

Supplementary Materials

Electronic Supplementary Information for An Iron(III) Complex with Pincer Ligand – Catalytic Water Oxidation through Controllable Ligand Exchange'

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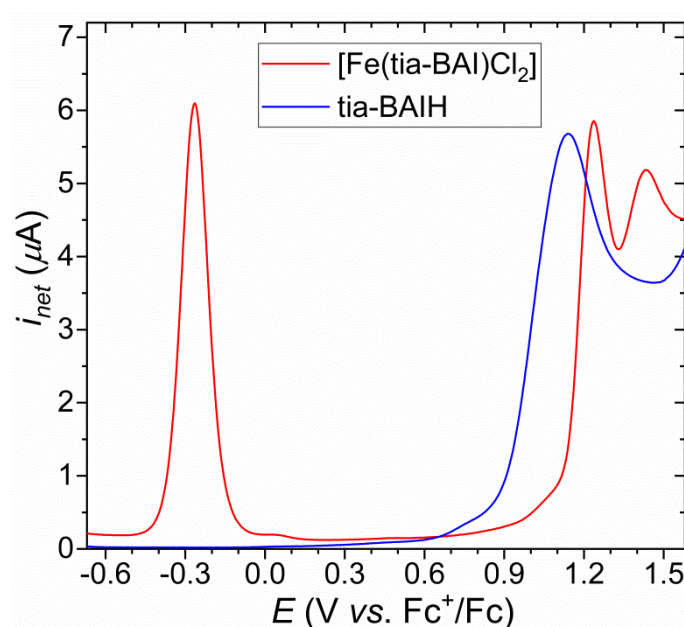


Figure 1. SWVs of the tia-BAIH ligand and the $[\text{Fe}^{\text{III}}\text{Cl}_2(\text{tia-BAI})]$ complex ($c = 0.2 \text{ mM}$) dissolved in acetone (BDD working electrode, under Ar, 0.1 M TBAP, 25 °C).

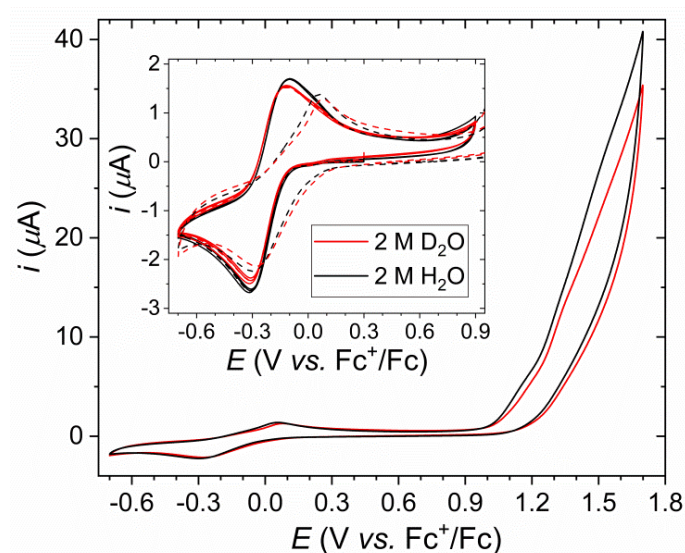


Figure 2. Comparison of CV scans for $[\text{Fe}^{\text{III}}\text{Cl}_2(\text{tia-BAI})]$ dissolved in acetone when 2 M of H_2O (black line) or D_2O (red line) is added, inset: CV scans of freshly prepared $[\text{Fe}^{\text{III}}\text{Cl}_2(\text{tia-BAI})]$ solutions used in the corresponding experiments (solid lines, $c = 0.2 \text{ mM}$) and CVs recorded after the addition of H_2O or D_2O (dashed lines, magnified view of the main figure). Cell setup: BDD working el., non-aqueous Ag^+/Ag ref. el., Pt counter-el., Ar atm., 25°C, 0.1 M TBAP.

Table S1. Selected binding energy values from the fitting of XP spectra of a freshly drop-casted complex/ITO sample, and of those collected after 4.5 h of CPE at +1.4 V *vs.* Ag/AgCl in borate buffer at pH 8.3 (in parenthesis). The associated chemical states of the elements are provided.^a

Elements / Component Peak	Binding Energy (eV)	Chemical State
1/ITO		
Fe 2p 1	709.0 (709.6)	Fe^{III}
Fe 2p 2	711.0 (711.3)	
Fe 2p 3	713.2 (713.0)	
Fe 2p 4	716.4 (716.2)	
Fe 3p	55.6 (55.6)	
N 1s 1	398.9 (399.5)	$\text{C}=\text{N}-\text{C}$ and $\text{Fe}-\text{N}_{\text{hc}}$
N 1s 2	400.9 (401.1)	$\text{C}-\text{NH}-\text{C}$
C 1s 1	284.8 (285.4)	
Cl 2p 1	198.5 (198.7)	Cl^-
Cl 2p 2	200.1 (200.3)	Cl^-
S 2p 1	164.4 (164.9)	S_{tia}
S 2p 2	165.6 (166.1)	S_{tia}

^athe same complex/ITO sample has been analyzed by SEM-EDX, then applied in CPE (Fig. 9), and re-analyzed.

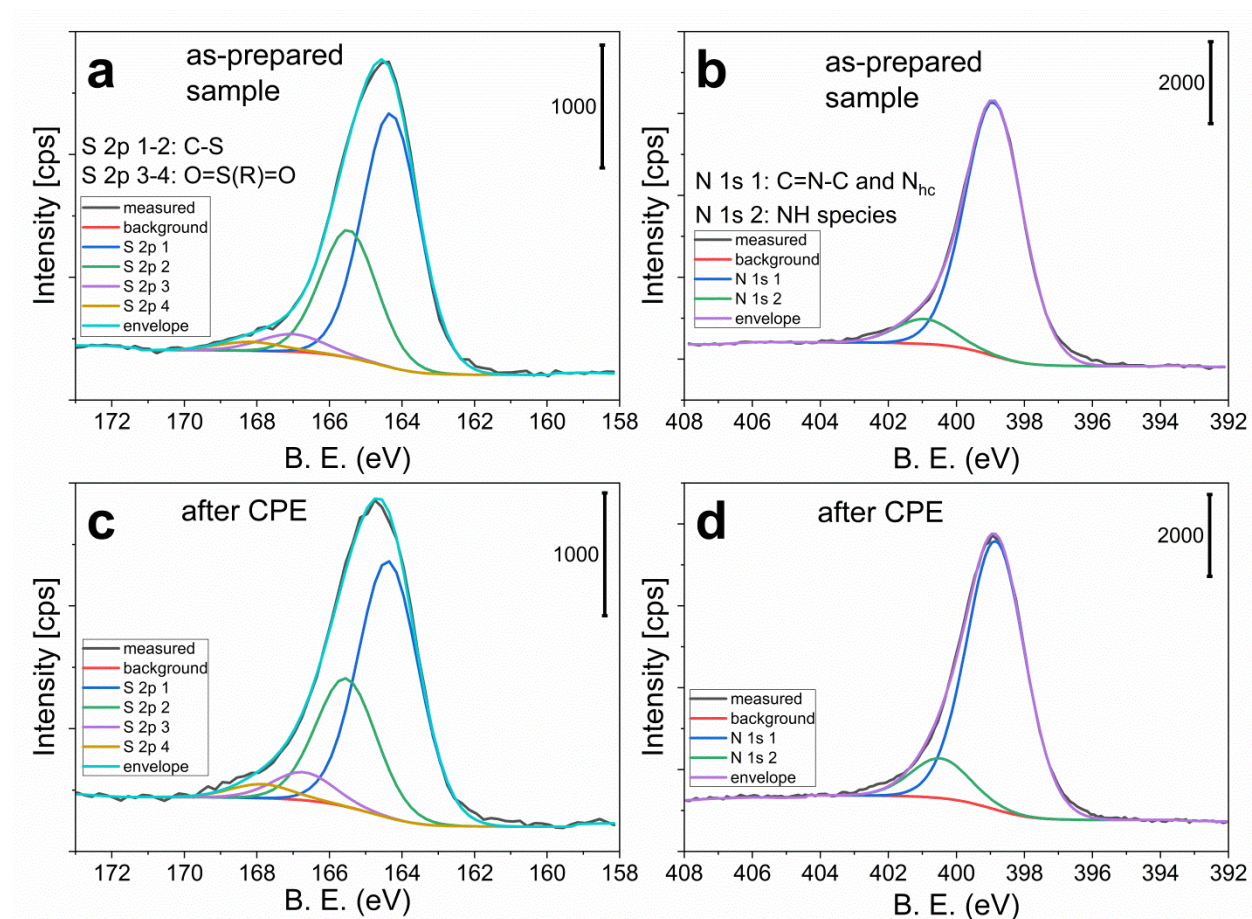


Figure 3. (a) The S 2p and (b) the N 1s binding energy region of XP spectra of the as-prepared complex/ITO with the fitted components; (c) and (d) the corresponding spectra after CPE (Fig. 8). For discussion see the text, for data see Tables 1 and S1.