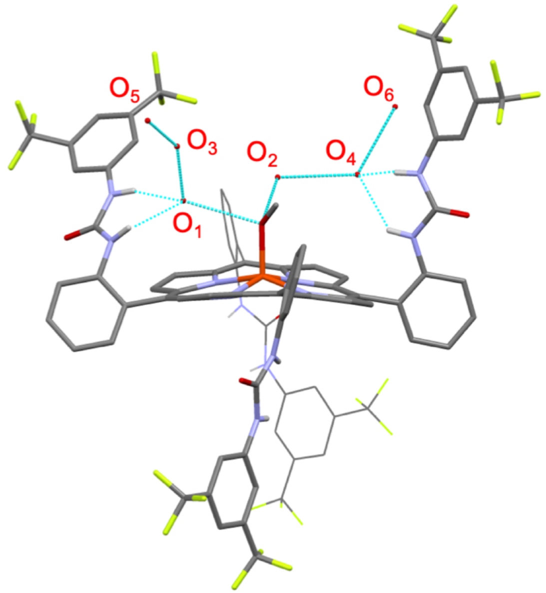
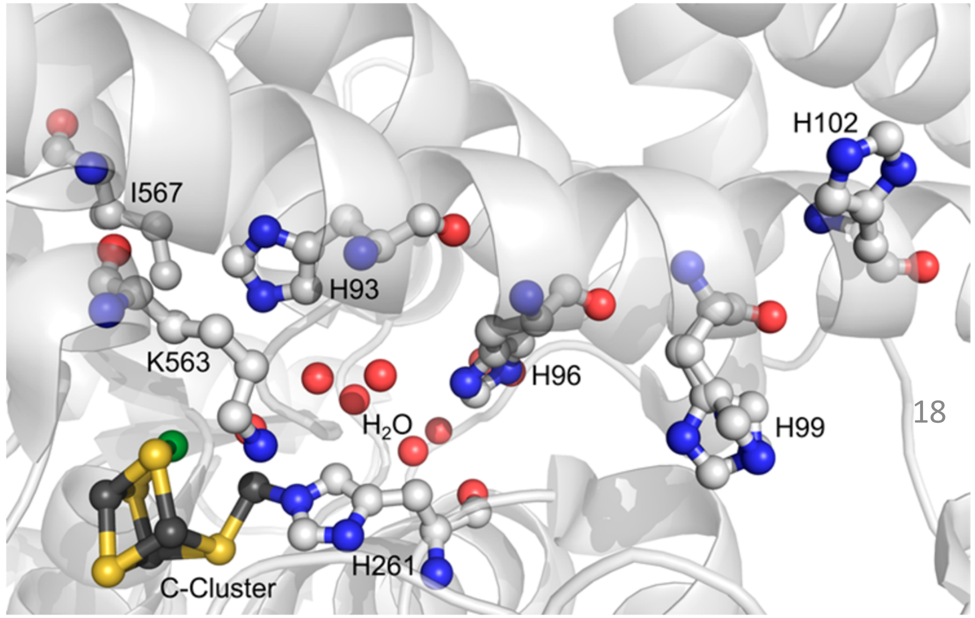
H_2O comme source de protons!!











Water as proton source!

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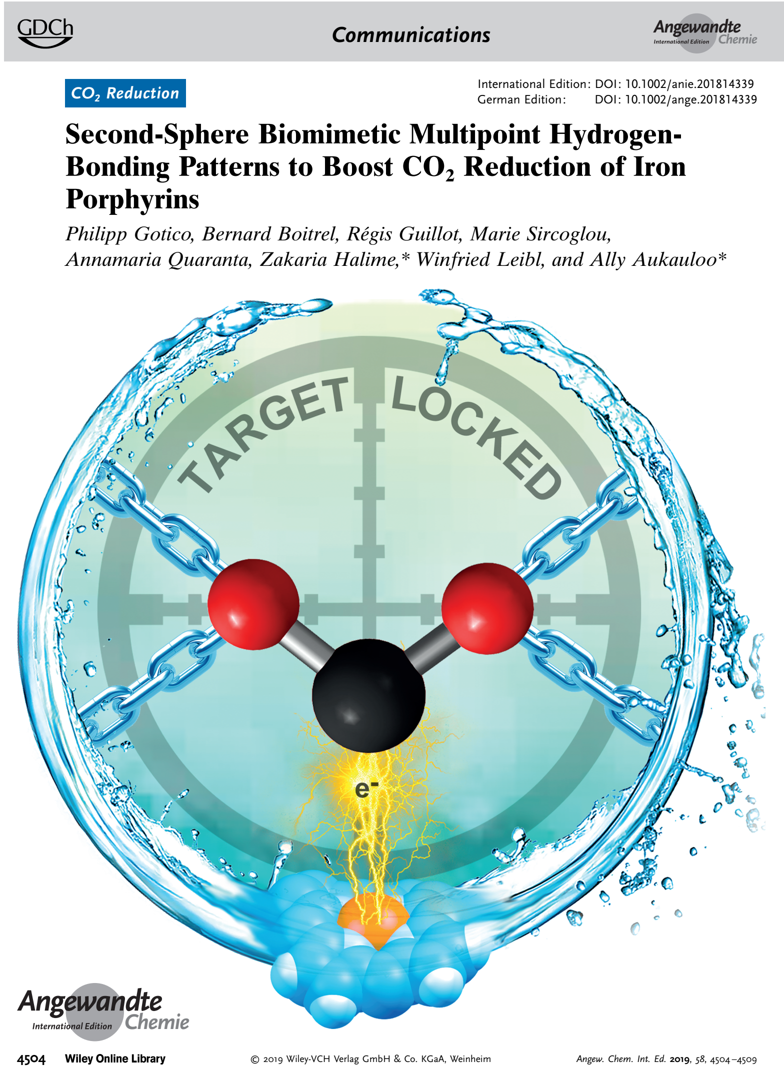
Performance électrochimique

- ✓ Increased CO_2 binding rate (k = 58 $M^{-1}s^{-1}$)
- ✓ Overpotential of 430 mV
- ✓ TOF of 2 760 s^{-1}
- ✓ TON of 3 280 000
- ✓ 91% Faradaic efficiency



GDCh **Communications** Angewandte Chemie

CO_2 Reduction

International Edition: DOI: 10.1002/anie.201814339
German Edition: DOI: 10.1002/ange.201814339

Second-Sphere Biomimetic Multipoint Hydrogen-Bonding Patterns to Boost CO_2 Reduction of Iron Porphyrins

Philipp Gotico, Bernard Boitrel, Régis Guillot, Marie Sircoglou, Annamaria Quaranta, Zakaria Halime, Winfried Leibl, and Ally Aukauloo**

Angewandte Chemie International Edition
4504 Wiley Online Library Angew. Chem. Int. Ed. 2019, 58, 4504–4509

Philipp Gotico et al. Angew. Chemie. Int Ed. 2019

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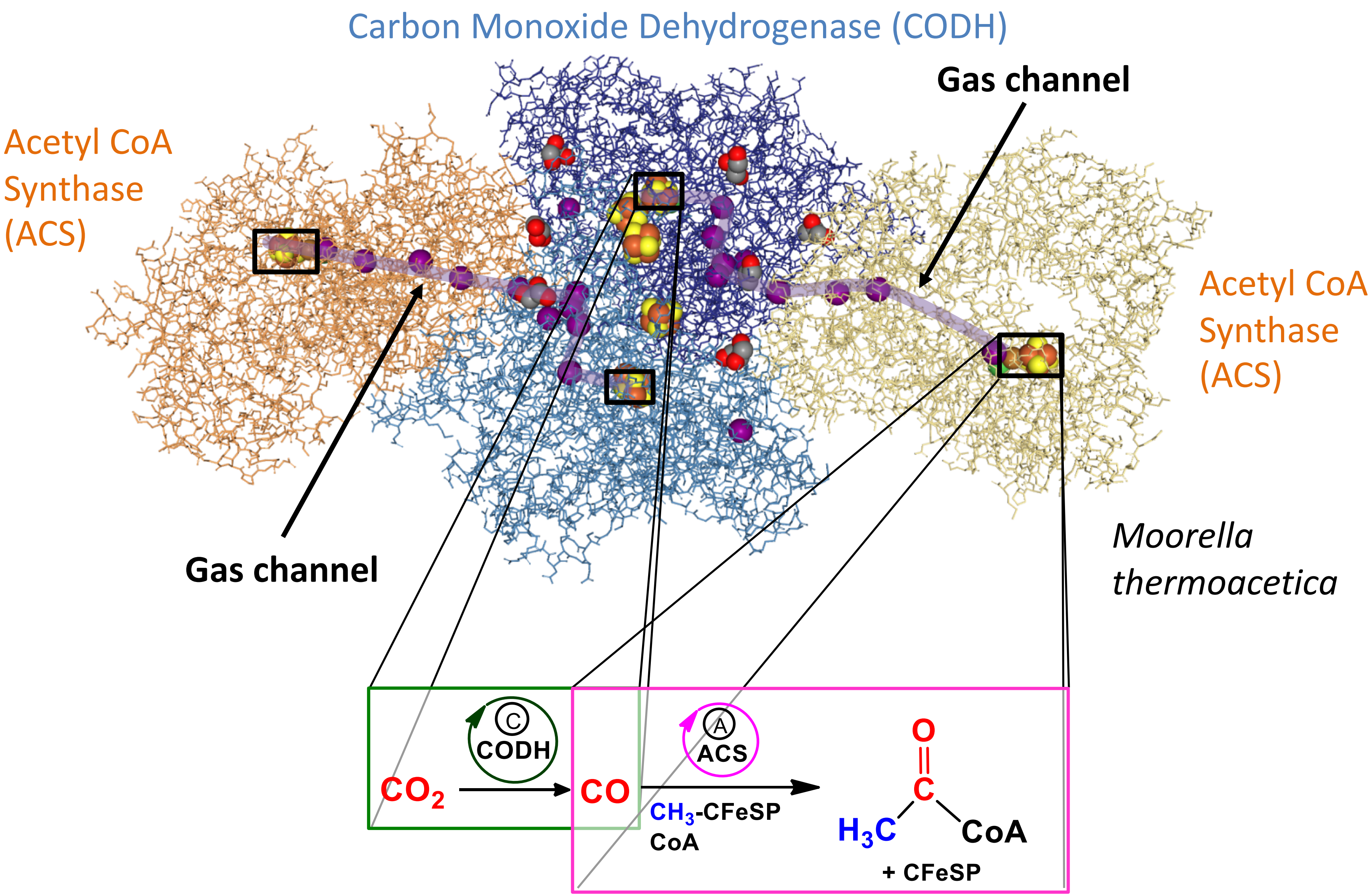
3 stratégie: Valorisation du monoxide de carbone



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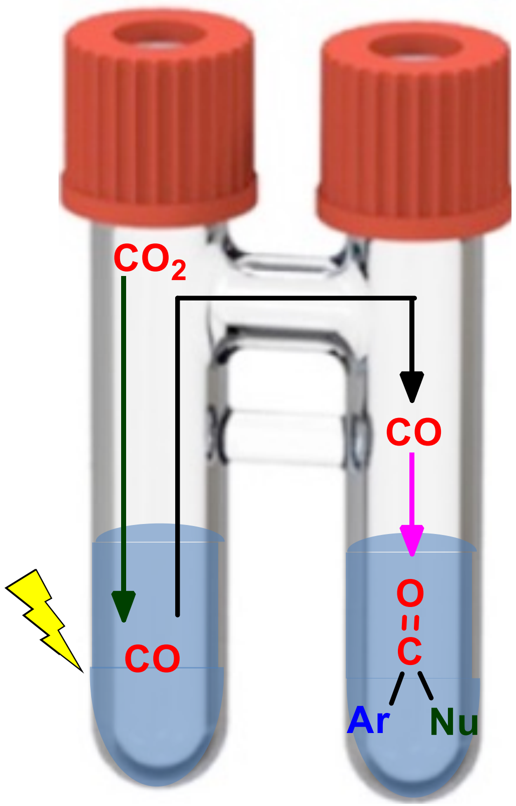
CFeSP = corrinoid iron-sulfur protein; CoA = coenzymeA

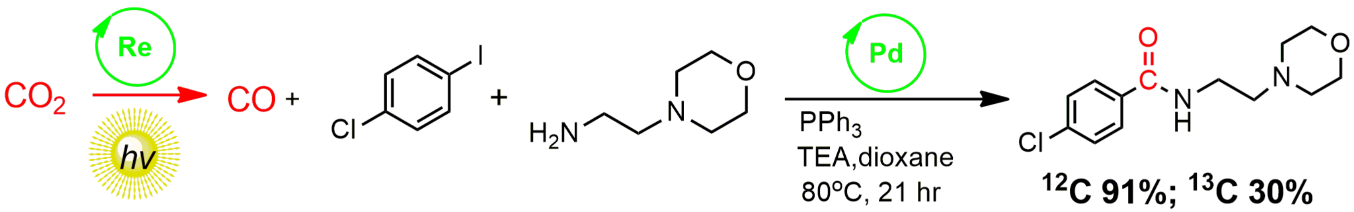
Valorisation du monoxide de carbone

Artificial Mimic

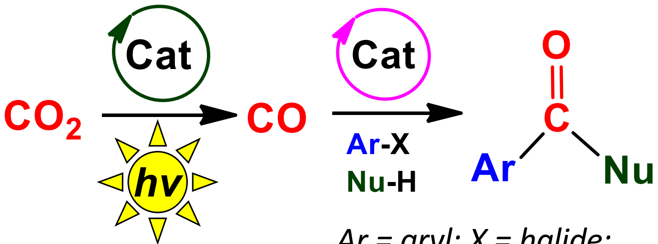


COware® two-chamber reactor was utilized to explore the possibility of a direct use of CO_2 in carbonylation chemistry under mild conditions

- ✓ One pot: avoid handling of toxic CO
- ✓ Eliminates the need for expensive CO precursors
- ✓ Lab-scale access for future researches on merging artificial photosynthesis and transformative chemistry



^{12}C 91%; ^{13}C 30%
Moclobemide drug
(reversible inhibitor of monoamine oxidase A)



Ar = aryl; X = halide;
Nu = nucleophile

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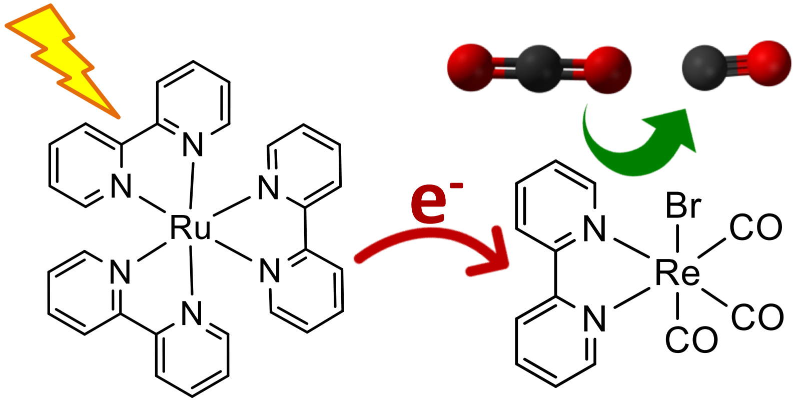
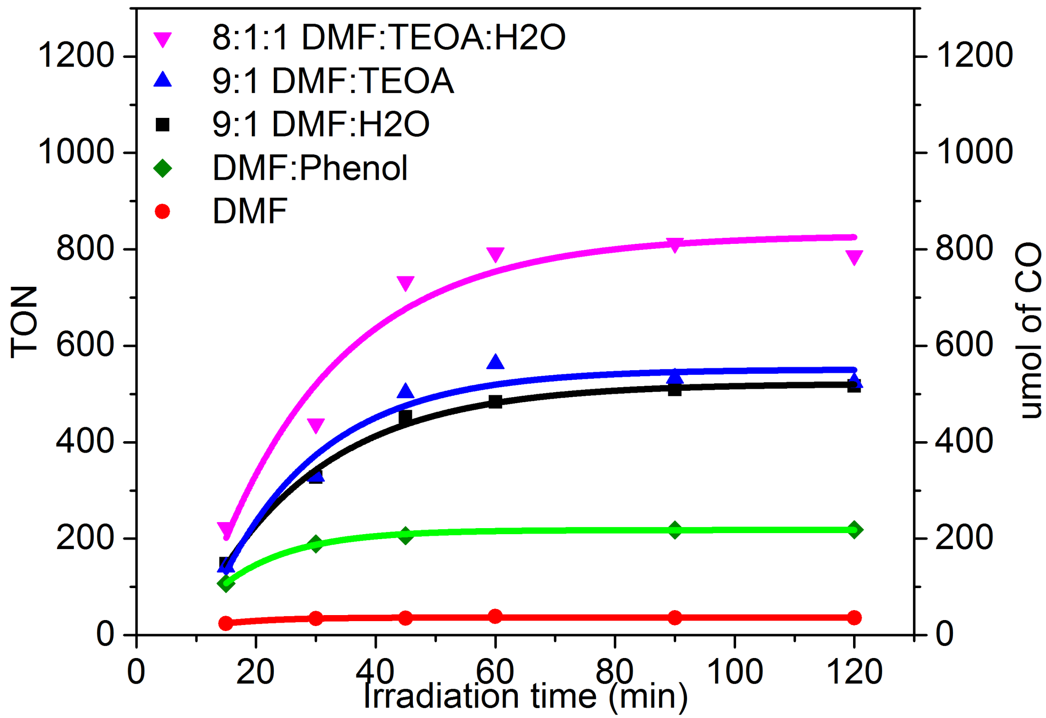
Gotico ChemPhotoChem 2017

Valorisation du monoxide de carbone

- ✓ **Sensitization in the visible region**
- ✓ **Electron transfer from the Ru photosensitizer to Re catalyst**
- ✓ **Optimized TON of 800**





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Artificial Photosynthesis Group