

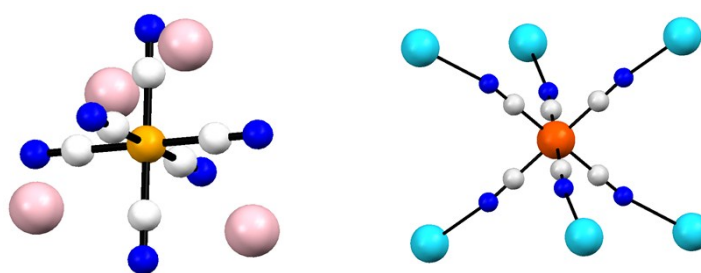
## Supporting information

### SII

#### Cluster design for DFT calculation:

Considering our goal to define the potassium ferrocyanate electronic structure, the most tricky question concerns the influence of potassium and water molecules surrounding the  $\text{Fe}(\text{CN})_6$  octahedron in solid state. Several structural studies are determined by XRD<sup>i,ii,iii</sup> or EXAFS<sup>iv</sup> report various differences for this system (depending on hydration, temperature, syntheses conditions). More in detail, one can see small Oh distortions due to external water molecules and  $\text{K}^+$ . In order to simplify calculations the Oh symmetry has been maintained for calculation. In order to stay in accordance with XRD data potassium cations can be positioned in several geometry. Three different tests was performed; (i) with octahedral  $\text{Fe}(\text{CN})_6$  and in Oh symmetry (no  $\text{K}^+$  and -4 charged system), (ii) octahedral  $\text{Fe}(\text{CN})_6$  and four  $\text{K}^+$  in Td symmetry (neutral system) and (iii) a  $\text{D}_{2h}$  geometry with two  $\text{K}^+$  in front of two cyano ligand and 2 in between the four other cyano (neutral system too). To determine the more accurate geometry, energy of the  $\nu_{\text{CN}}$  vibration has been calculated and compared to experimental value (Aldrich  $\text{K}_4\{\text{Fe}(\text{CN})_6\}$ ,  $4\text{H}_2\text{O}$  :  $\nu_{\text{CN}}=2044\text{ cm}^{-1}$ ).

Finely the  $\text{K}_4\{\text{Fe}(\text{CN})_6\}$  cluster with  $\text{K}^+$  cation in tetraedrical positions (**SI. 1**) selected as a reference structure to the calculate electronic structure due both to a better agreement between calculated distances those measured (**SI 1**) and the more accurate calculated vibrational mode  $\nu_{\text{CN}}=2027\text{ cm}^{-1}$ .



**Figure SI :** a)  $\text{K}_4\text{Fe}(\text{CN})_6$  cluster used for electronic structure calculation.

b) Cluster  $\text{Fe}-(\mu\text{CN})_6\text{-Th}_6\text{-}\delta_x$ . Punctual charges doesn't appears for clarity.

*Orange atoms are for iron, white are carbon, dark blue is nitrogen, pink is potassium and light blue is thorium.*

The punctual charges called  $\delta$  were previously determined by a Mulliken analysis apply to another DFT calculation with a cluster centred on thorium ( $\text{Th}(\text{NC})_6(\text{H}_2\text{O})_3$ ), are  $\delta_{\text{O}} = -0.33$  et  $\delta_{\text{N}} = -0.43$  and are also positioned at the EXAFS's determined position for N and O.

<b>Analyses</b>	<b>d Fe-C (Å)</b>					<b>d C-N (Å)</b>				
DFT (this work)	1.921					1.178				
EXAFS (solution)	1.920					1.180				
EXAFS (solid)	1.920					1.170				
DRX (Cc)	1.909	1.914	1.922	1.926	1.944	1.181	1.164	1.167	1.144	1.098
DRX (C2/c)	1.916	1.917	1.920	1.942		1.162	1.16	1.156	1.100	

Table 1 : Distances obtained by xxxxx compared to experimental one.

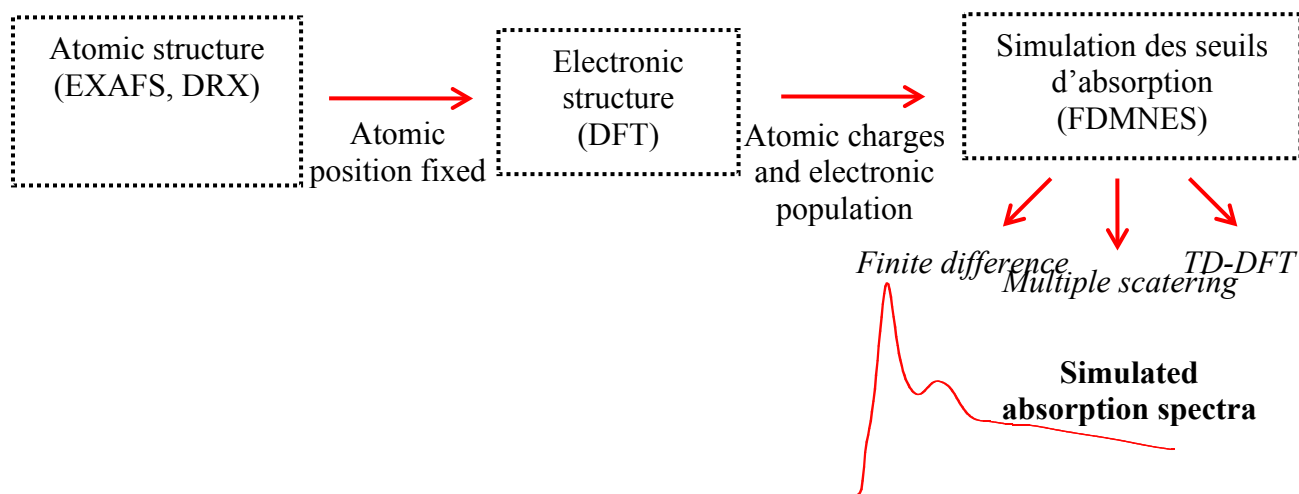
*XANES simulation, methodology and electronic configuration tests*

Figure S2 :Schematic representation of the methodology used for simulation of XANES spectrum

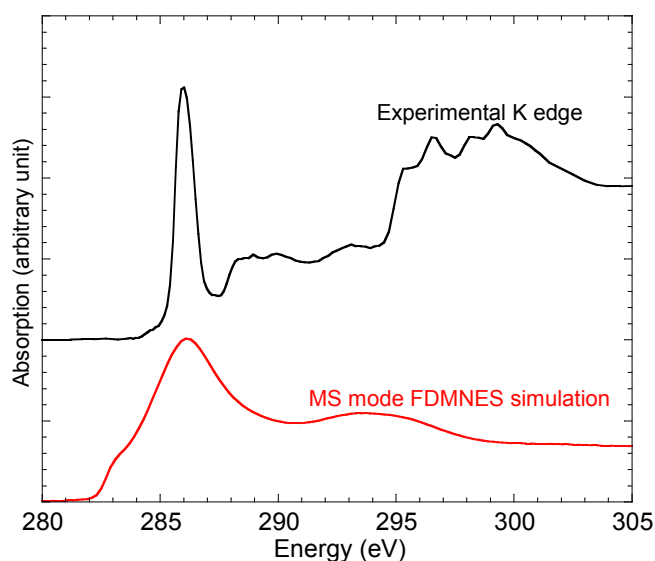


Figure S3 : Simulation with multiple scattering approach at carbon K edge. FDMNES calculation based on the DFT structure.

This simulation clearly shows that the muffin tin approximation is not adapted to light element K edge spectrum because, it is not taking into account the effect strong modification of potentials geometry due to the formation of covalent bonding.

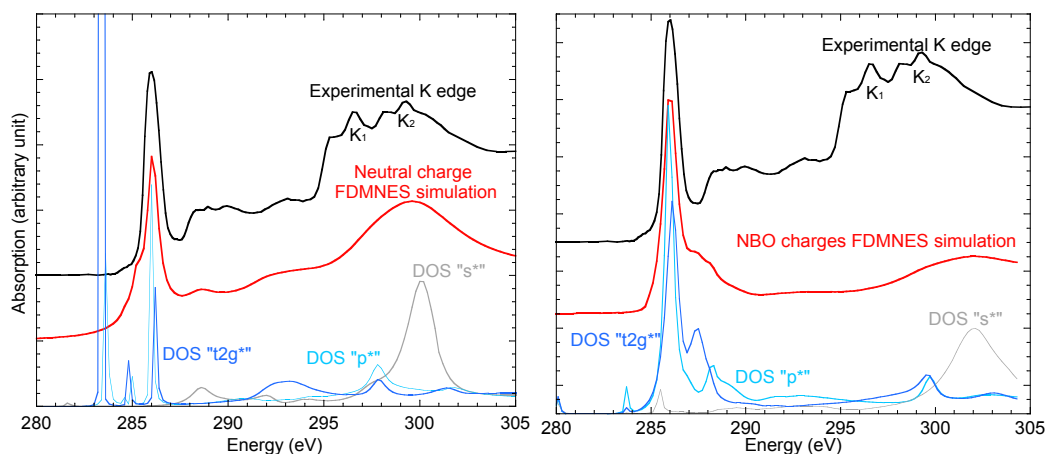


Figure S5 : Simulation with finite difference method approach at carbon K edge. FDMNES calculation based on the DFT structure and NBO analysis charges.

Figure S4 : Simulation with finite difference method approach at carbon K edge. FDMNES calculation based on the DFT structure and neutral atomic charges.

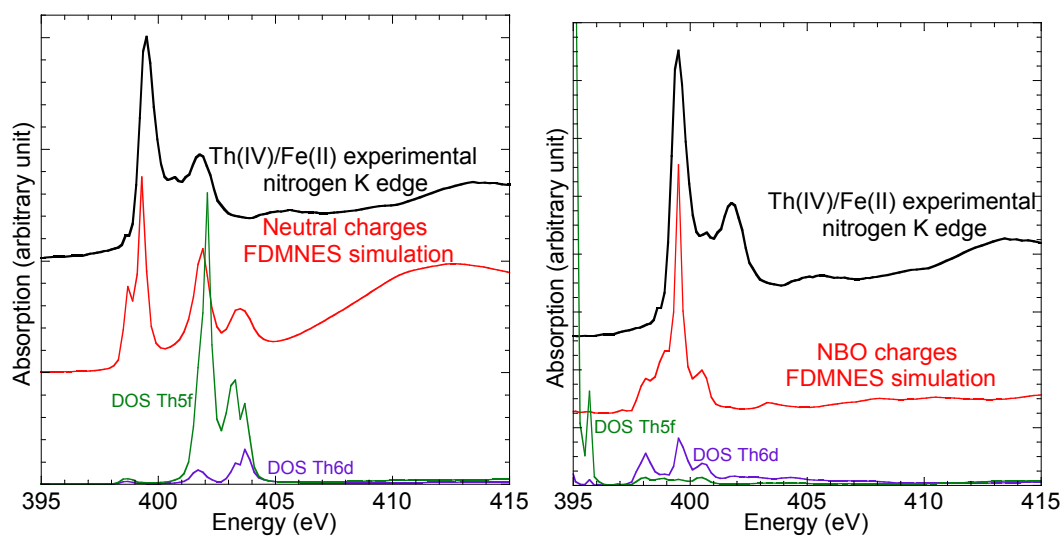
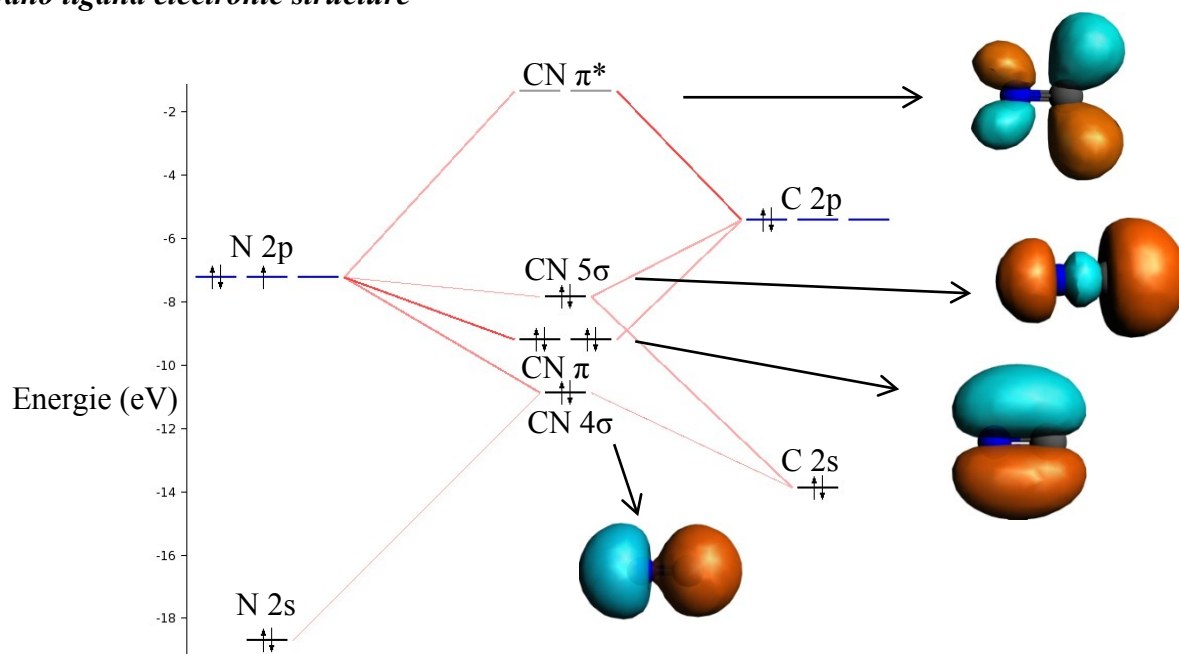


Figure S7 : Simulation with finite difference method approach at carbon K edge for Th(IV)/Fe(II). FDMNES calculation based on the DFT structure and NBO analysis charges.

Figure S6 : Simulation with finite difference method approach at carbon K edge for Th(IV)/Fe(II). FDMNES calculation based on the DFT structure and neutral charges.

### SI3 Cyano ligand electronic structure



FigureS1 : Molecular interaction diagram of cyano ligand ( $\text{CN}^-$ ).

### SI.4 XAS simulation dependece on cyano bridge geometry

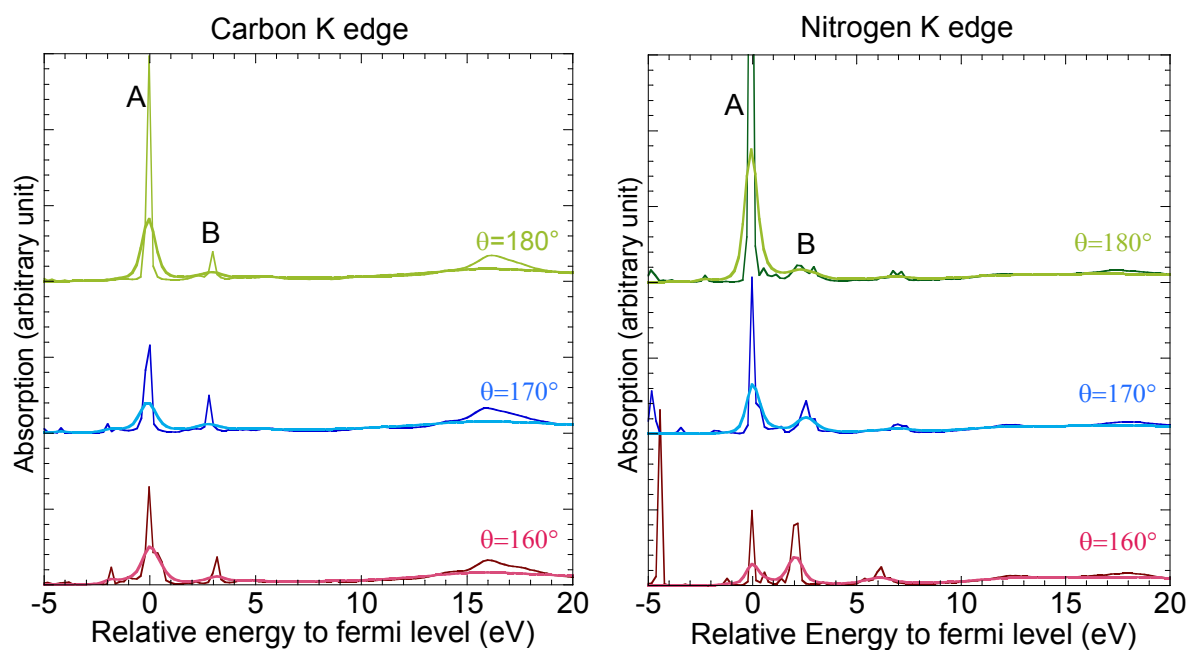


Figure S8 : Simulation with finite difference method approach at carbon K edge and nitrogen K edge dependent of the cyano bridge linearity.

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<sup>i</sup> A = Figgis & al. *Aust.J.Chem.* **1978**.

<sup>ii</sup> B = Murioka & al. *J.Phys.Soc.Jpn.***1985**.

<sup>iii</sup> M.J.Willians; R.E.Wasylinshen; R.McDonald. *Inorg.Chem.* **2009**,Vol xx,No XX.

<sup>iv</sup> Hayakawa & al. *JACS.* **2004**.