Electron Transfer at the Liquid-Liquid Interface, between Lu(III) Bisphthalocyanines in a Solvent and Fe(III)/Fe(II) in Water. Studies at a Micro-Interface and at Solvent Film Electrodes.

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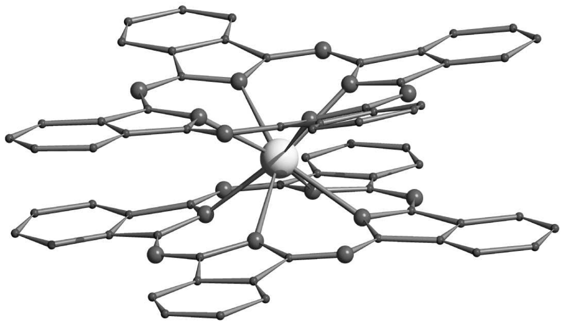

Figure 1 : Lu[Pc]$_2$

The lanthanide bisphthalocyanines present many reversible one-electron redox systems, observable in nonaqueous media ; the potentials of the first oxidation and reduction processes of the molecule are separated by 0.4 V. These potentials can be modified through the substitution of electron-donating or –withdrawing groups on the peripheral benzene rings of the macrocycles. The lutetium complexes (Figure 1) constitute a family of molecules having adjustable redox properties, interesting for many studies and particularly for the investigation of the electron transfer through the liquid-liquid interface (Figure 2); the bisphthalocyanines are insoluble in aqueous phases.

The following reversible interfacial electron exchange as been studied, with $Fe^{III}(CN)_6^{3-}/Fe^{II}(CN)_6^{4-}$ in water and various lutetium bisphthalocyanines in a solvent :

$$Fe(CN)_6{}^{3-}{}_W + LuPc_{2\,S} \leftrightarrow Fe(CN)_6{}^{4-}{}_W + LuPc_2{}^{+}{}_S$$

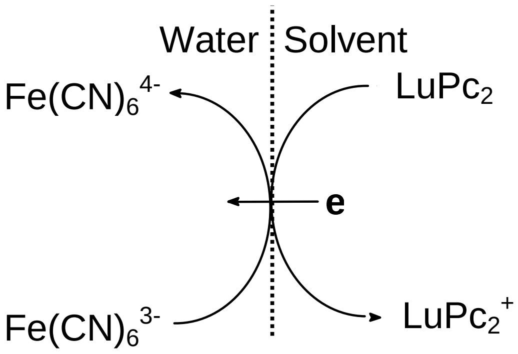

Figure 2 : Electron transfer at the liquid-liquid interface.

Thermodynamic parameters, such as the potential of the interfacial reaction, that is the Gibbs energy, have been measured by voltammetry, as well as kinetics (α, the electron transfer coefficient and k_{obs}, the apparent rate constant). This has been examined, using an ultramicro liquid-liquid interface (Figure 3). Similarly to what is observed with solid UME's, voltammetry can be performed under two diffusion regimes, depending on the scan rate.

From the present study, it is clear that some molecular factors play an important role in these interfacial redox reactions. For example, the substitution by polyether chains on the periphery of the macrocyclic ligands slows down the electron exchange rate.

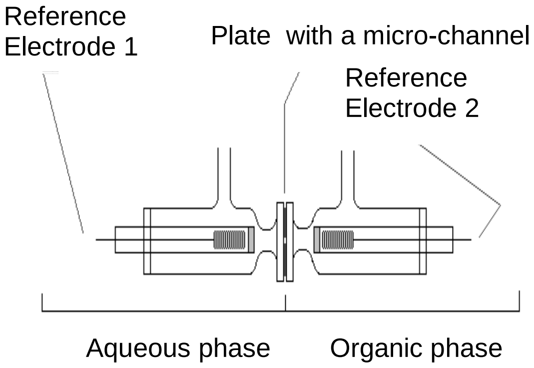

Figure 3 : The liquid-liquid cell

The electron transfer is also observable when the compounds are deposited at the surface of an electrode, in contact with an aqueous solution, as Langmuir-Blodgett films or in thin layers of solutions in organic solvents. In such cases however, the ions of the aqueous medium play a role in the electron exchange at the modified electrode, because ionic species have to cross the interface to counterbalance the charges produced by the oxidation or reduction of Lu[Pc]$_2$ at the surface of the electrode. The electron transfer at the modified electrode is dependent on the ion exchange at the interface between the aqueous phase and the solvent layer, or the L-B film (Figure 4).

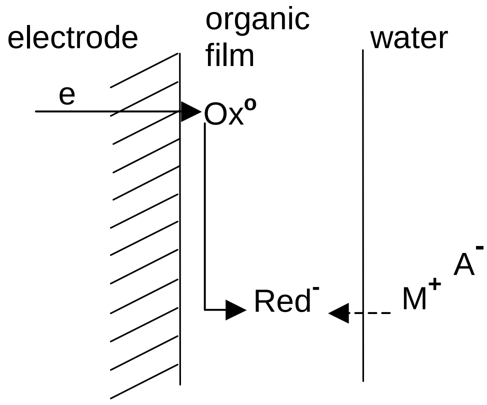

Figure 4 : The organic film electrode.

Lu(III)bisphthalocyanines are eminently suitable for such studies because the molecules can be reduced as well as oxidized, so that the transfer of anions as well as the exchange of cations can be examined at the interface between the aqueous phase and the organic film.