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Supporting Information

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**New Trends in the Chemistry of Iron(III)-Citrate Complexes. Correlations Between X-ray Structures and Solution Species Probed by Electrospray Mass Spectrometry and Kinetics of Iron Uptake from Citrate by Iron Chelators.**

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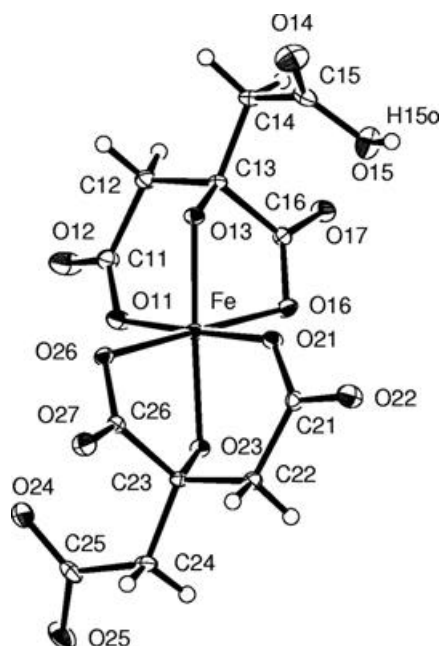
**Table S1.** Selected interatomic distances (Å) and bond angles (°) in the  $[\text{Fe}_2(\text{cit})_2(\text{H}_2\text{O})_2]^{2-}$  complex of the compounds **1** to **5**.

compound	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
base	py	im	pic	neo	neo
Fe...Fe'	3.120(1)	3.108(1)	3.123(1)	3.126(1)	3.121(1)
Fe-O1	1.987(3)	2.000(2)	1.999(2)	2.001(2)	1.998(3)
Fe-O3	2.038(3)	2.042(2)	2.040(2)	2.027(2)	2.012(2)
Fe-O3'	1.995(2)	1.992(2)	1.989(2)	2.000(2)	2.013(3)
Fe-O4'	1.987(2)	1.976(2)	1.977(2)	1.963(2)	1.960(2)
Fe-O6	2.017(2)	1.996(2)	2.024(2)	2.023(2)	2.013(2)
Fe-O8	2.033(2)	2.019(2)	1.993(2)	2.028(2)	2.021(3)
Fe-O3-Fe'	101.3(1)	100.8(1)	101.7(1)	101.9(1)	101.7(1)
O3-Fe-O3'	78.7(1)	79.23(7)	78.35(7)	78.15(8)	78.3(1)

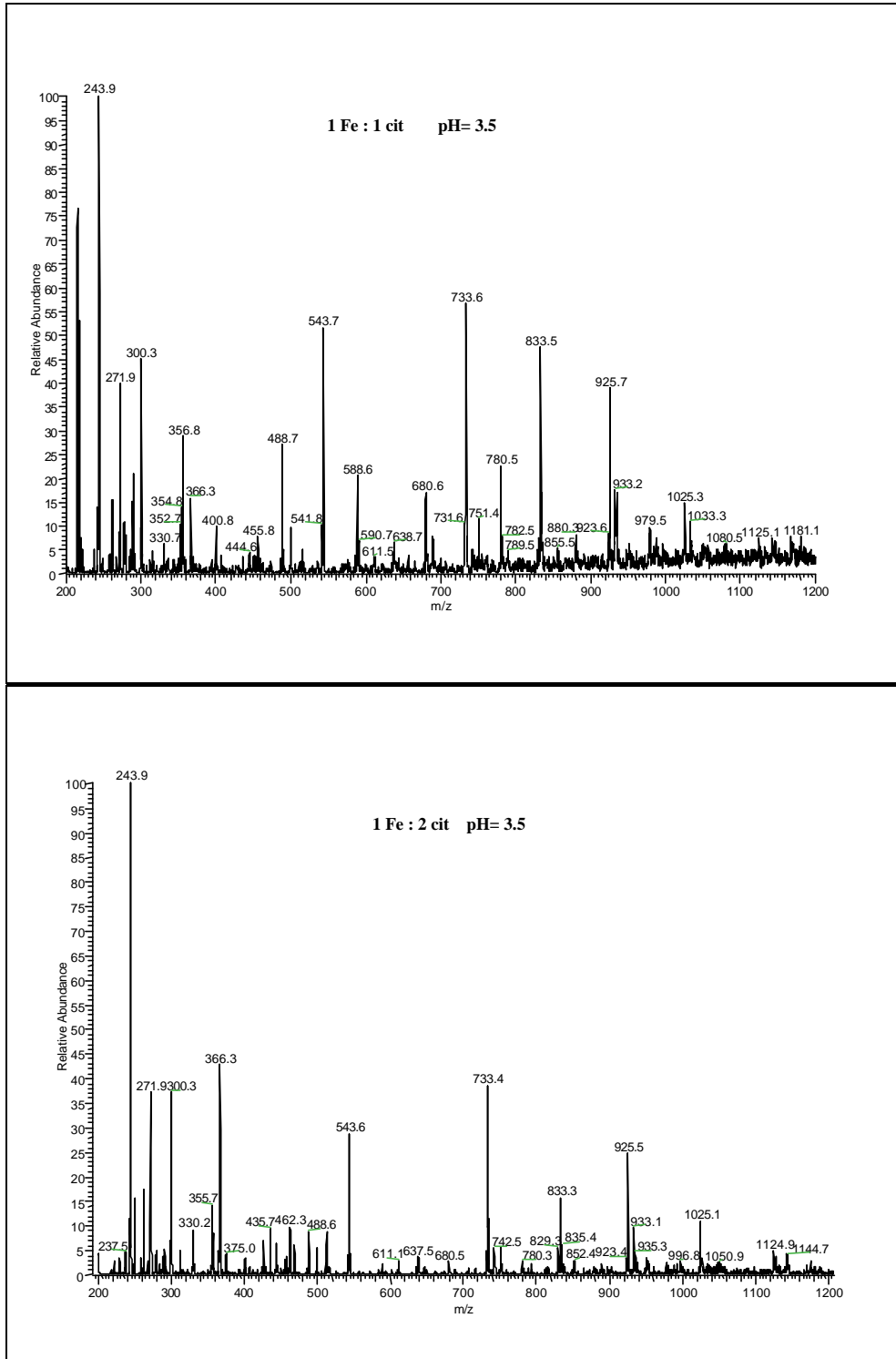
**Table S2.** Selected bond distances (Å) in the compounds **6** to **8**.

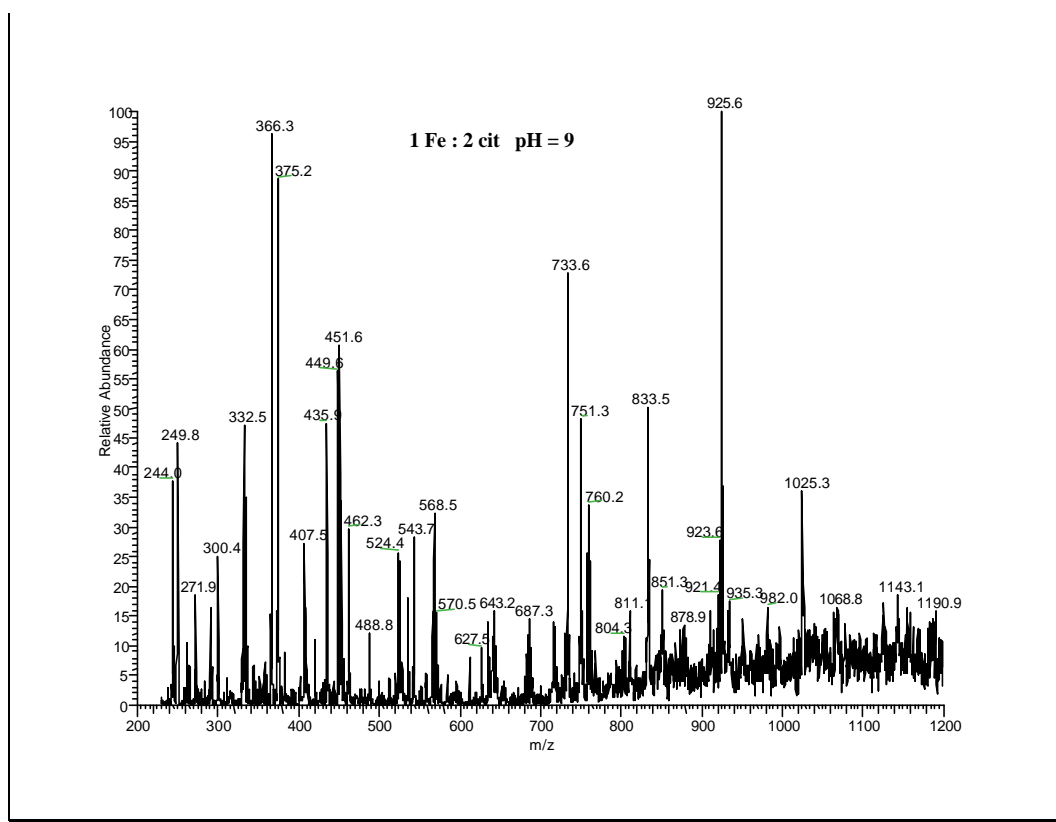
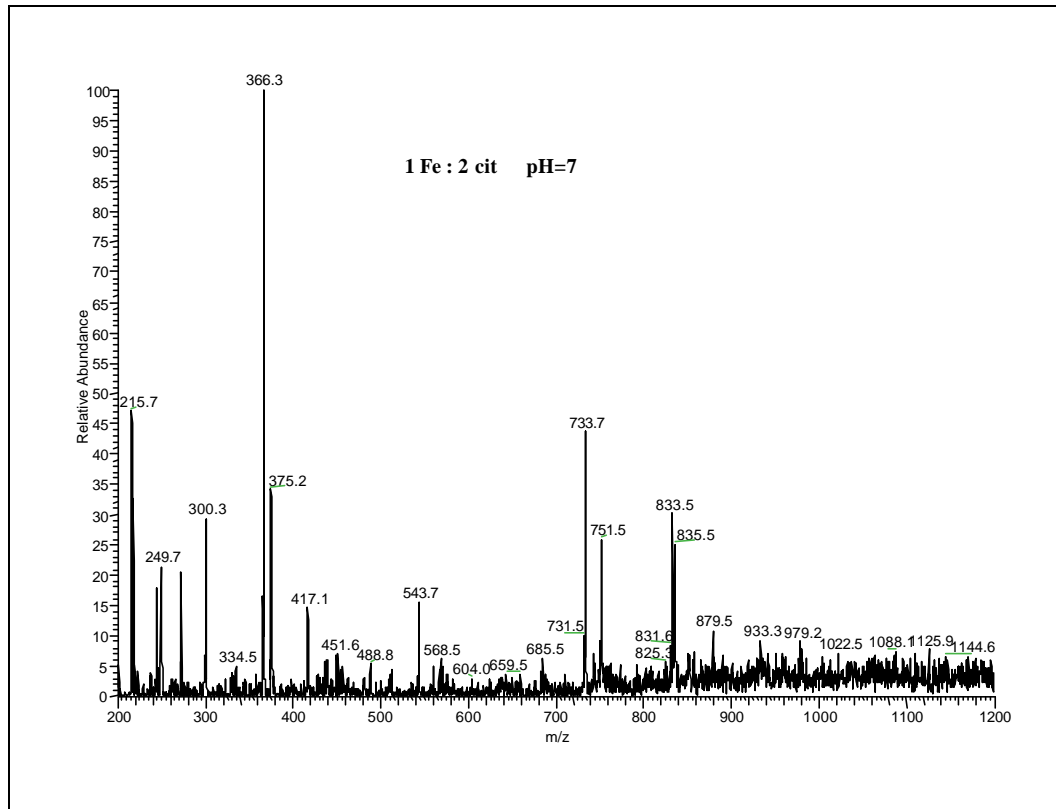
compound <b>6</b>			
Fe1-O13	2.051(2)	Fe2-O13	2.034(2)
Fe1-O16	1.960(2)	Fe2-O11	1.957(2)
Fe1-O23	2.023(2)	Fe2-O23	2.069(2)
Fe1-O26	1.978(2)	Fe2-O21	1.963(2)
Fe1-O31	1.938(2)	Fe2-O36	1.977(2)
Fe1-O33	2.037(2)	Fe2-O33	2.020(2)
compound <b>7</b>		compound <b>8</b>	
Fe-O1	2.055(1)	Fe-O11	2.035(1)
Fe-O3	1.943(1)	Fe-O13	1.932(1)
Fe-O6	1.995(1)	Fe-O16	2.007(1)
		Fe-O21	2.064(1)
		Fe-O23	1.944(1)
		Fe-O26	2.019(1)

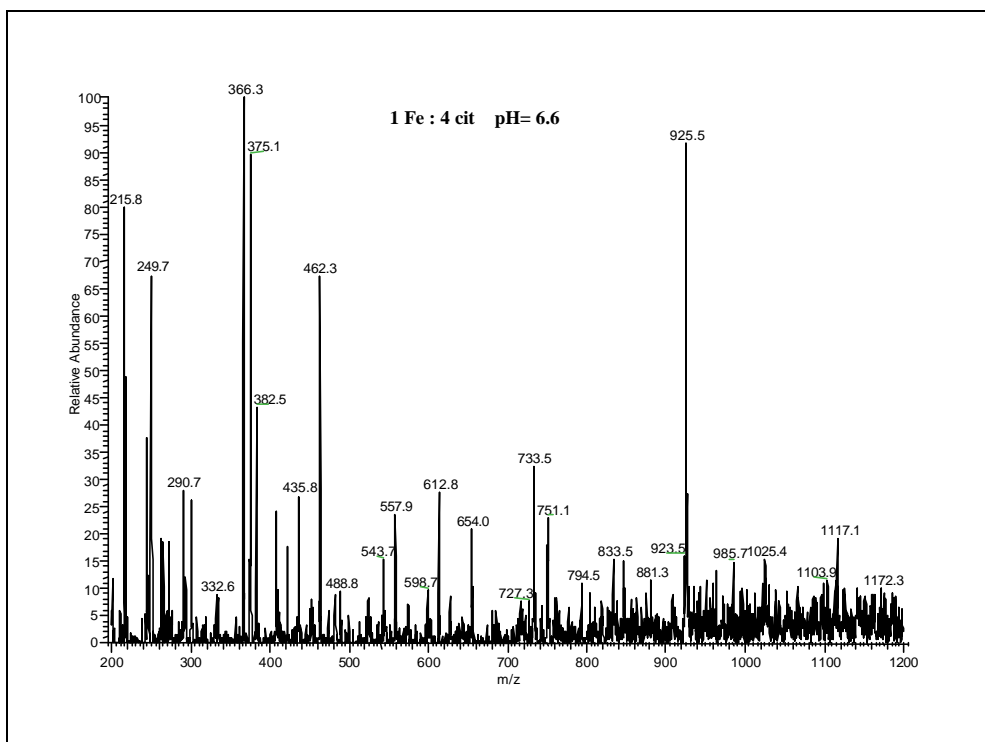
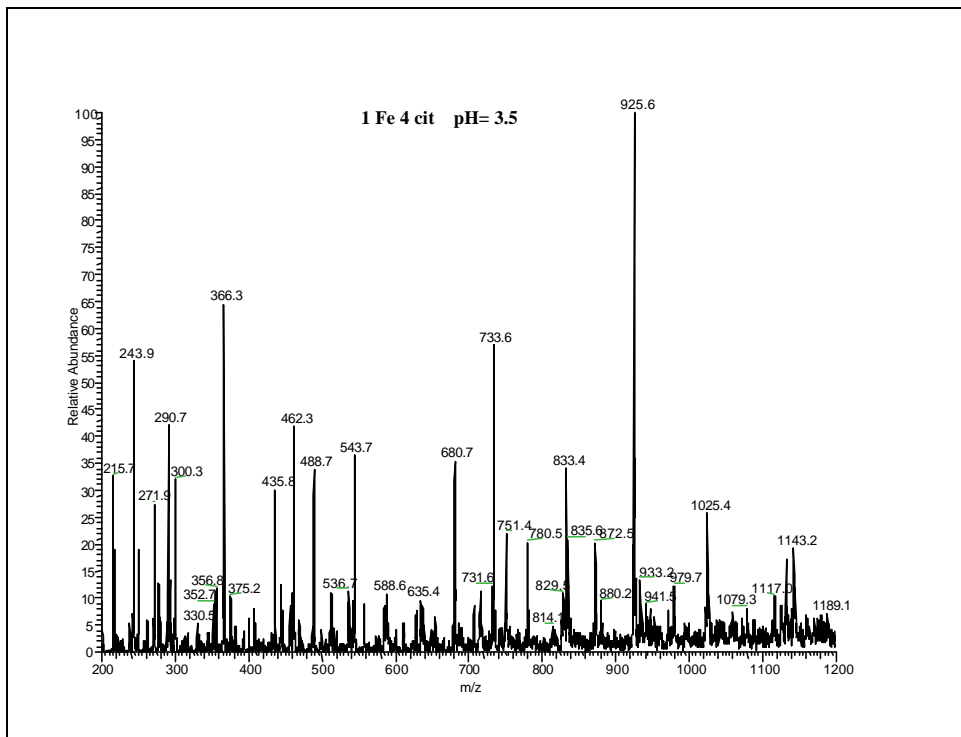
**Figure S1.** ORTEP representation, of the  $[\text{Fe}(\text{Hcit})(\text{cit})]^{4-}$  anion in the compound **8**.

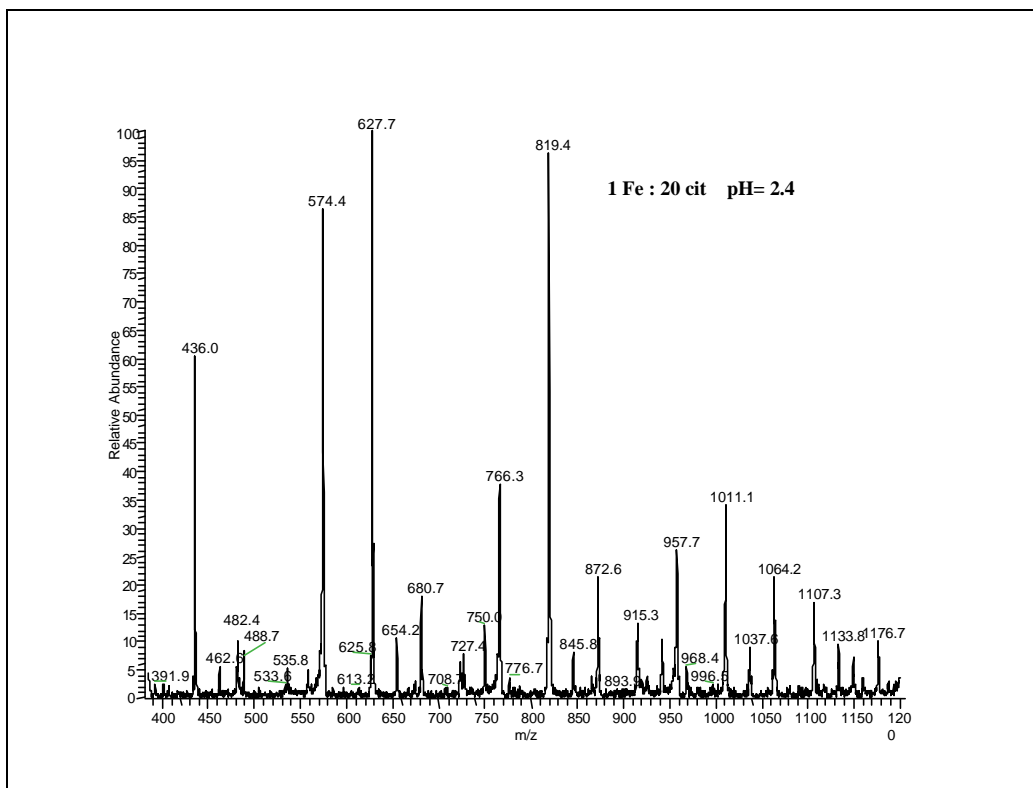
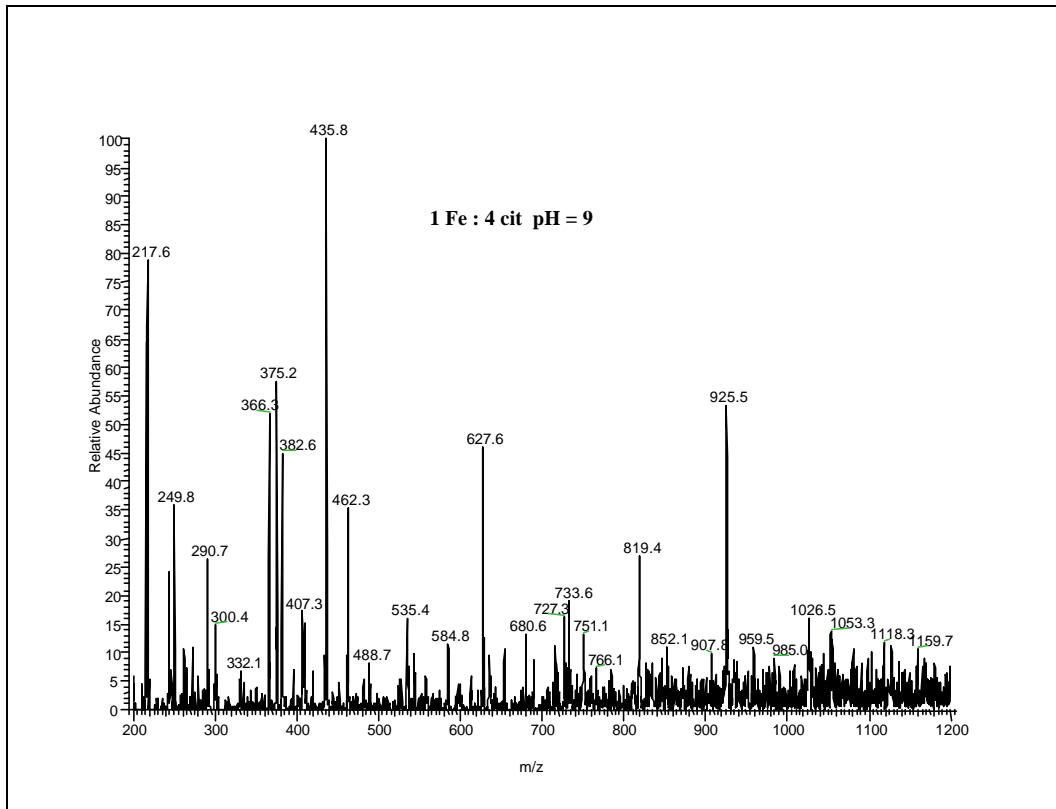


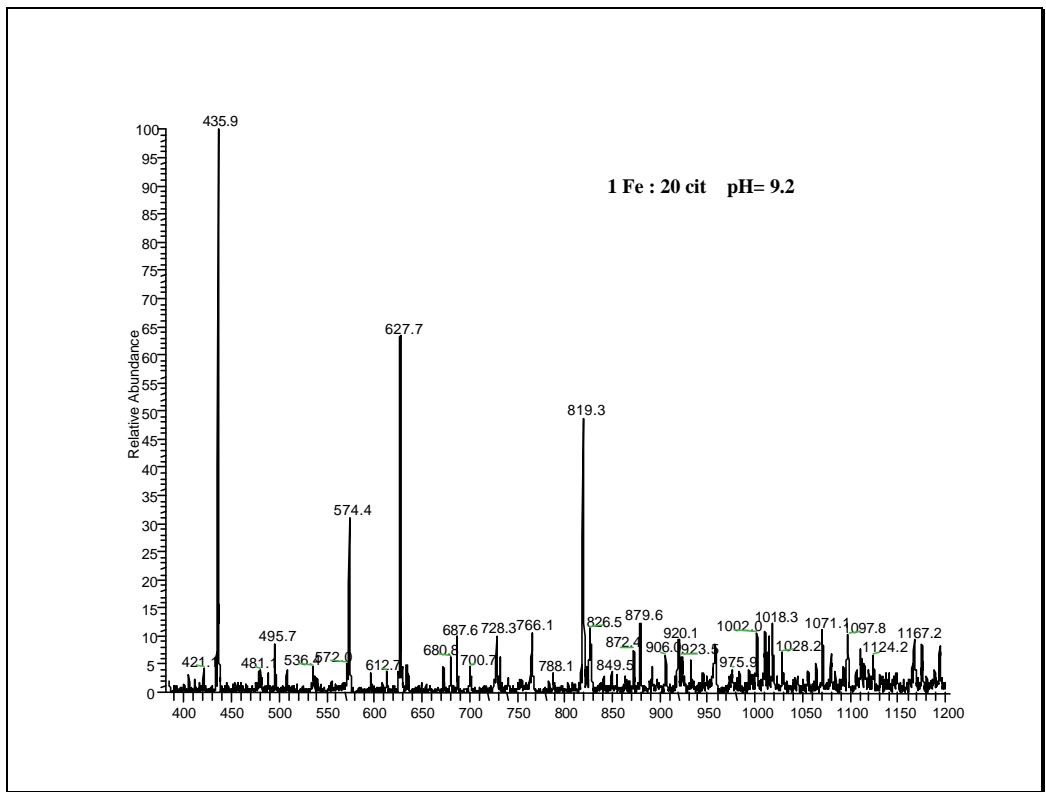
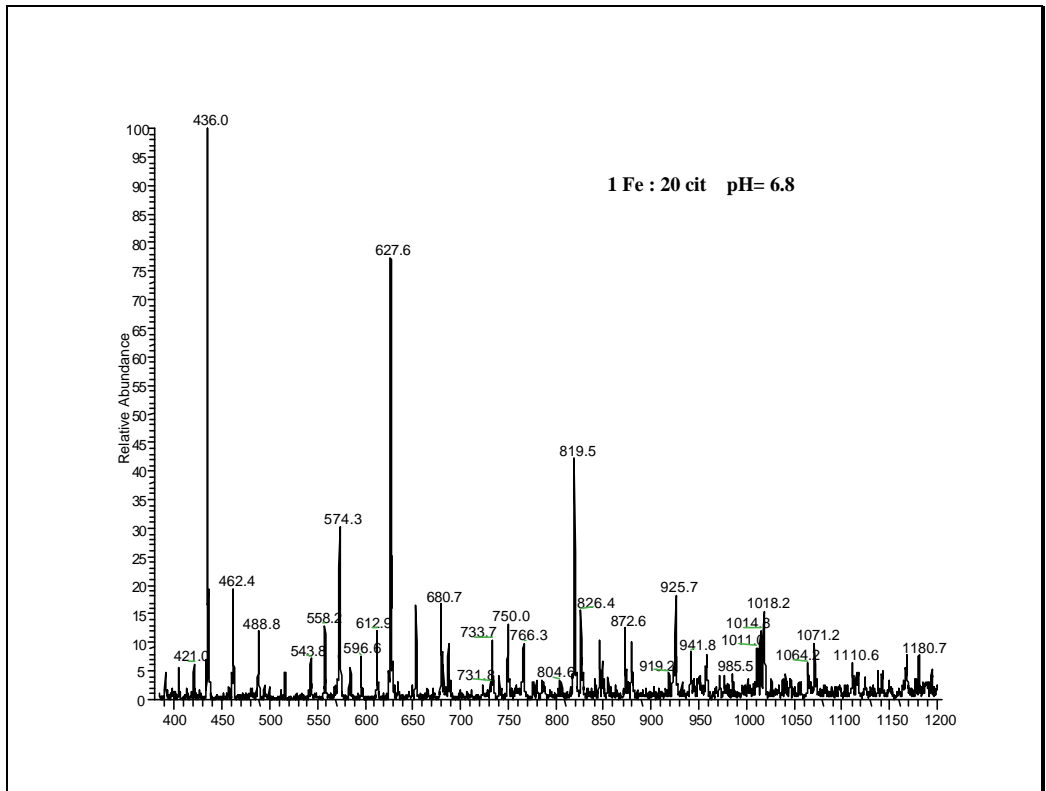
**Figure S2. ESI-MS spectra**

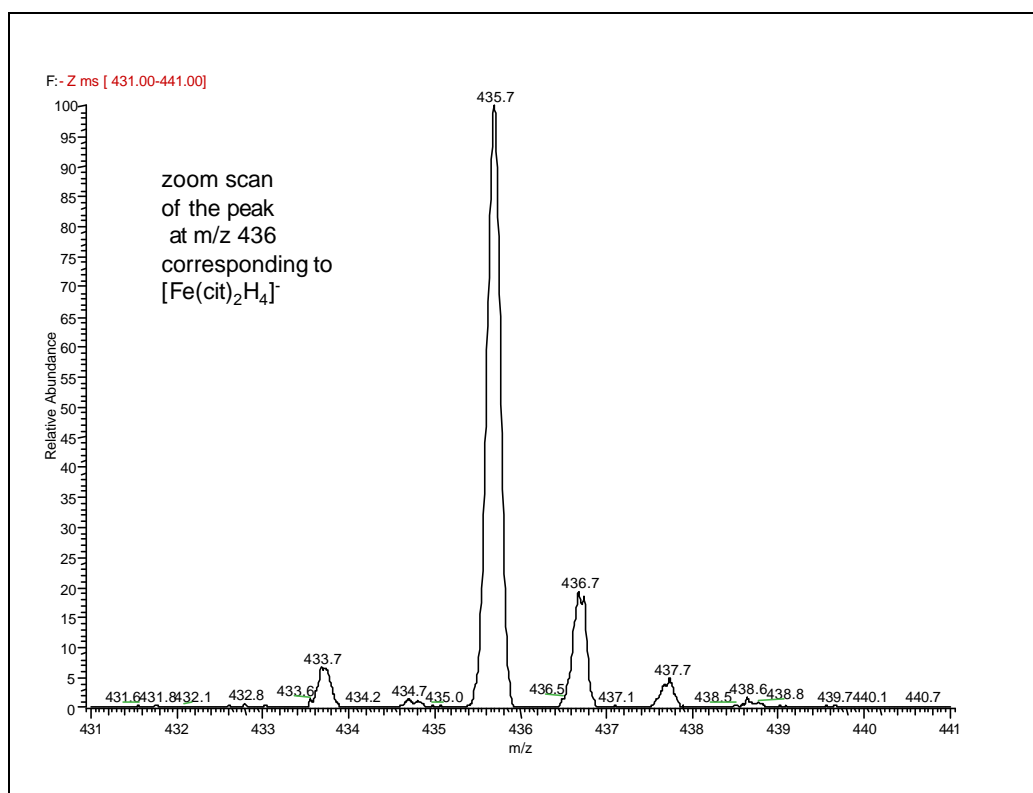
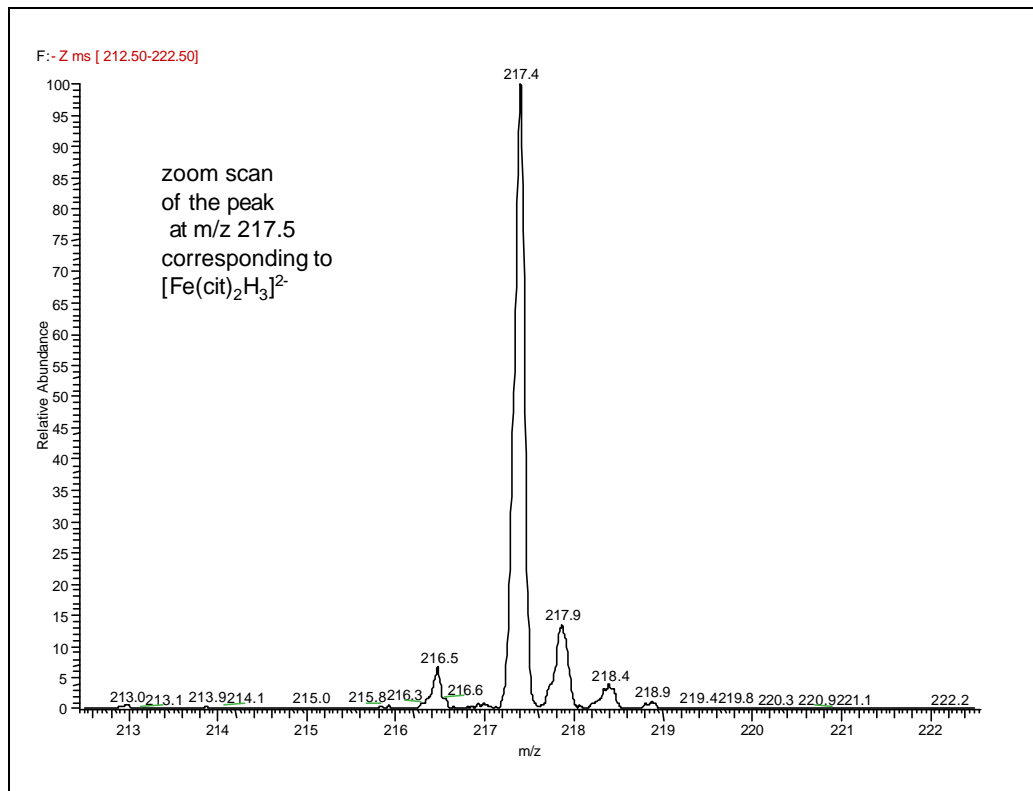


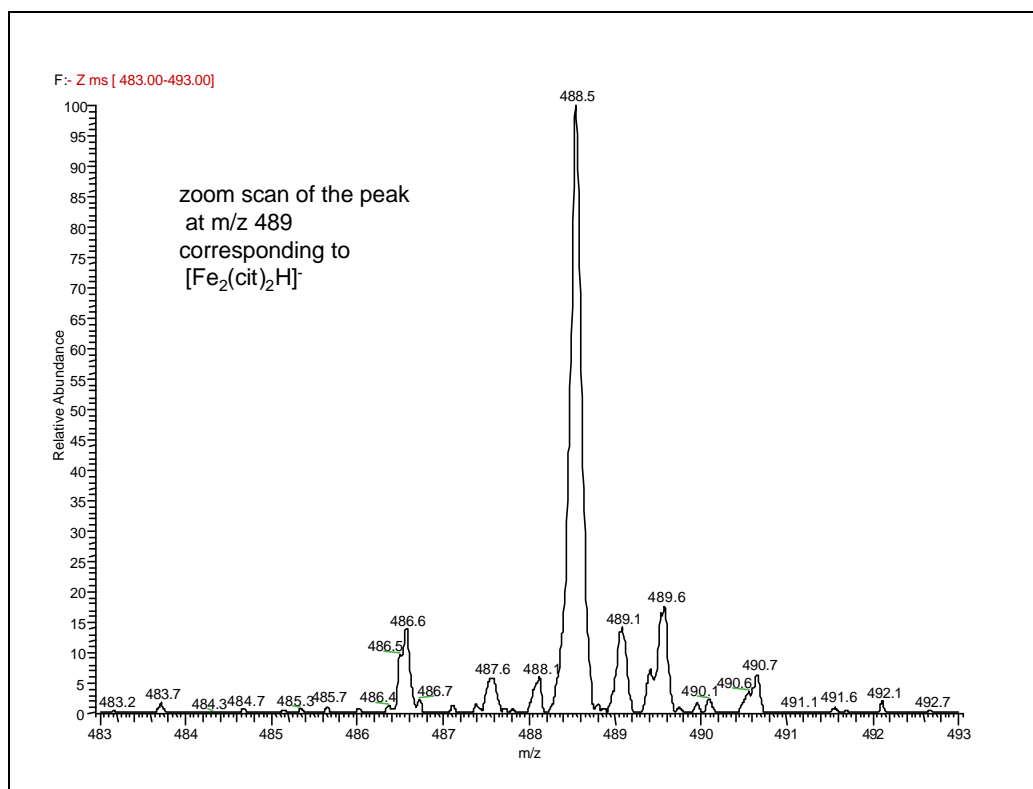
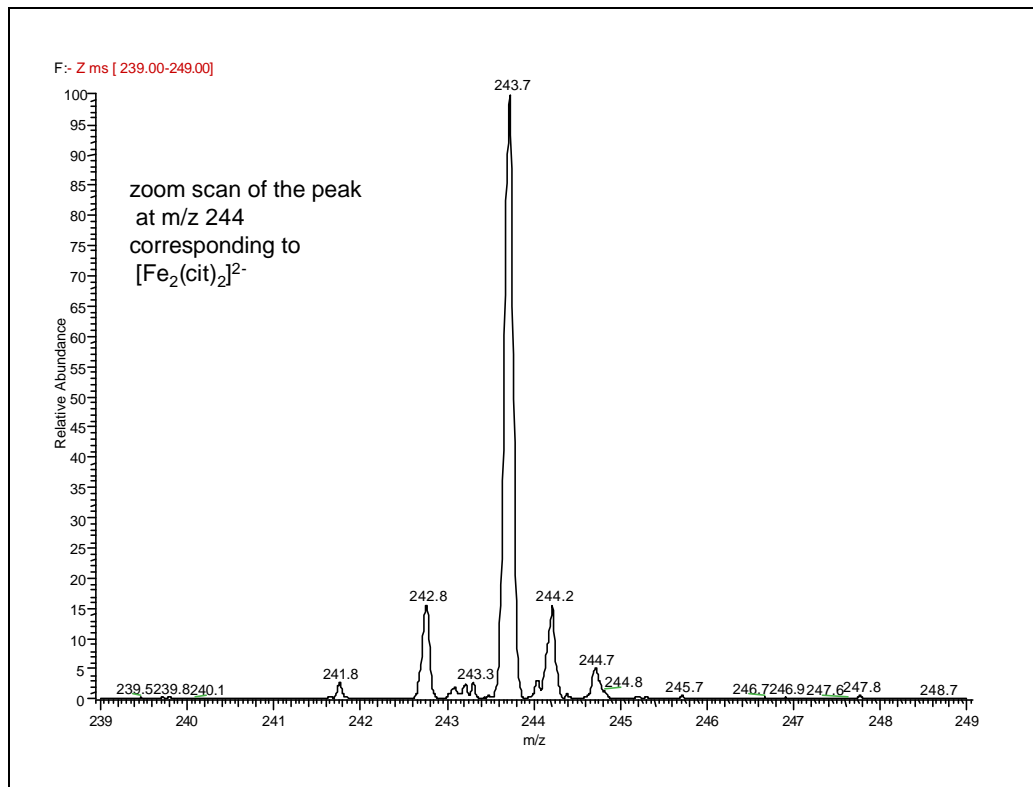


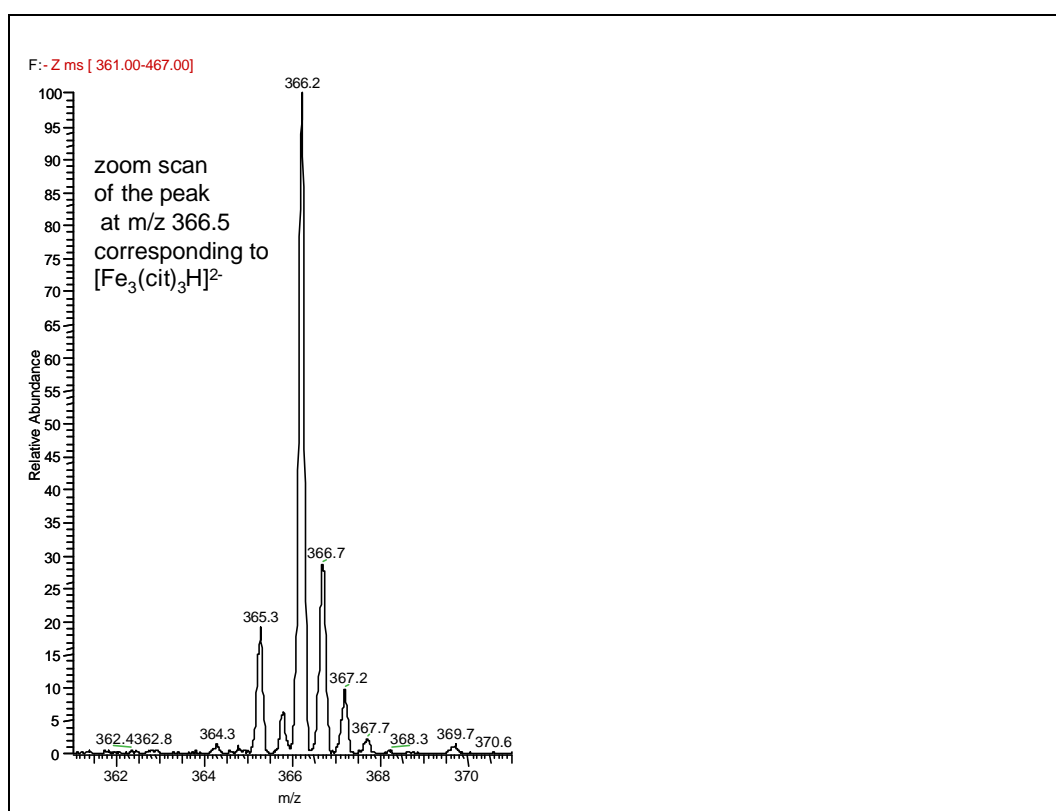
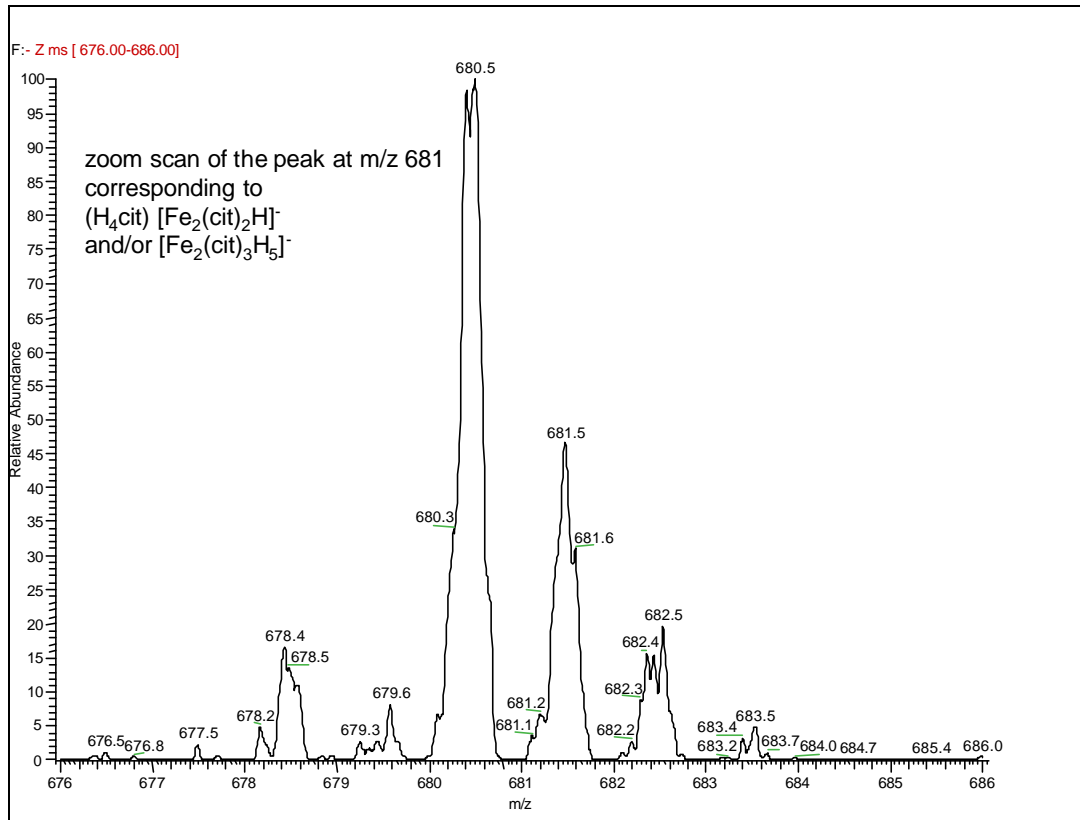


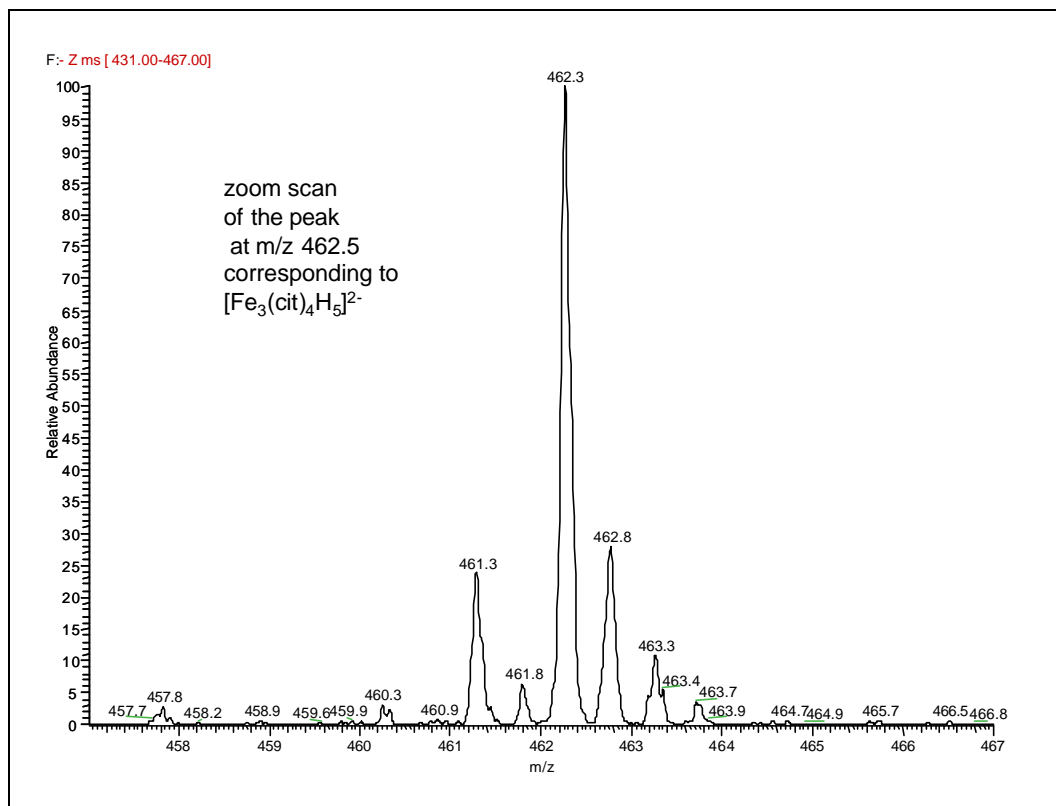
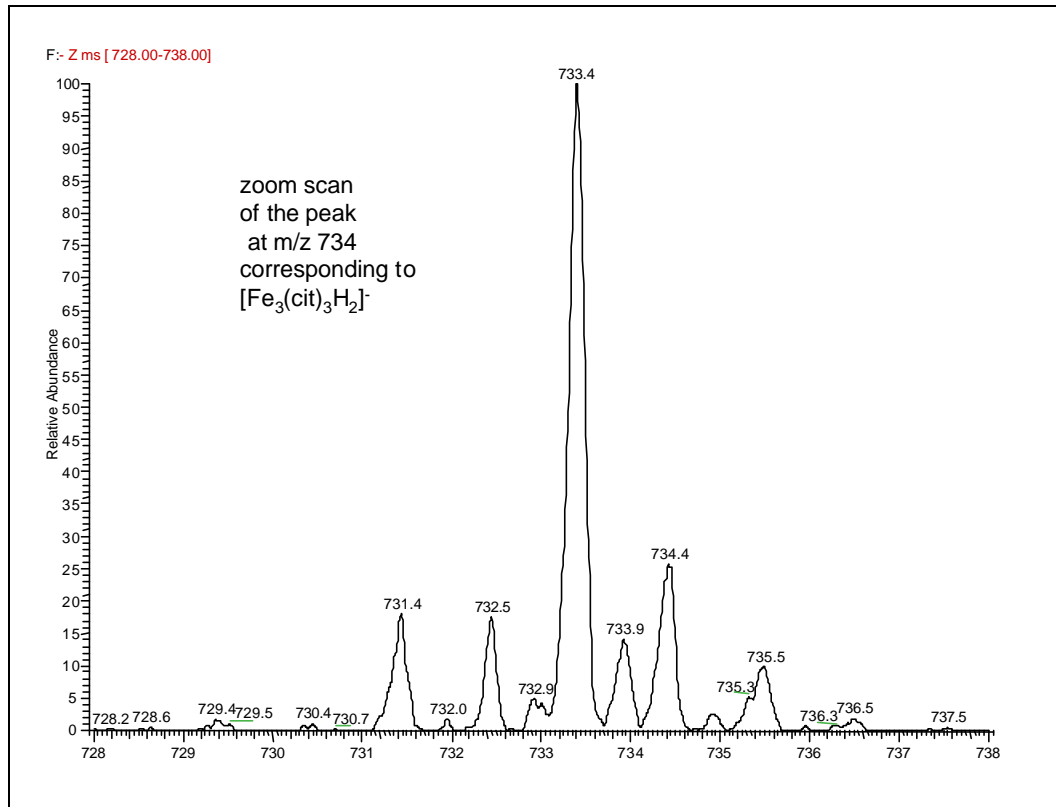


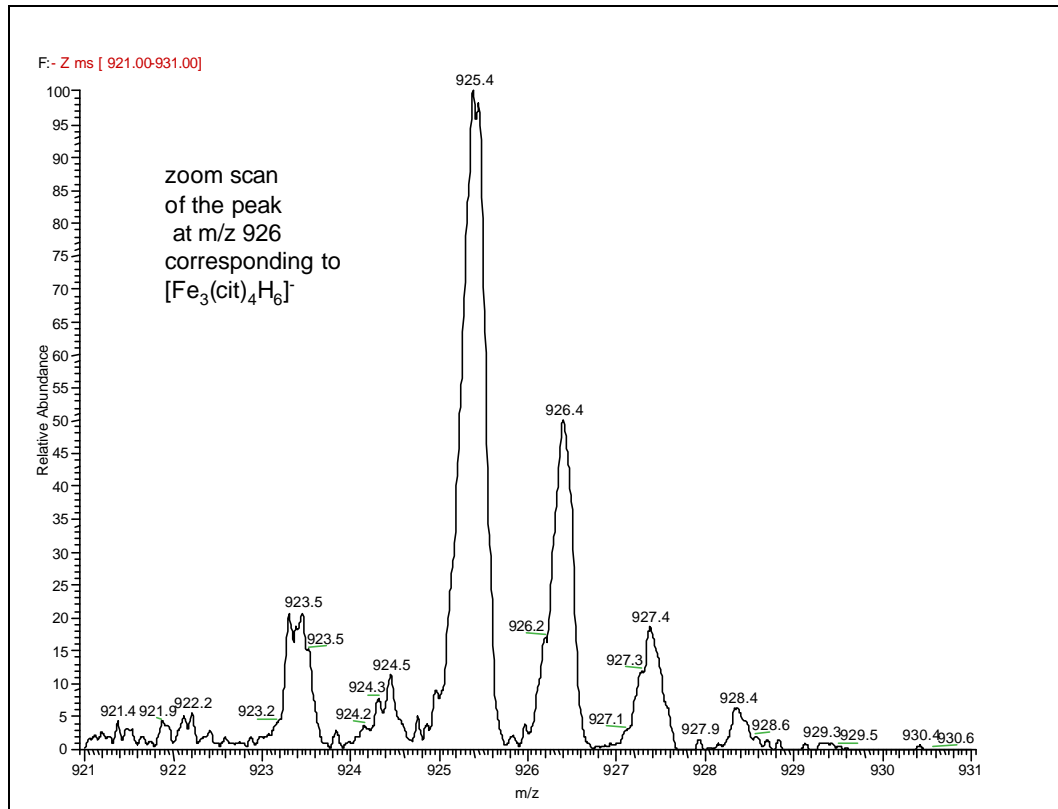




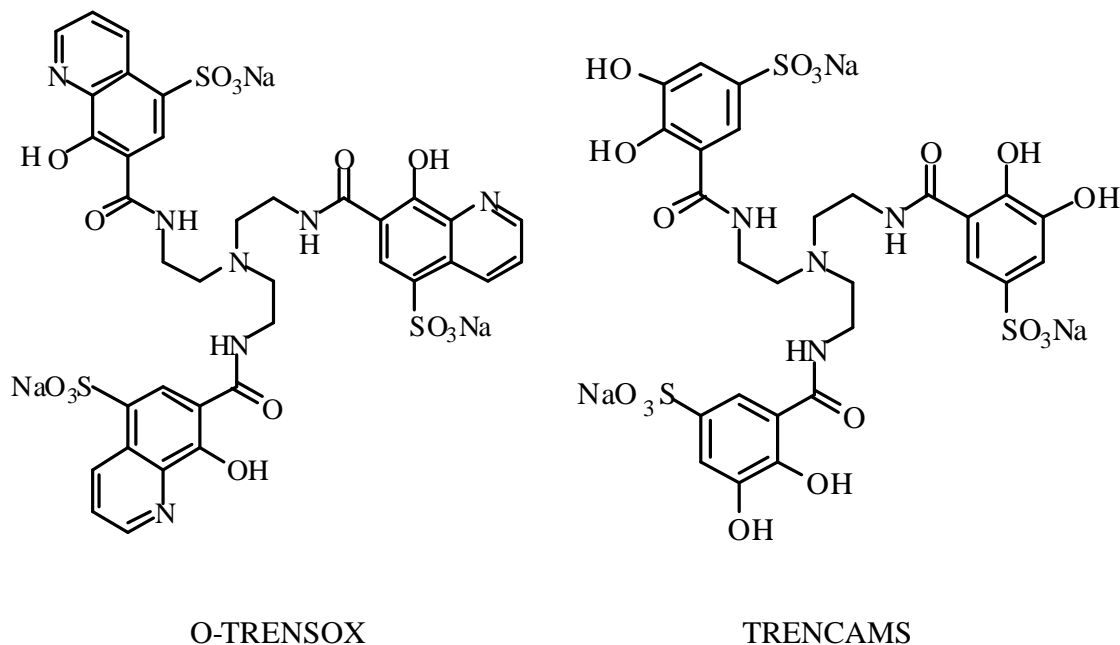








**Figure S3.** Chemical formulae of the ligands



**Table S3.** Pseudo-first-order rate constants (observed and calculated according to equation 4) for the fast stage of the transfer of Fe<sup>III</sup> from citrate to TRENCAMS at pH = 7.4, I = 0.1 M (NaCl) and 25°C; [Fe<sup>III</sup>] = 0.02 mM.

[L] M	[cit] M	$k_1^{\text{obs}} \text{ s}^{-1}$	$k_1^{\text{calc}} \text{ s}^{-1}$
0.0004	0.0004	0.048	0.0463
0.0006	0.0004	0.078	0.0694
0.0008	0.0004	0.094	0.0926
0.0010	0.0004	0.110	0.1157
0.0002	0.0016	0.018	0.0164
0.0004	0.0016	0.034	0.0329
0.0006	0.0016	0.051	0.0493
0.0008	0.0016	0.066	0.0658
0.0010	0.0016	0.082	0.0822
0.0004	0.0002	0.053	0.0496
0.0004	0.0006	0.041	0.0433
0.0004	0.0008	0.038	0.0407
0.0004	0.0012	0.035	0.0364

**Table S4.** Pseudo-first-order rate constants (observed and calculated according to equation 4) for the fast stage of the transfer of Fe from citrate to O-TRENTOX at pH = 7.4, I = 0.1 M (NaCl) and 25°C;  $[\text{Fe}^{\text{III}}] = 0.02 \text{ mM}$ .

[L] M	[cit] M	$k_1^{\text{obs}} \text{ s}^{-1}$	$k_1^{\text{calc}} \text{ s}^{-1}$
0.0002	0.0004	0.050	0.0443
0.0004	0.0004	0.093	0.0888
0.0006	0.0004	0.156	0.1331
0.0008	0.0004	0.180	0.1775
0.0010	0.0004	0.22	0.2219
0.0012	0.0004	0.25	0.2663
0.0002	0.0016	0.047	0.0393
0.0004	0.0016	0.076	0.0787
0.0006	0.0016	0.126	0.1180
0.0008	0.0016	0.160	0.1573
0.0010	0.0016	0.190	0.1967
0.0004	0.0002	0.110	0.0907
0.0004	0.0008	0.086	0.0851
0.0004	0.0012	0.082	0.0818

**Table S5.** Pseudo-first-order rate constants for the slow stage of the transfer of  $\text{Fe}^{\text{III}}$  from citrate to TRENTOX at pH = 7.4, I = 0.1 M (NaCl) and 25°C;  $[\text{Fe}^{\text{III}}] = 0.02 \text{ mM}$ .

[L] M	$k_2^{\text{obs}}$ ([Fe]:[cit] = 1:5)	$k_2^{\text{obs}}$ ([Fe]:[cit] = 1:20)	$k_2^{\text{obs}}$ ([Fe]:[cit] = 1:80)
0.0018		0.0046	0.0051
0.0015		0.0044	0.0045
0.0012	0.0045	0.0042	0.0042
0.0010	0.0041	0.00345	0.0038
0.0008	0.0037	0.00301	
0.0006	0.0029	0.00285	0.00267
0.0004	0.0022	0.00196	0.0024
0.0002	0.0013		

**Table S6.** Pseudo-first-order rate constants observed for the slow stage of the transfer of Fe from citrate to O-TRENTOX at pH = 7.4, I = 0.1 M (NaCl) and 25°C;  $[\text{Fe}^{\text{III}}] = 0.02 \text{ mM}$ .

[L] M	$k_2^{\text{obs}}$ ([Fe]:[cit] = 1:5)	$k_2^{\text{obs}}$ ([Fe]:[cit] = 1:20)	$k_2^{\text{obs}}$ ([Fe]:[cit] = 1:80)
0.0018		0.00527	
0.0015	0.00352	0.00420	0.0031
0.0012	0.00283	0.00325	0.0022
0.0010	0.00269	0.00266	0.00198
0.0008	0.00191	0.00215	0.00175
0.0006	0.00179	0.00166	0.00110
0.0004	0.00106	0.00098	0.000767