

## *Supporting Information*

### **Proton-Coupled Intervalence Charge Transfer. Concerted Processes.**

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## 1. Experimental Details

**Chemicals.** Acetonitrile (Fluka, > 99.5 %, stored on molecular sieves), the supporting electrolyte  $\text{NBu}_4\text{PF}_6$  (Fluka, puriss.),  $\text{NEt}_3$  (Prolabo, HPLC grade),  $\text{HNEt}_3\text{Cl}$  (Aldrich, 98%), pyrrolidine (Aldrich, 99%),  $\text{HClO}_4$  (Prolabo, Normapur), methanol and  $\text{CD}_3\text{OD}$  (Eurisco-top, 100%) were used as received.

**Cyclic voltammetry.** The working electrode was a 3-mm diameter glassy carbon (GC) electrode disk (Tokai) carefully polished and ultrasonically rinsed in absolute ethanol before use. The counter-electrode was a platinum wire and the reference electrode an aqueous SCE electrode. All experiments were carried out under argon at  $23^\circ\text{C}$ , the double-wall jacketed cell being thermostated by circulation of water. Cyclic voltammograms were obtained by use of a Metrohm AUTOLAB instrument.

**UV-vis.** Spectra were recorded on a Specord S600 spectrophotometer (Analytik Jena) at room temperature with a 0.5 cm quartz cuvette.

## 2. Construction of the Pourbaix diagram (fig 1S):

CV recorded in absence of base allows the determination of the  $\text{Fe}^{\text{III}}\text{Fe}^{\text{III}}\text{LH}/\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}\text{LH}$  and  $\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}\text{LH}/\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}\text{LH}$  standard potential thus giving rise to horizontal lines **1** and **2** in the Pourbaix diagram.

CV recorded in large excess of base ( $\text{NEt}_3$ ) allows the determination of the  $\text{Fe}^{\text{III}}\text{Fe}^{\text{III}}\text{L}/\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}\text{L}$  and estimation of the  $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}\text{L}/\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}\text{L}$  standard potential thus giving rise to horizontal lines **3** and **4** in the Pourbaix diagram.

UV-vis determination of the  $pK_a$  of the  $\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}\text{LH}/\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}\text{L}$  gives rise to the vertical line **5** joining lines 2 and 3.

Diagonal lines **6** and **7** joining lines **1** and **3** and **2** and **4** respectively corresponds to  $1 e^- - 1 H^+$  processes thus corresponding to a  $RT/F \ln(10)$  slope. Drawing those lines from **2-5** and **3-5** corners allows the determination of both  $pK_{\text{Fe}^{\text{III}}\text{Fe}^{\text{III}}\text{LH}} = 9.9$  and  $pK_{\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}\text{LH}} \square 27.9$ .

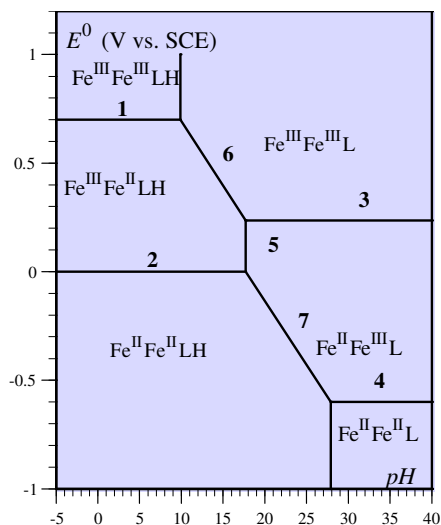


Fig. 1S. Pourbaix diagram.

## 3. Data with pyrrolidine as a base:

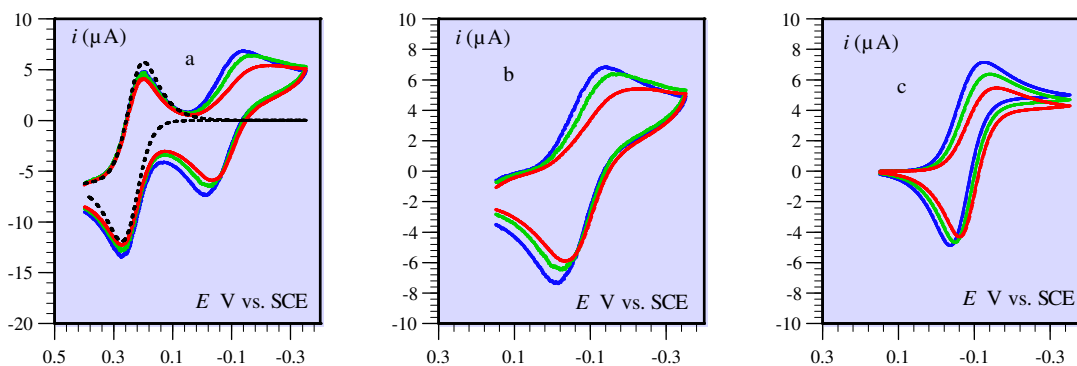


Fig. 2S. Cyclic voltammetry of 1 mM  $\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}\text{LH}$  complex after a 10 s pre-electrolysis at 0.4 V in presence of 2 mM  $^+\text{HB}$  (B = pyrrolidine;  $^+\text{HB}$  is obtained by mixing  $\text{HClO}_4$  and an equal amount of B).  $v = 0.05 \text{ V/s}$ . a: experiments (except dotted black line: first wave simulation), b: second wave after subtraction of the first wave. c: simulation with  $k_f = 10^4 \text{ M}^{-1}\text{s}^{-1}$ . Blue:  $[\text{B}] = 2 \text{ mM}$ ; Green:  $[\text{B}] = 3 \text{ mM}$ ; Red:  $[\text{B}] = 5 \text{ mM}$ .

#### 4. Additional data for KIE :

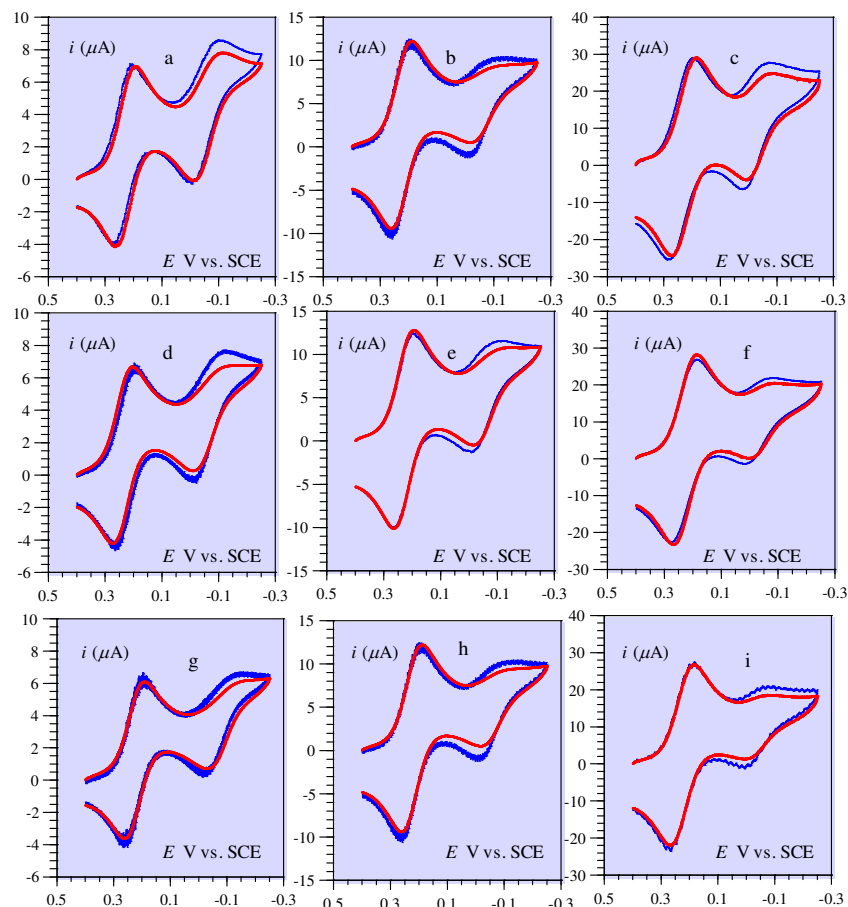


Fig. 3S. Cyclic voltammetry of 0.65 mM  $\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}\text{LH}$  complex after a 10 s pre-electrolysis at 0.4 V in presence of 2 mM  $^+\text{HNEt}_3$ . Blue: in presence of 1% MeOH. Red: in presence of 1% MeOD. a, b, c:  $[\text{NEt}_3] = 4$  mM; d, e, f:  $[\text{NEt}_3] = 8$  mM; g, h, i:  $[\text{NEt}_3] = 12$  mM. a, d, g:  $v = 0.05$  V/s. b, e, h:  $v = 0.2$  V/s. c, f, i:  $v = 1$  V/s. Current at the starting potential was set to zero for the sake of an easier comparison.

#### 5. Determination of the equilibrium constant $K$ in deuterated medium:

The constant  $K$  in deuterated medium is obtained from the variation of its UV-Vis spectrum upon addition of  $\text{NEt}_3$  (figure 4S) in presence

of 1% MeOD using the following equation: 
$$\frac{A - A_{n=0}}{A_{n \rightarrow \infty} - A_{n=0}} = \left[ n + 1 - \sqrt{(n+1)^2 - 4n(1-K)} \right] / [2(1-K)]$$

where  $n$  is the number of triethylamine equivalents.  $K$  is found equal to 0.1 as in the case of hydrogenated medium.

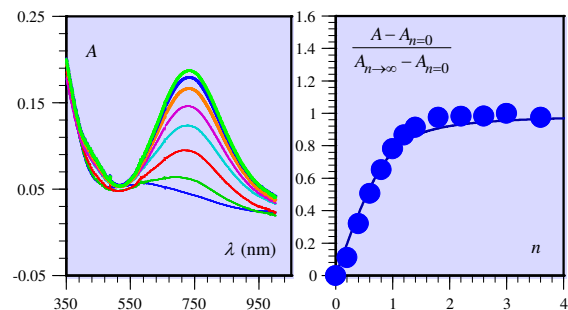
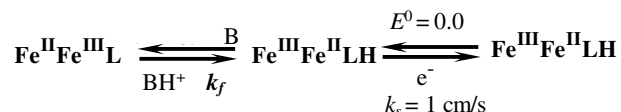


Fig 4S. left: Increase of the UV-Vis band of the  $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}\text{L}$  complex upon addition of  $\text{NEt}_3$  in presence of 1% MeOD. Right: variation of the normalized peak absorbance with the number of  $\text{NEt}_3$  equivalents,  $n$ .

## 6. Simulations

The second waves of the voltammograms shown in figures 3, 2S and 5S have been simulated according to the CE mechanism depicted in the scheme below. The rate constant  $k_f$  was used as the only adjustable variable in the simulation. Initial concentrations of the various species were calculated according to the introduced concentrations of complex and the equilibrium constant. The diffusion coefficients were taken as equal  $10^{-5} \text{ cm}^2\text{s}^{-1}$  and  $5 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$  for of all complexes on the one hand and B and  ${}^+\text{HB}$  on the other. Finite diffusion with a convection layer of 0.01 cm was considered to take into account natural convection in order to get a correct description of the pre-electrolysis procedure (finite diffusion procedure is an option available in Digilich CV-properties).



Below, simulations are compared to experimental data (figure 5S) and  $k_f$  were estimated for both hydrogenated and deuterated media. The second waves observed in figures 3, 2S and 5S are extracted from the whole voltammograms through subtraction of the simulated first wave. Simulation of this first wave was obtained from the reaction shown below starting with  $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}\text{L}$  species. The diffusion coefficients were taken as equal  $10^{-5} \text{ cm}^2\text{s}^{-1}$ . Finite diffusion with a convection layer of 0.01 cm was considered to take into account natural convection. Simulation of the 10 seconds pre-electrolysis at 0.4 V was obtained by performing a first scan (at 0.01 V/s) between 0.5 V and 0.4 V. Simulation fits well with the experimental first wave (see figure 3a).

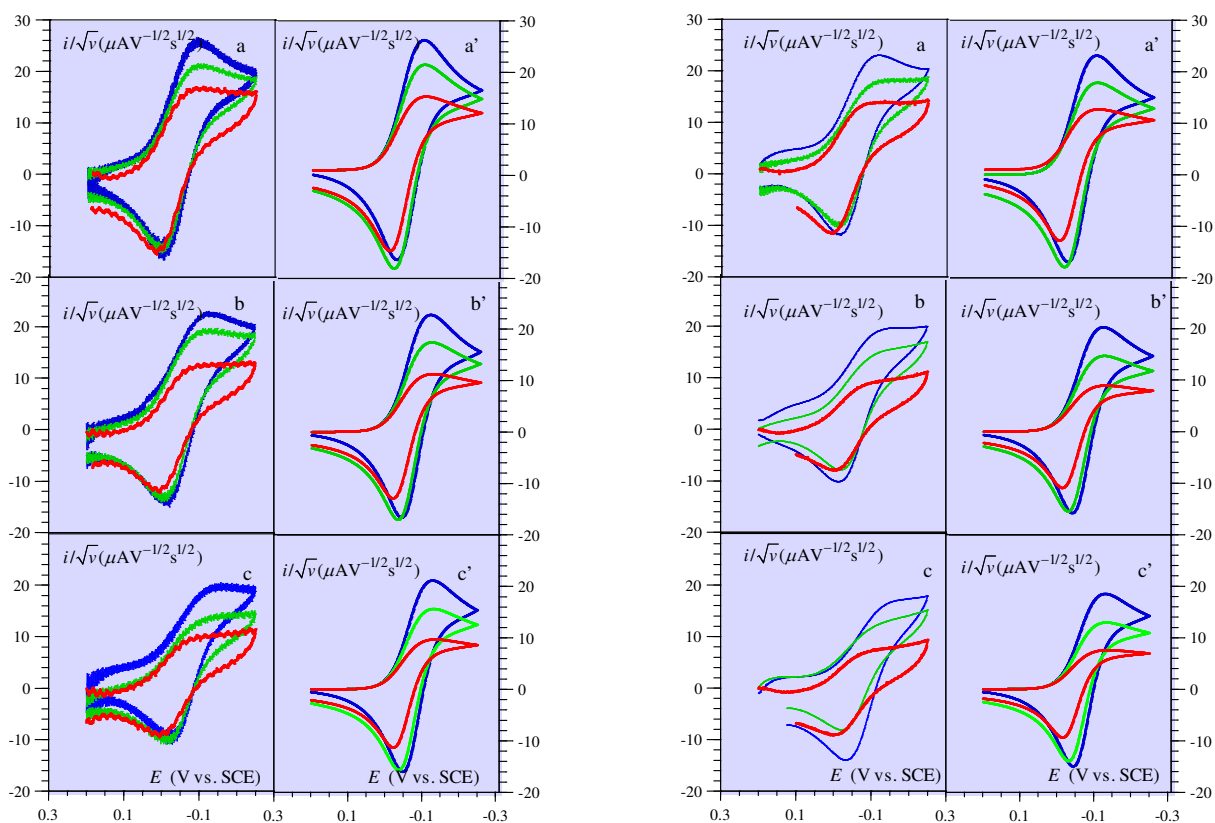
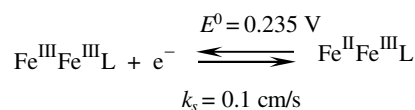


Fig. 5S. Cyclic voltammetry of 0.65 mM  $\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}\text{LH}$  complex in the same conditions as in figure 3 after subtraction of the simulated first wave. Left: in the presence of 1% MeOH; right: in the presence of 1% MeOD. Scan rates (V/s): 0.05 (blue) 0.2 (green) 1 (red).  $[\text{}^+\text{HNEt}_3]=2 \text{ mM}$ . a, a':  $[\text{NEt}_3] = 4 \text{ mM}$ , b, b':  $[\text{NEt}_3] = 8 \text{ mM}$ , b', b':  $[\text{NEt}_3] = 12 \text{ mM}$ . a, b, c: experimental, a', b', c': simulated: left:  $k_f = 3 \cdot 10^4 \text{ M}^{-1}\text{s}^{-1}$ . Right:  $k_f = 1.5 \cdot 10^4 \text{ M}^{-1}\text{s}^{-1}$ .