**Supporting information**

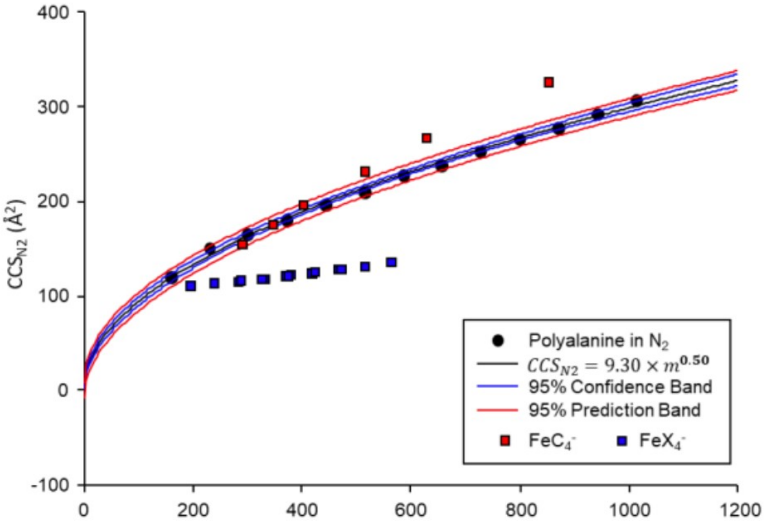


**Figure S1**. TWIMS calibration curve involving $^{DT,1st}CCS_{N2}$ values of negatively charged polyalanine ions[1] used as calibrating substances. The CCS/mass ratio values of clusters do not line up with the CCS-mass trend of the calibrating substances, which can lead to inaccuracies on CCS measurement[2].

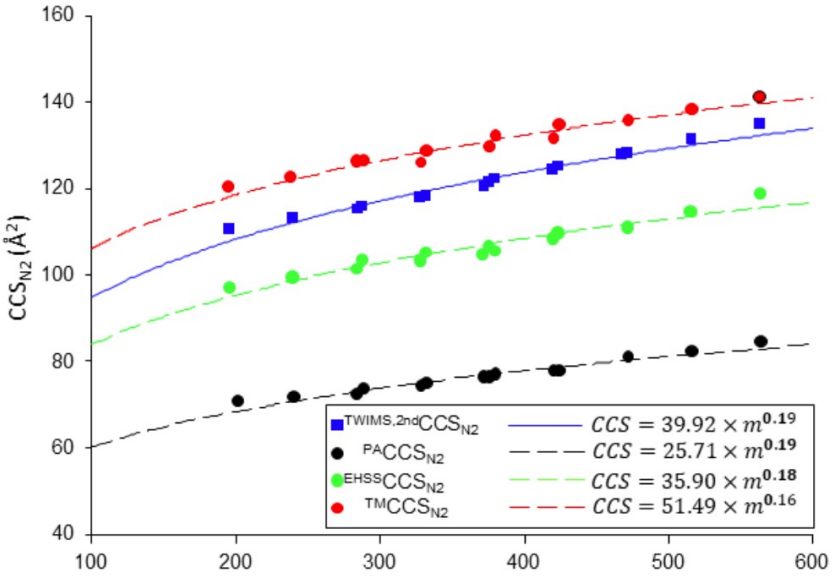


**Figure S2.** Experimental (dots) and theoretical (dashed lines) CCS-mass trends of $FeX_4^-$. Experimental TWIMS, $^{2nd}CCS_{N2}$-mass trend, theoretical $^{PA}CCS^{N2}$-mass trend, theoretical $^{EHSS}CCS_{N2}$-mass trend, and $^{TM}CCS_{N2}$-mass trend are represented in blue, black, green and red respectively. Similar *Pow* parameters are determined for each trend.

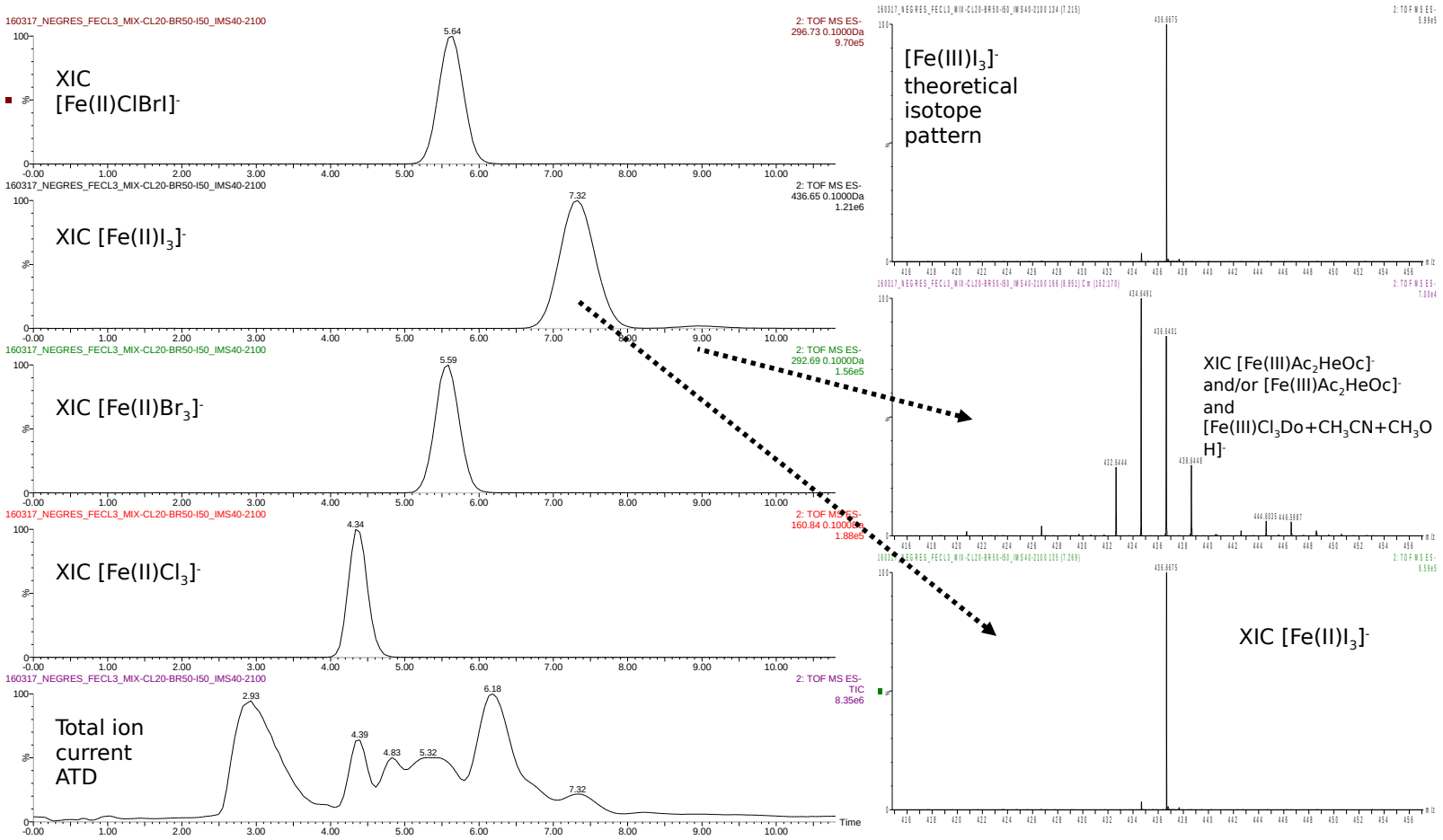


**Figure S3**: Arrival time distribution (ATD) of Fe(II) and halides ligands obtained by electrospray using negative ionization mode. Right section show the theoretical and experimental mass spectra for extract ion current (XIC) at m/z: 436.65±0.1 at their respective drift time ($[Fe(III)I_3]^-$ iron-carboxylates and/or iron hybrid complexes and 7.32 and 9ms respectively).

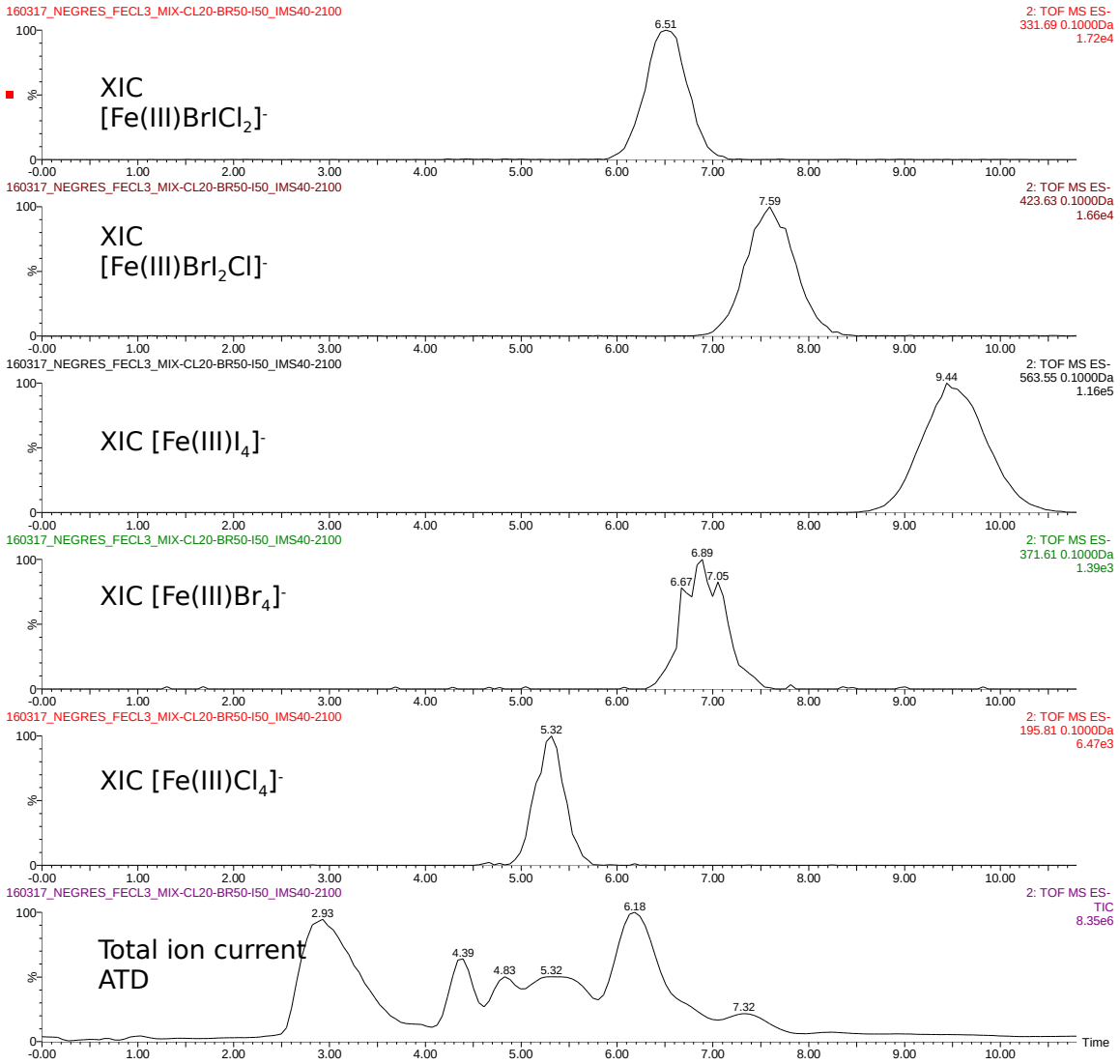


**Figure S4**: Arrival time distribution of Fe(III) and halides ligands obtained by electrospray using negative ionization mode

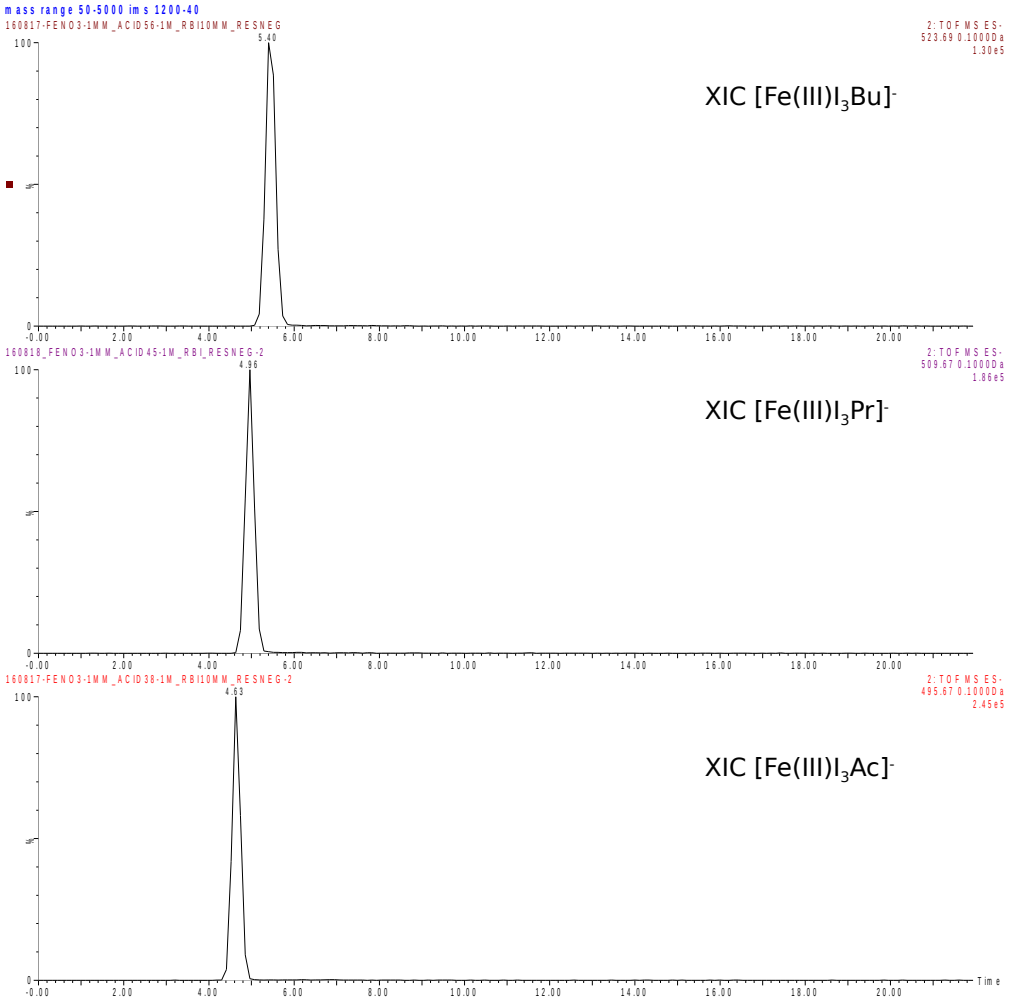


**Figure S5**: Arrival time distribution of hybrid iron complexes of Fe(III), iodide, and carboxylates ligands obtained by electrospray using negative ionization mode.

**References:**

1. Forsythe et al., Analyst (2015) 140:6853-6861, Collision cross section calibrants for negative ion mode traveling wave ion mobility-mass spectrometry

2. Haler et al., Analytical chemistry (2017) 89,22:12076-12086, Comprehensive Ion Mobility Calibration: Poly(ethylene oxide) Polymer Calibrants and General Strategies