Supplementary Material (ESI) for Faraday Discussions
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Supporting Information

Proton-coupled electron transfers in biomimetic water bound metal complexes. The electrochemical approach.

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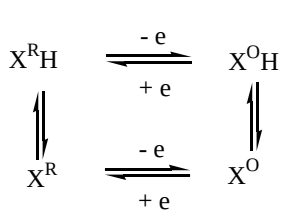
A. Criteria for Proton transfer at equilibrium

Square scheme mechanism:



Scheme S1.

1**. PET pathway**

We consider a situation where $pK_{X^RH} > 14$

We assume that at each *pH* there is a buffer which pKa is $pH = pK_{a,Z}$ and thus $K_{PT}^{PET} = \frac{k_p^{ap}}{k_{-p}^{ap}} = 10^{pH - pK_{X^RH}} < 1$

$$X^RH \underset{k_{-p}^{ap}}{\overset{k_p^{ap}}{\rightleftharpoons}} X^R$$

The zone diagram [1] (figure S1) depends upon two parameters : $K_{PT}^{PET} = 10^{pH - pK_{X^RH}}$ and $\lambda = \frac{RT}{F}\frac{\left(k_p^{ap} + k_{-p}^{ap}\right)[Z]}{v} \simeq \frac{RT}{F}\frac{k_{dif}[Z]}{v}$ It can be seen on this diagram that as soon as $\log\lambda > 2$, the boundary between DE and KE zone is given by $\log K_{PT}^{PET} = 0.75 - 0.5\log\lambda$.

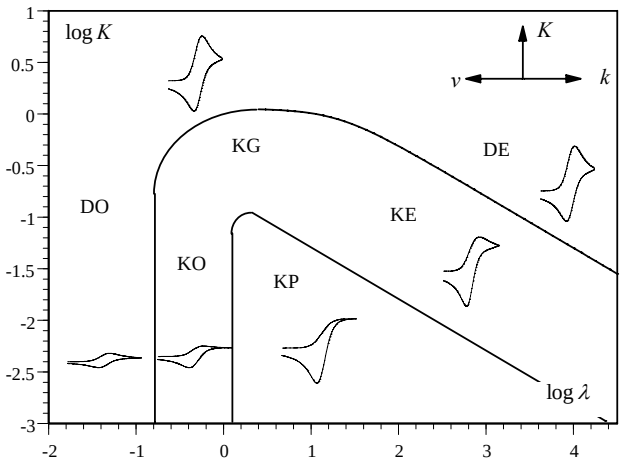


Figure S1.

2. EPT pathway

We consider a situation where $pK_{X^OH} < 0$.

We assume that at each *pH* there is a buffer which *pKa* is $pH = pK_{a,Z}$ and thus $K_{PT}^{EPT} = \frac{k_p^{ap}}{k_{-p}^{ap}} = 10^{pH - pK_{X^OH}} < 1$

$$X^OH \underset{k_{-p}^{ap}}{\overset{k_p^{ap}}{\rightleftharpoons}} X^O$$

The zone diagram [2] (figure S2) depends upon two parameters : $K_{PT}^{EPT} = 10^{pH - pK_{X^OH}}$ and $\lambda = \frac{RT}{F}\frac{\left(k_p^{ap} + k_{-p}^{ap}\right)[Z]}{v} \simeq \frac{RT}{F}\frac{k_{dif}[Z]}{v}$ It can be seen on this diagram that as soon as $\log\lambda > 1.5$, the boundary between DE and KE zone is given by $\log K_{PT}^{EPT} = -0.75 - 0.5\log\lambda$.

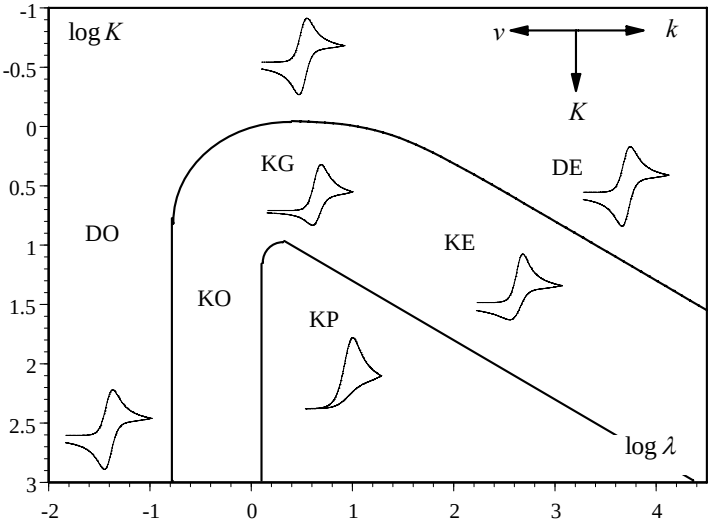


Figure S2.

B. Behavior at pH < 6: UV-vis experiments

At low pH characteristic bands of the complex (250 nm and 288 nm) disappear at the expense of a new band at 274 nm showing a modification of the complex. Bands at 274 nm and 288 nm have been identified as characteristics of phenol and phenolate respectively by comparison of free phenol and phenolate in aqueous solution.

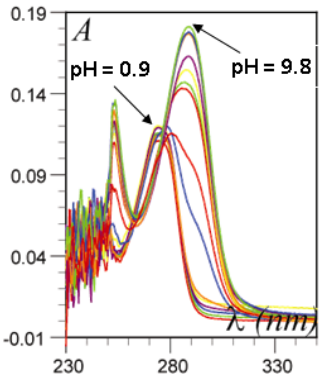


Figure S3. UV-vis spectra for $[Mn^{II}LNH(H_2O)]^{2+}$ (c=3.10^{-5} M) in aqueous media (cuve length= 1cm)

pH is ajusted by small addition of concentrated HBF_4 or concentrated NaOH.

pH = 0.9, 1.5, 2.1, 3.1, 4, 4.9, 5.3, 5.8, 6.3, 7.3, 6.1, 7.5, 8.1, 8.9, 9.8.

C. Cyclic voltammograms at various scan rates

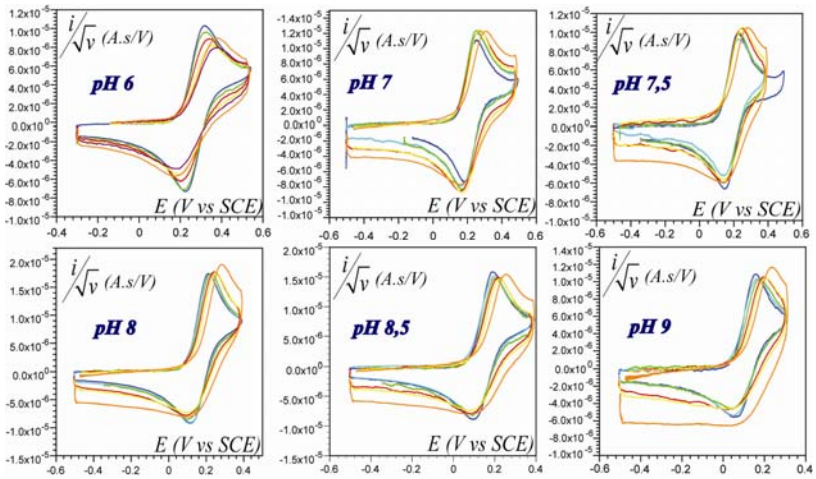


Figure S4. Voltammograms for $[Mn^{II}LNH(H_2O)]^{2+}$ oxidation in MES, HEPES et TABS 0.1 M buffers at various scan rates and pH. Glassy carbon electrode (1mm) , under argon. (dark blue) : 0.2 V/s, (blue) : 0.5 V/s, (green) : 1 V/s, (red) : 5 V/s (yellow) : 10 V/s, (magenta) : 20 V/s, (orange): 50 V/s

D. References

1. Savéant, J-M. In *Elements of Molecular and Biomolecular Electrochemistry*, Wiley-Interscience; Hoboken: 2006 p 93.
2. Savéant, J-M., Vianelo, E. *Electrochim. Acta*, **1967**, *12*, 629.