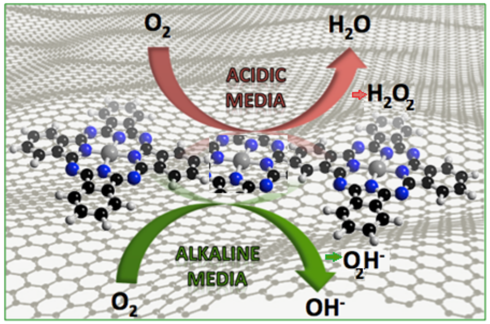
AVANCES Y PERSPECTIVAS DE LA GENERACIÓN FOTOVOLTAICA Y ALMACENAMIENTO DE LA ENERGÍA SOLAR

Curauma, Marzo 2, 2018

Reactivity descriptors for the electrocatalytic activity of MN4 molecular catalysts for O_2 reduction and other reactions relevant to energy conversion



José H. Zagal

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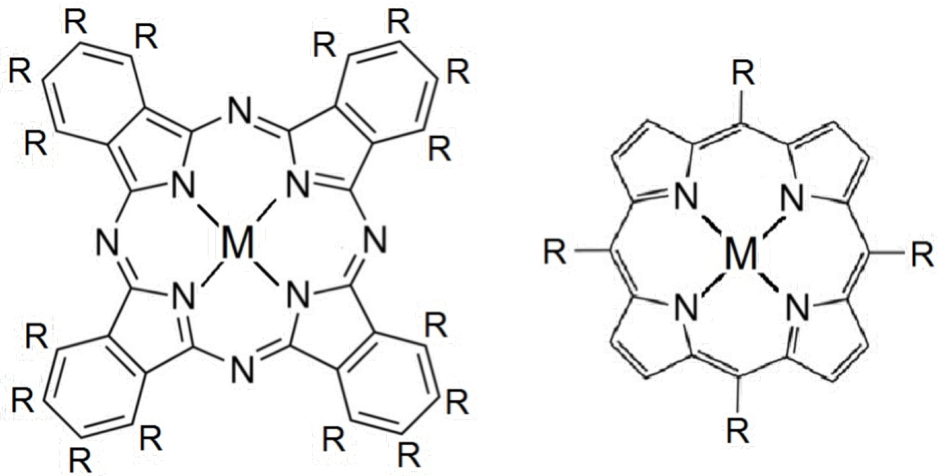
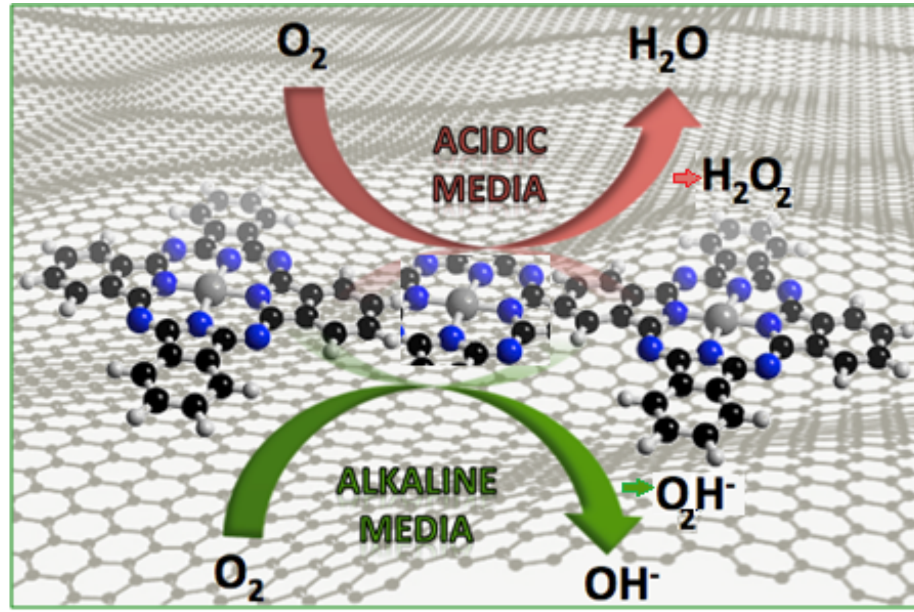
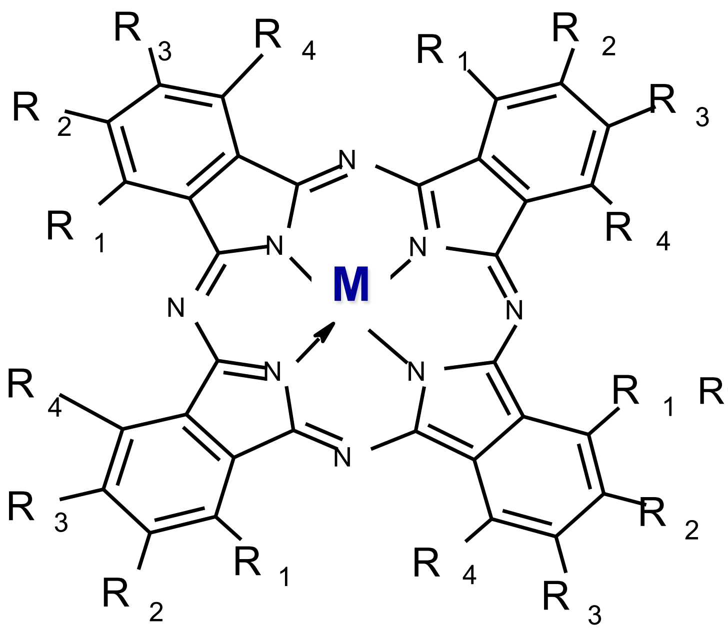




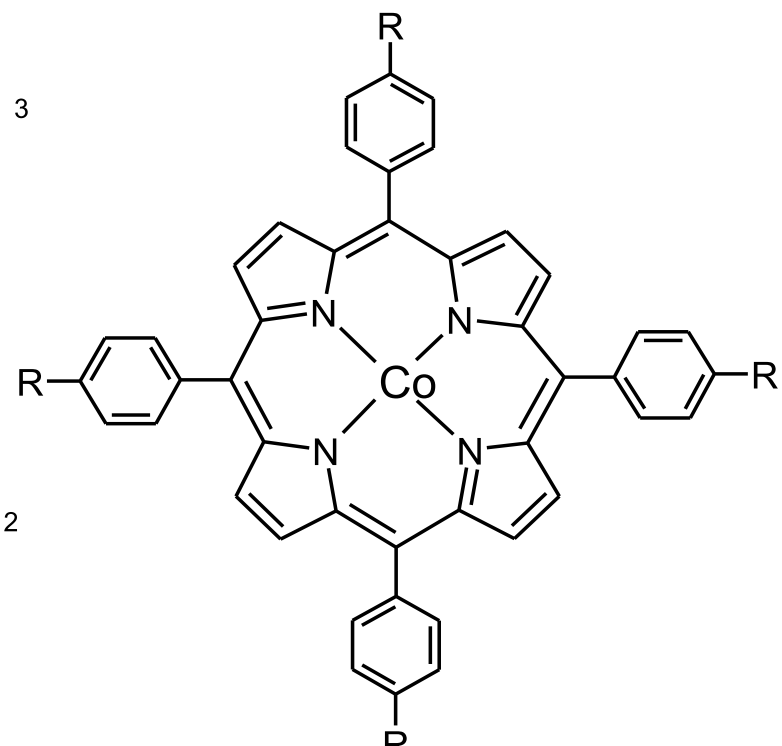
Structure of MN_4 typical molecular versatile catalysts: metal phthalocyanines (left) and metal porphyrin (right). M=Cr, Mn, Fe, Co, Ni.

N-4 MACROCYCLICS COMPLEXES (bioinspired versatile electrocatalysts) Models for O_2 reduction

N-4 MACROCYCLICS COMPLEXES (bioinspired versatile electrocatalysts)



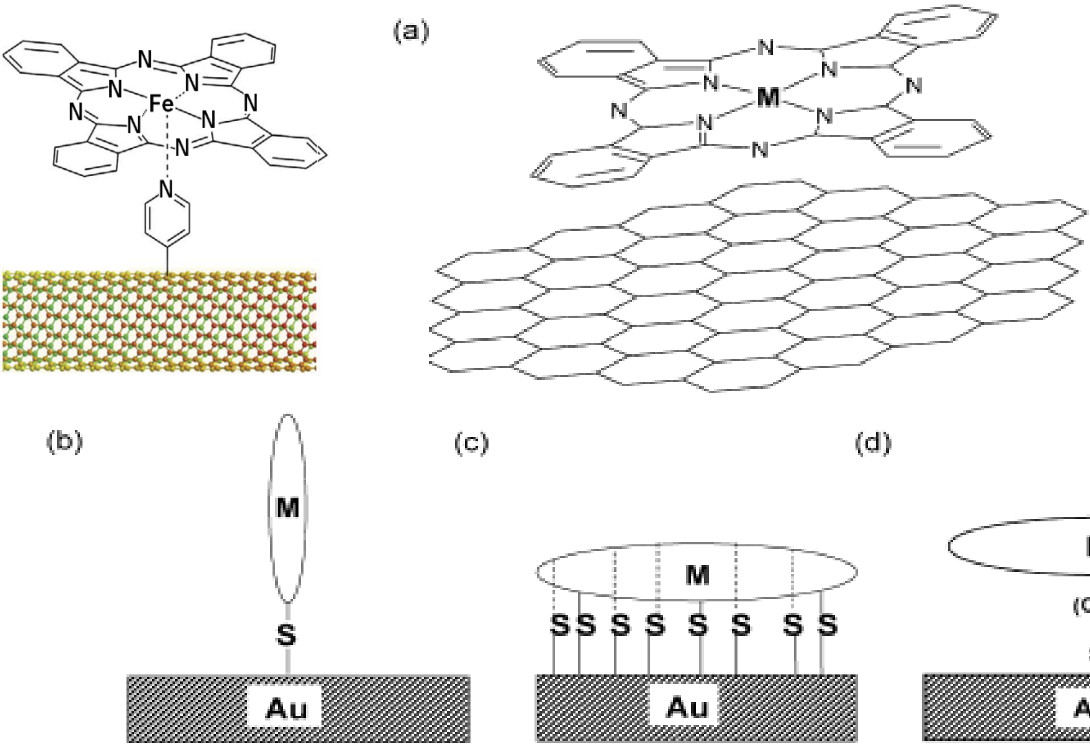
Metallophthalocyanines

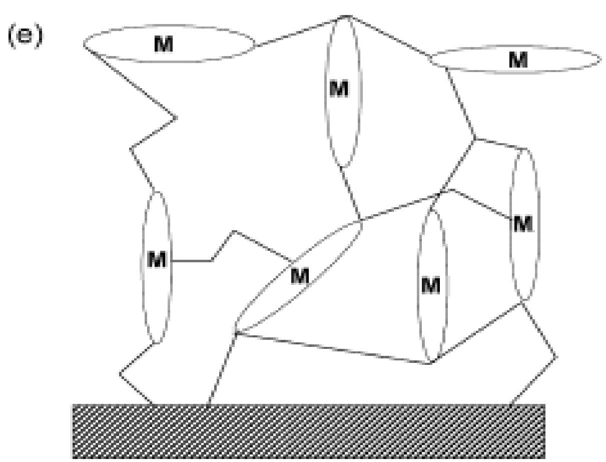


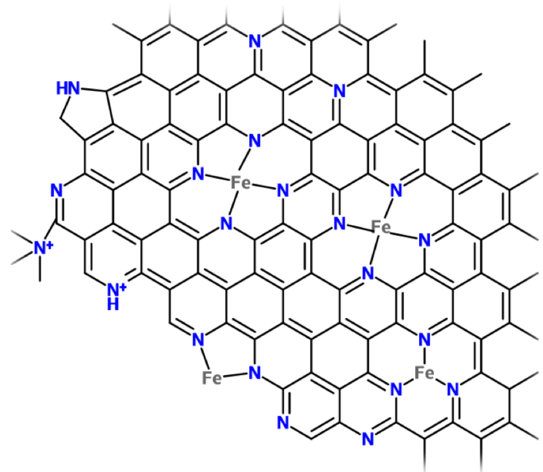
Metallotetraphenylporphyrins

R. Jasinski, Nature, 1965

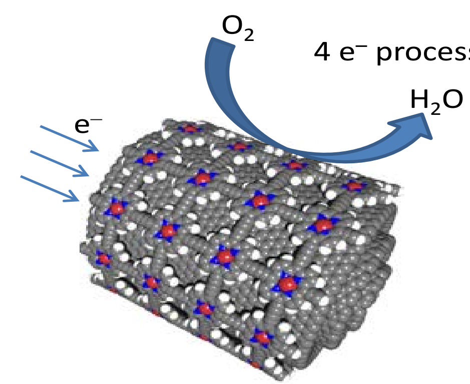
J.H. Zagal et al. / Coordination Chemistry Reviews xxx (2010) xxx–xxx

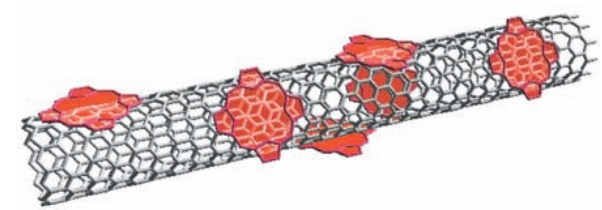


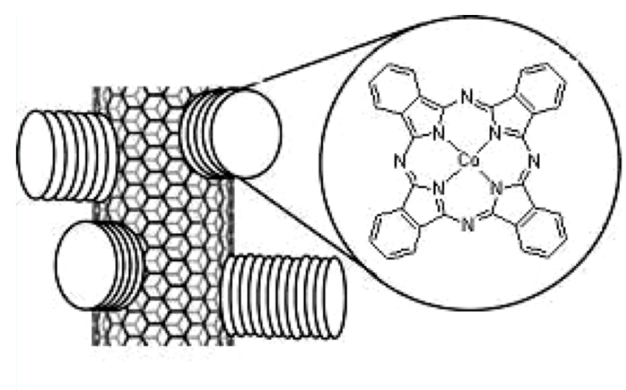




Bourgeteau et al.







Different surface configurations of intact MN4 catalysts on electrodes

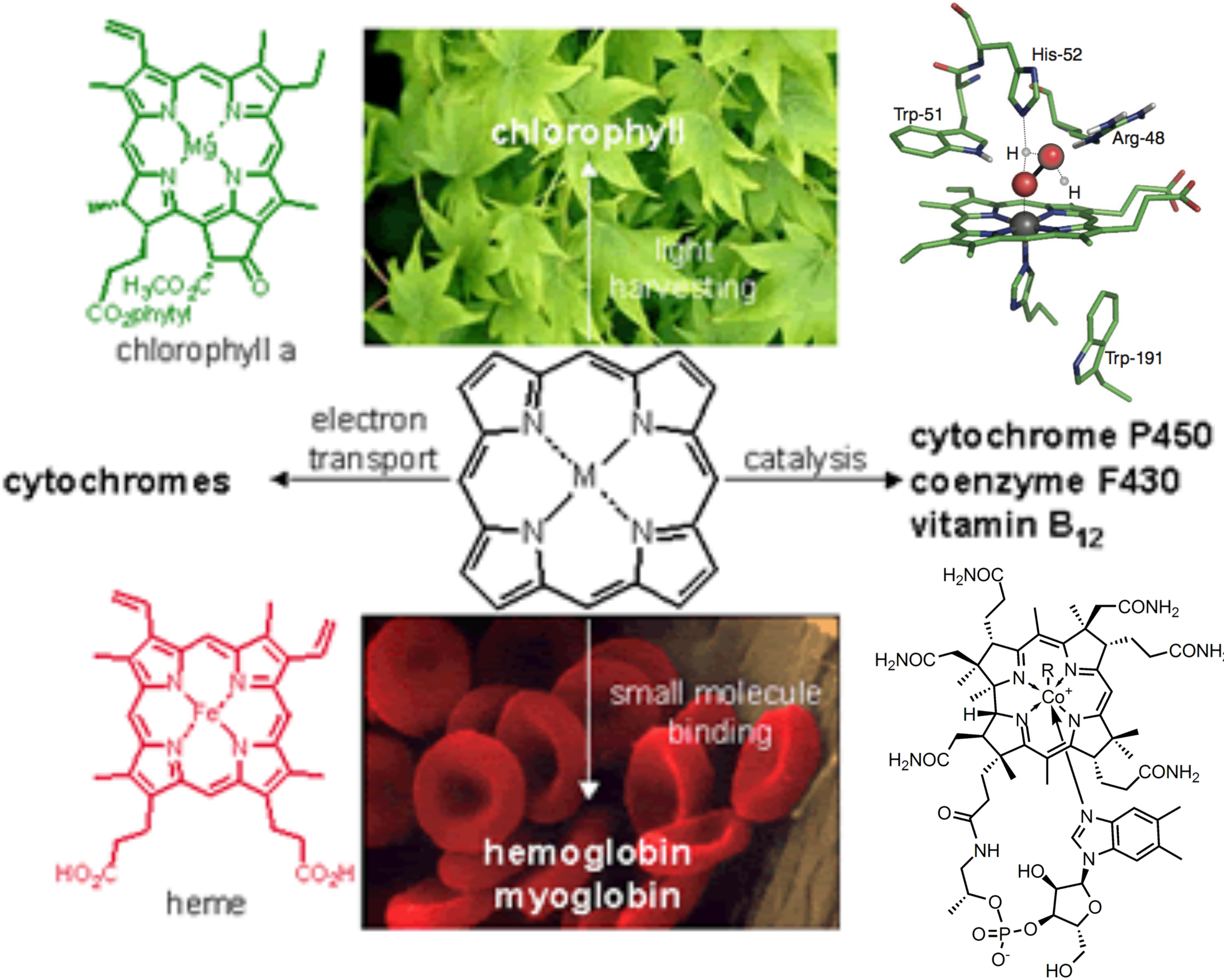
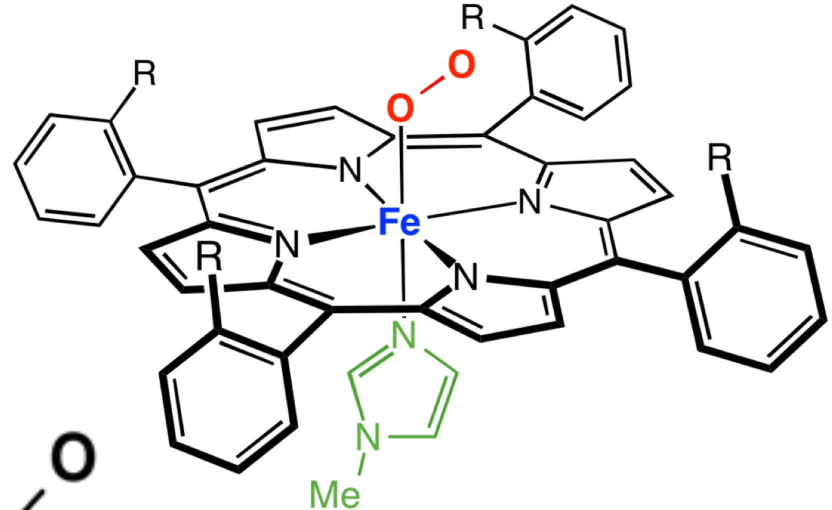
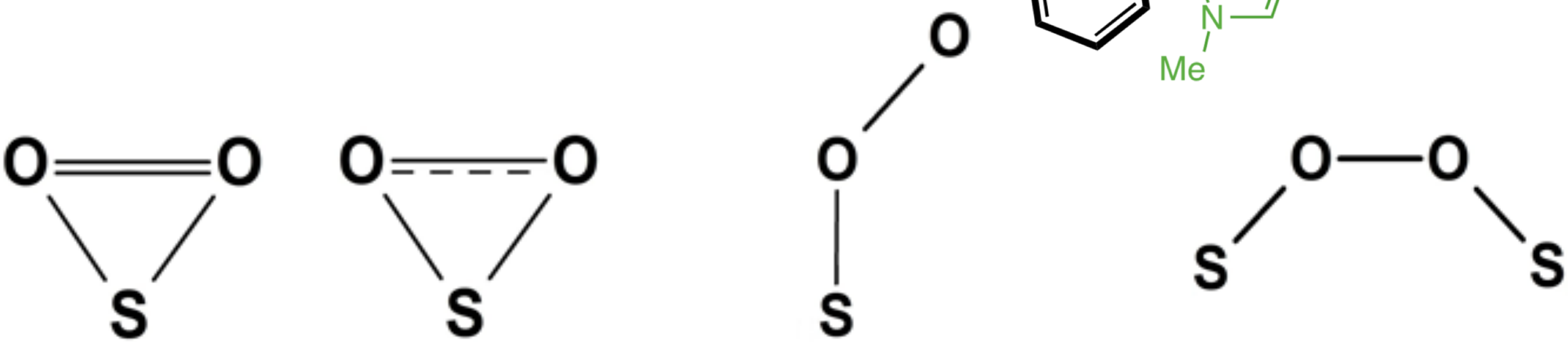


Figure 1. Diverse functions of metalloporphyrins in Nature

Inner sphere O_2 reduction



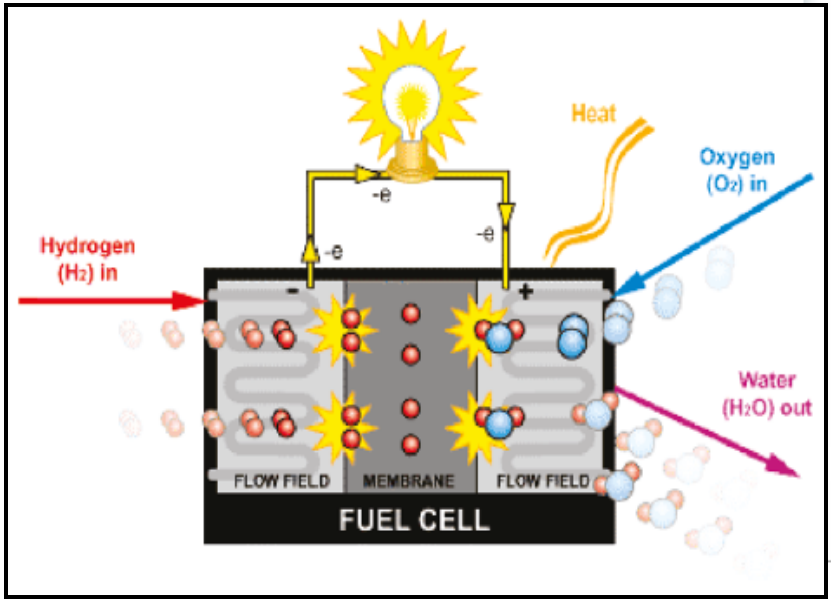


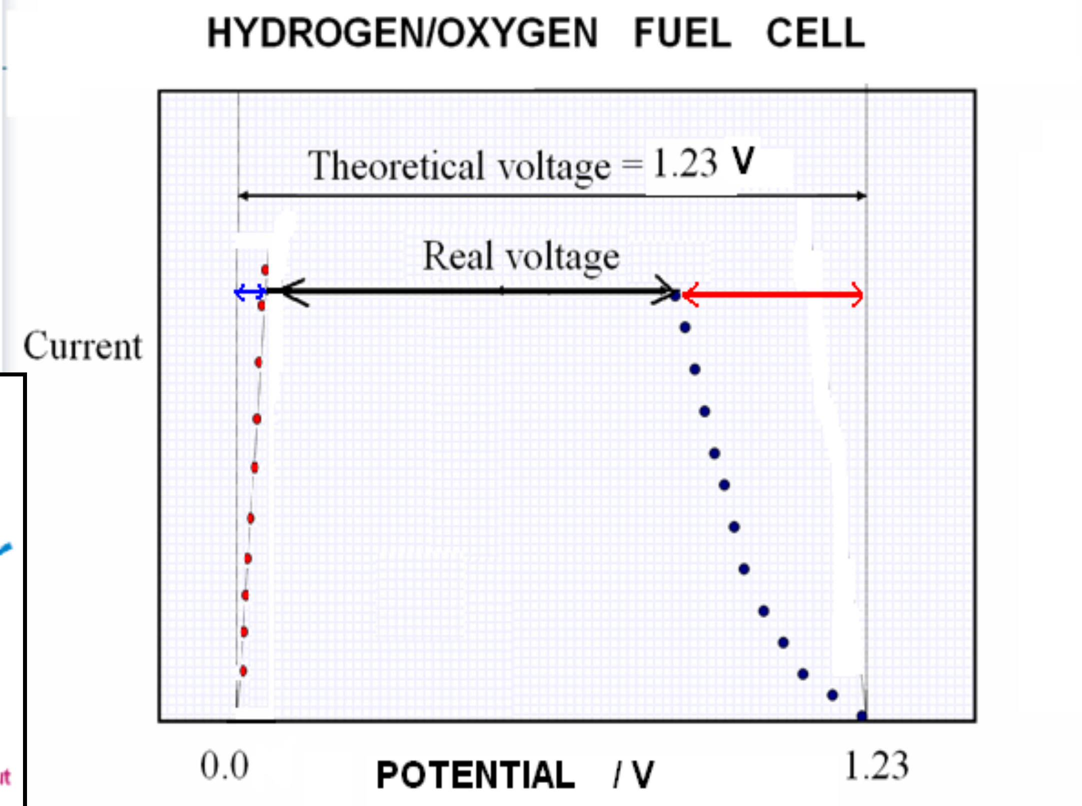
$O_2 + 4e + 4H^+ \text{------}\rightarrow 2H_2O$ Eo= 1.230 V Fuel cells

$O_2 + 2e + 2H^+ \text{-----}\rightarrow H_2O_2$ Eo = 0.695 V

$O_2 + e \text{-----}\rightarrow O_2-$ Eo = -0.695 V Li batteries

Low cost catalysts are required to avoid the use of expensive noble catalysts for O_2 cathode in fuel cells . $$$$$$$



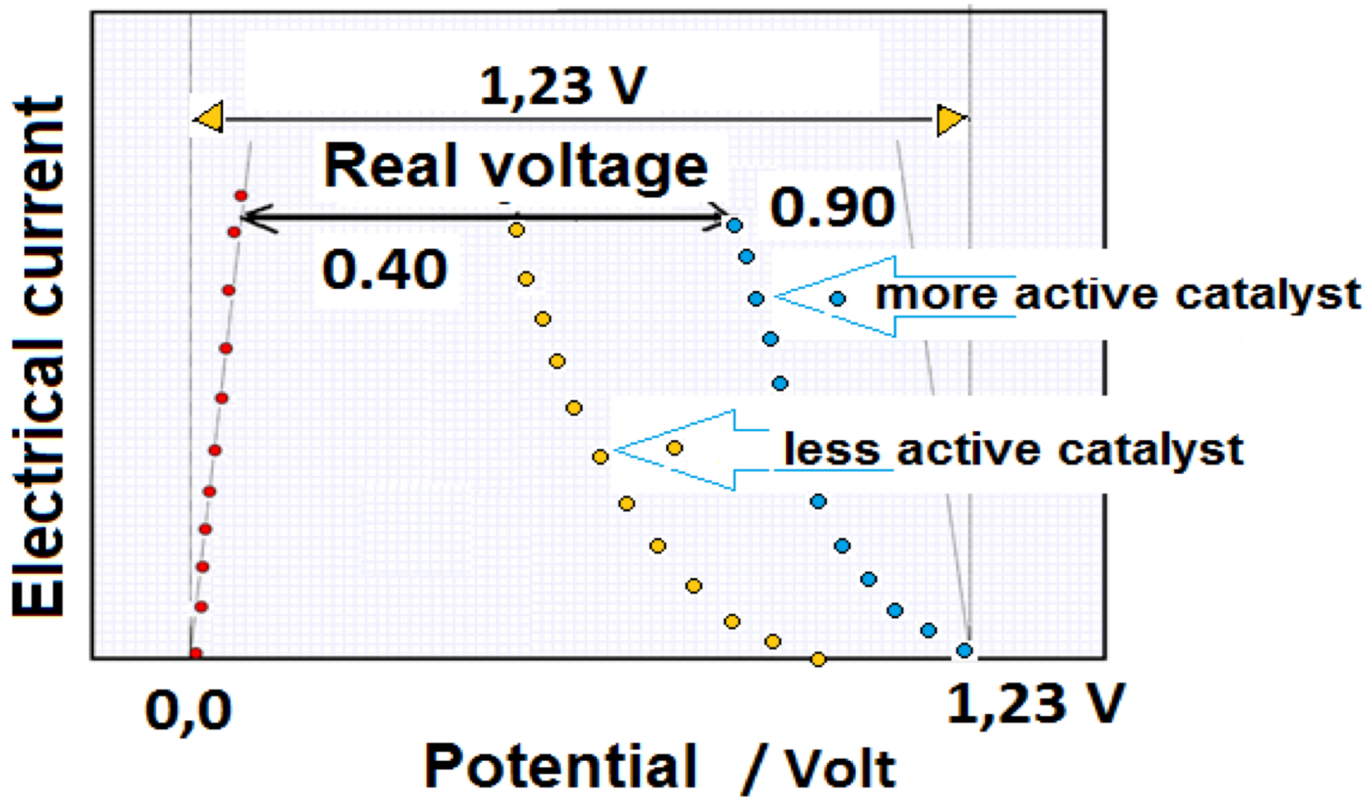


$2H_2 - 4e^- \rightarrow 4H^+$

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Power = Current x Voltage / Watts

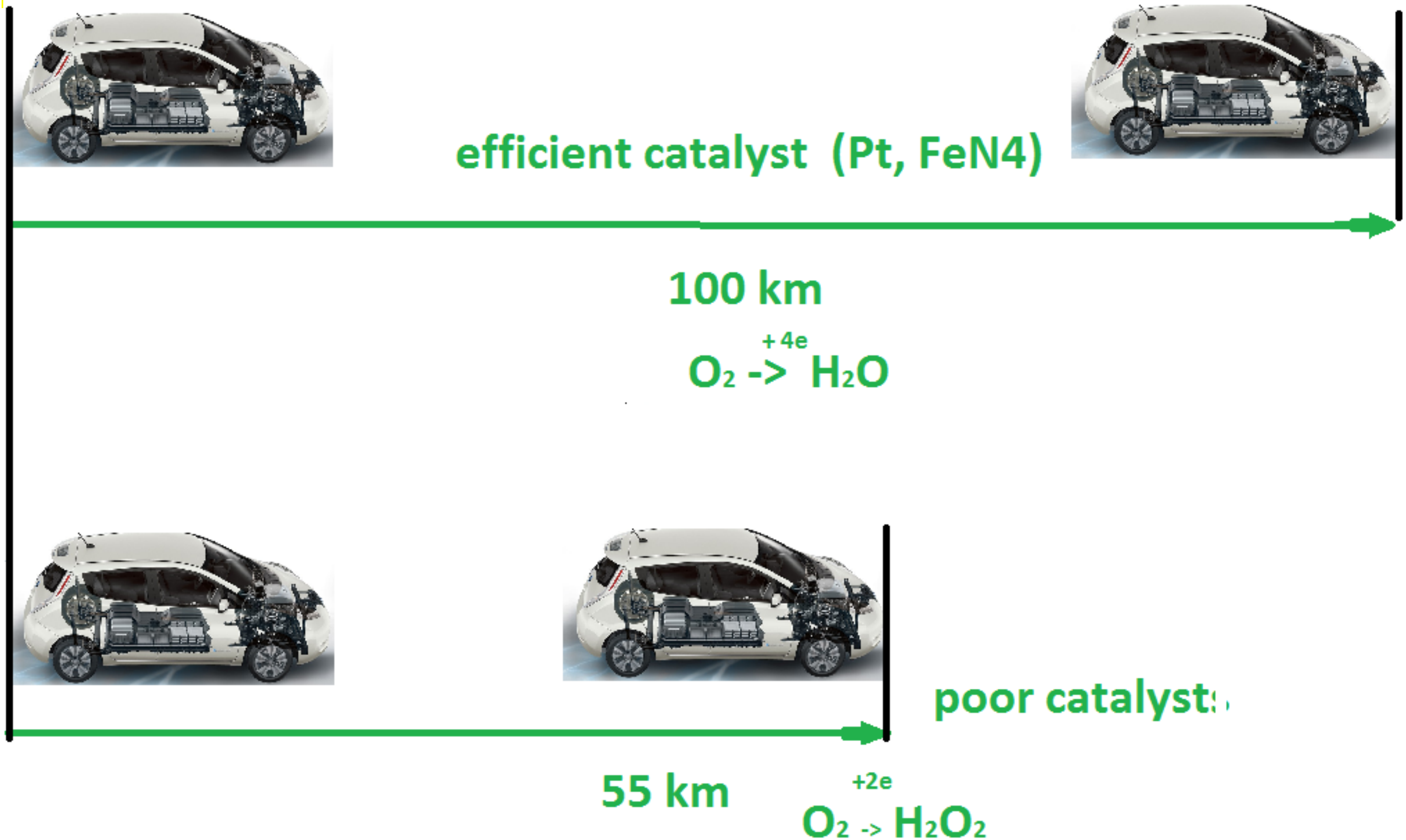
The role of the catalyst is crucial. Not only increases the rate of the reaction…it increases the voltage of the cell

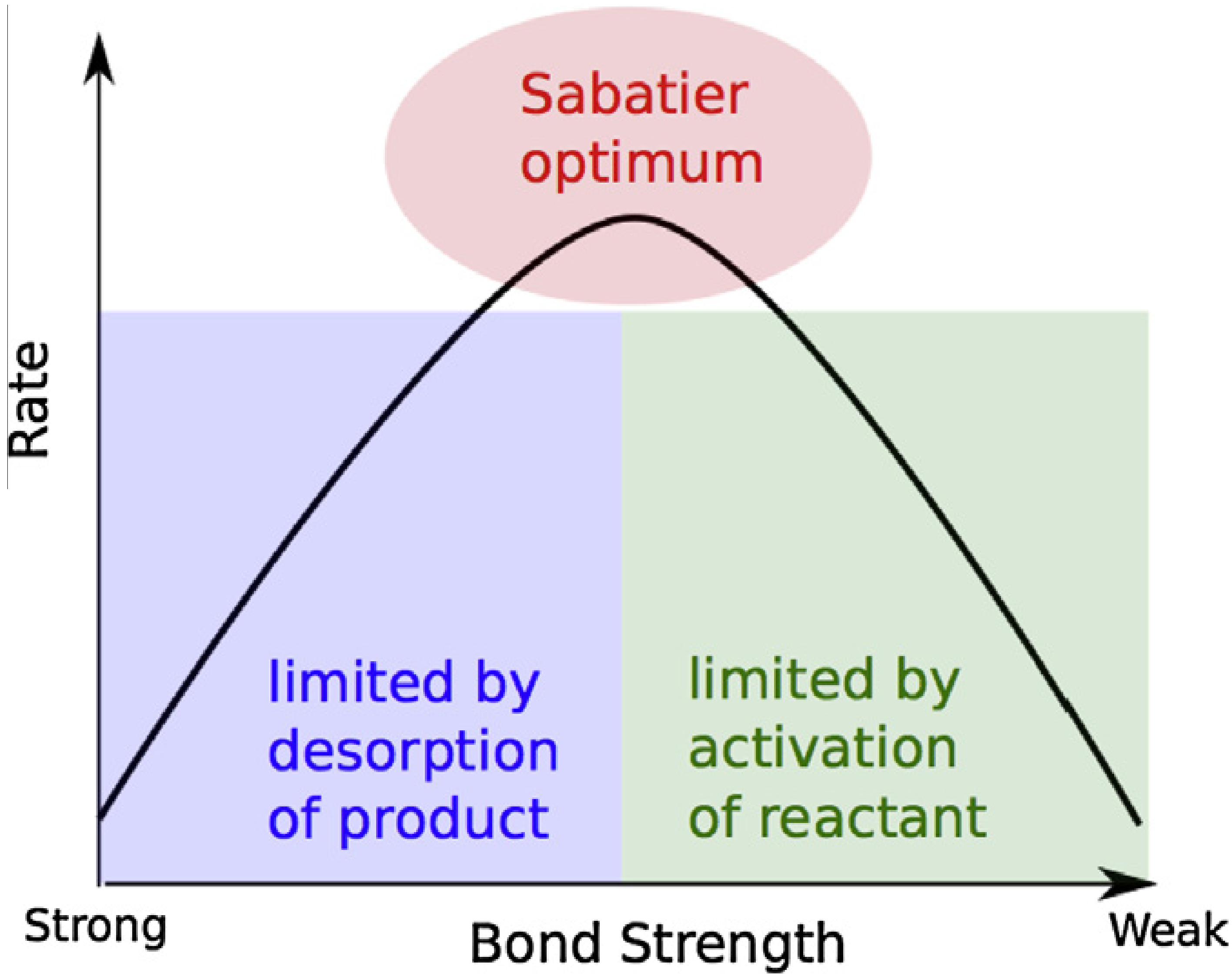


$2H_2 - 4e \rightarrow 4H^+$
Oxidation

$O_2 + 4H^+ + 4e \rightarrow 2H_2O$
Reduction

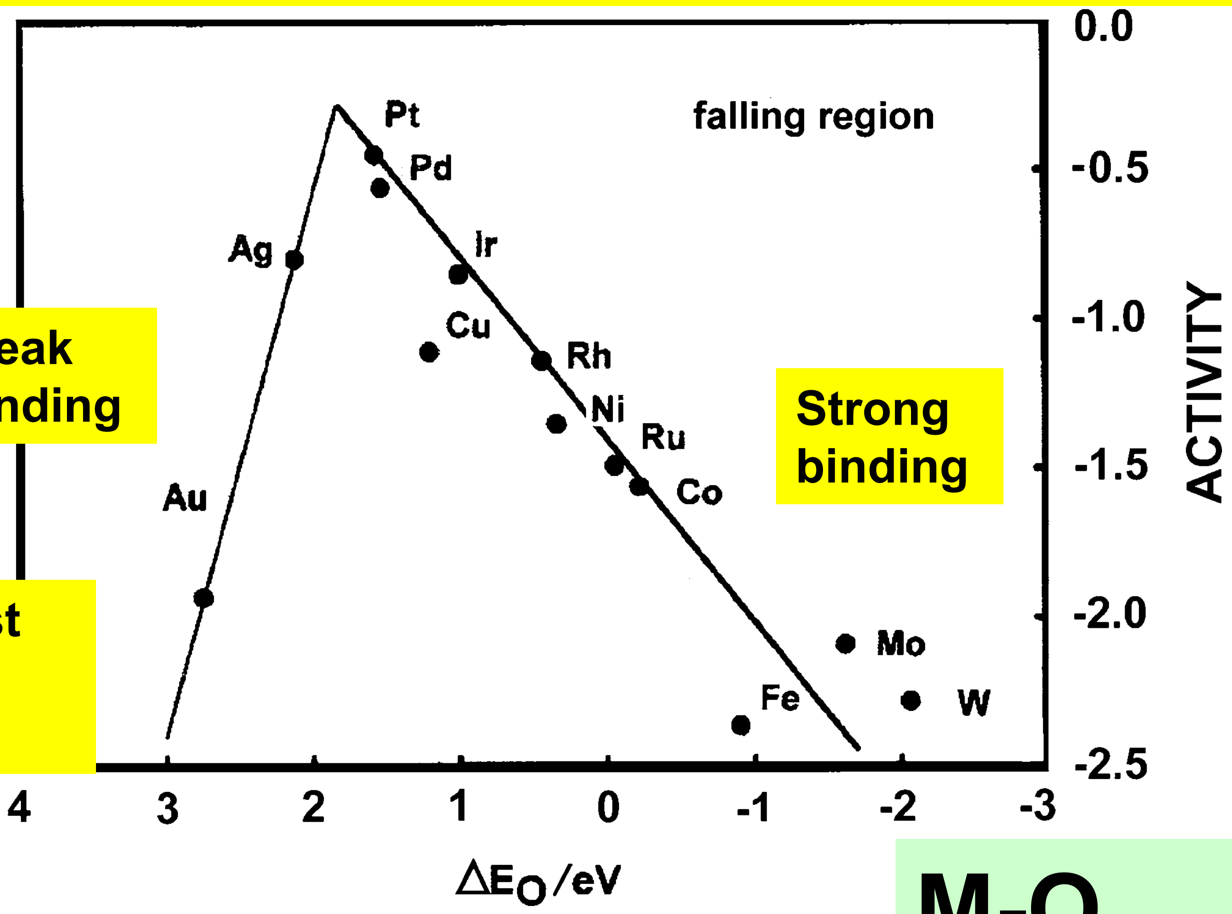
Influence of type of O_2 catalyst on the performance of a fuel-cell electric car





. Schematic representation of the qualitative Sabatier principle.

SEMI-THEORETICAL VOLCANO PLOT from Norksov et al. For O_2 reduction



Weak binding

Strong binding

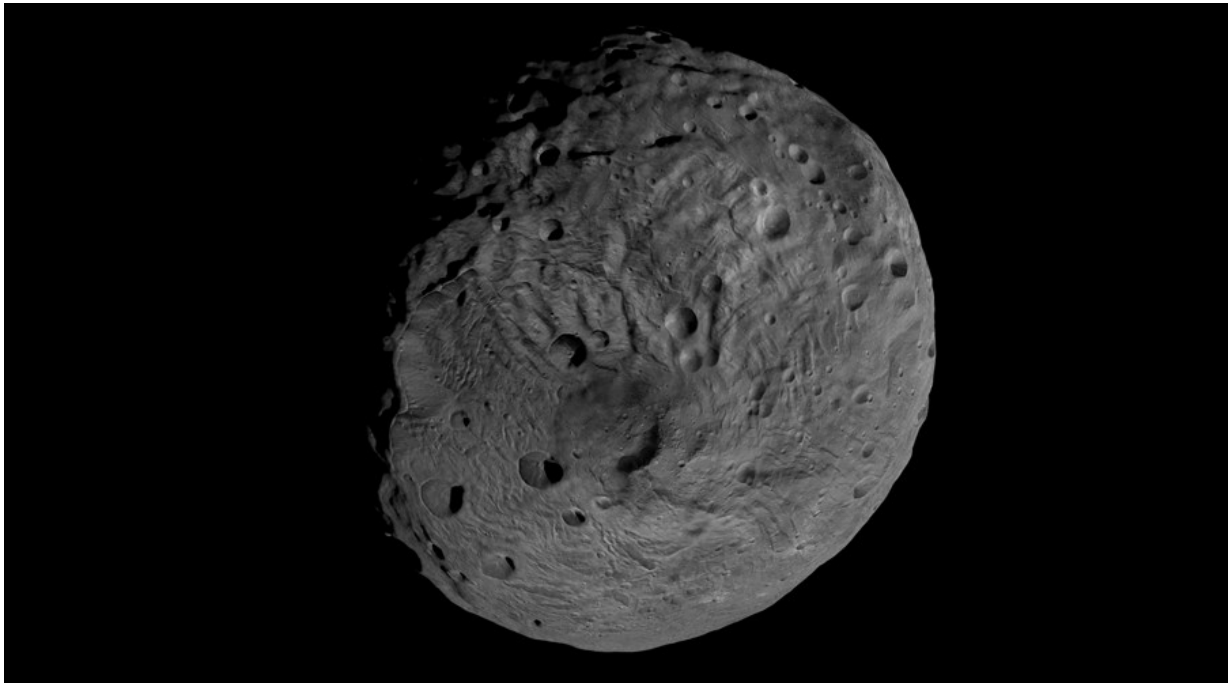
Pt is the best Catalysts, but….

M-O_2

Fig. 8 Volcano plot for the reduction of O_2 plotted versus the oxygen binding energy. Adapted from Nørskov et al. [106]

- **An asteroid believed to be carrying up to 90 million tons of platinum in its core, as well as other rare and precious materials, passed our planet in July 2015.**
- **.**
  The platinum-rich asteroid officially named 2011 UW158, is 452 meters by 1,011 meters in size and passed Earth at a distance of an estimated 2.4 million kilometers, according to the Goldstone Radar Observatory. It was 30 times closer to Earth than the closest planet of the Solar system. 'Platinum' asteroid potentially worth $5.4 trillion

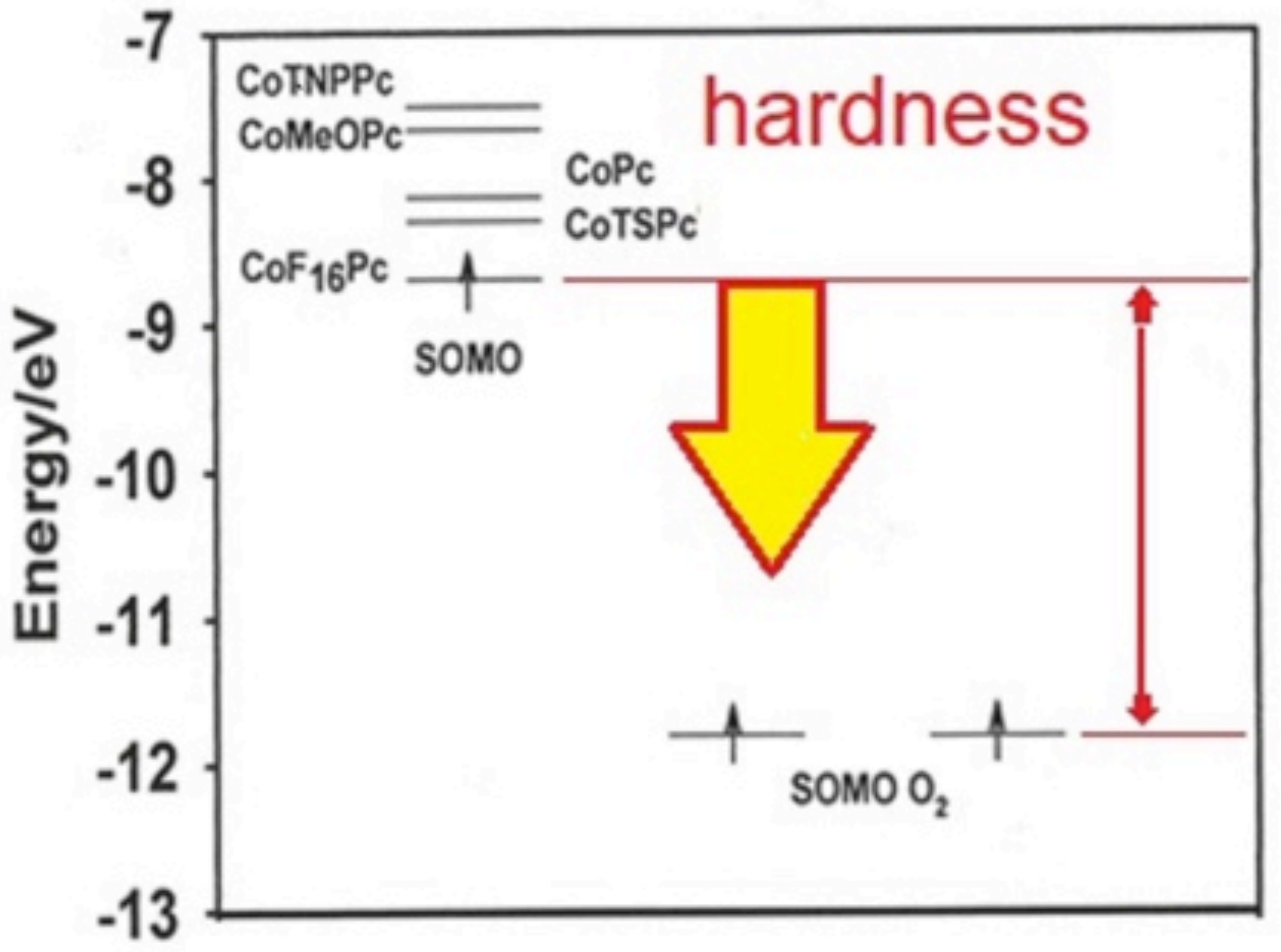
Pt is expensive on earth but..



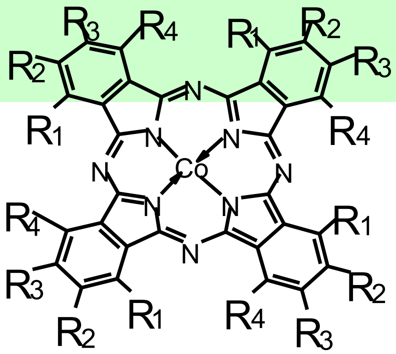
REACTIVITY DESCRIPTORS OF MN4 MOLECULAR CATALYSTS FOR ORR

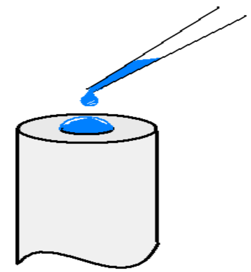
- Classical descriptor: M-O_2 binding energy
- Donor acceptor intermolecular hardness (M-O_2 hardness, frontier orbital energy gap)
- M(III)/(II) formal potential of the catalyst
- Factors that affect these parameters:
- Electron-withdrawing power of the N_4 ligand
- Presence of an e-withdrawing axial ligand.

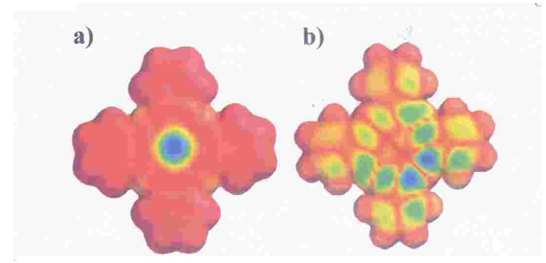
Donor acceptor intermolecular hardness ($M\text{-}O_2$ hardness, frontier orbital energy gap)

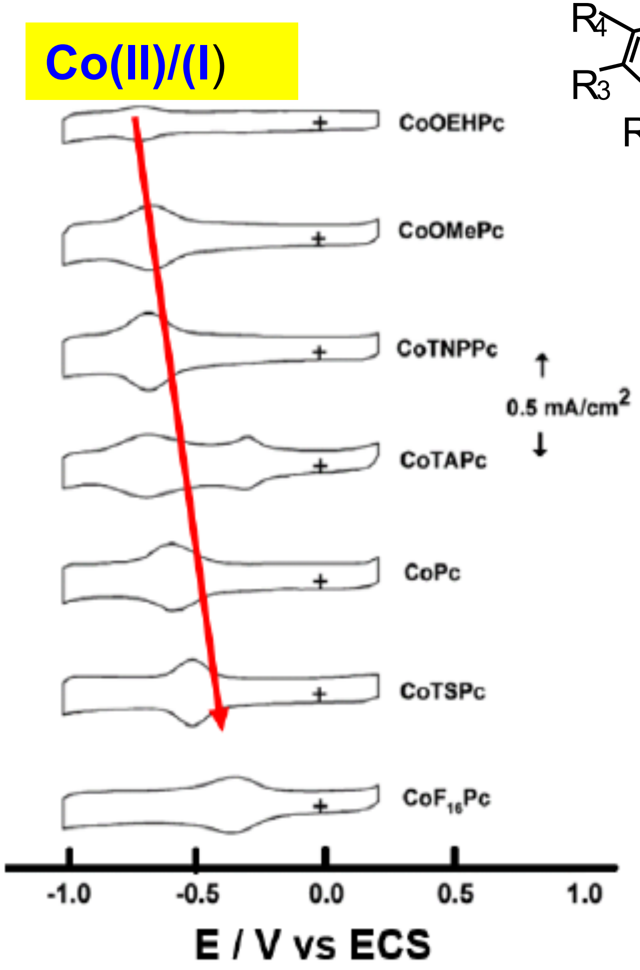


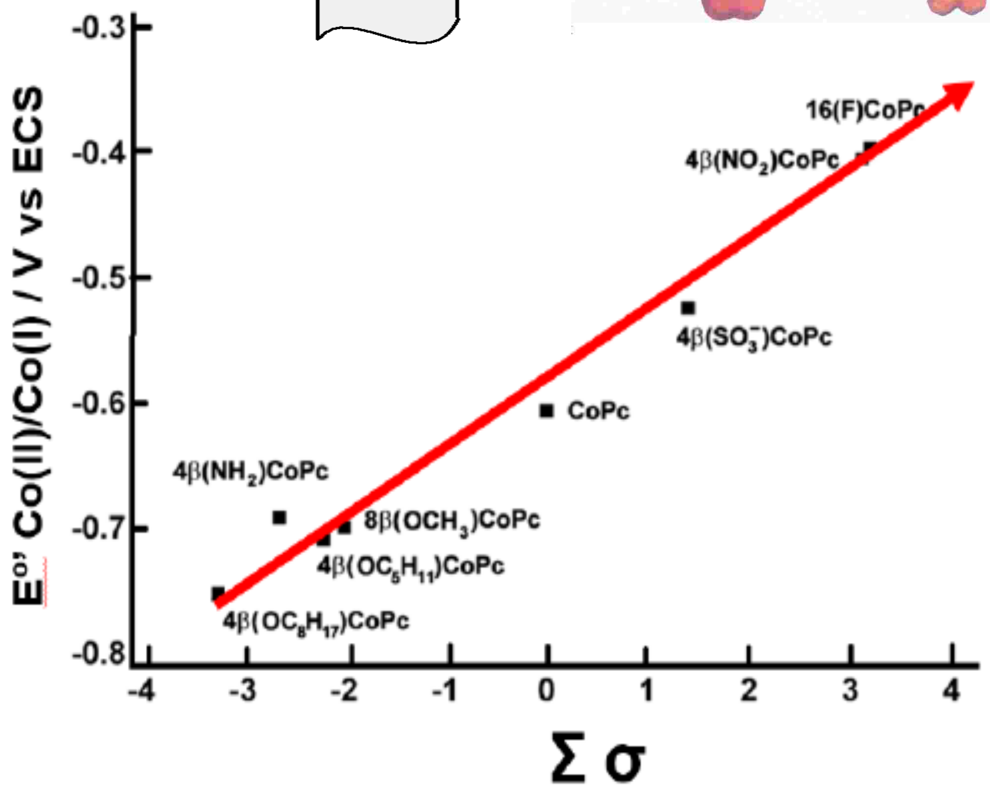
Tuning the Co(II)/(I) redox potential with groups on the ligand



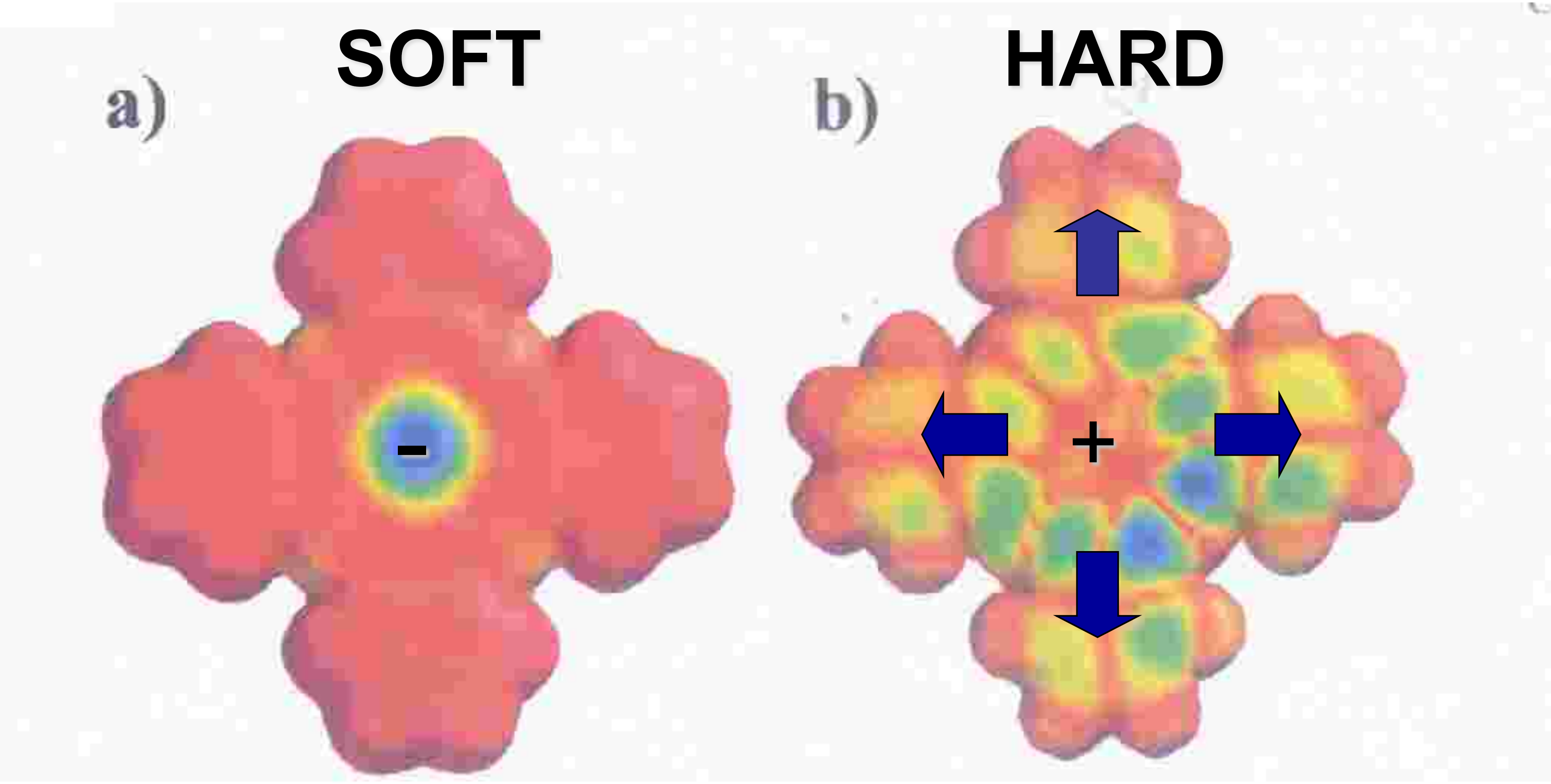








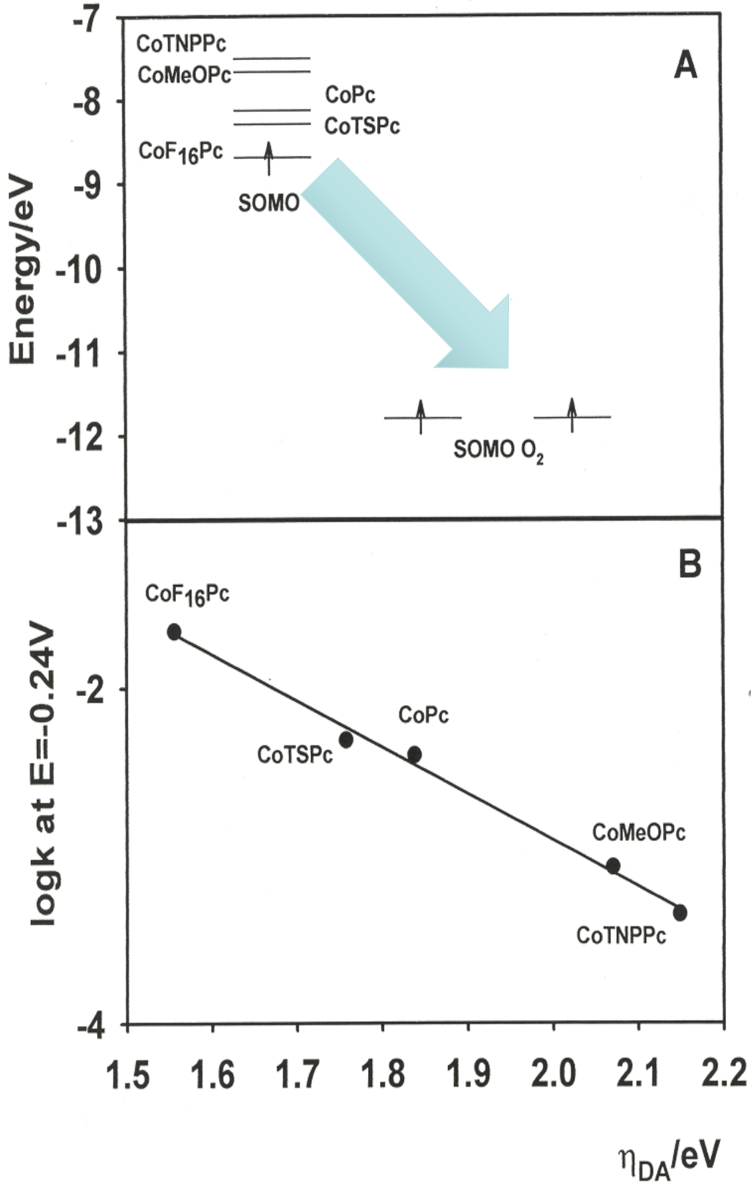
G.Cardenas-Jiron, J.H.Zagal, J.Phys. Chem. (2003)

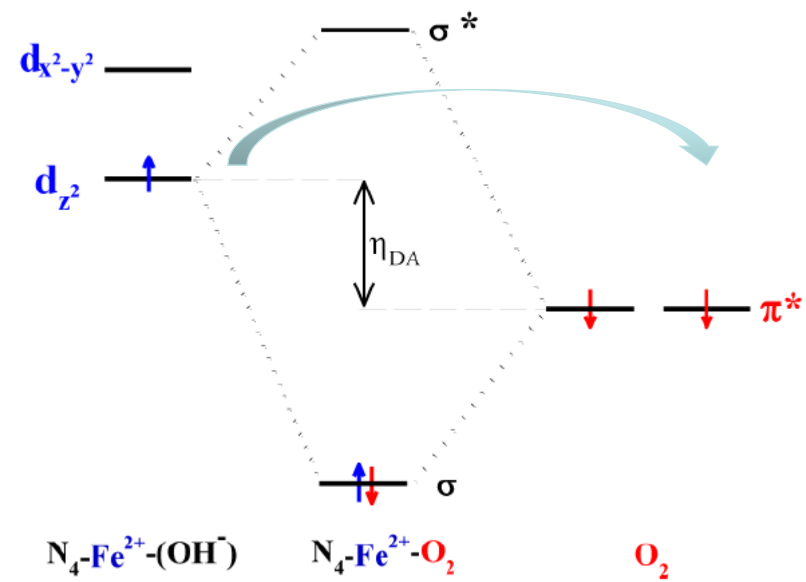


Co-Pc

Co-F_{16}Pc

Donor-acceptor Intermolecular hardness. Parr & Pearson. Higher reactivity for less hard systems

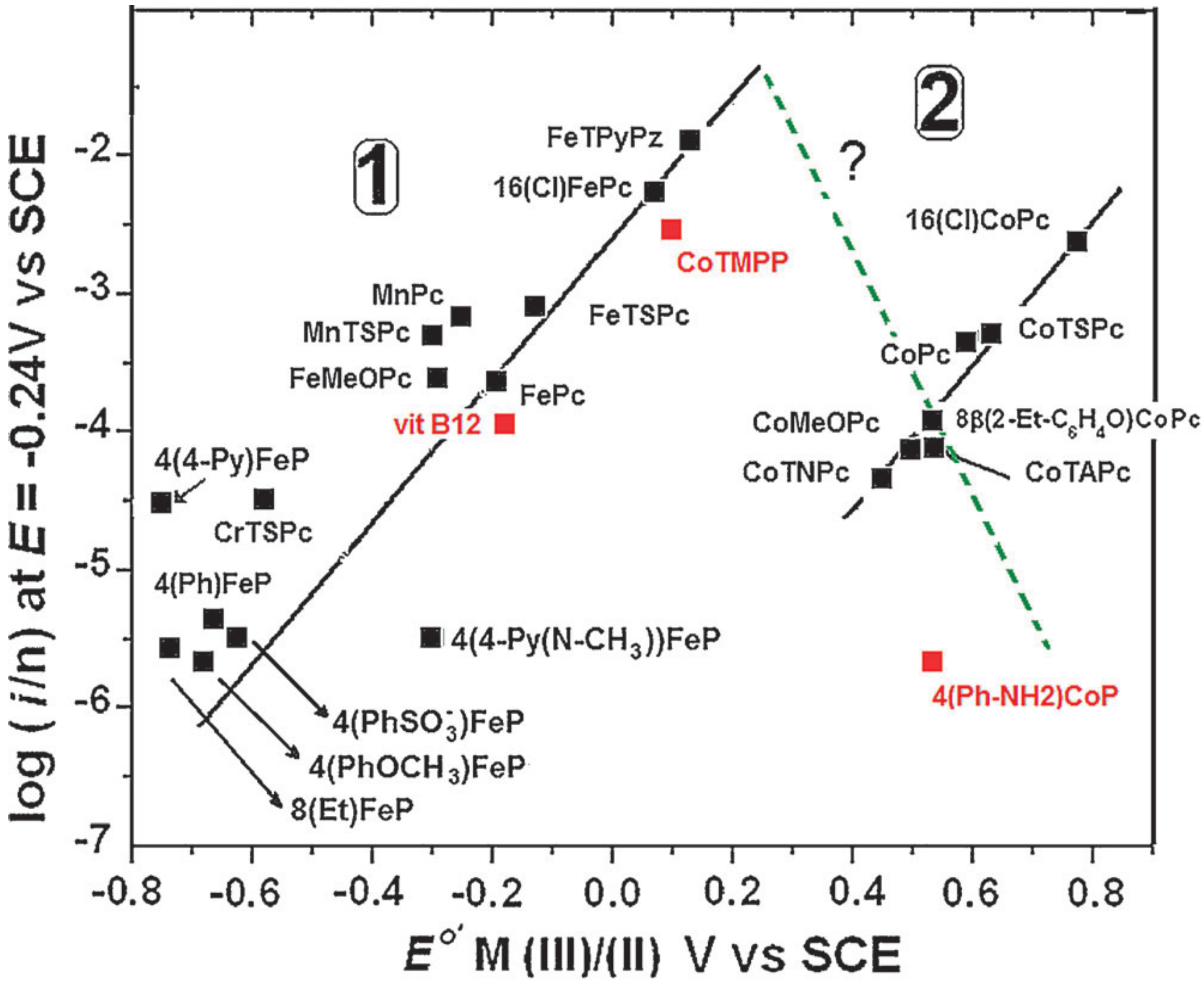




Mukerjee et al.
JACS, 135 (2013), 15443

Fig (A) Relative energies of frontier orbitals of O_2 and Co-Pcs. (B) Plot of log k vs. η_{DA} for oxygen electroreduction catalyzed by different Co-Pcs adsorbed on OPG. Apparent rate constants obtained at -0.24 V vs SCE Zagal & Cardenas J Phys Chem, 2003

EFECT OF M(III)/(II) REDOX POTENTIAL:Volcano plots of catalytic activities for the ORR in alkaline media) for different MN4 catalysts at E = 0.24 V versus SCE, Zagal & Koper, Angewandte Chemie, (2016)



J.H. Zagal/Coord. Chem. Rev. 119 (1992) 89–136

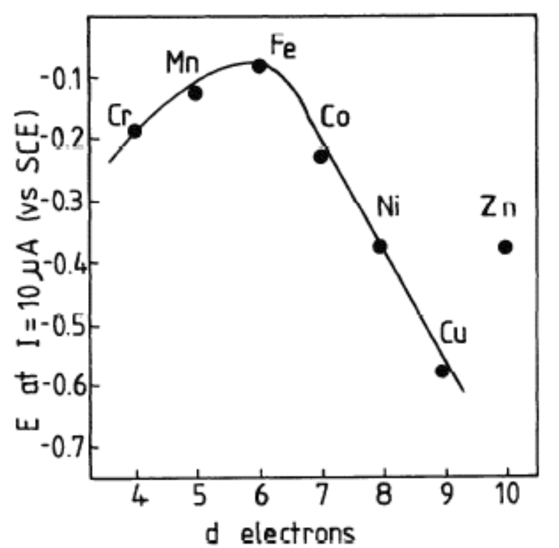
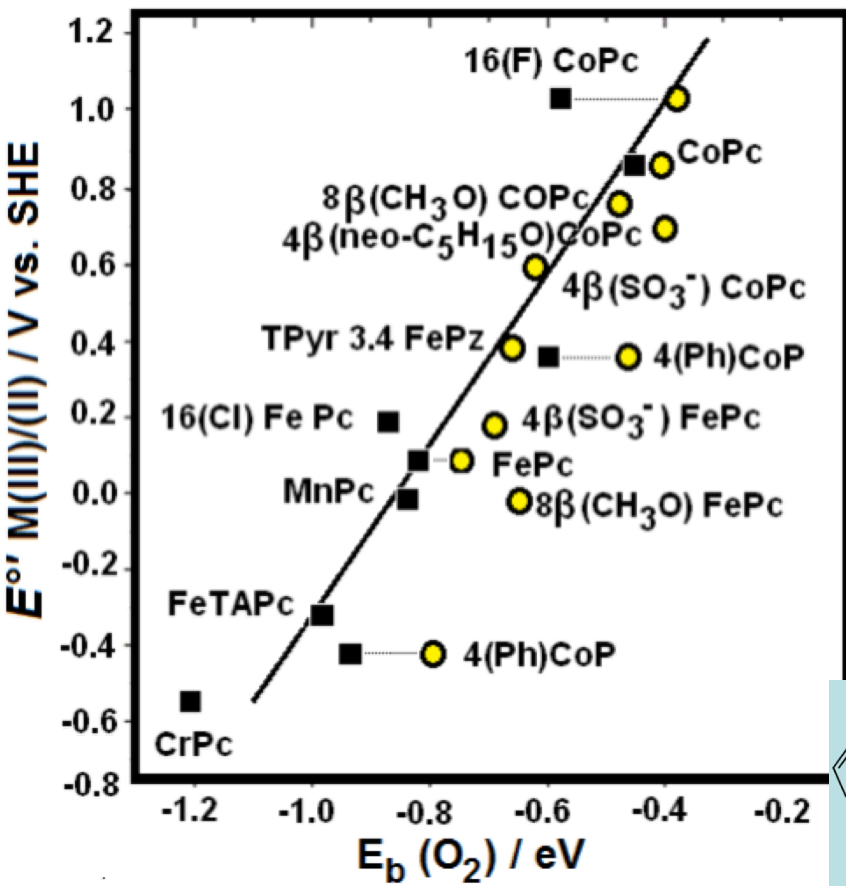
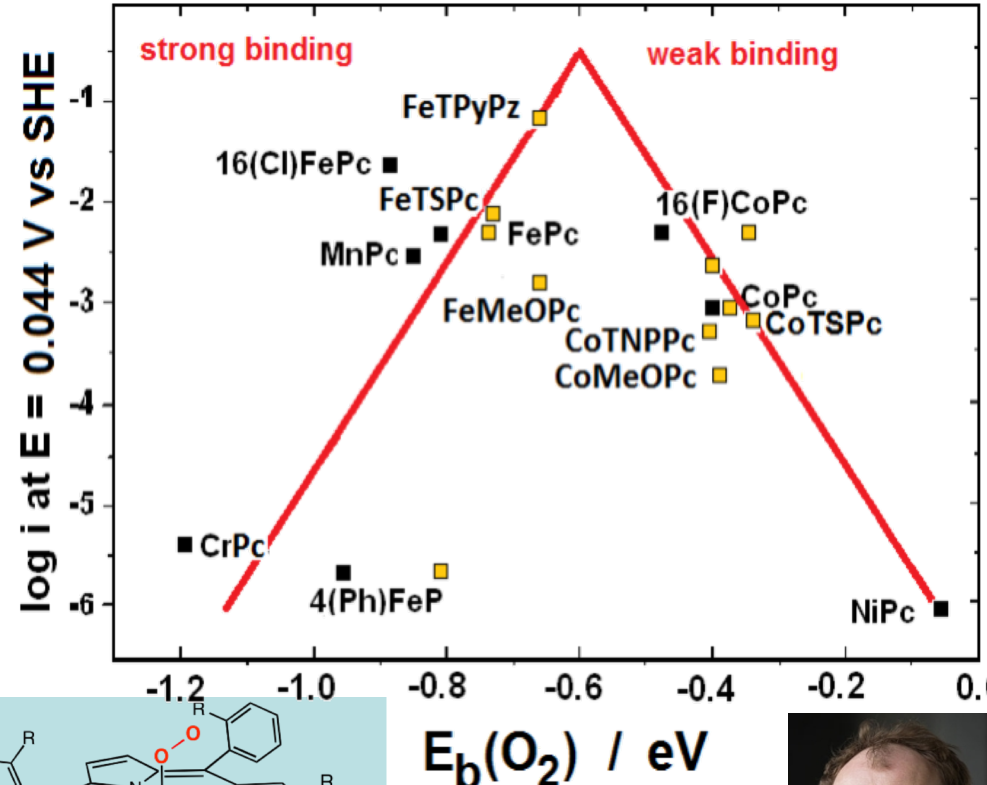


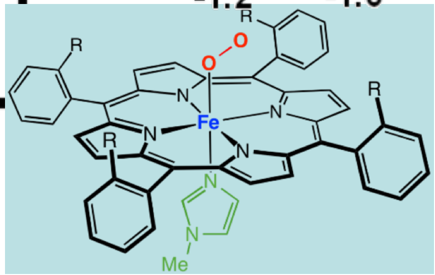
Fig. 14. Electrocatalytic activity of different M(II)-TSPs for O_2 reduction in 0.1 M aque function of the number of d electrons. (Adapted from refs. 137 and 205.)

M-O_2 binding

MN4 complexes adsorbed on graphite

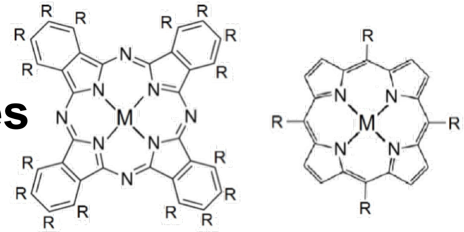




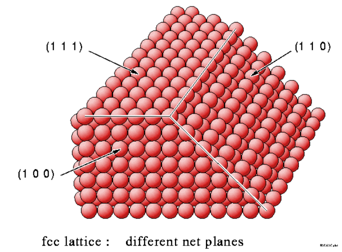


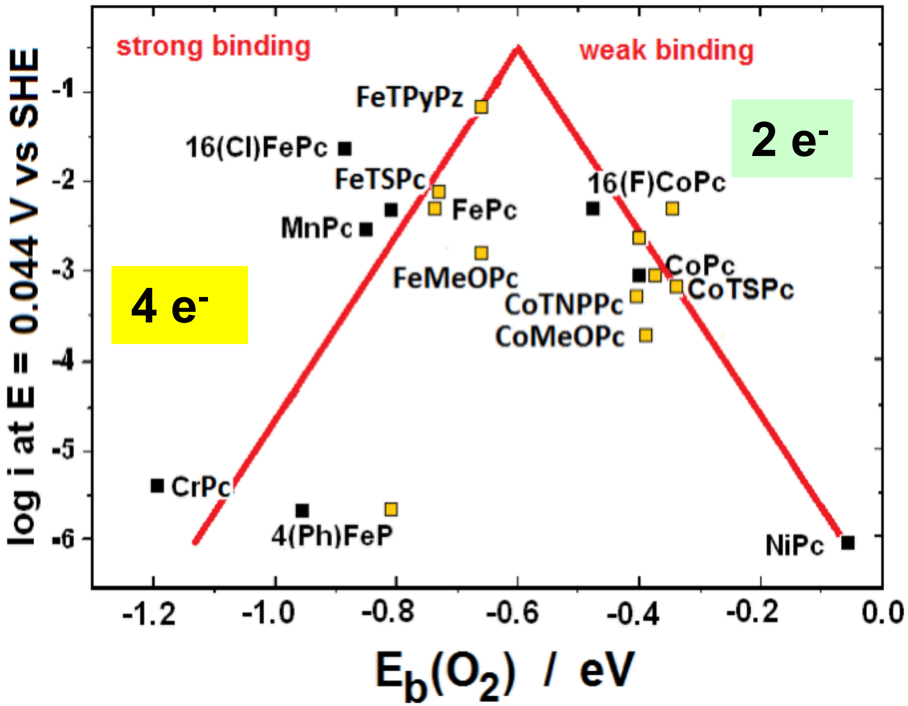
Left: correlation between the M-O_2 binding energy and the M(III)/(II) redox potential . **Right:** Volcano correlation for ORR (pH=13) for different MN4 catalyst versus the MO2 binding energy. **Zagal & Koper** Angewandte Chemie Int.Ed. 55 (2016) 14510. DFT data from Wang et al. J. Chem. Phys. 2013, 139, 204 and Zhang et al. J. Phys. Chem. C 2007, 111, 7084

MN4 Metal complexes



Pure metals





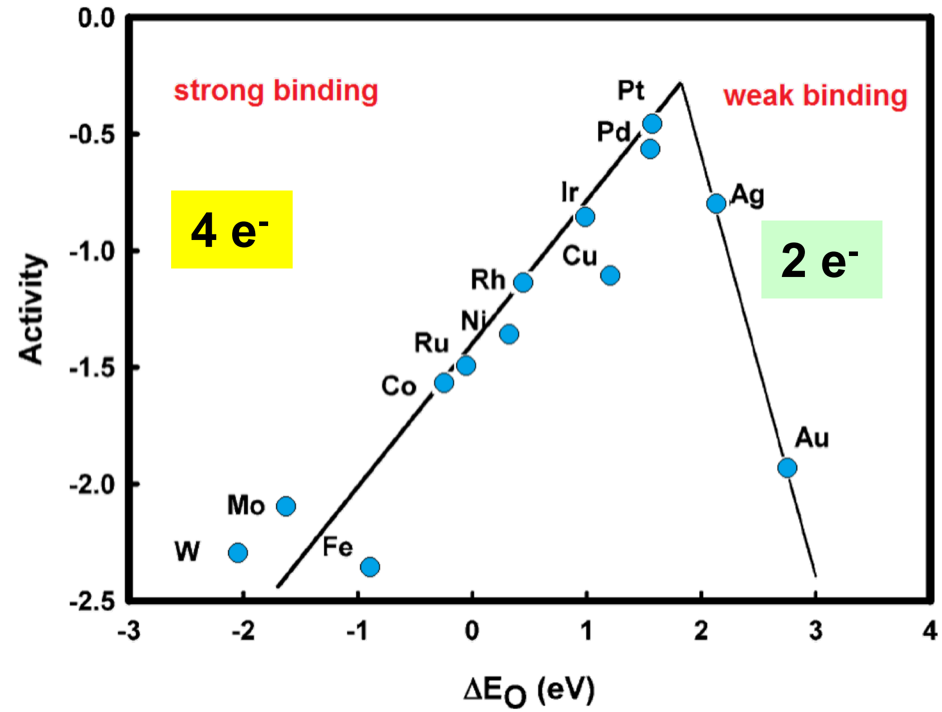


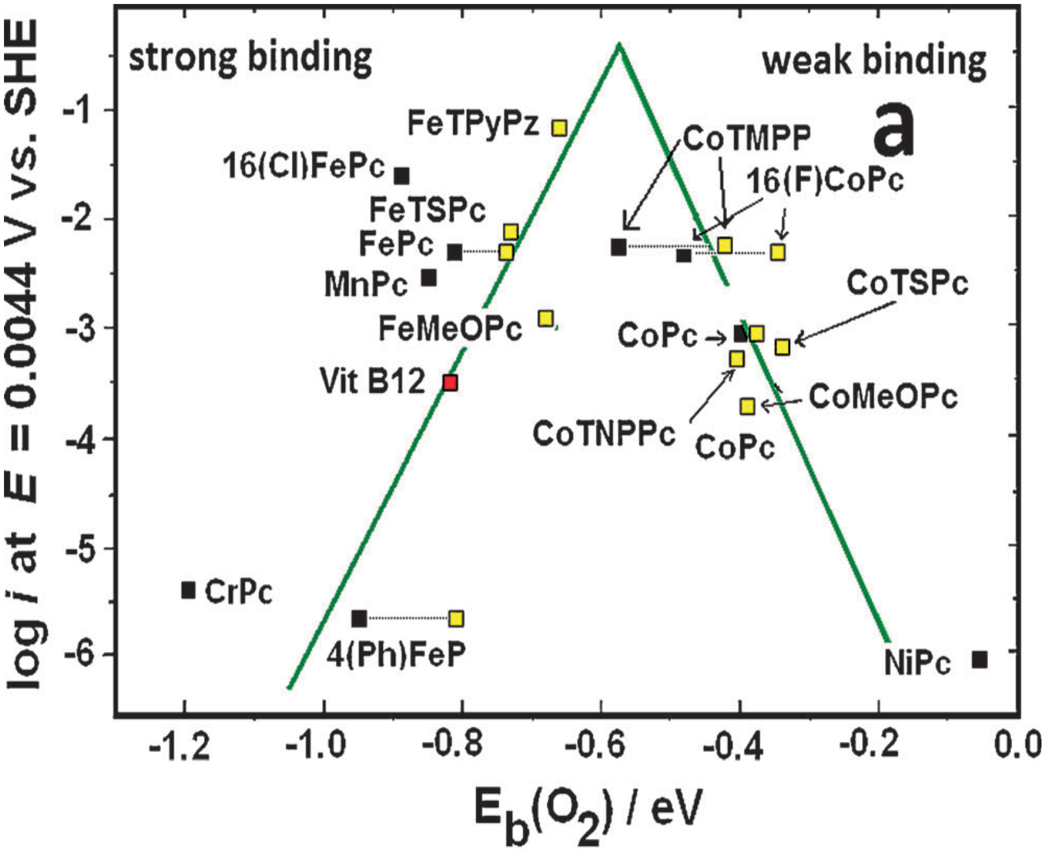
Figure 3. Activity volcano for ORR on different MN4 catalystsfrom Zagal & Koper, Angewandte Chemie Int.Ed. 55 (2016) 14510

Figure 4. Volcano correlation Taken from Norskov et al. J Phys Chem B 108 (2004) 17886.

$O_2 + 4e + 4H^+ \text{------}\rightarrow 2H_2O$ Eo= 1.230 V

$O_2 + 2e + 2H^+ \text{-----}\rightarrow H_2O_2$ Eo = 0.695 V

Does the maximum corresponds to an optimum interaction of M with O_2 red. intermediates?



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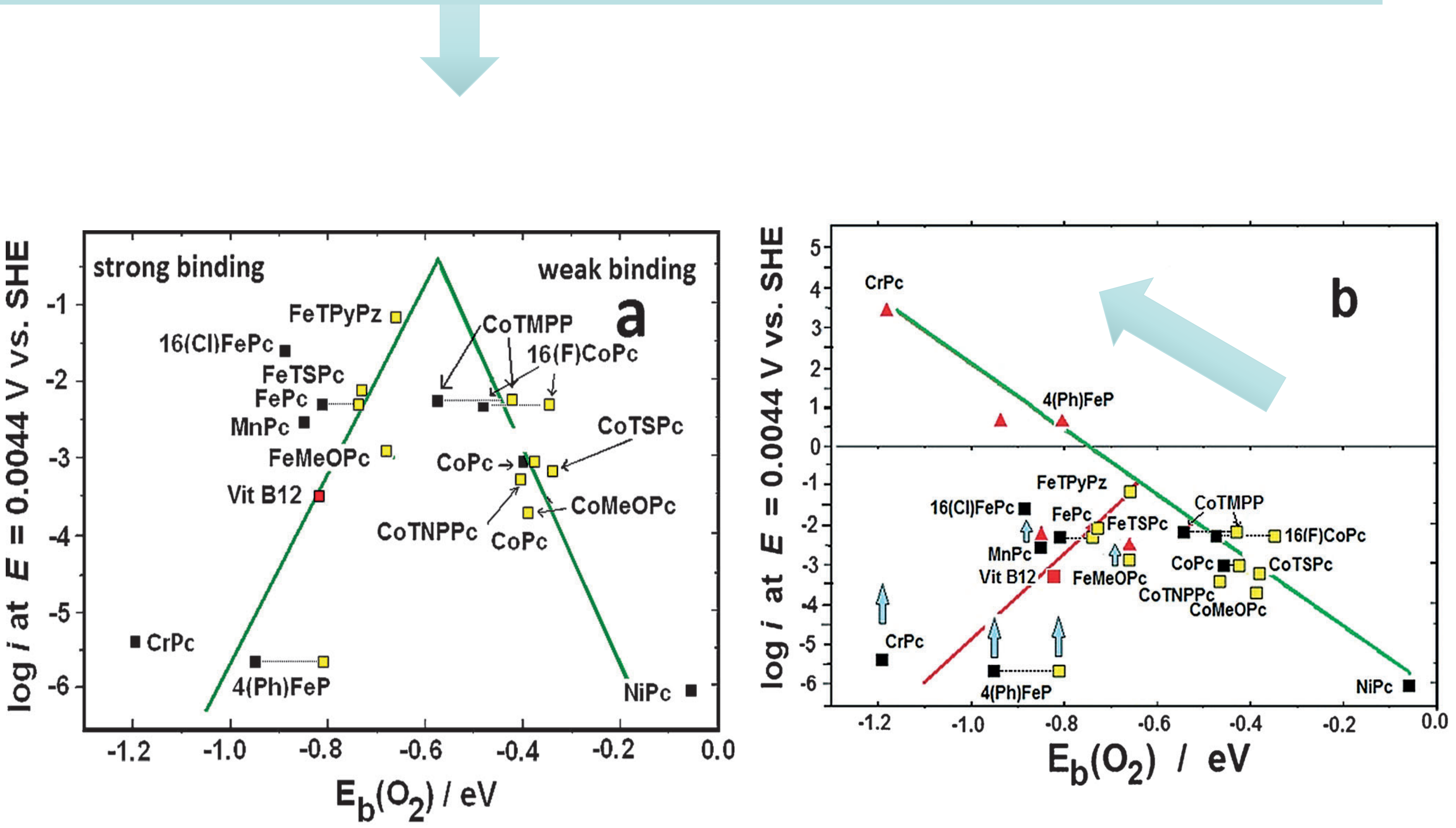
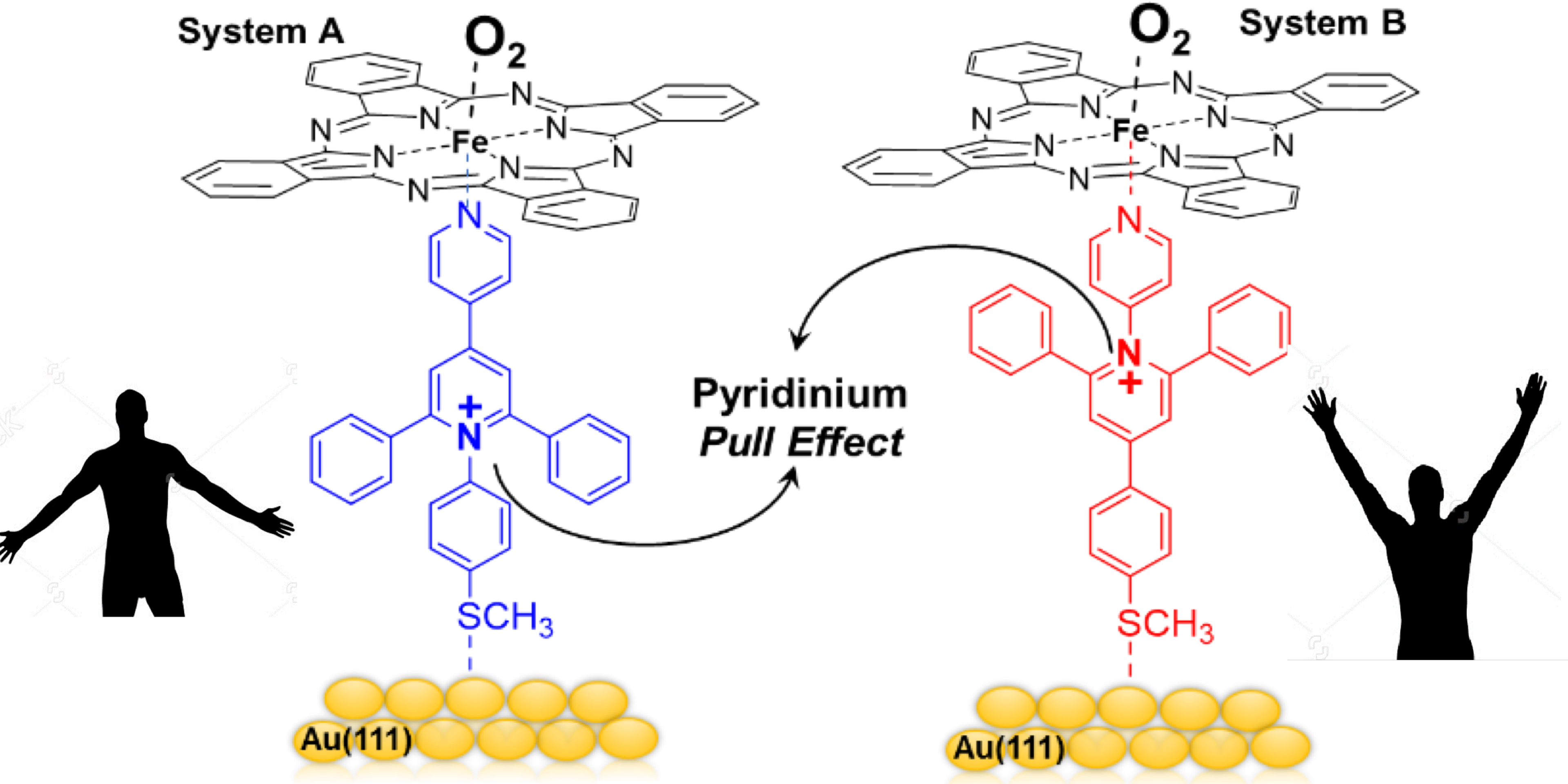
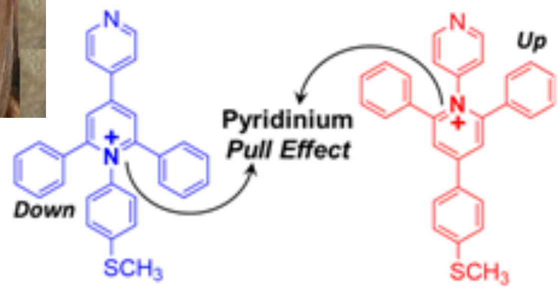
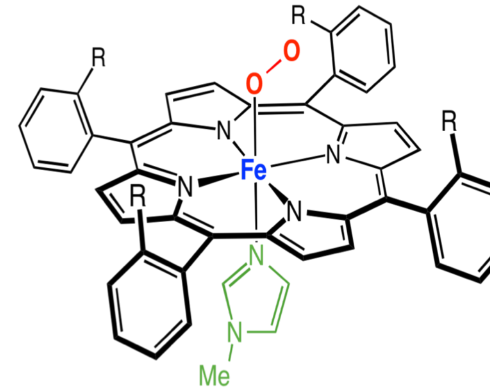


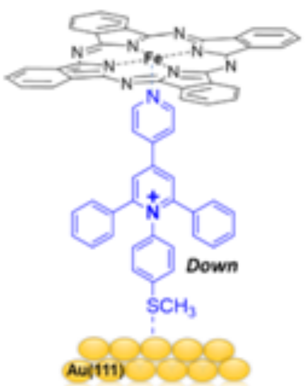
Biomimetic O_2 reduction on UP and DOWN configurations of back ligand



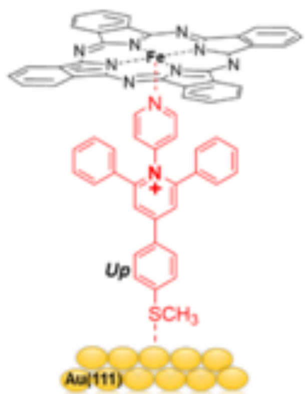
Ingrid Ponce & Ana Pizarro



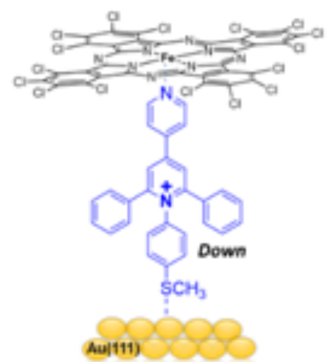




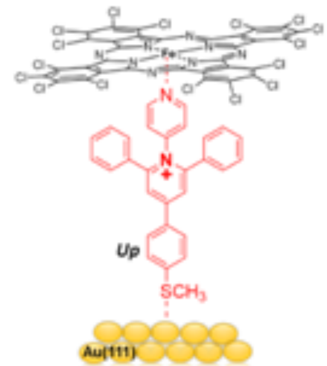
Au(111)/Down/FePc



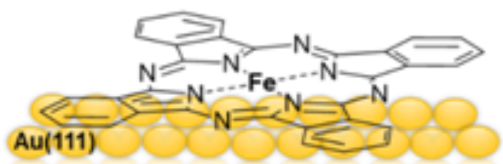
Au(111)/Up/FePc



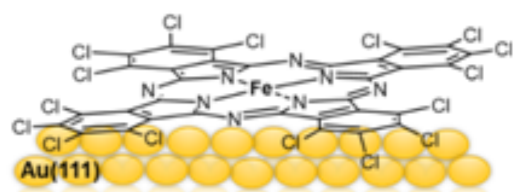
Au(111)/Down/16(Cl)FePc



Au(111)/Up/16(Cl)FePc

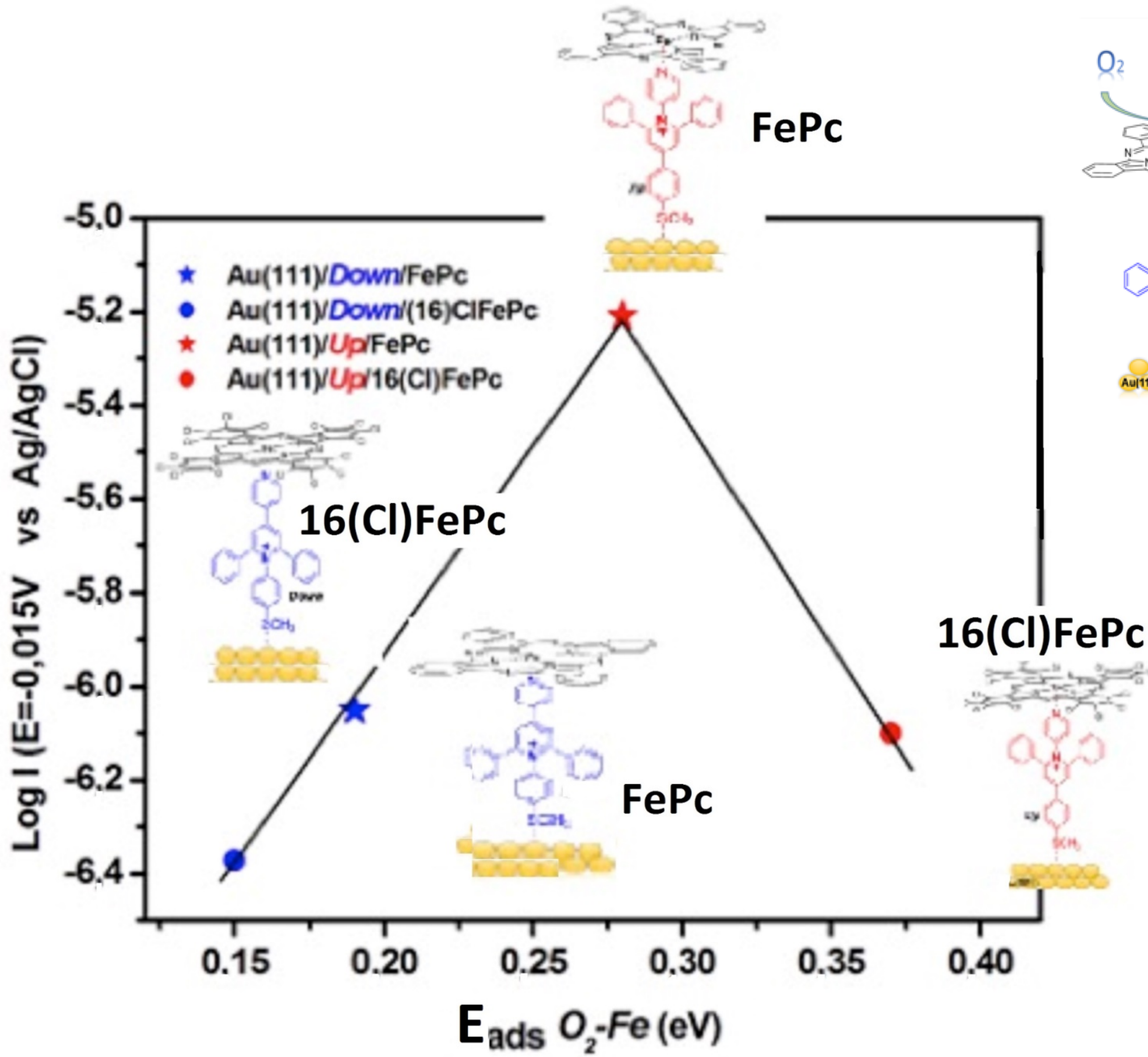


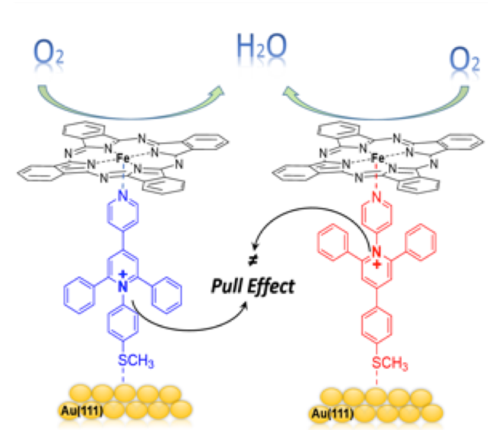
Au(111)/FePc



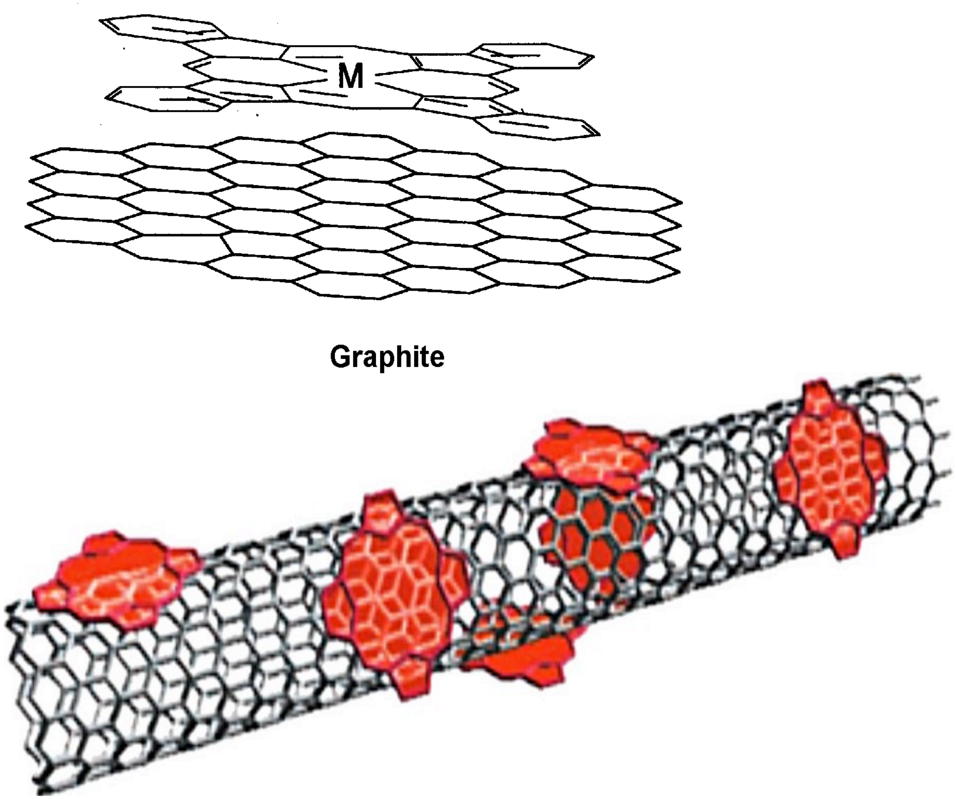
Au(111)/ 16(Cl)FePc

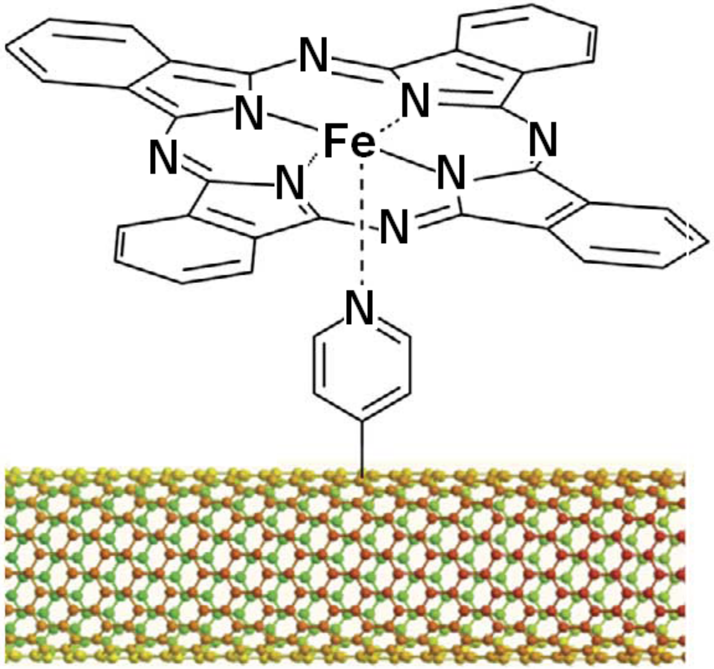
Activity Volcano plot for ORR (0.1 M NaOH) on two complexes: FePc and 16(Cl)FePc in different configurations. P





MN4 CATALYSTS ADSORBED ONTO SWCNT/MWCNT and ANCHORED by a AXIAL LIGAND. ORR CATALYTIC ACTIVITY

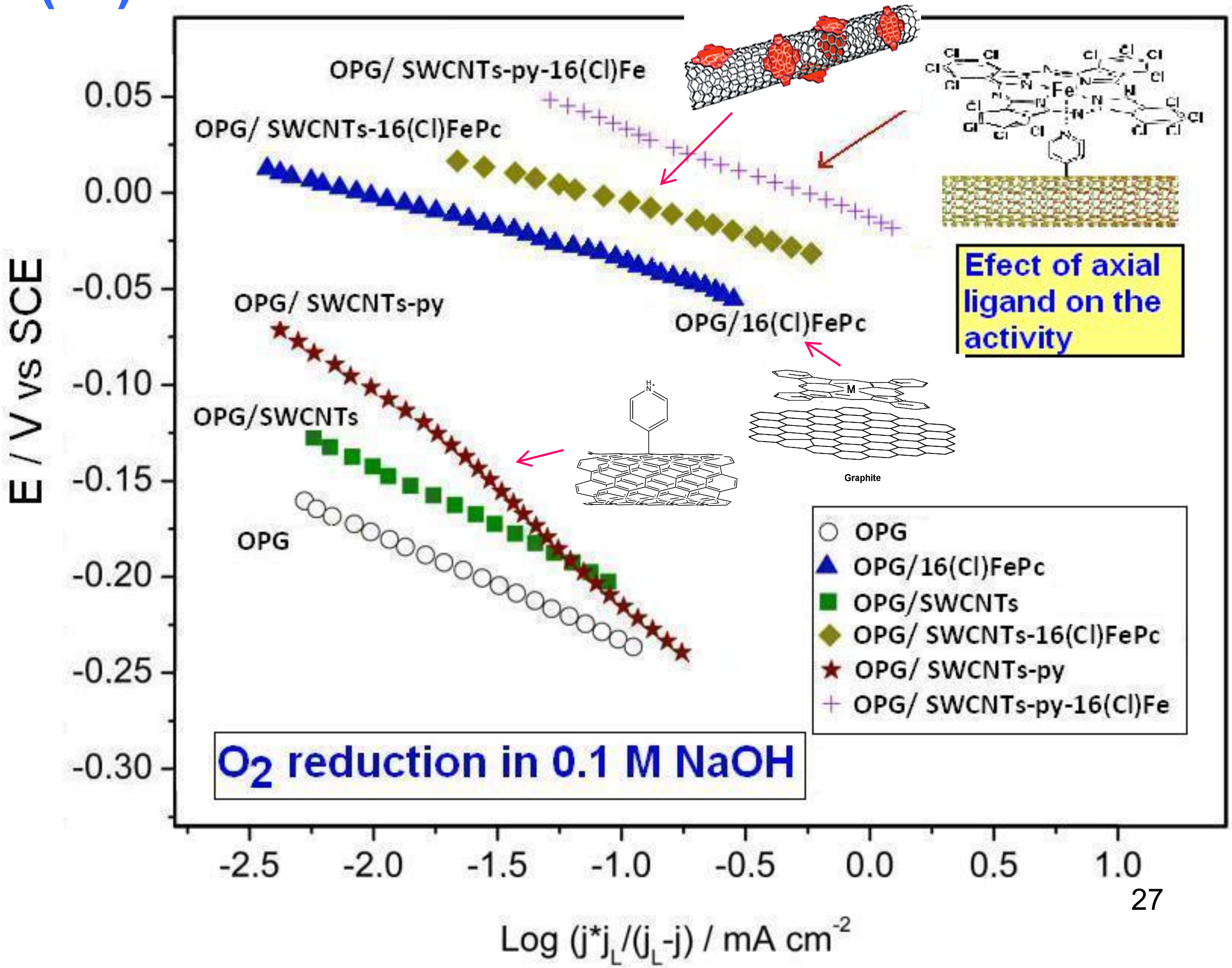




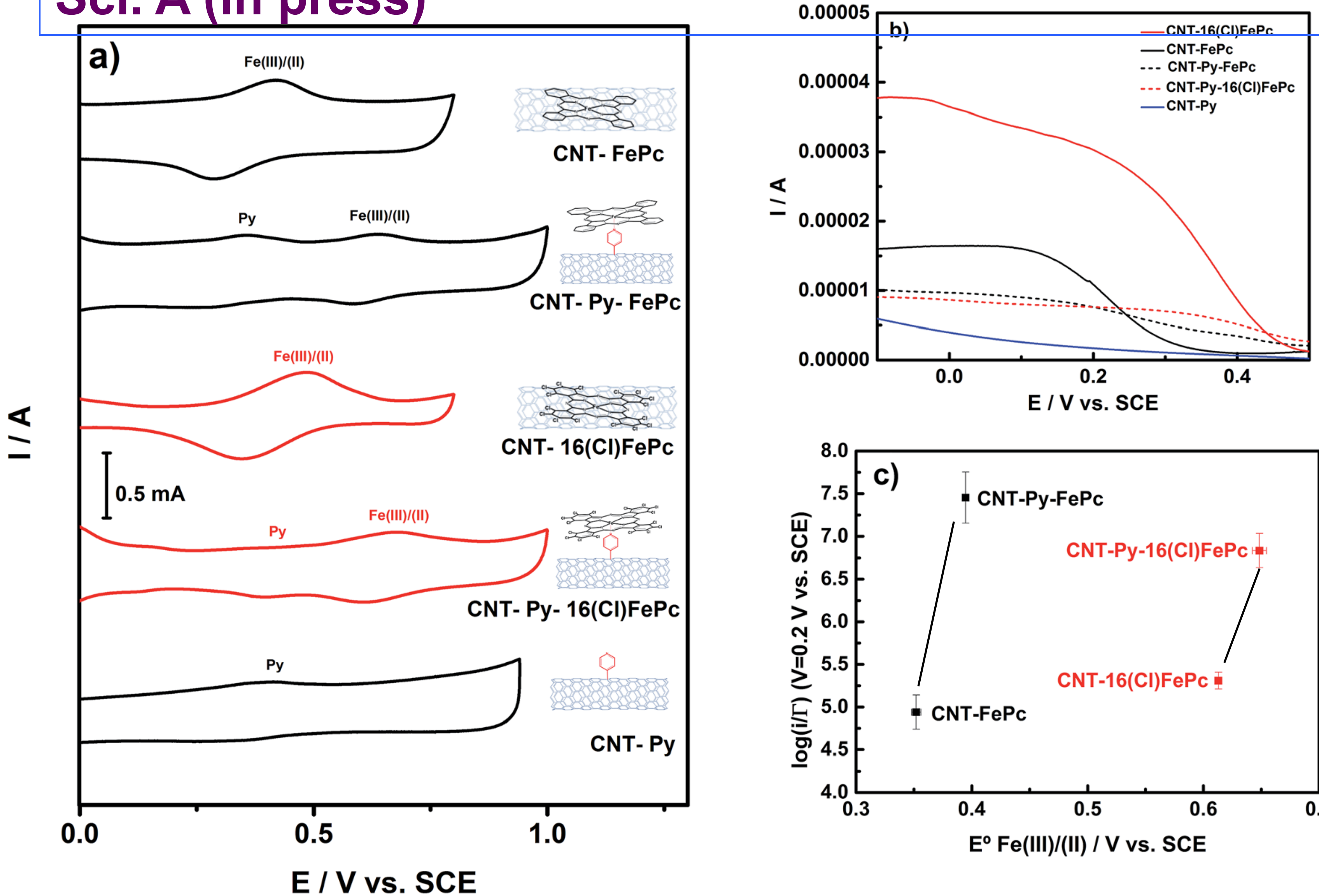
C. A. Gutierrez, F.J. Recio, J. H.Zagal et al. Electrocatalysis **(2014)**

Ruiguo Cao, Ranjit Thapa, et al. Nature Communications 4, 2076, **(2014)**

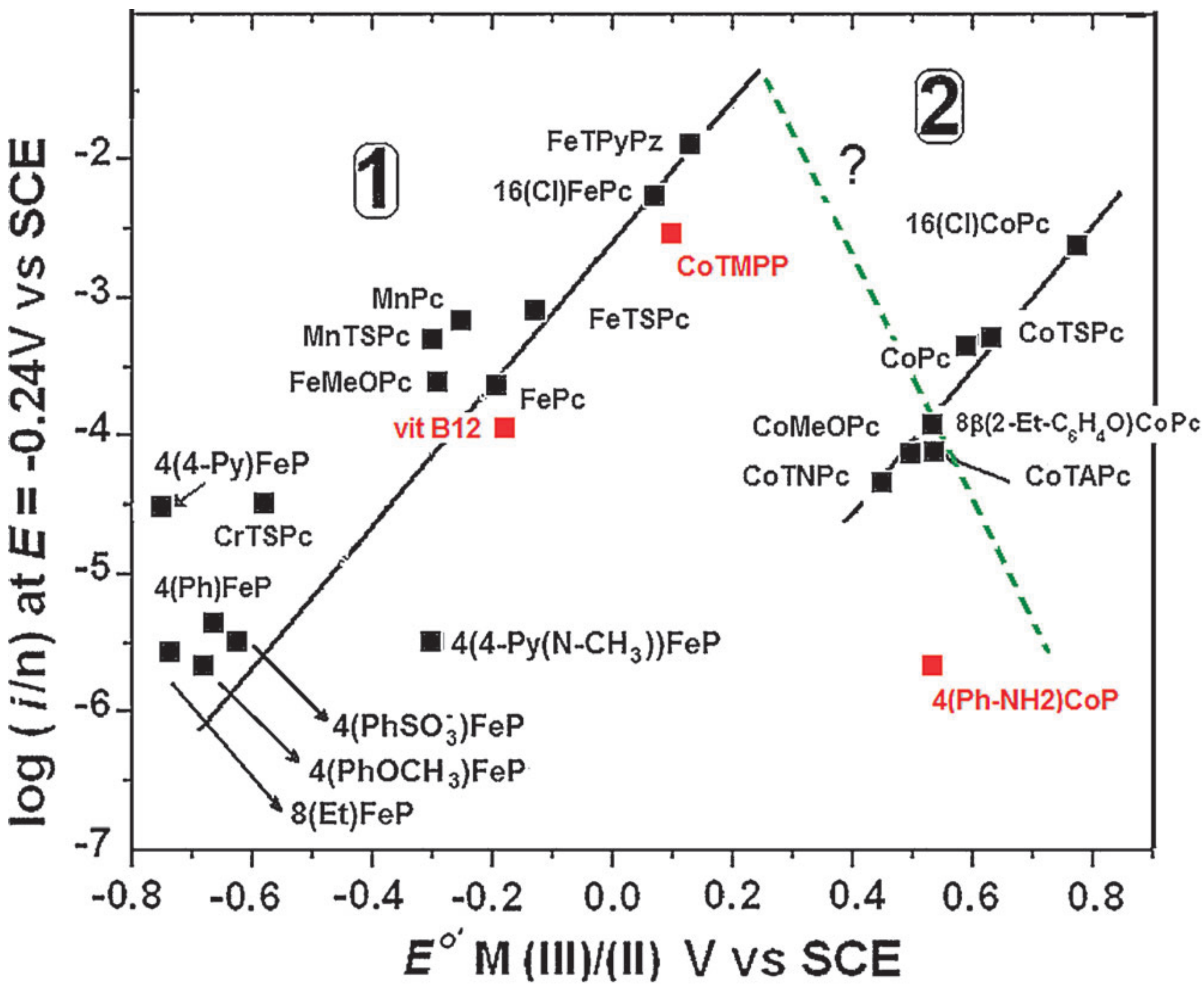
Tafel plots for ORR on different electrodes with and without 16(Cl)FePc



ORR in 0.1 M H_2SO_4 on FeN4 with and without axial ligand , anchored on CNT Zagal, Tasca et al J. Mat. Sci. A (in press)



EFECT OF M(III)/(II) REDOX POTENTIAL:Volcano plots of catalytic activities for the ORR in alkaline media) for different MN4 catalysts at E = 0.24 V versus SCE, Zagal & Koper, Angewandte Chemie, (2016)



J.H. Zagal/Coord. Chem. Rev. 119 (1992) 89–136

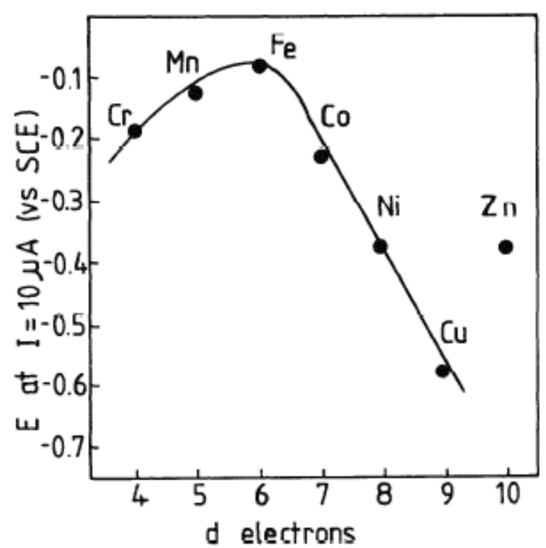
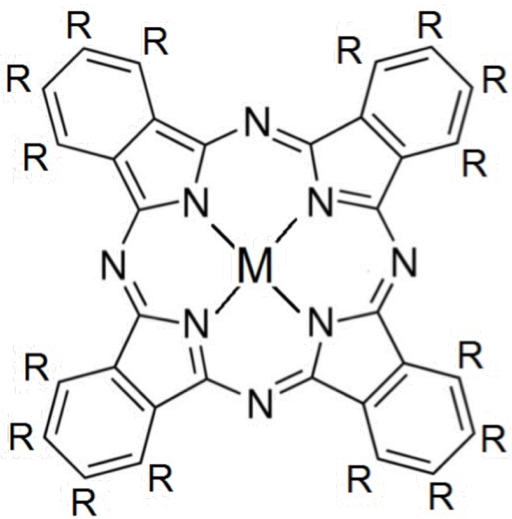
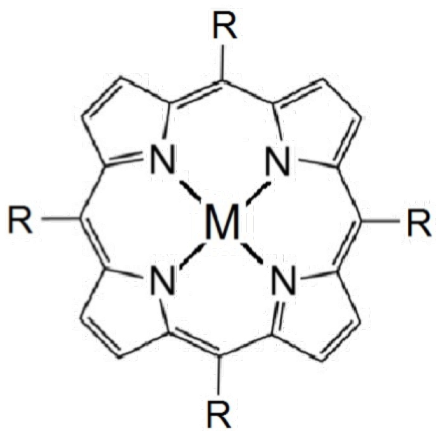
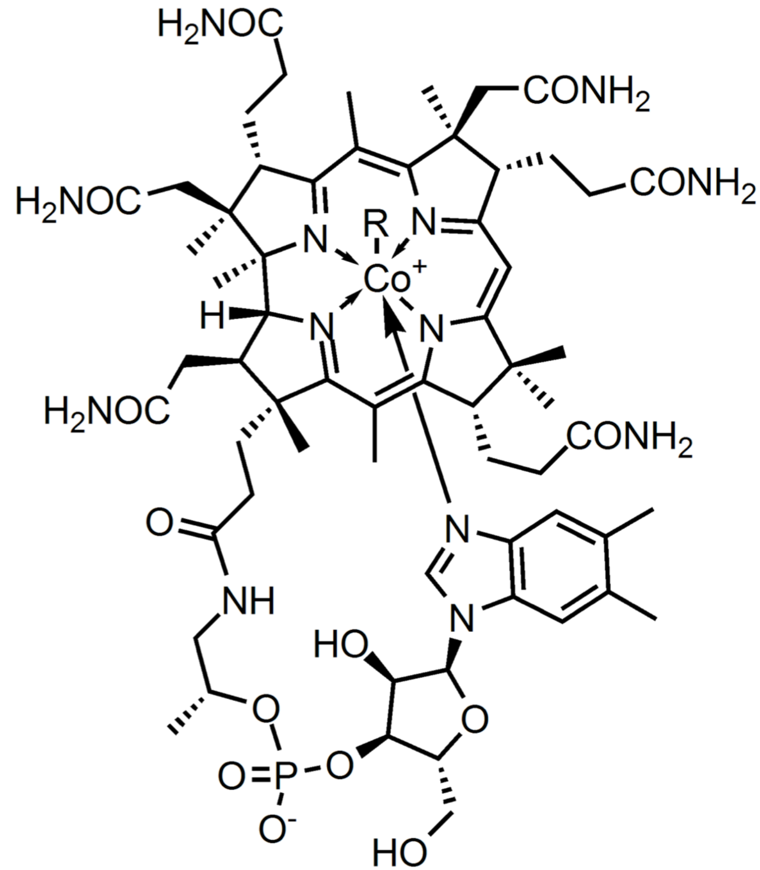


Fig. 14. Electrocatalytic activity of different M(II)-TSPs for O_2 reduction in 0.1 M aqueo[us ...] function of the number of d electrons. (Adapted from refs. 137 and 205.)

Metal phthalocyanines, metal porphyrins and vitamin B12





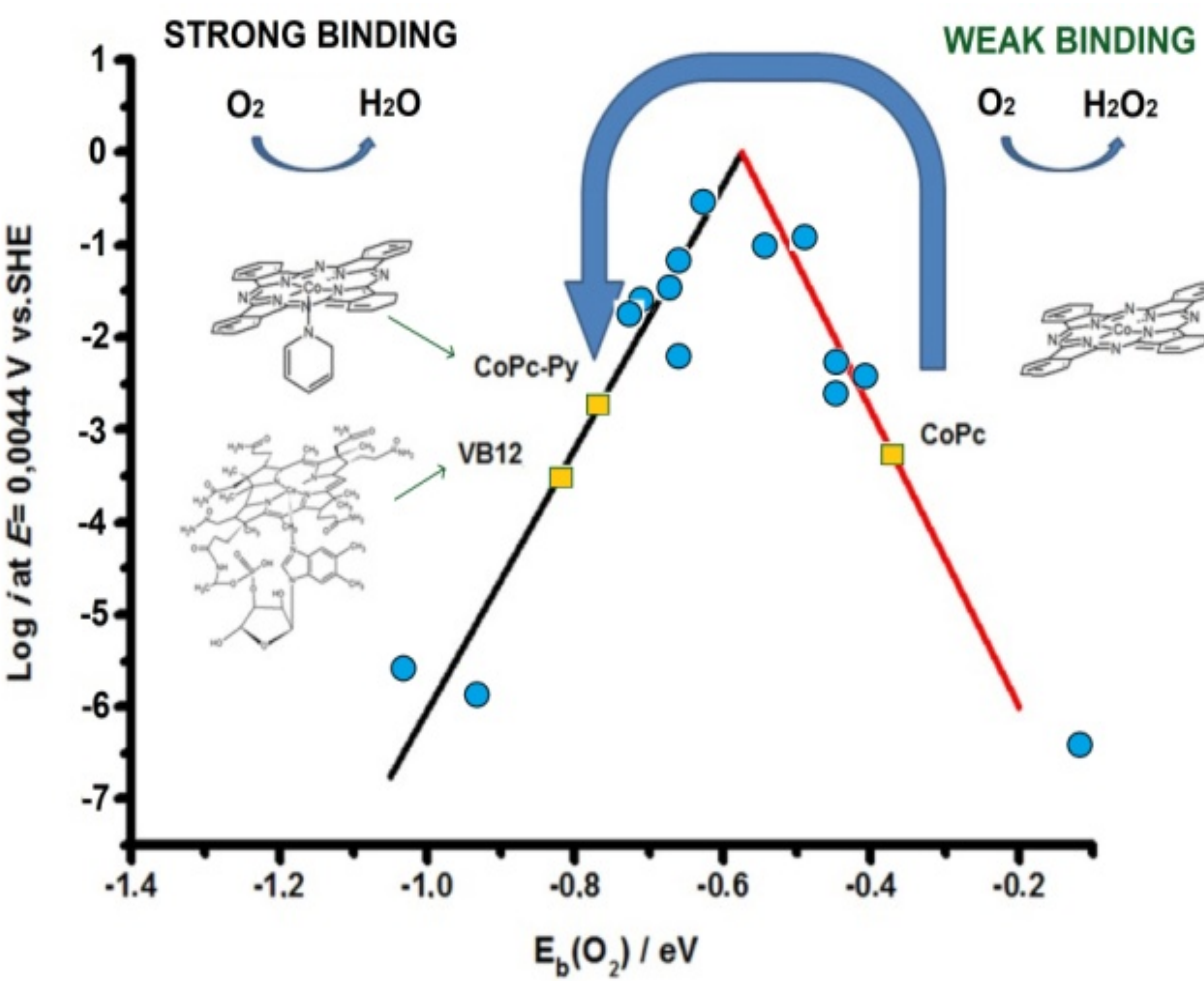


R = 5'-deoxyadenosyl, Me, OH, CN

CoPc = 2 e (gives peroxide)

Vit B12 = gives 4 e, gives H_2O

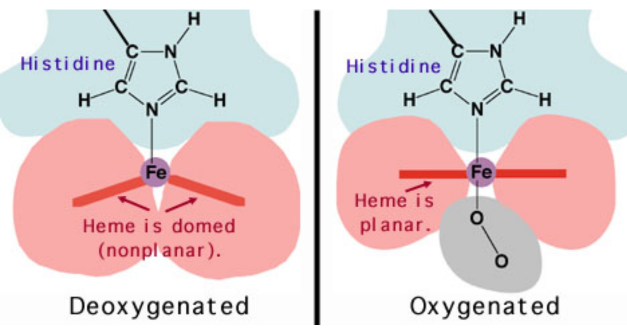
CoPc climbs the volcano correlation and goes from weak binding to strong binding faavouring the 4-e reduction of O_2

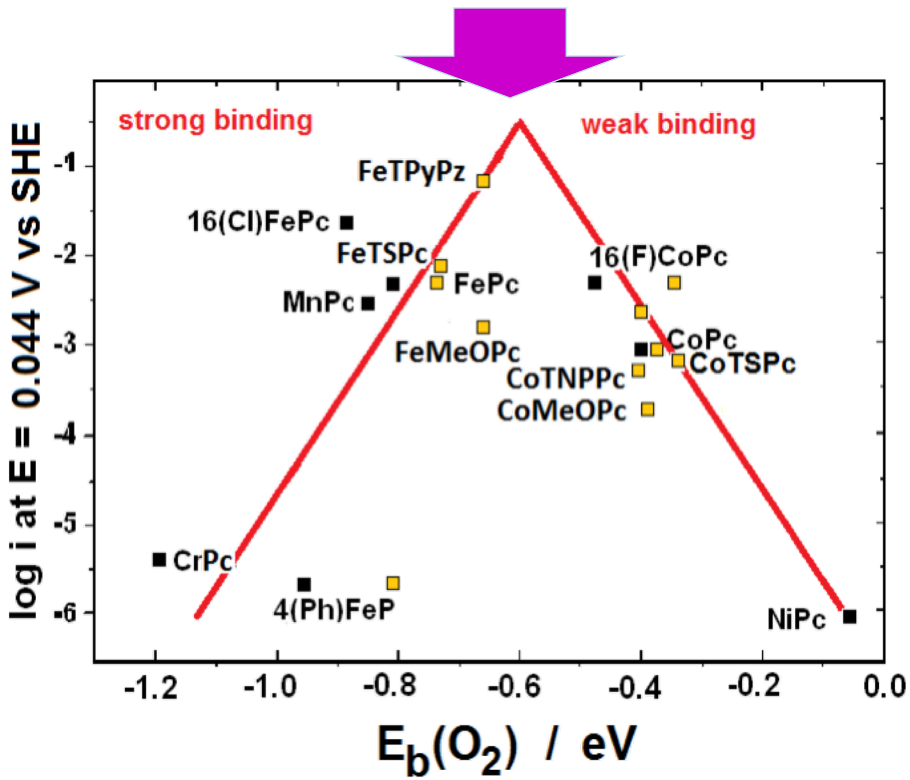


Zagal, Tasca , Electrochim. Acta (2018)

Crucial step in electrocatalysis:

(i) $O_2 + M + e \rightarrow M\text{-}O_2^-$ $\Delta G_{ad} = 0$ $K = 1$





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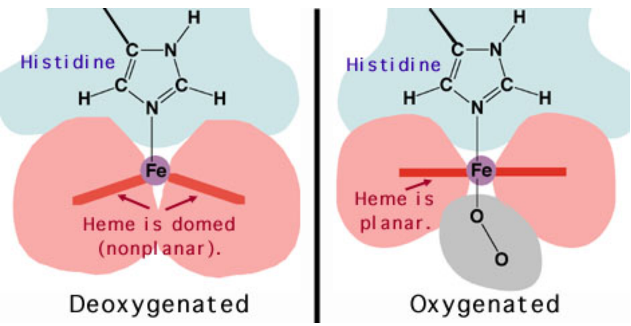
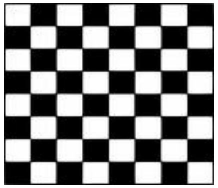
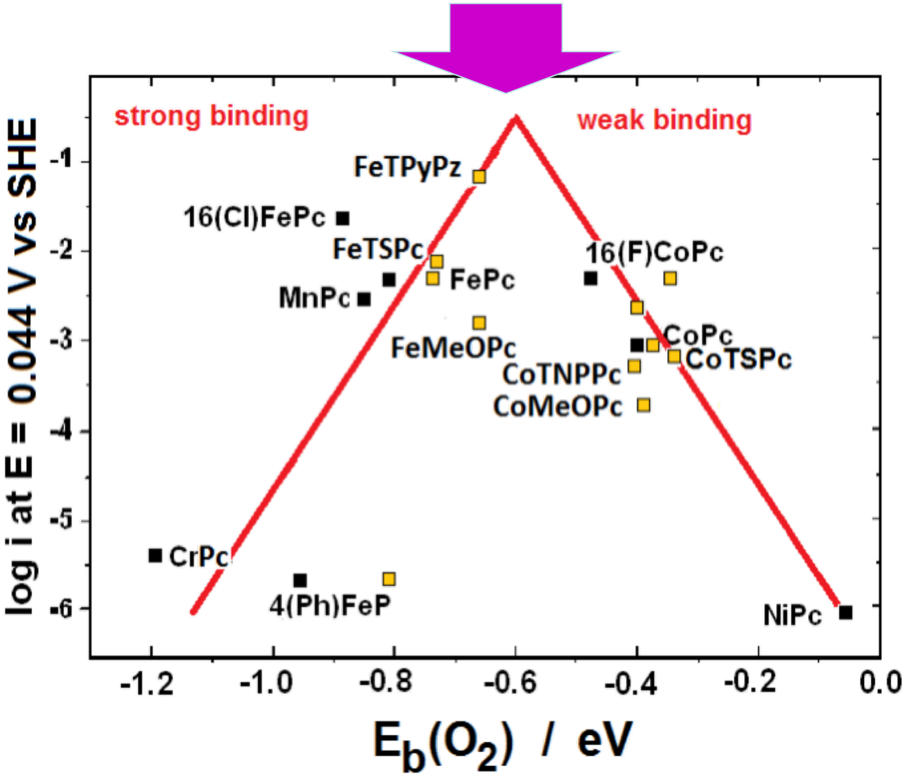
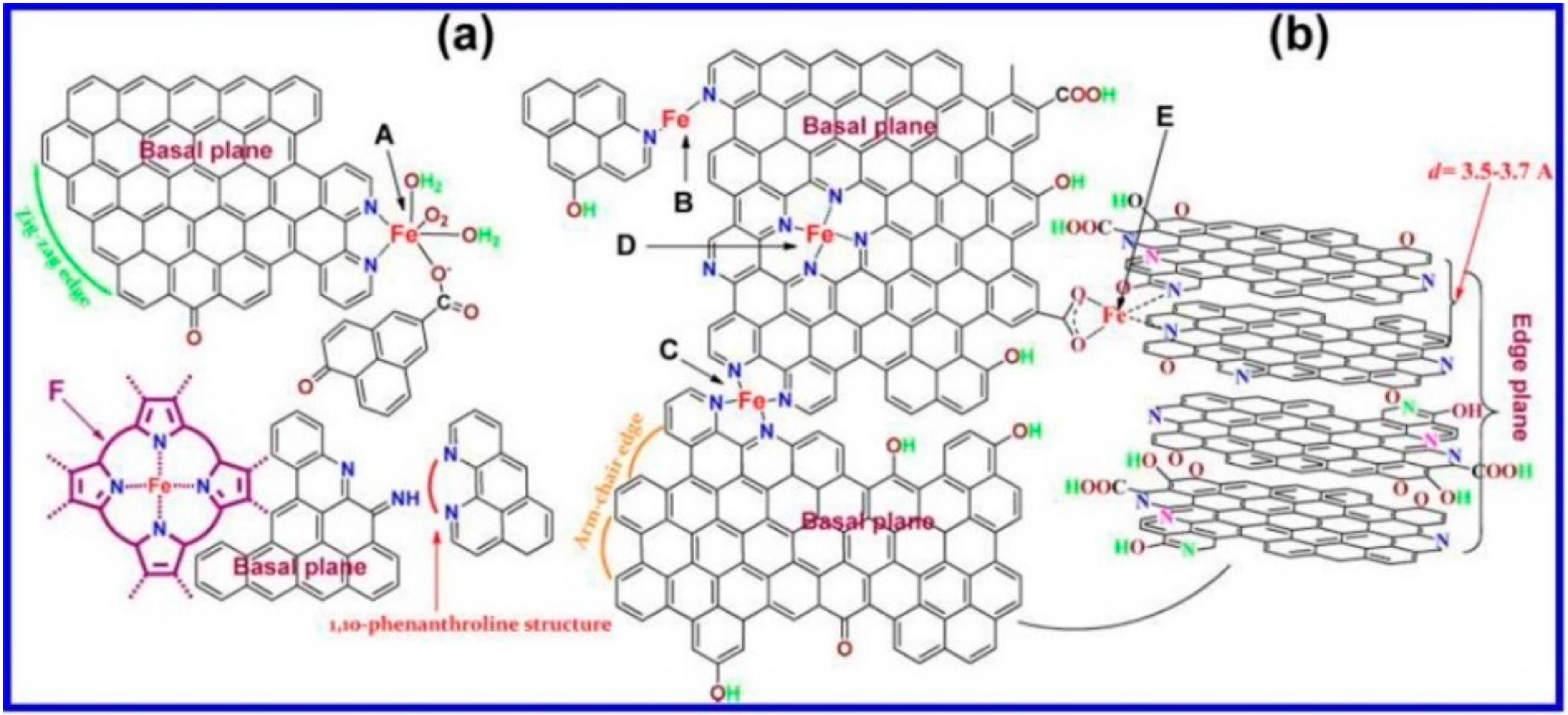






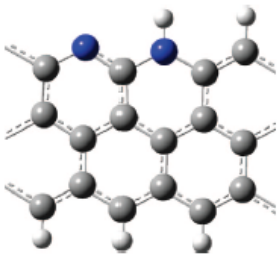
MNx PYROLYZED CATALYSTS. These are the best candiadtes for fuel cell applications, but there still problems. Possible Iron Active Site Structures on Nanocrystal Graphite: (a) top and (b) side view

J.Liu et al.*Catalysts* ***2015, 5, 1167***



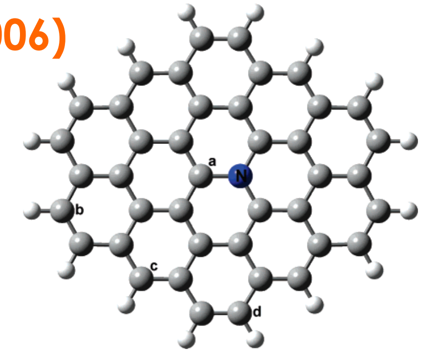
PGM-free Electrocatalysts Structure P.Atanassov

"Metal-free"

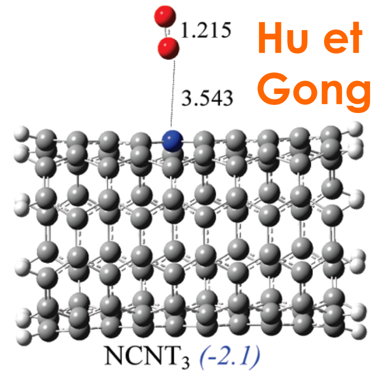


Kurak and Anderson (2009)

Sidik et al. (2006)
Li et al. (2010)

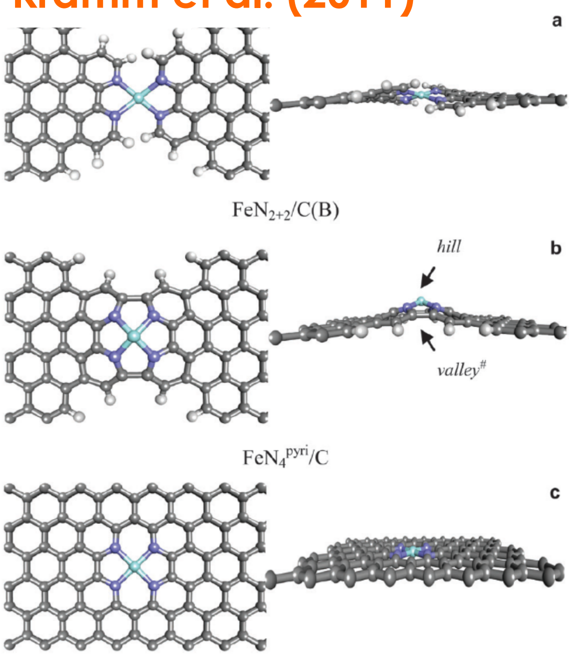


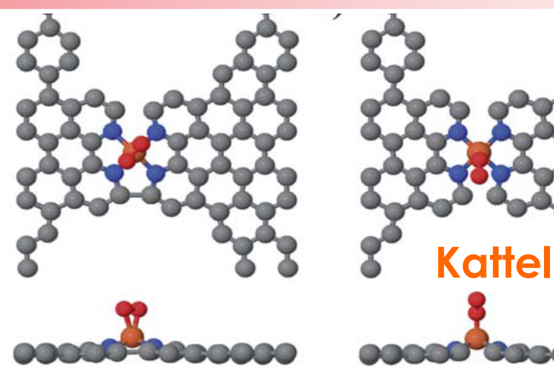
Hu et al. (2010)
Gong et al. (2009)



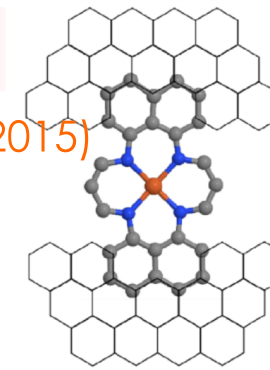
… or transition metal-centered

Kramm et al. (2011)

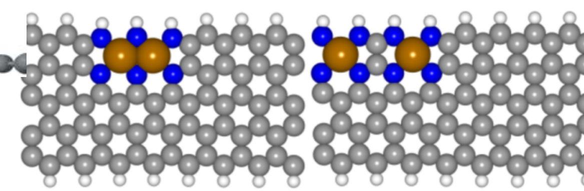




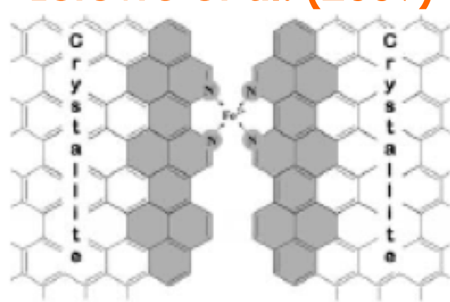
Zitolo et al. (2015)



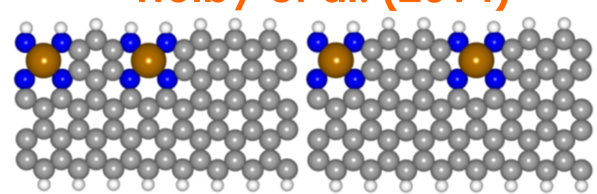
Kattel et al. (2014)



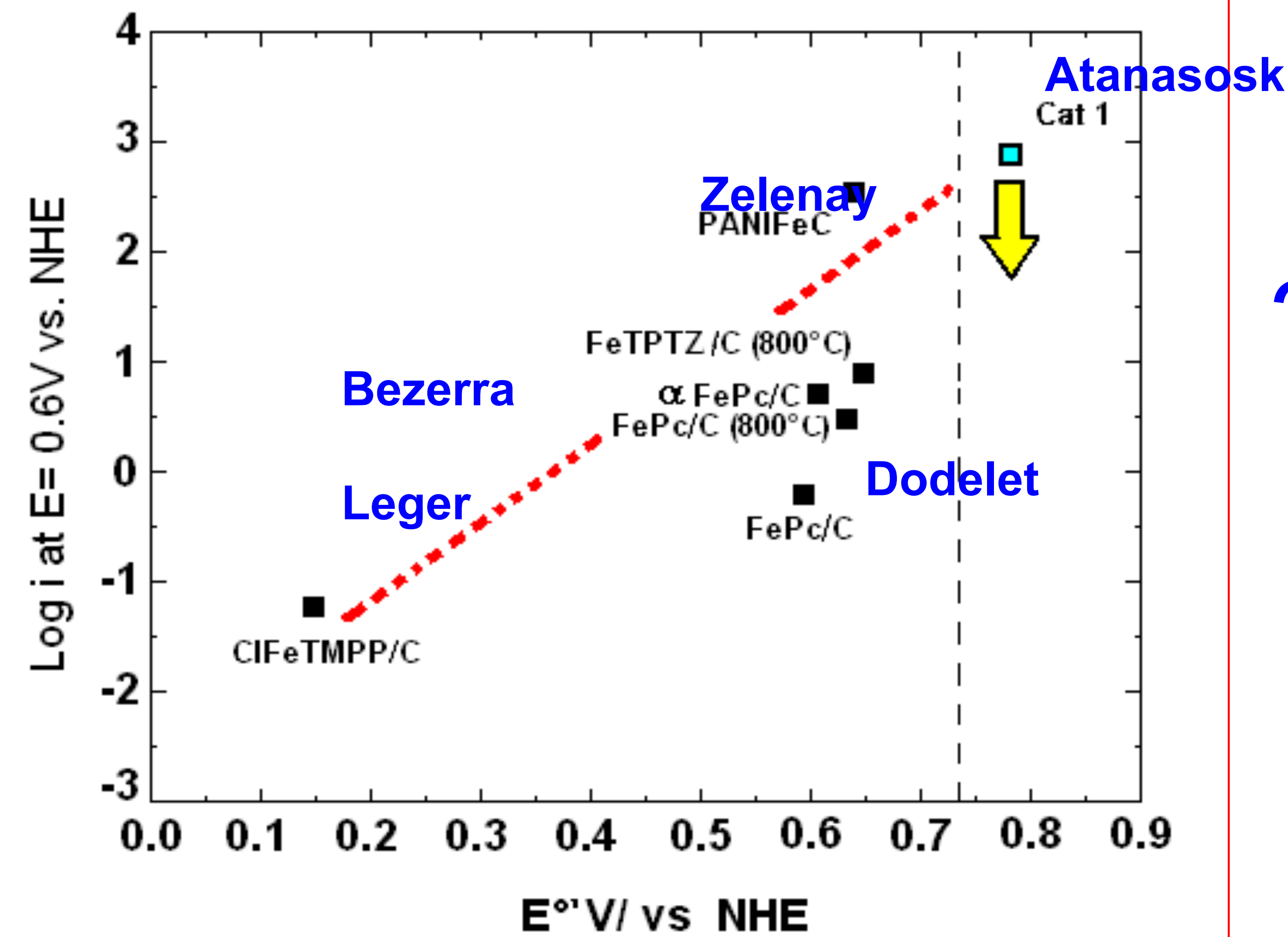
Lefevre et al. (2009)



Holby et al. (2014)



Trends in reactivity of pyrolized MNX catalysts (v.the redox potential up to 1000C° O2 reduction in acid (0.05 M H_2SO_4)



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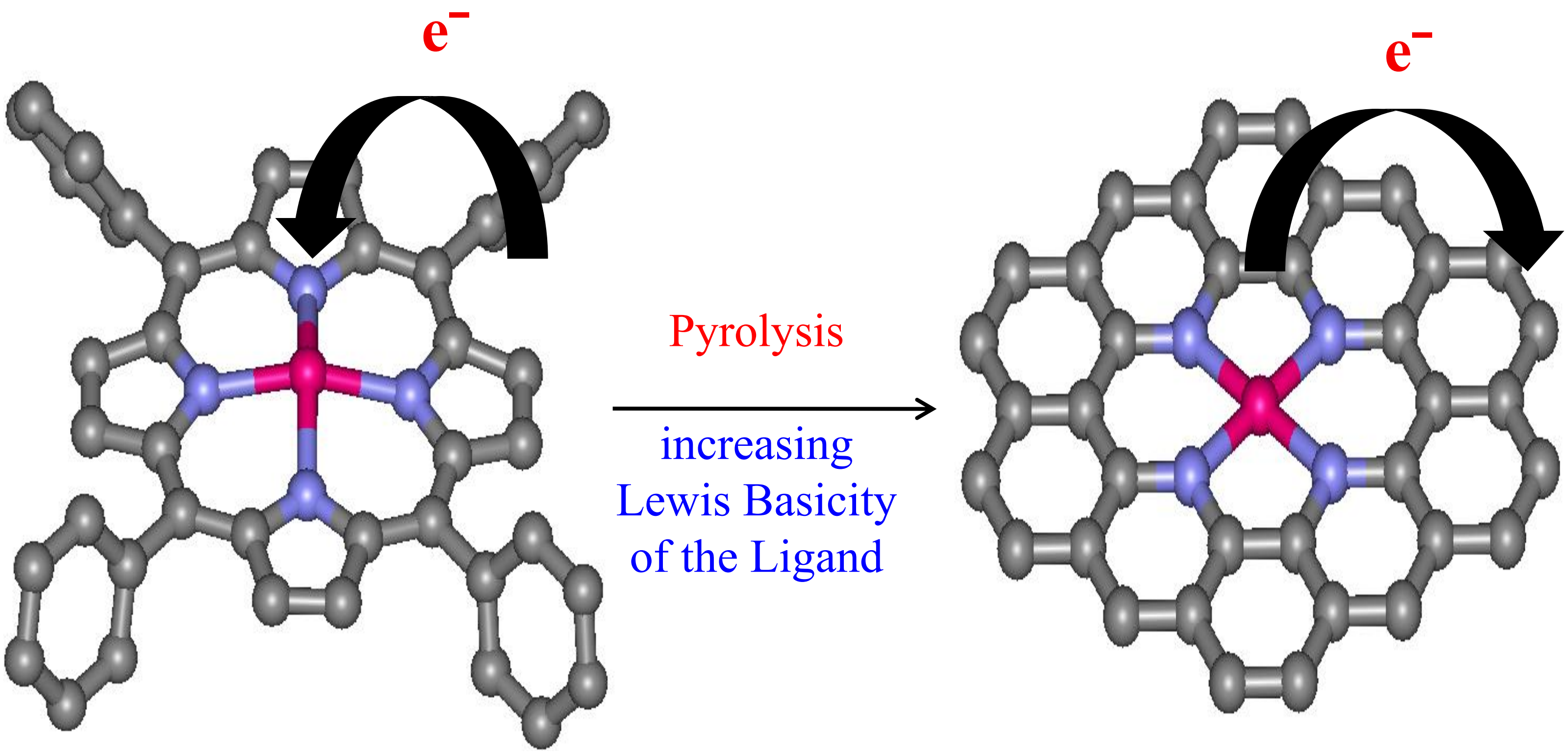
B90 *Electrochemical and Solid-State Letters*, **15** (6) B90-B92 (2012)
1099-0062/2012/15(6)/B90/3/$28.00 © The Electrochemical Society

A Possible Interpretation for the High Catalytic Activity of Heat-Treated Non-Precious Metal Nx/C Catalysts for O_2 Reduction in Terms of Their Formal Potentials

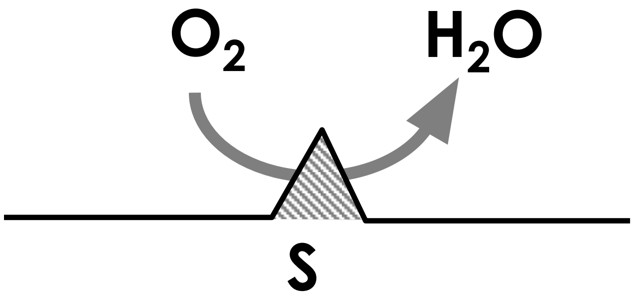
José H. Zagal,*,z Ingrid Ponce, Daniela Baez, Ricardo Venegas, Jorge Pavez,* Maritza Paez,*

usach

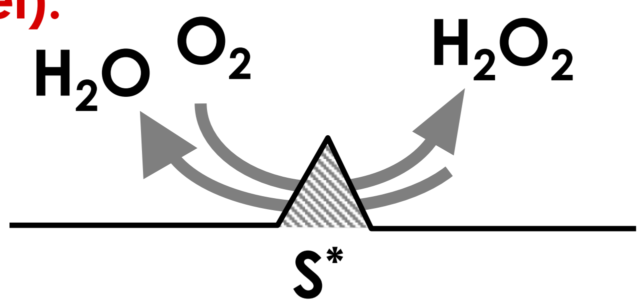
Pyrolized catalysts: High activity attributed to modification of the chemical environment around the metal aupon pyrolysis (up to 1000° C) S- Mukerjee et al. : Effect of Lewis Basicity of Ligand on Redox Potential, JACS (2013). Dramatic shift of Fe(III)/(II) upon pyrolysis



ORR on PGM-free Electrocatalysts Plamen Atanassov

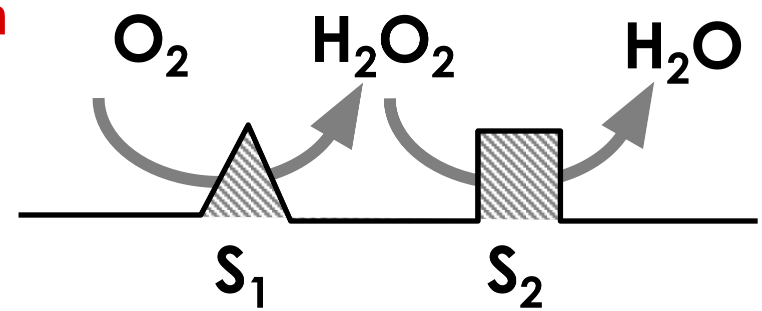


Single site direct (parallel):
4 e⁻ mechanism



Single site consequential:
2 x 2e⁻ mechanism

Transition Metal-containing PGM-free catalysts derived from Nitrogen-Carbon family, regardless of the synthetic route are highly chemically heterogeneous (and morphologically heterogeneous as well).
It is not realistic to assume a simple active site, but rather a competition between several sites.



Dual site consequential:
2 x 2e⁻ bi-functional mechanism

Transition metal appears to be associated (but is not strictly needed) for the reduction of O_2 to H_2O_2. Transition metal appears to be required for the reduction of O_2 to H_2O (4 e⁻ stoichiometry), yet there is agreement on the mechanism (2 x 2 e⁻ or 4 e⁻) and the number of active sites required for ORR completion.

Systematic Tuning of Heme Redox Potentials and its effects on O_2 reduction rates

Marschall, Robinson ,Lu ,JACS (2014)

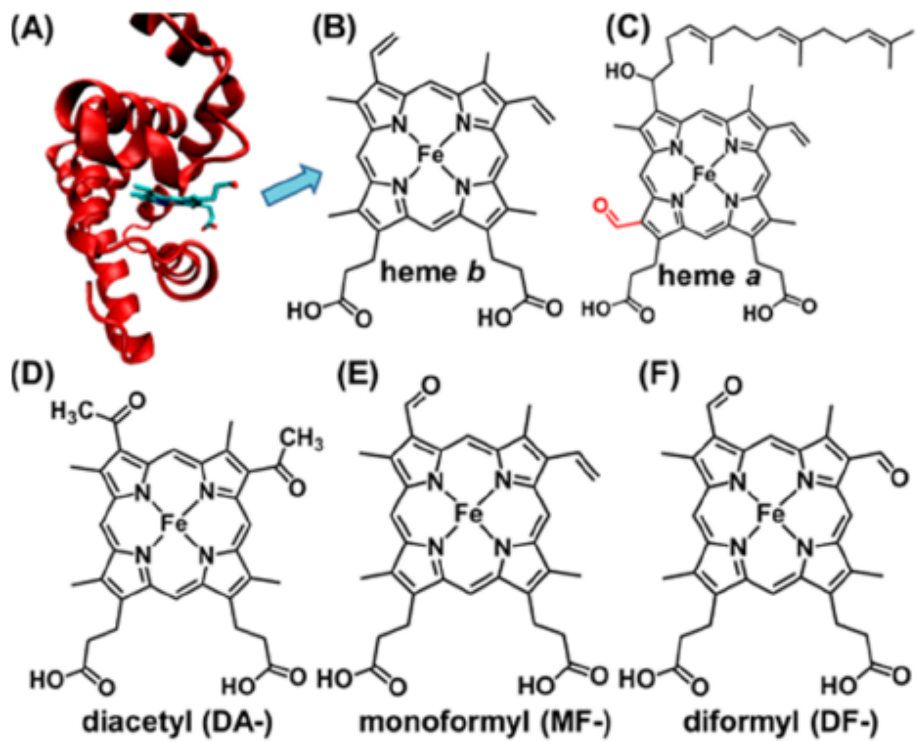


Figure 3. (A) Protein scaffold of F33Y-Cu$_B$Mb. (B) Heme *b* cofacto present in F33Y-Cu$_B$Mb. (C) Heme *a* present in the catalytic site o bovine CcO. (D) Diacetyl heme (E) Monofomyl heme and (F Diformyl heme incorporated in F33Y-Cu$_B$Mb apo-protein.

Journal of the American Chemical Society

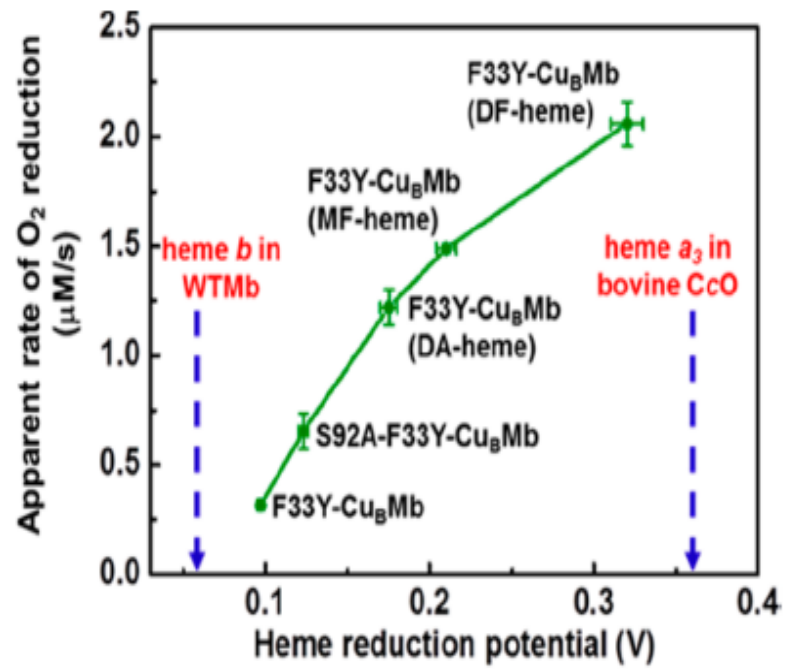


Figure 5. Variation of O_2 reduction activity with heme $E°$ for F33Y-Cu$_B$Mb variants. Dotted blue line indicates $E°$ of WTMb and bovine CcO.

The same trends is found , i.e. The more positive the redox potentilas the higher the activity

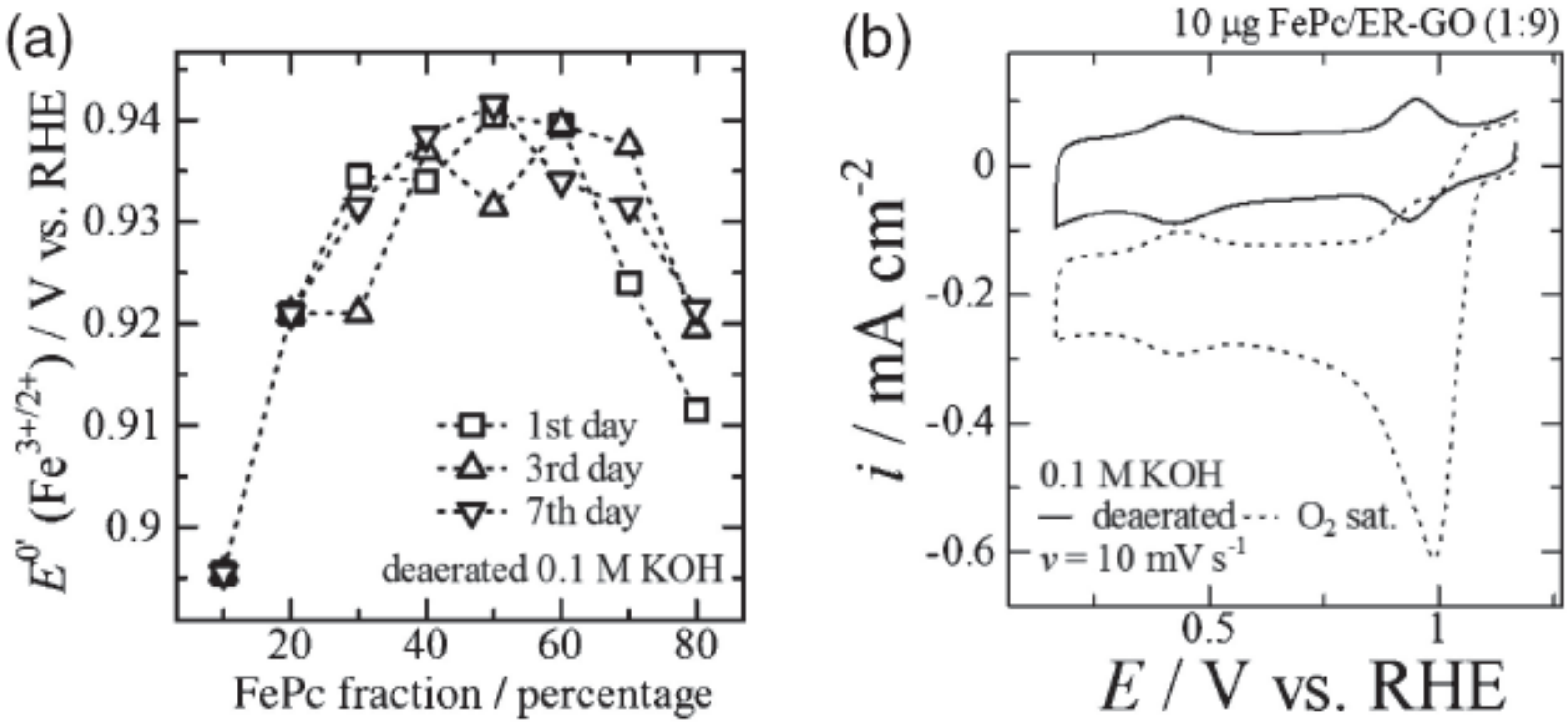


Figure 3. (a) The relationship between $E^{0'}(Fe^{3+/2+})$ of FePc and its fraction in FePc/GO composite. Open squares, open triangles, open inverse triangles indicate the data obtained for electrodes fabricated with aged FePc-GO mixture solution for 1, 3 and 7 days. (b) Cyclic voltammograms of 10% FePc/ER-GO/GC in deaerated (solid) and O_2 saturated (dotted) 0.1 M KOH solution. The deposited amount of FePc-GO was 10 μg.

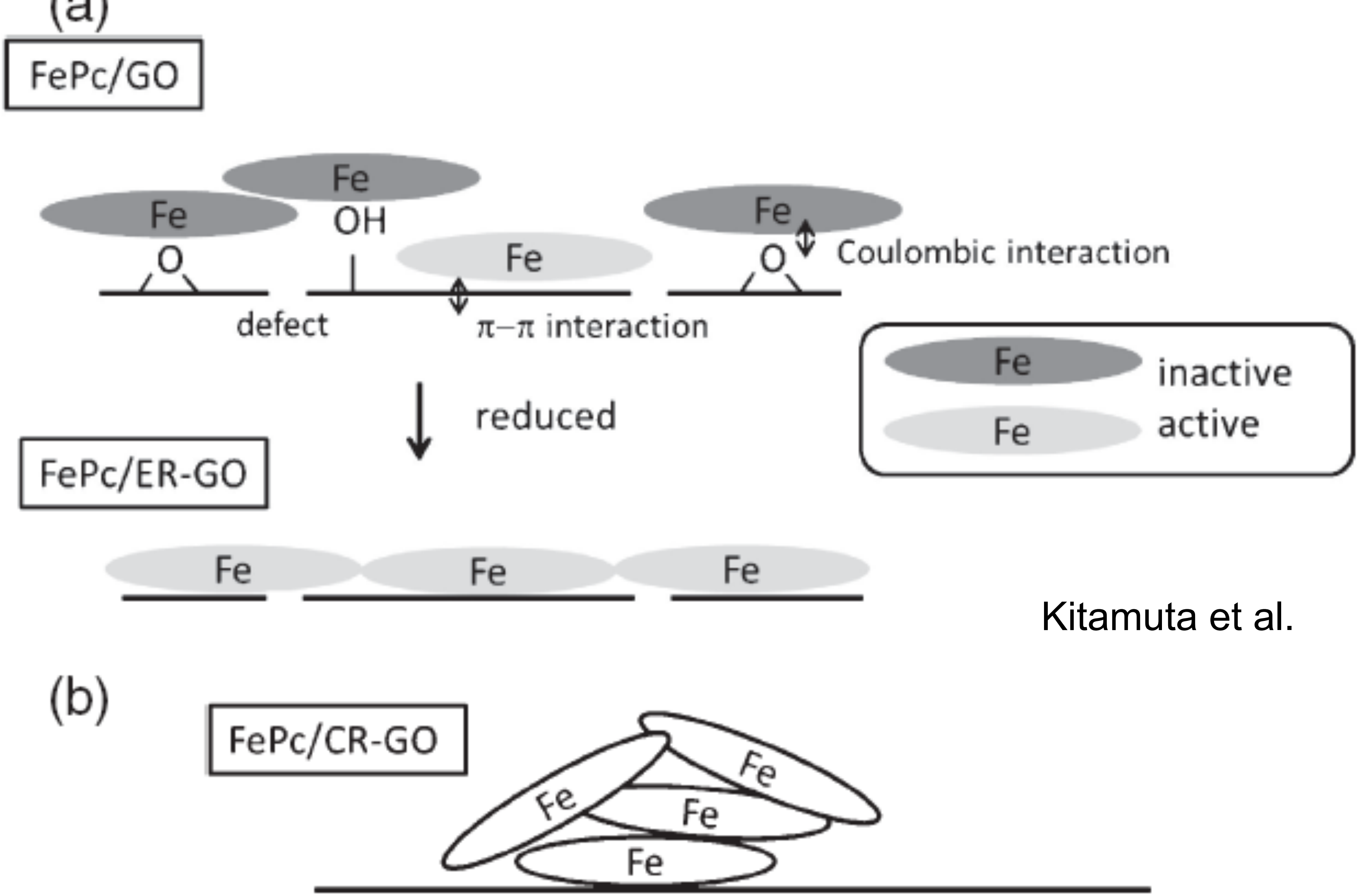


Figure 2. (a) Schematic images of the interaction between FePc and GO or ER-GO. The FePc in pale and deep colors indicates electroactive and inactive states, respectively. (b) the images of FePc/CR-GO.

The Electrochemical Society of Japan http://dx.doi.org/10.5796/electrochemistry.83.37

Article Electrochemistry, **83(5)**, 376–380 (2015)

On the Formal Redox Potential of Oxygen Reduction Reaction at Iron Phthalocyanine/Graphene Composite Electrode in Alkaline Media

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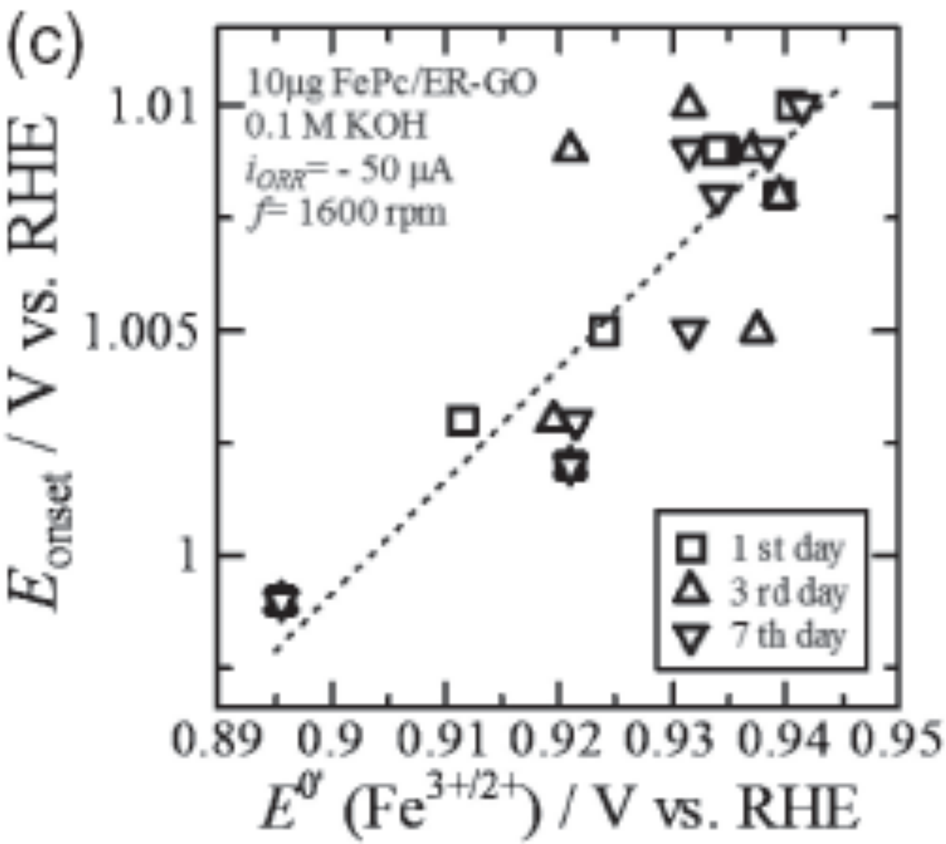
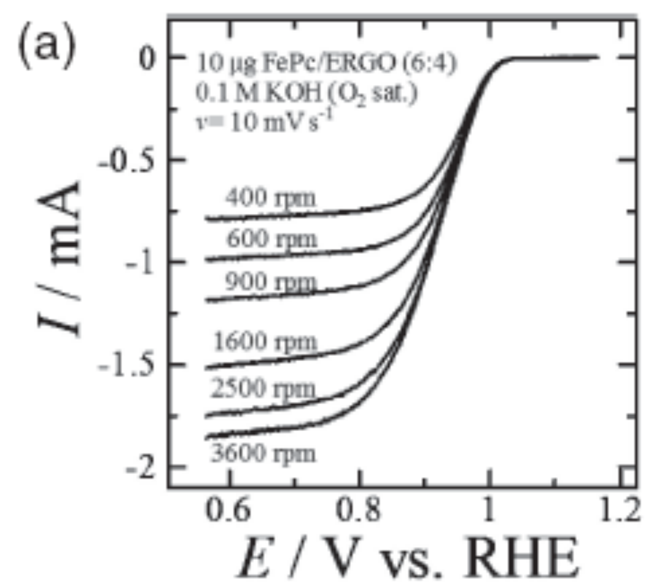
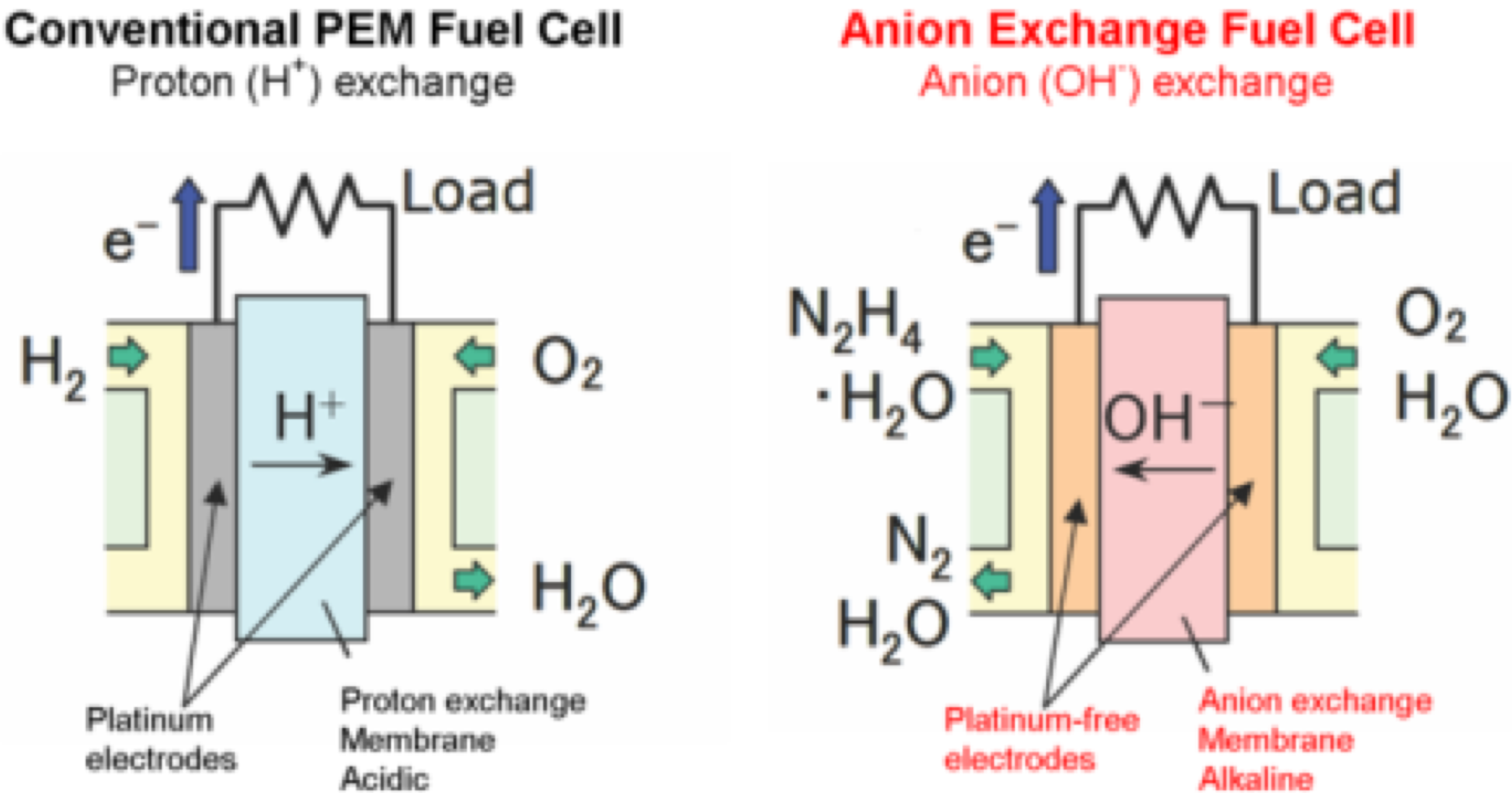
Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan

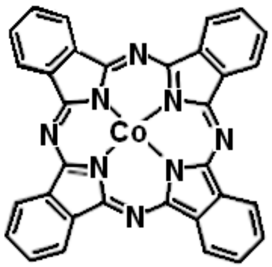
* *Corresponding author: kitamura@echem.titech.ac.jp*



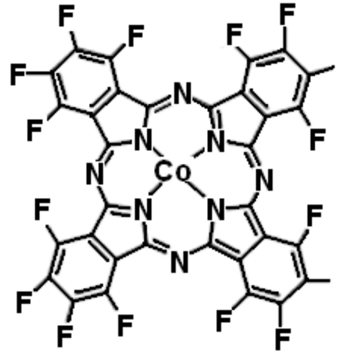


Hydrazine oxidation Dahiatsu Motor Co.
Pt-free fuel cell



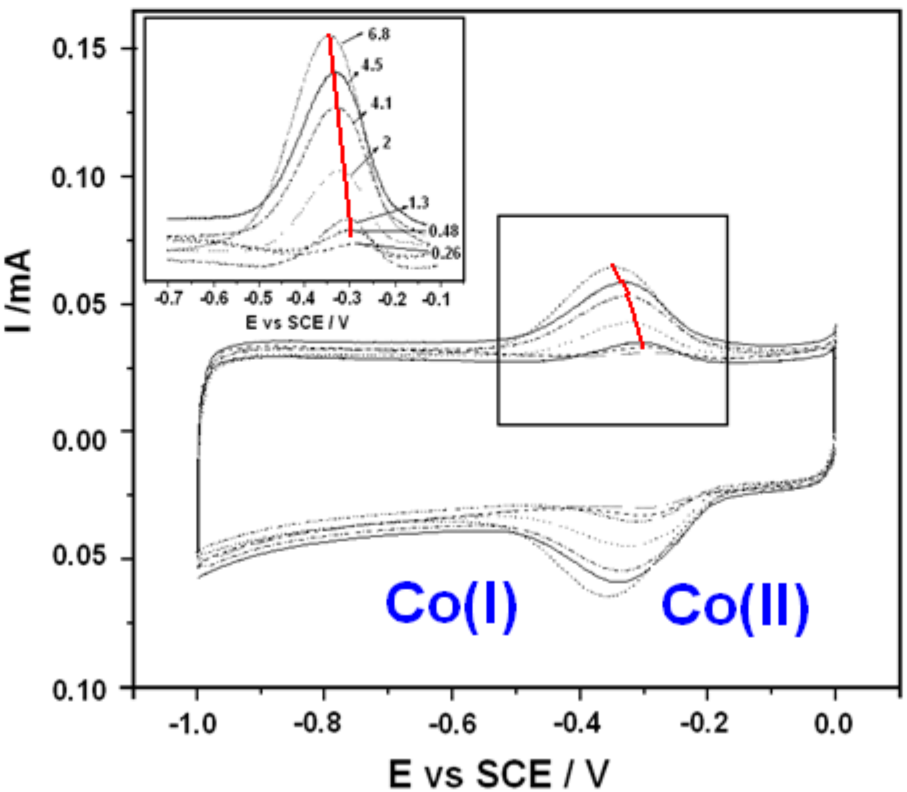


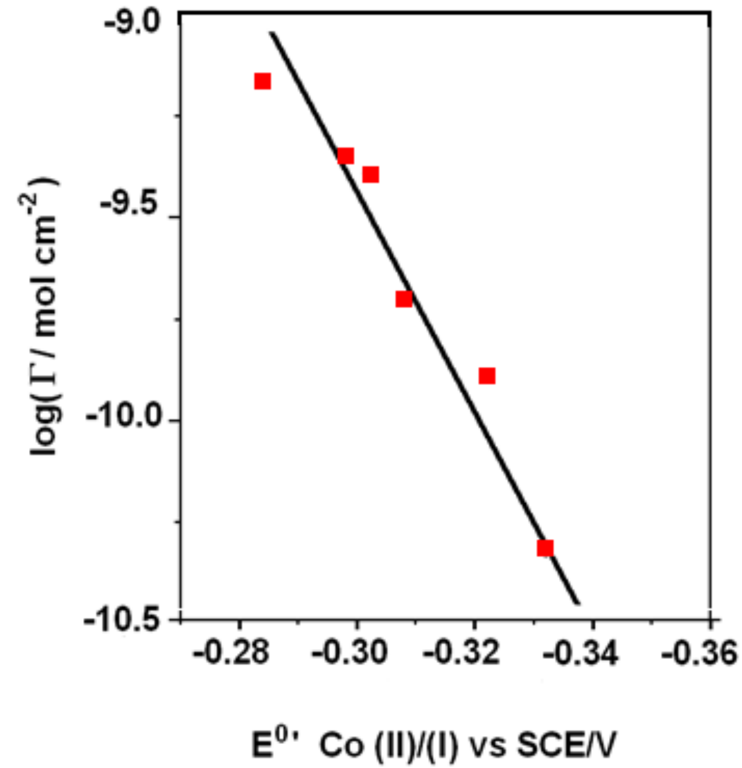
CoPc



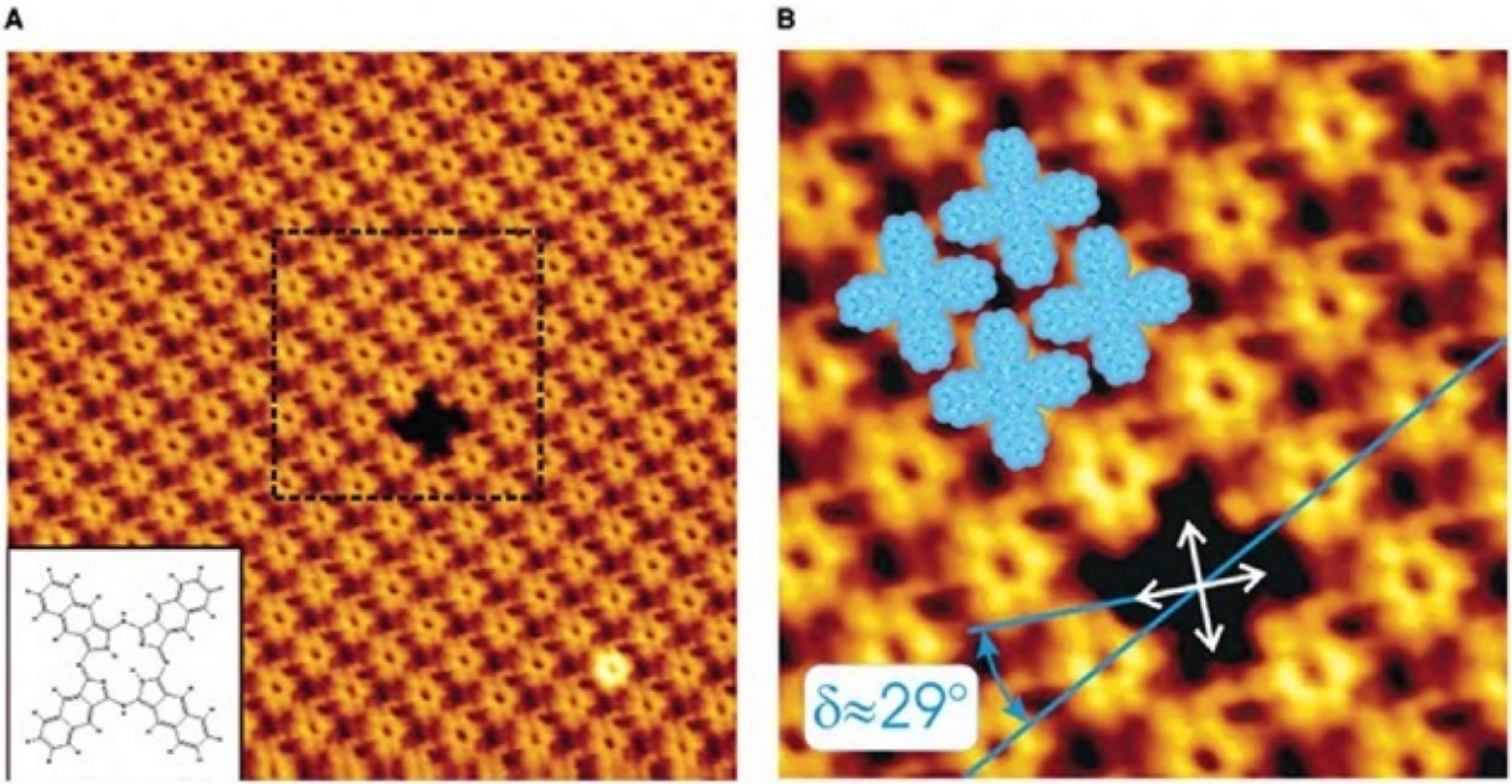
$CoF_{16}Pc$

Co(II)/(I) redox process shifts to more positive potentials with surface concentration.

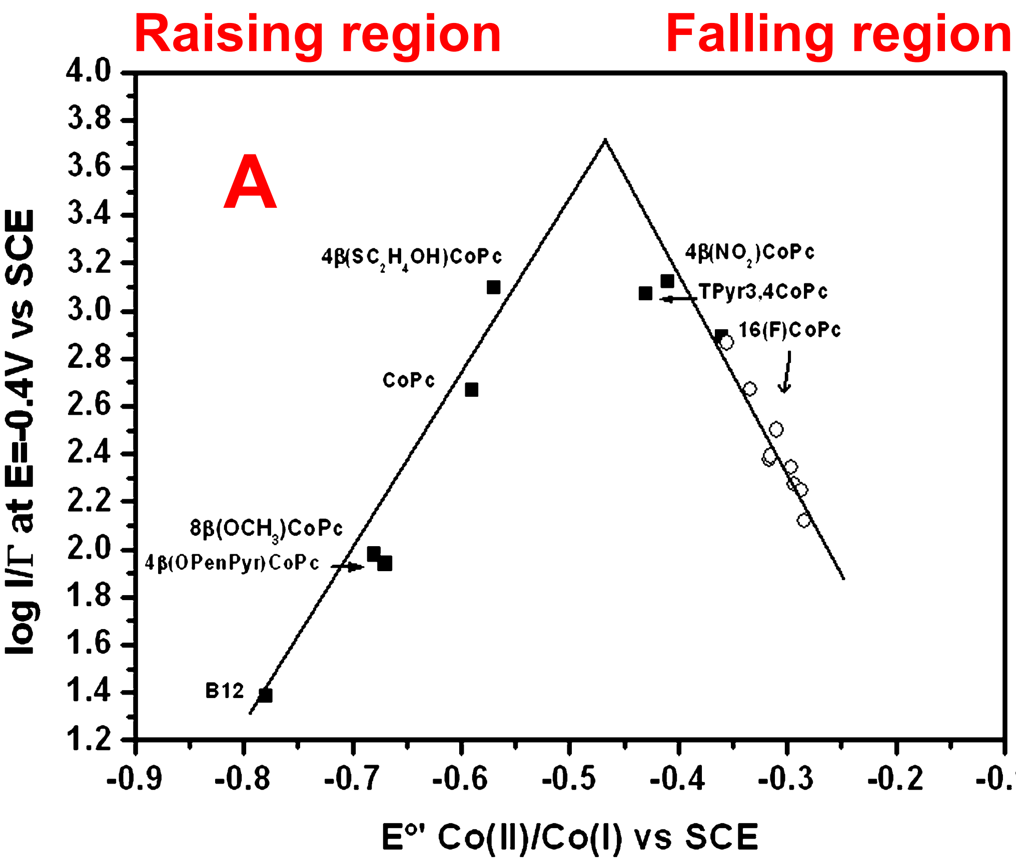


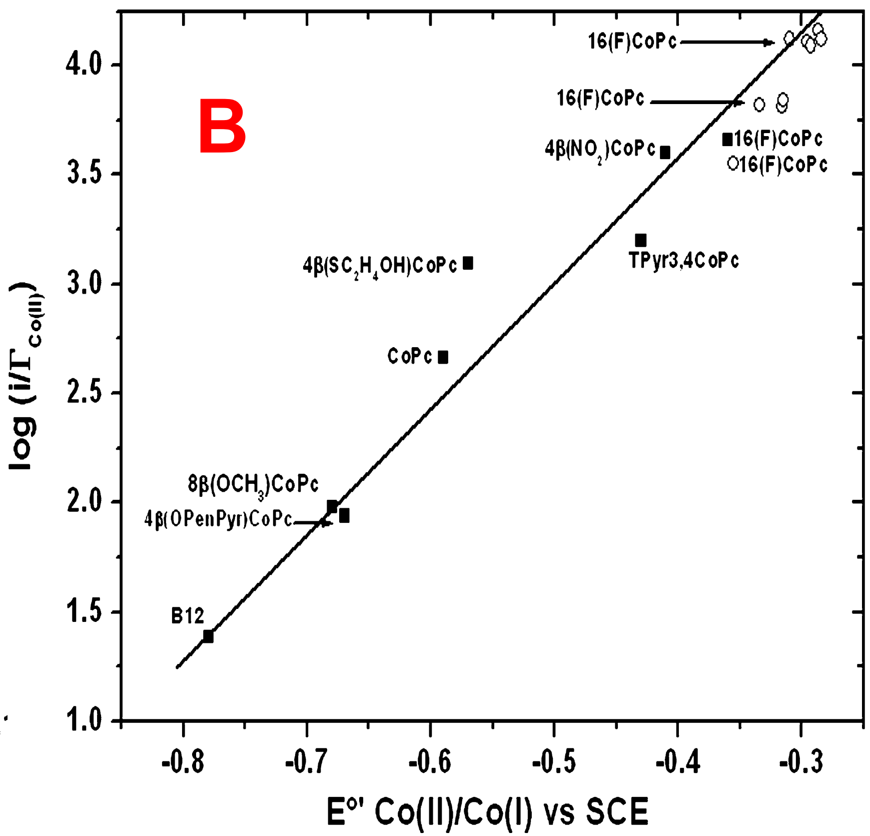


The interaction between neighboring CoF16Pc affects the electron density on the Co center and this is not observed with other phthalocyanines



Volcano vs Linear correlation for N_2H_4 oxidation on CoN4/OPG when the Nernstian surface concentration of $[Co(II)]_{ad}$ is considered





(A) Rates plotted versus E^o and **(B)** rates corrected for the real number of Co(II) surface active sites

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Electrochemistry Communications

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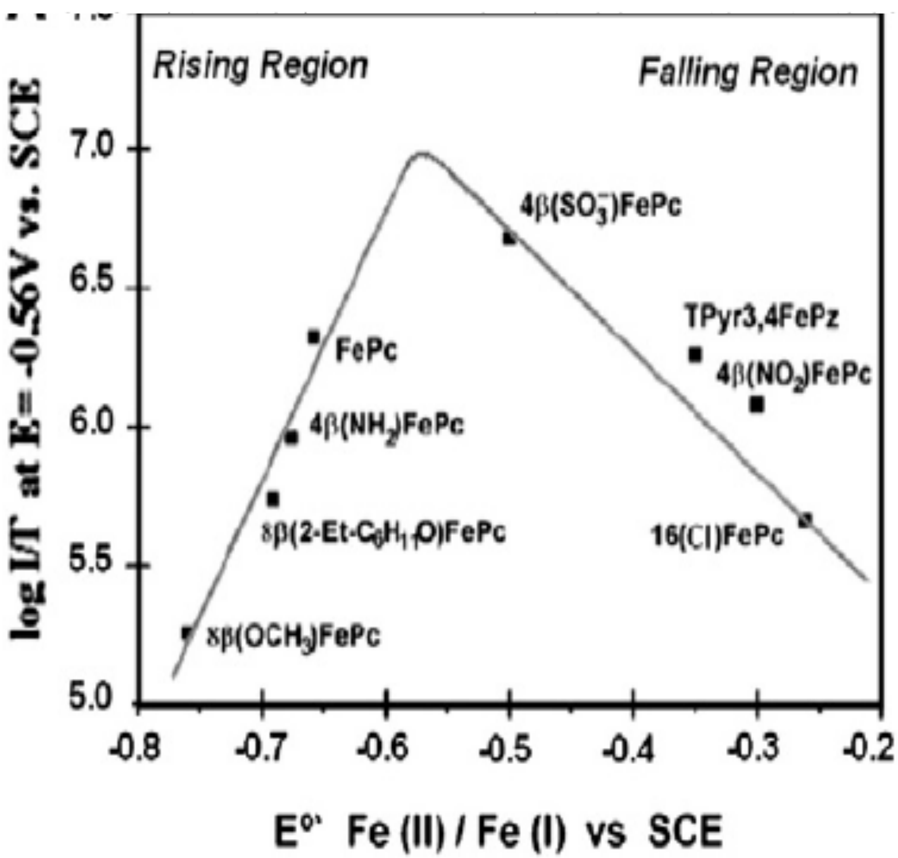
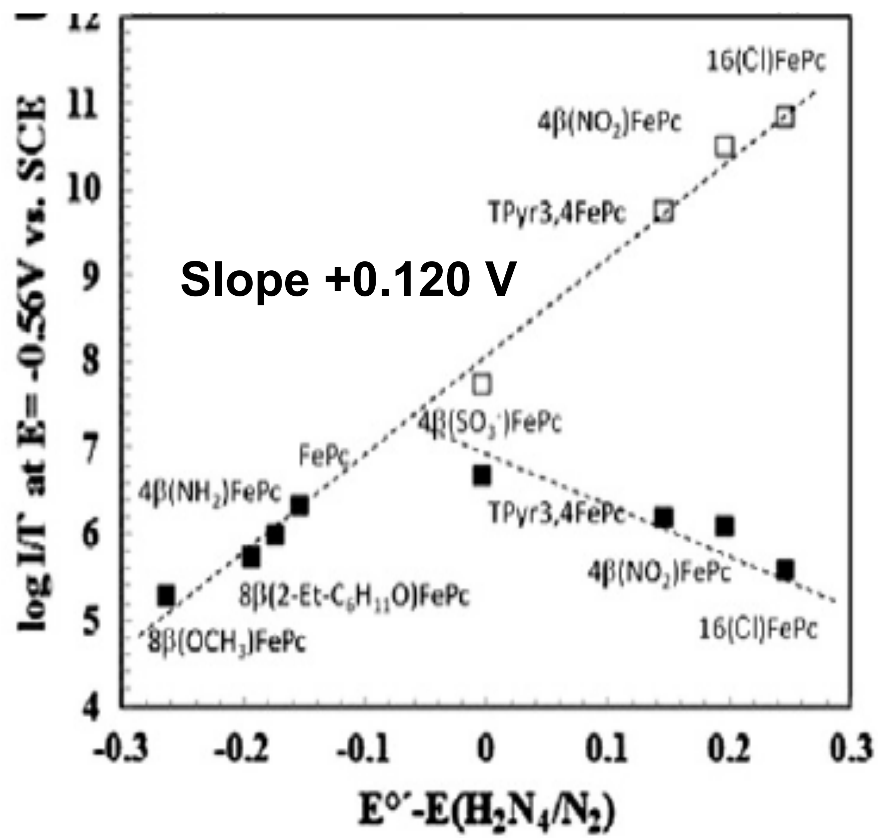
Tuning the Fe(II)/(I) formal potential of the FeN_4 catalysts adsorbed on graphite electrodes to the reversible potential of the reaction for maximum activity: Hydrazine oxidation

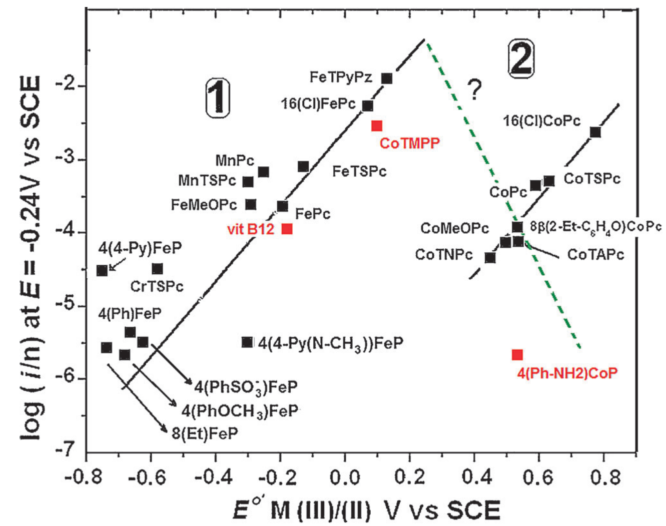
Francisco Javier Recio [a], Paulina Cañete [a], Federico Tasca [a], Cristian Linares-Flores [b], José Heráclito Zagal [a,*]





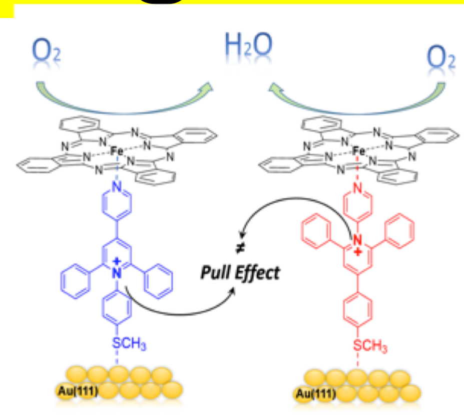
Conclusions

- The M(III)/(II) redox potential
- Is an experimental reactivity descriptor.
- The redox potential needs to be “tuned” to obtain the highest catalytic activity and this is true for many reactions
- The donor-acceptor intermolecular hardness predicts reactivity trends..
- Interesting similarities between volcano correlations for MN4 catalysys and those for pure metals.

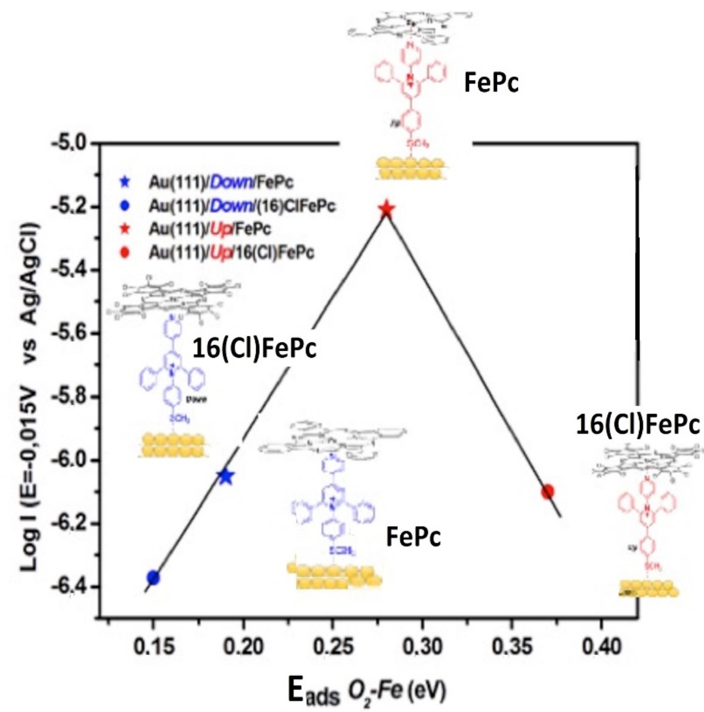


Conclusions Axial ligand

- The maximum in the volcano
- correlation is non-Sabatier.
- For ORR and N_2H_4 oxidation
- Enhancement in activity by
- Axila ligand might be due to
- A shift of M(III)/(II) redox pot.

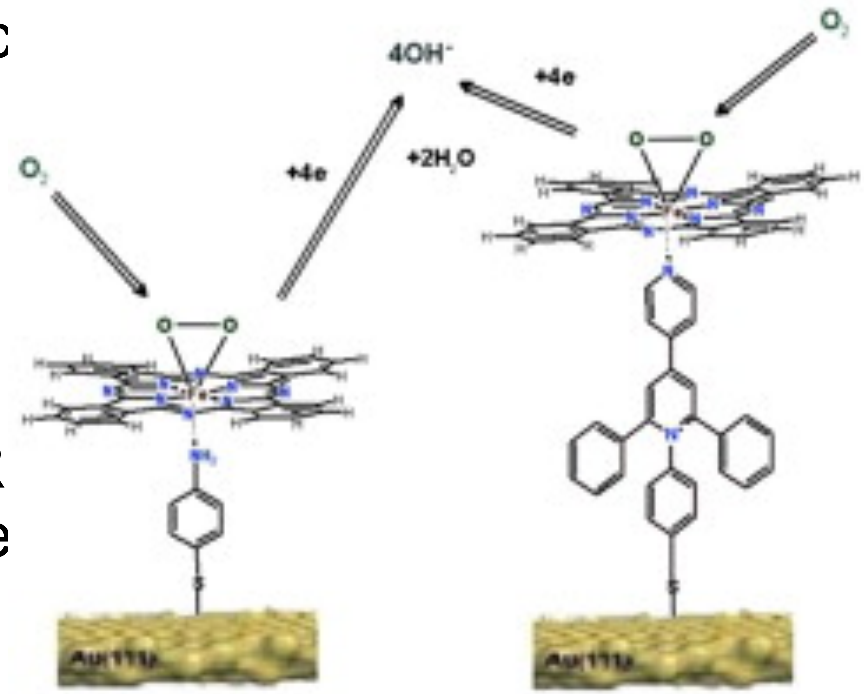


- The falling side of the volcano **cannot be attributed to high surface coverage** of adsorbed intermediates but to the lack of active sites in the **M(II)** active state.



Conclusions

- There is a substantial enhancement in the catalytic activity of both FePc and CoPc complexes for ORR when linked to a Au(111) surface via pre-formed SAM of aromatic thiols.
- Both complexes retain their selectivity to catalyze the ORR i.e FePc via 4-electrons to give water whereas CoPc only promotes the ORR via 2-electrons to peroxide



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Fondo Nacional de Desarrollo Científico y Tecnológico

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Fundacion *Copec*

- **THANK YOU VERY MUCH FOR YOUR ATTENTION!**

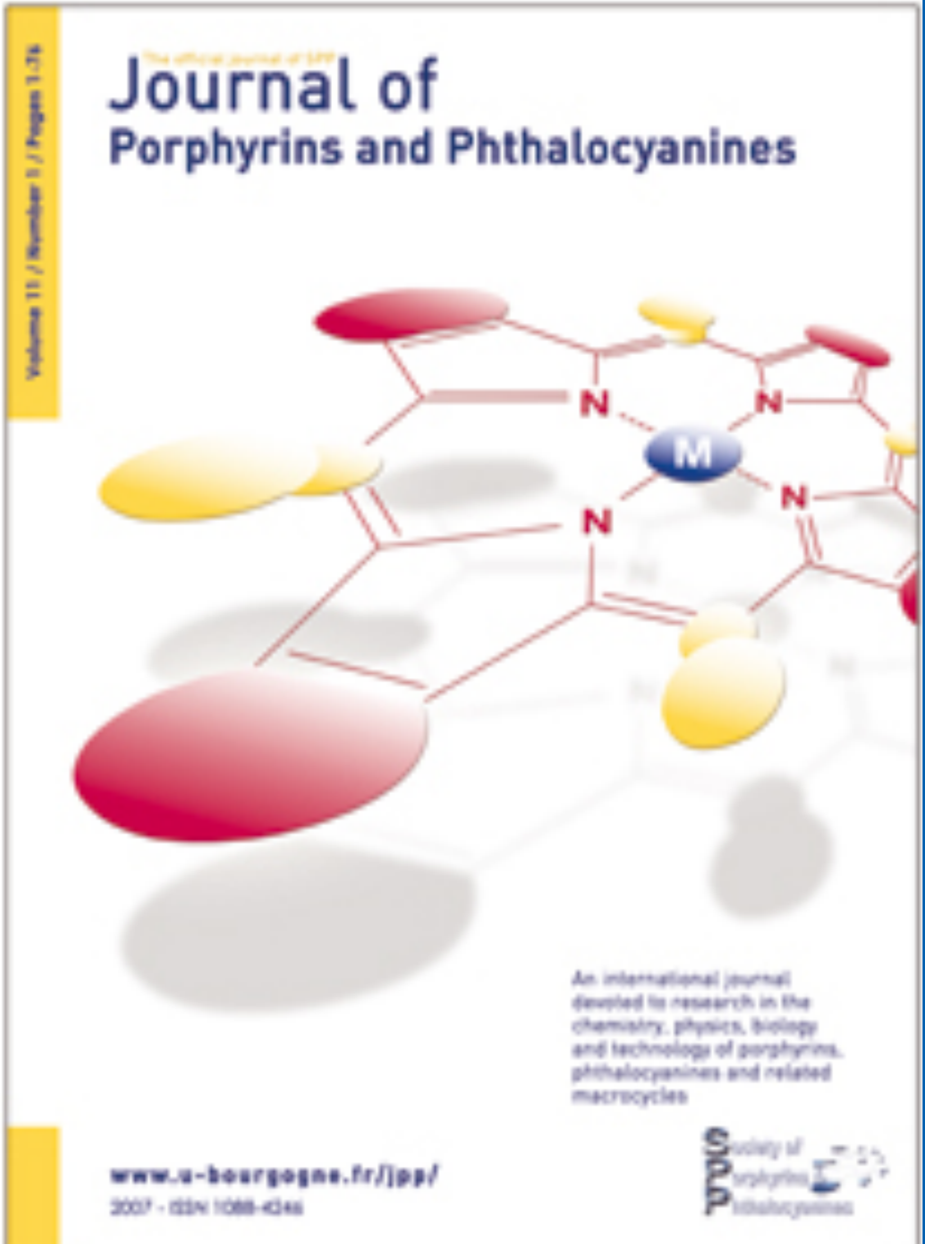
Simplified Mechanism for ORR catalyzed by adsorbed metal macrocyclics in alkaline media

$[M(III)OH]_{ad}$ +e ⇆ $[M(II)]_{ad}$ + OH^- fast (1)

$[M(II)]_{ad}$ + O_2 + e → $[M(III)\ O_2^-]_{ad}$ **r.d.s.** (2)

$[M(III)\ O_2^-]_{ad}$ + e → prods. + $[M(II)]_{ad}$ (3) rds

Step 2 is related to ΔG°_{ad} of O_2 Binding to M(II) active sites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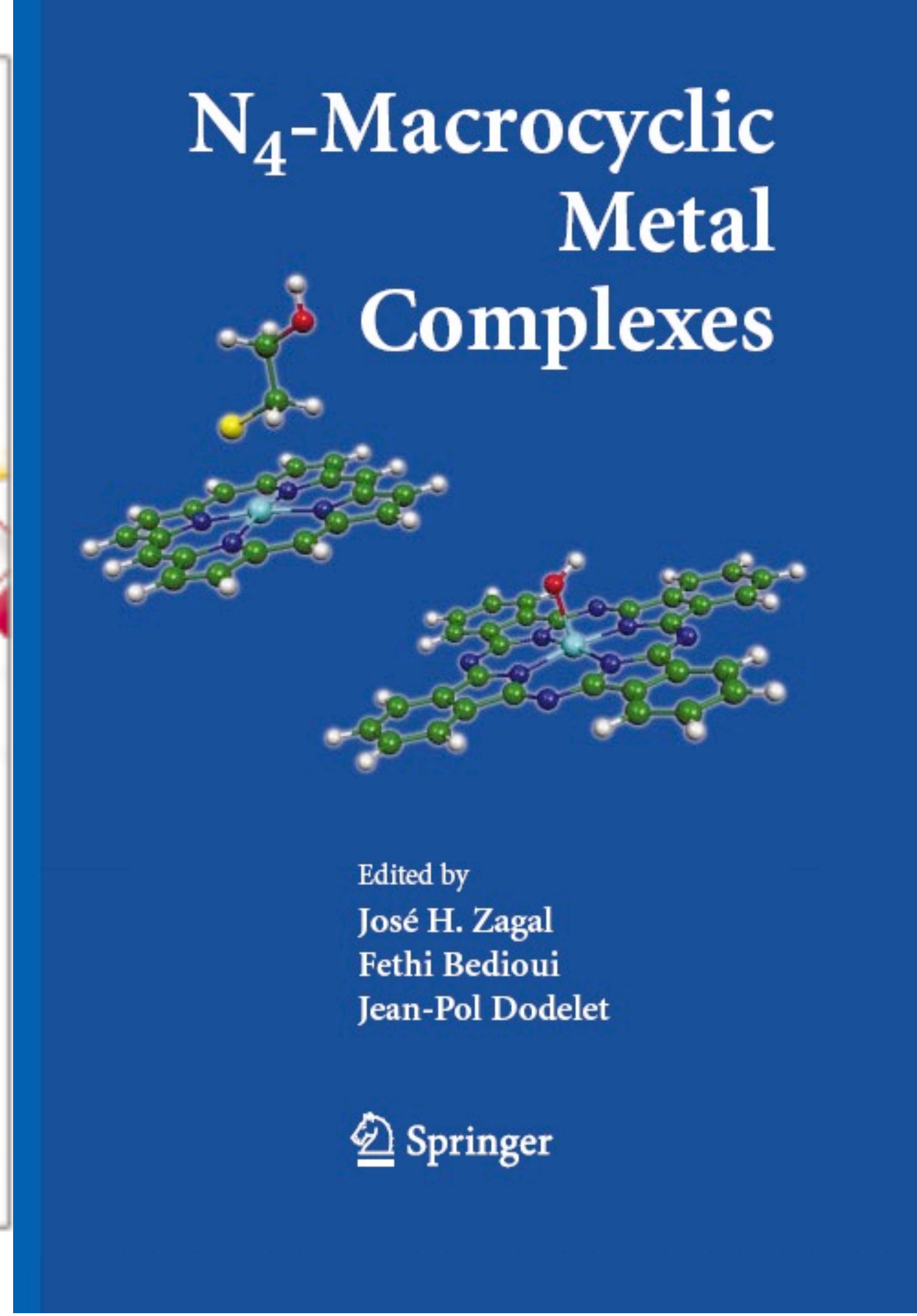
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Complexes
Edited by
José H. Zagal
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