Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

A Systematic Investigation of the Relaxation Properties of Fe(III)-EDTA Derivatives and Their Potential as MRI Contrast Agents

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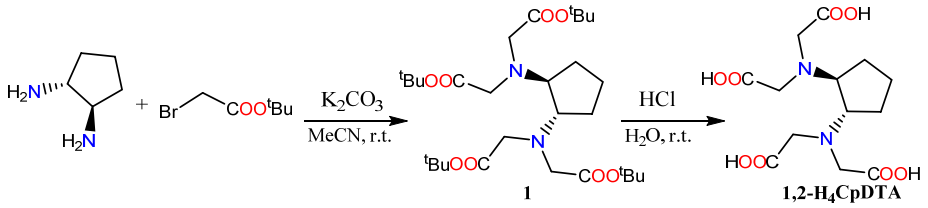


Scheme S1: Synthesis of **1,2-H_4CpDTA**.

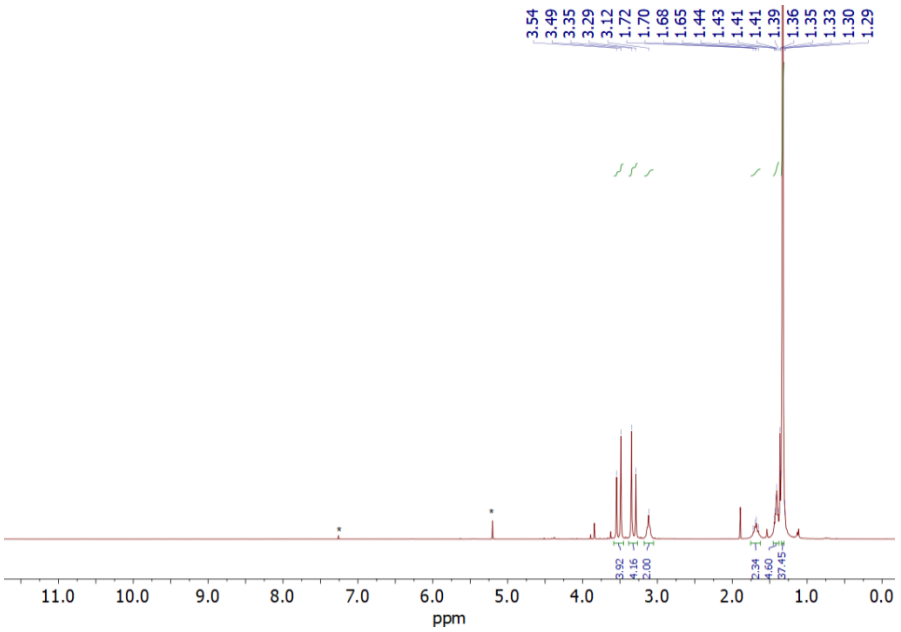


Figure S1: ^{1}H NMR spectrum of compound **1** (300 MHz, $CDCl_3$, 298 K).

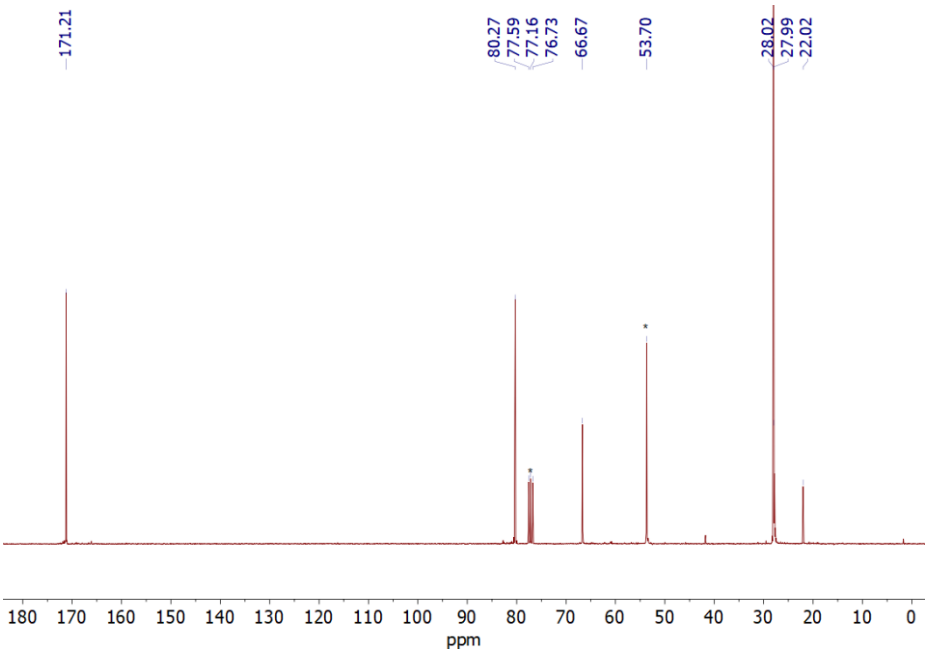


Figure S2: ^{13}C NMR spectrum of compound **1** (75 MHz, $CDCl_3$, 298 K).

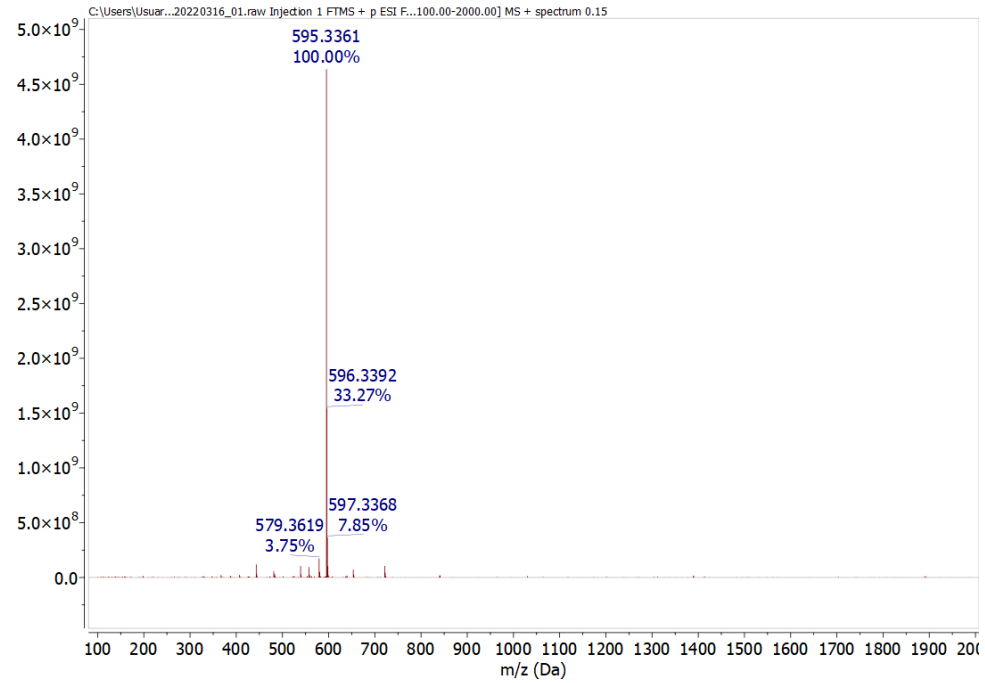


Figure S3: Experimental high resolution mass spectrum (ESI^+) of compound **1**.

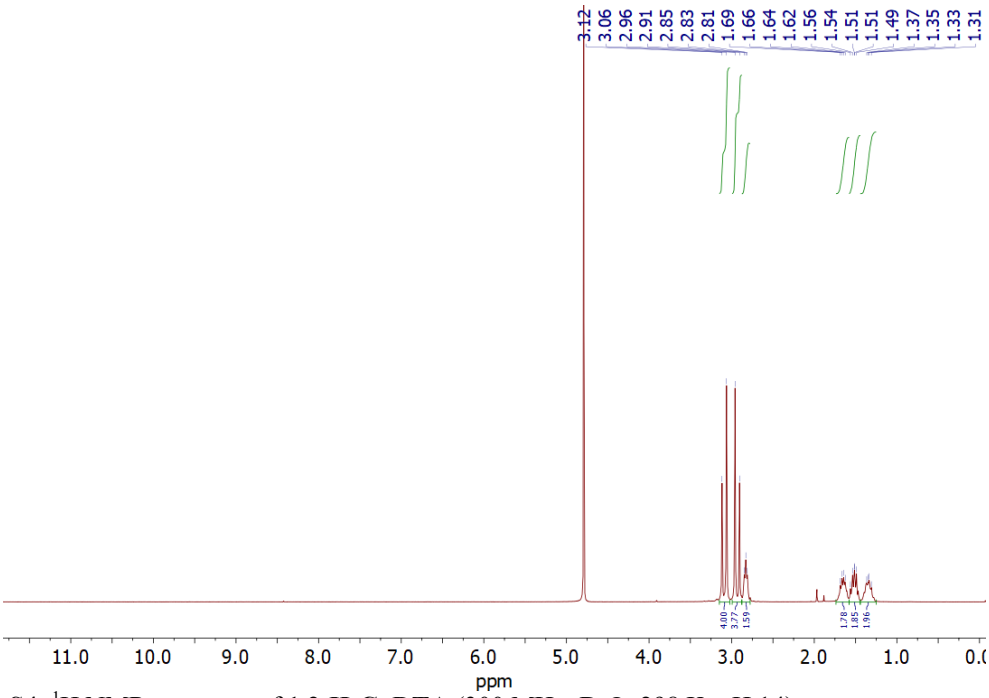


Figure S4: ^1H NMR spectrum of **1,2-H_4CpDTA** (300 MHz, D_2O, 298 K, pH 14).

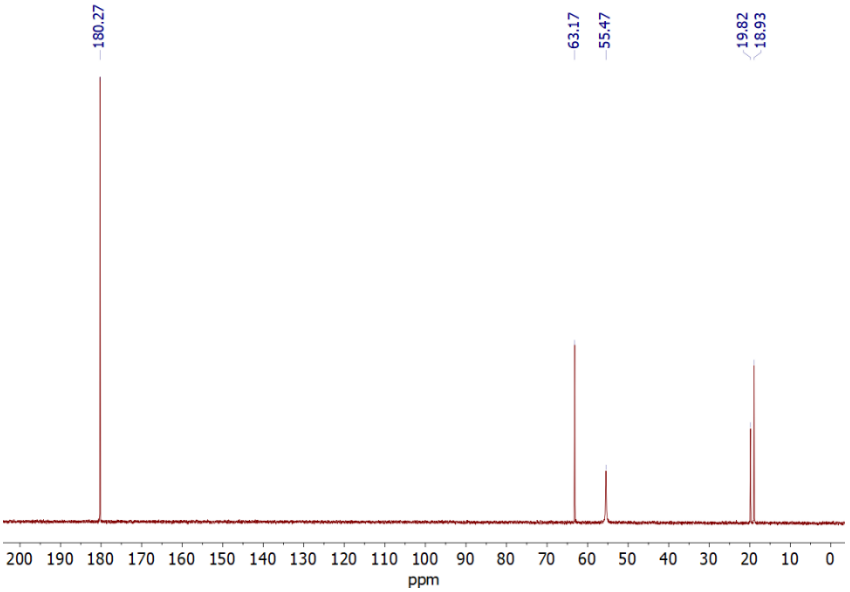


Figure S5: ^{13}C NMR spectrum of **1,2-H$_4$CpDTA** (75 MHz, D_2O, 298 K, pH 14).

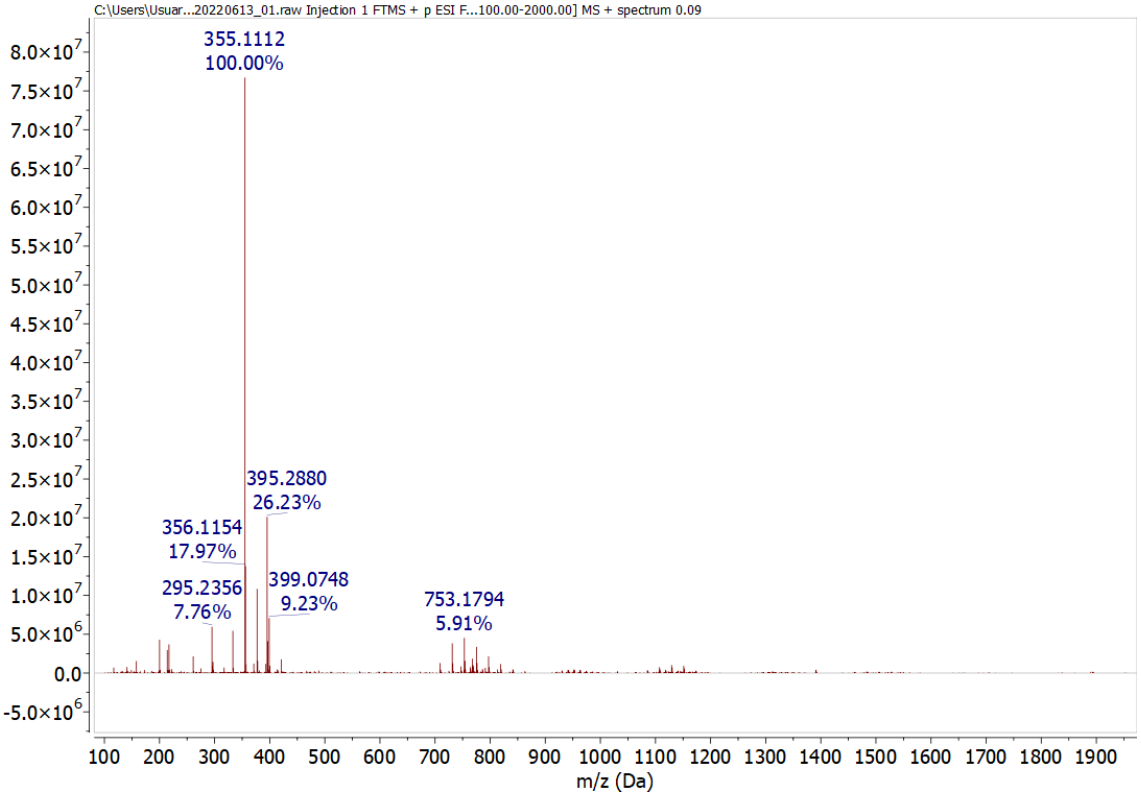
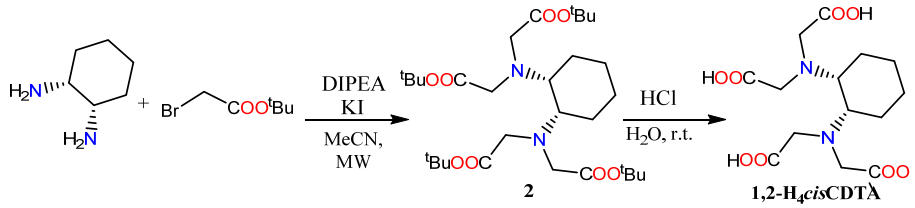


Figure S6: Experimental high resolution mass spectrum (ESI$^+$) of **1,2-H$_4$CpDTA**.



Scheme S2: Synthesis of **1,2-*c*-H_4CDTA**.

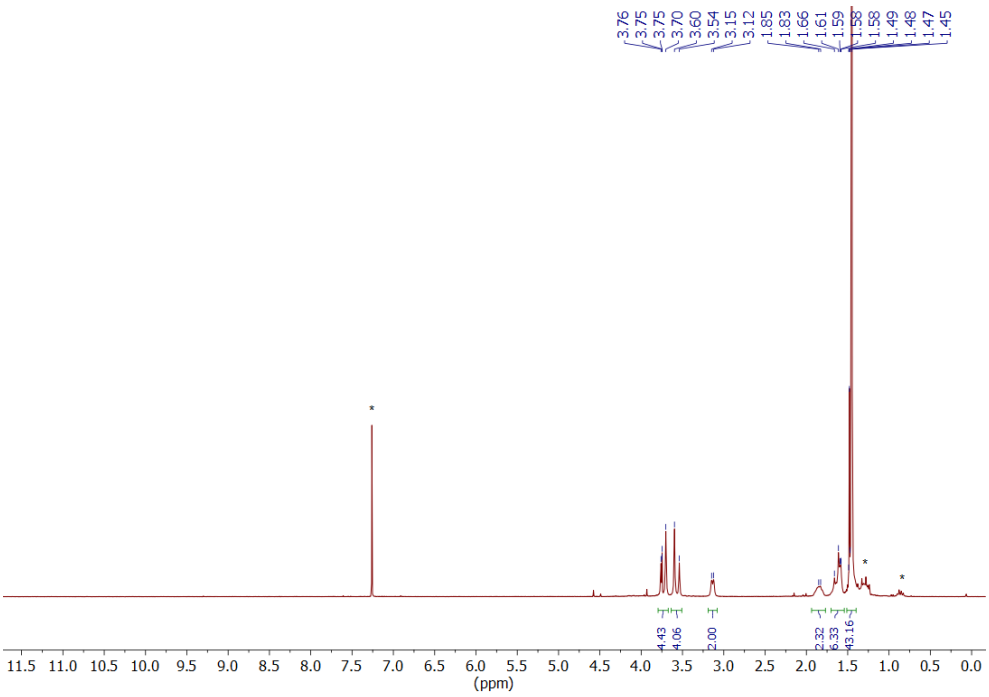


Figure S7: ^{1}H NMR spectrum of compound **2** (300 MHz, $CDCl_3$, 298 K). *Solvent residues

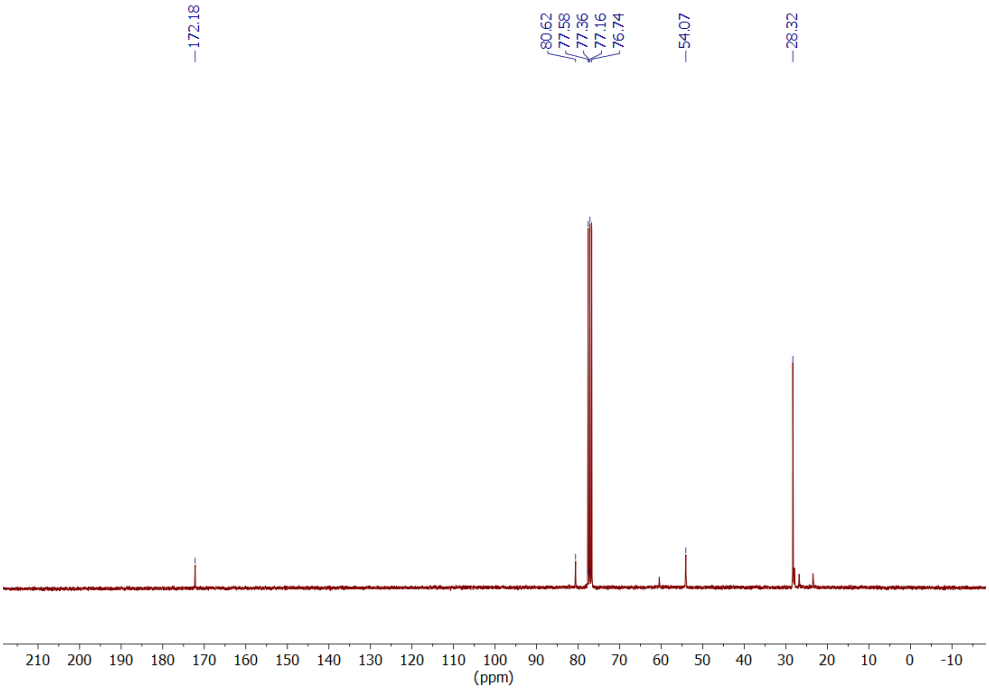


Figure S8: ^{13}C NMR spectrum of compound **2** (75 MHz, $CDCl_3$, 298 K).

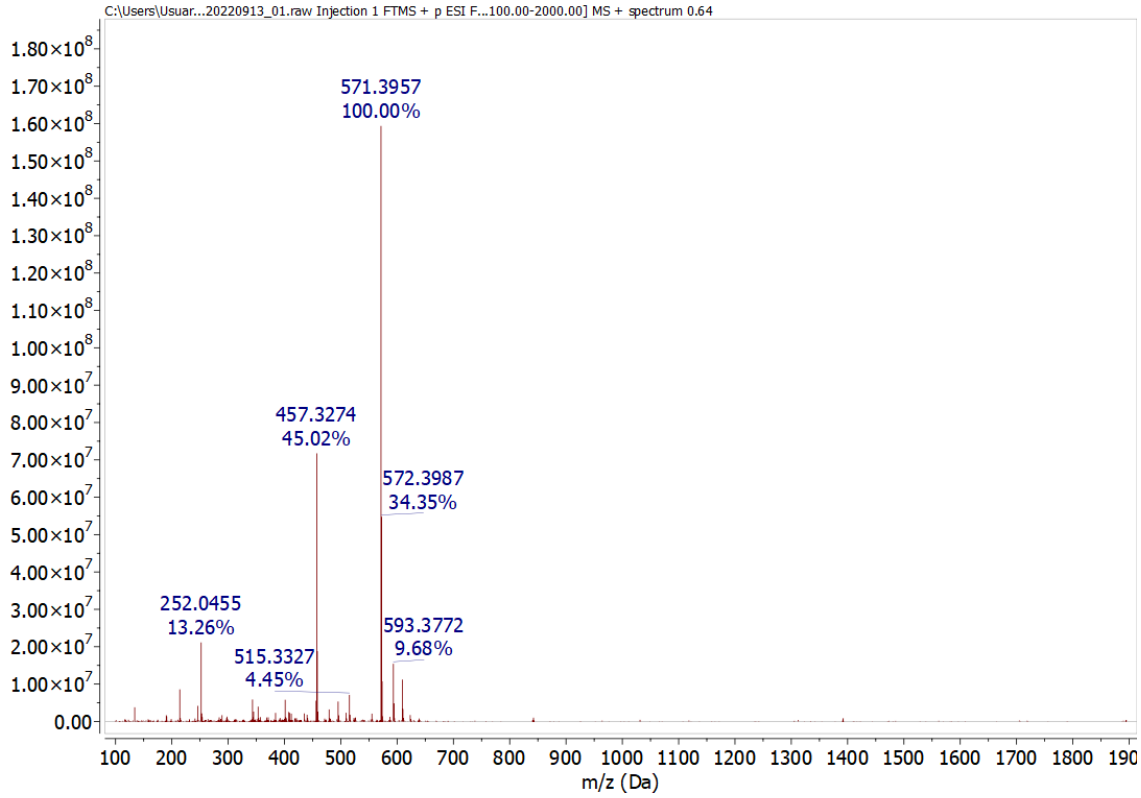


Figure S9: Experimental high resolution mass spectrum (ESI^+) of compound **2**.

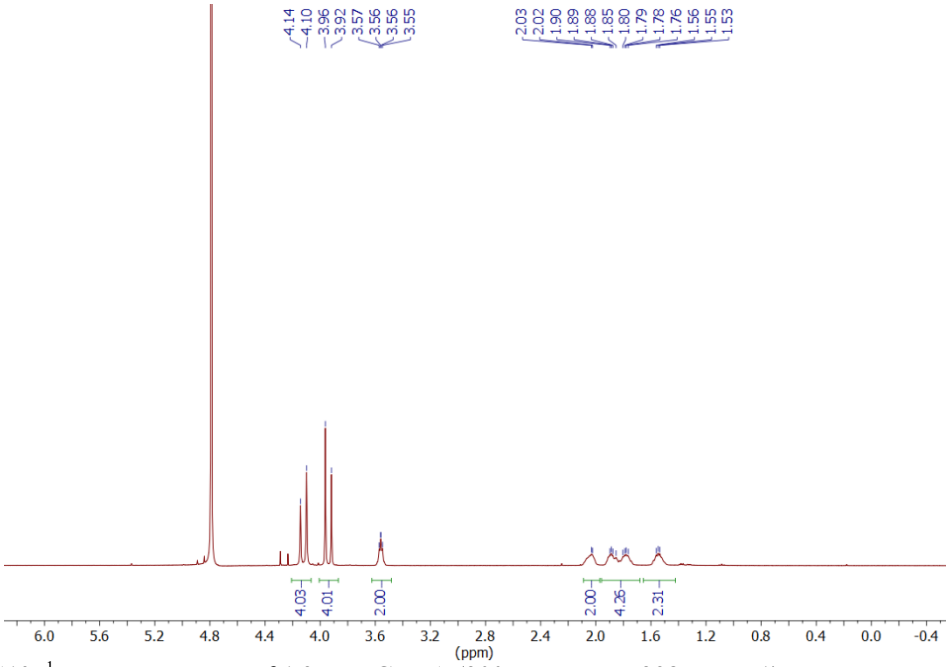


Figure S10: ^1H NMR spectrum of **1,2-*c*-H_4CDTA** (300 MHz, D_2O, 298 K, pH 1).

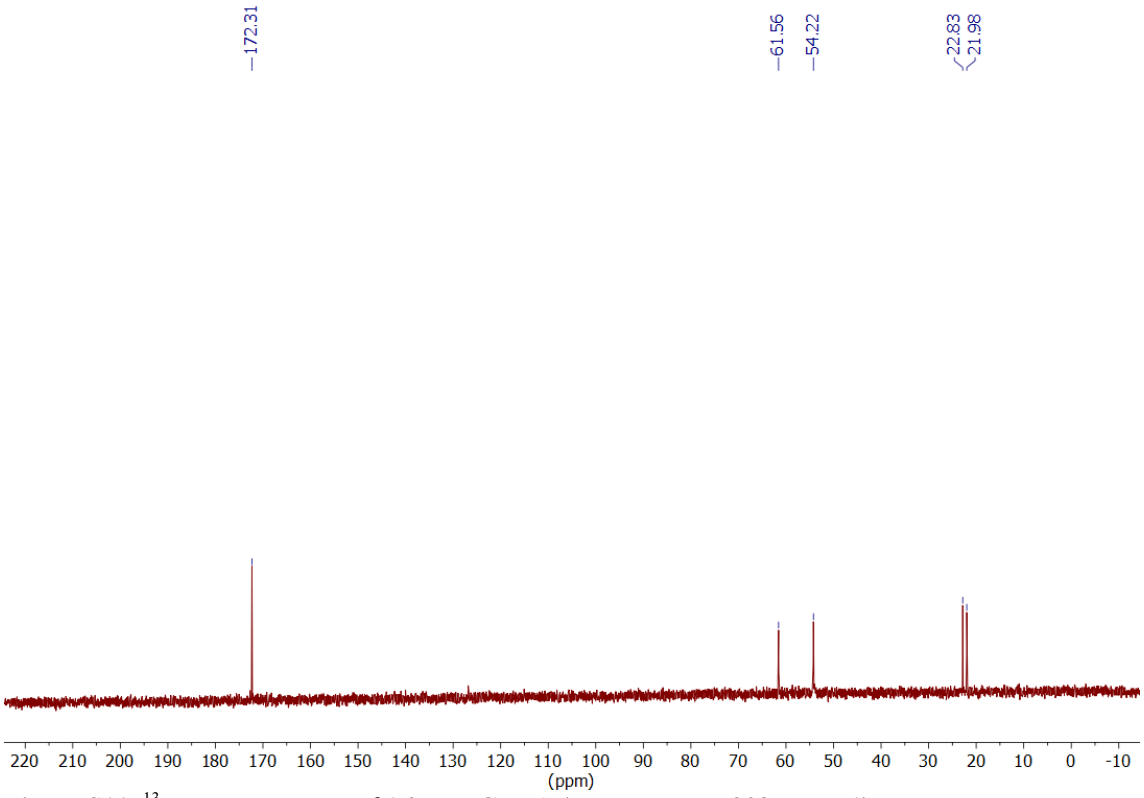


Figure S11: ^{13}C NMR spectrum of **1,2-*c*-H$_4$CDTA** (75 MHz, D_2O, 298 K, pH 1).

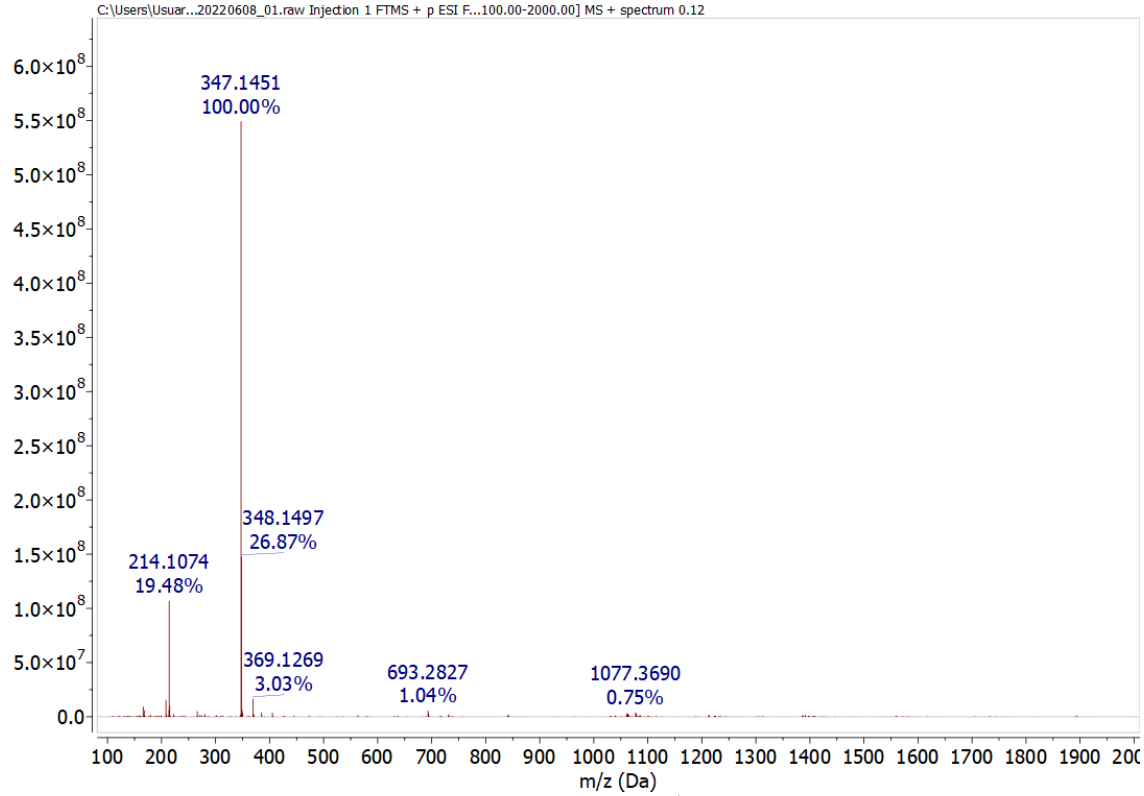
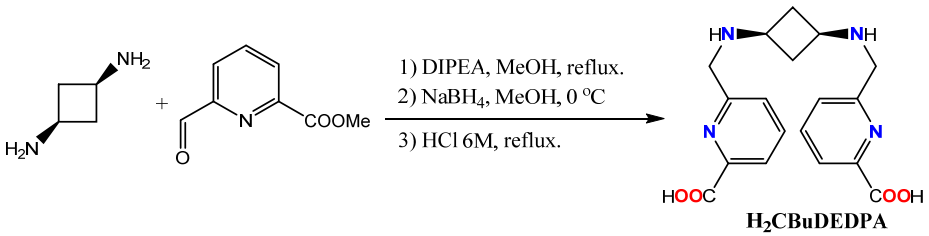


Figure S12: Experimental high resolution mass spectrum (ESI$^+$) of **1,2-*c*-H$_4$CDTA**.



Scheme S3: Synthesis of **H_2CBuDEDPA**.

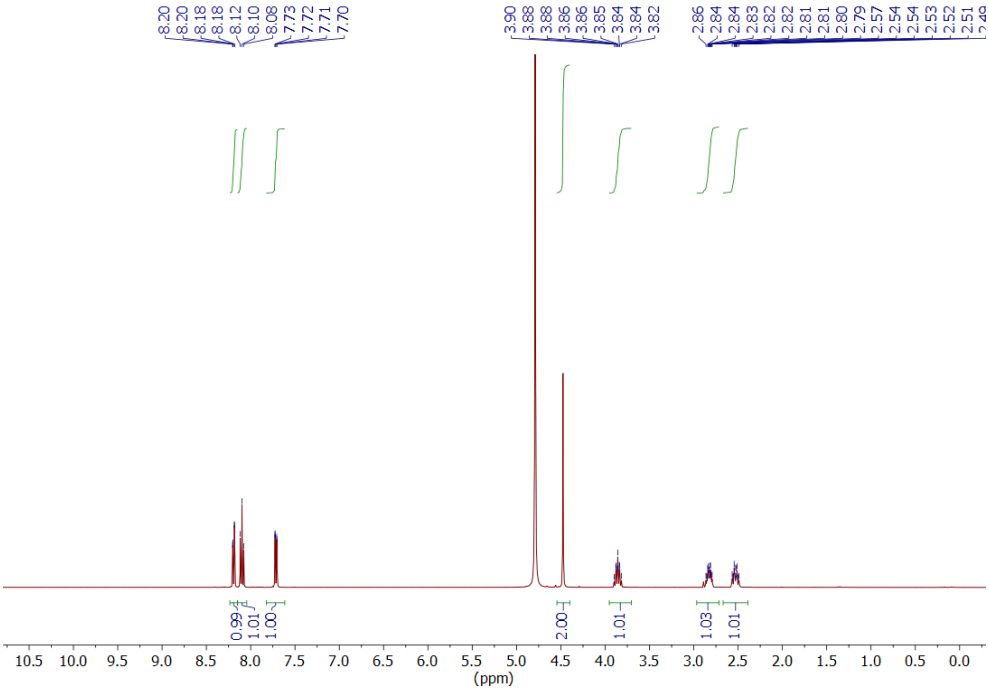


Figure S13: ^{1}H NMR spectrum of **H_2CBuDEDPA** (400 MHz, D_2O, pH 2, 298 K).

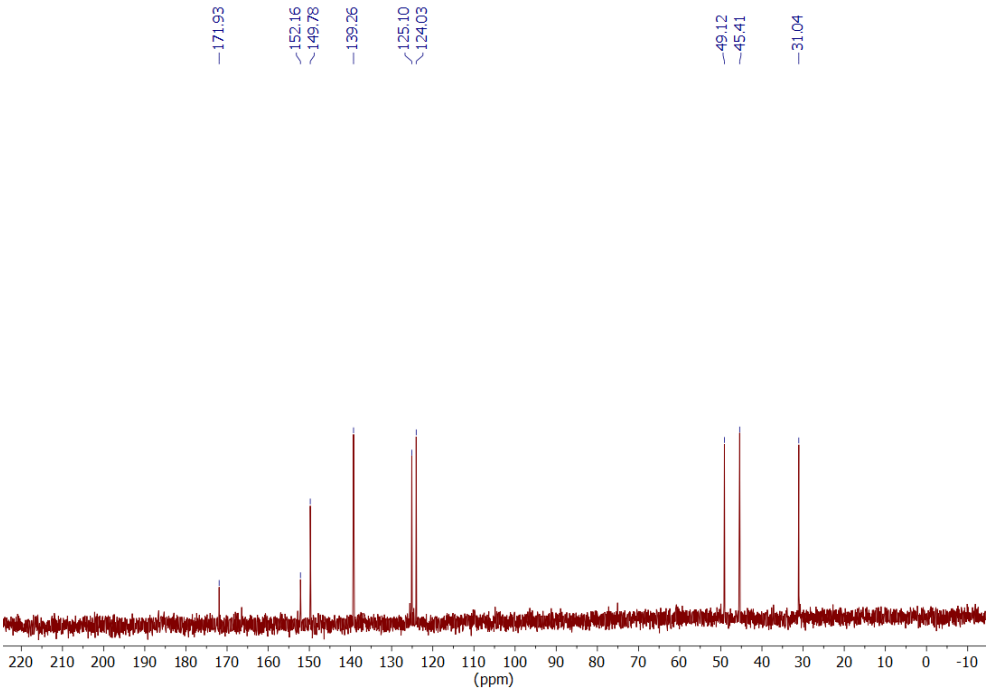


Figure S14: ^{13}C NMR spectrum of **H_2CBuDEDPA** (400 MHz, D_2O, pH 2, 298 K).

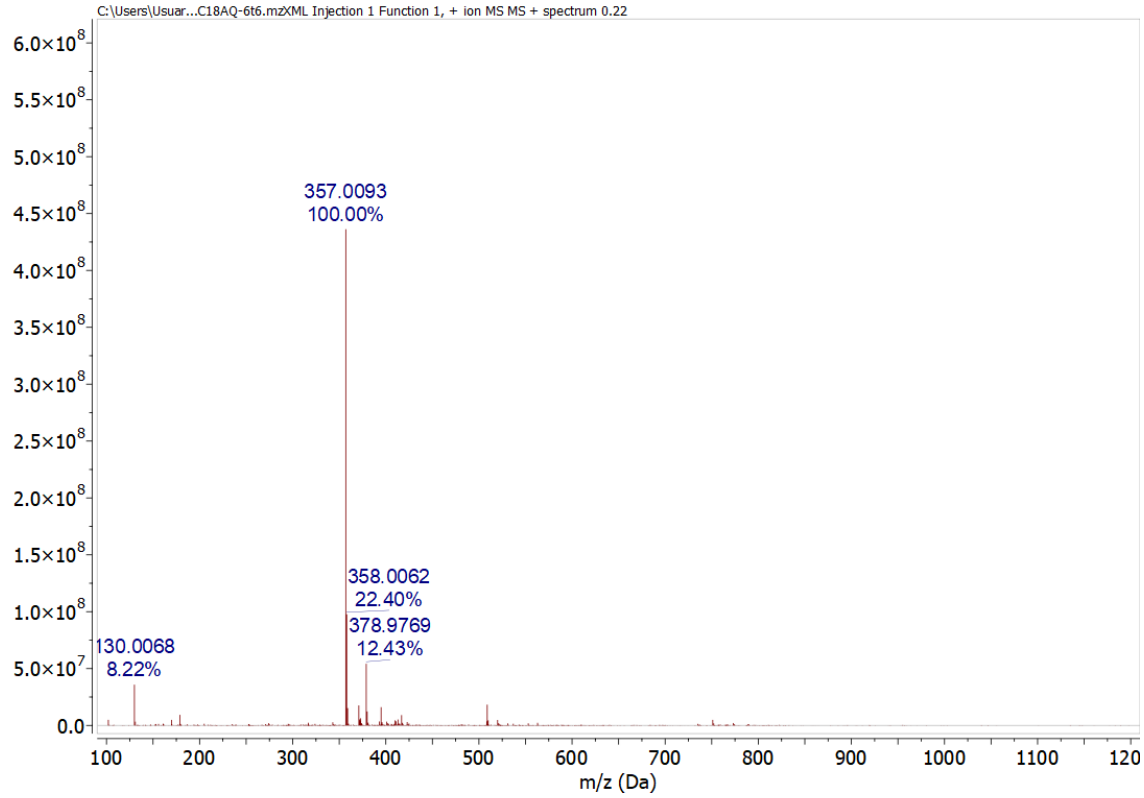


Figure S15: Experimental high resolution mass spectrum (ESI$^+$) of **H_2CBuDEDPA**.

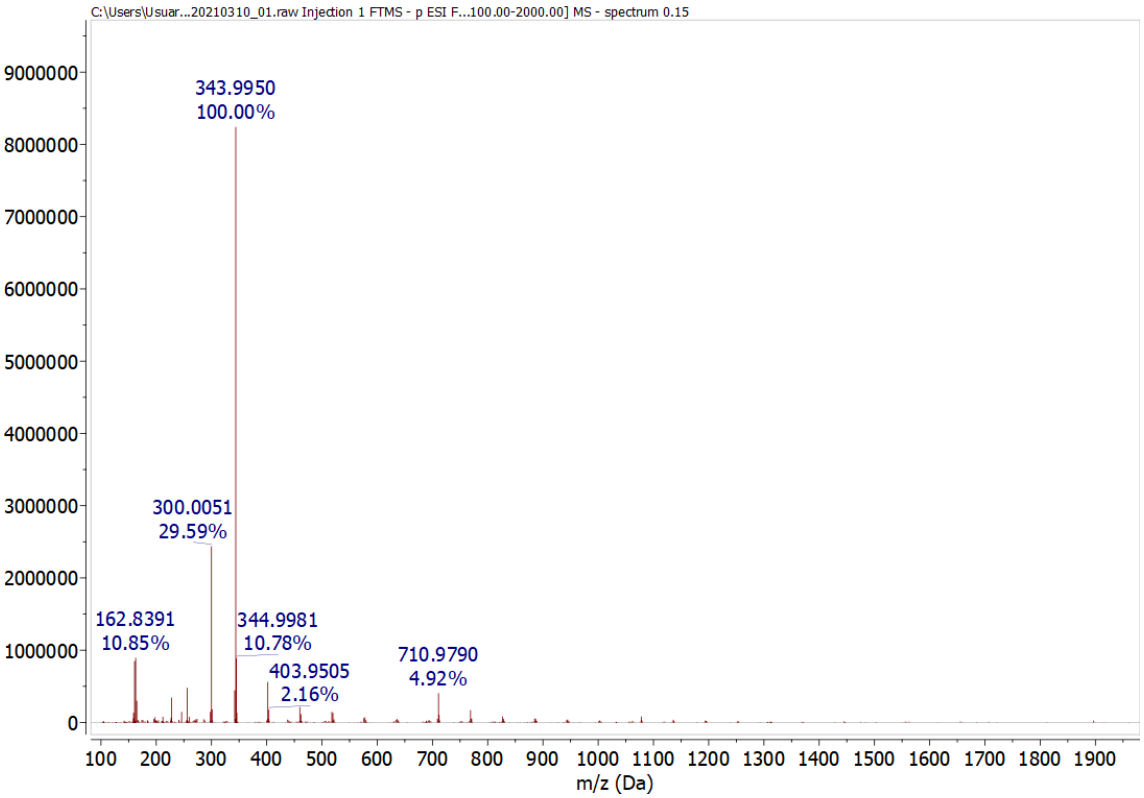


Figure S16: Experimental high resolution mass spectrum (ESI$^+$) of [**Fe(EDTA)**]$^-$.

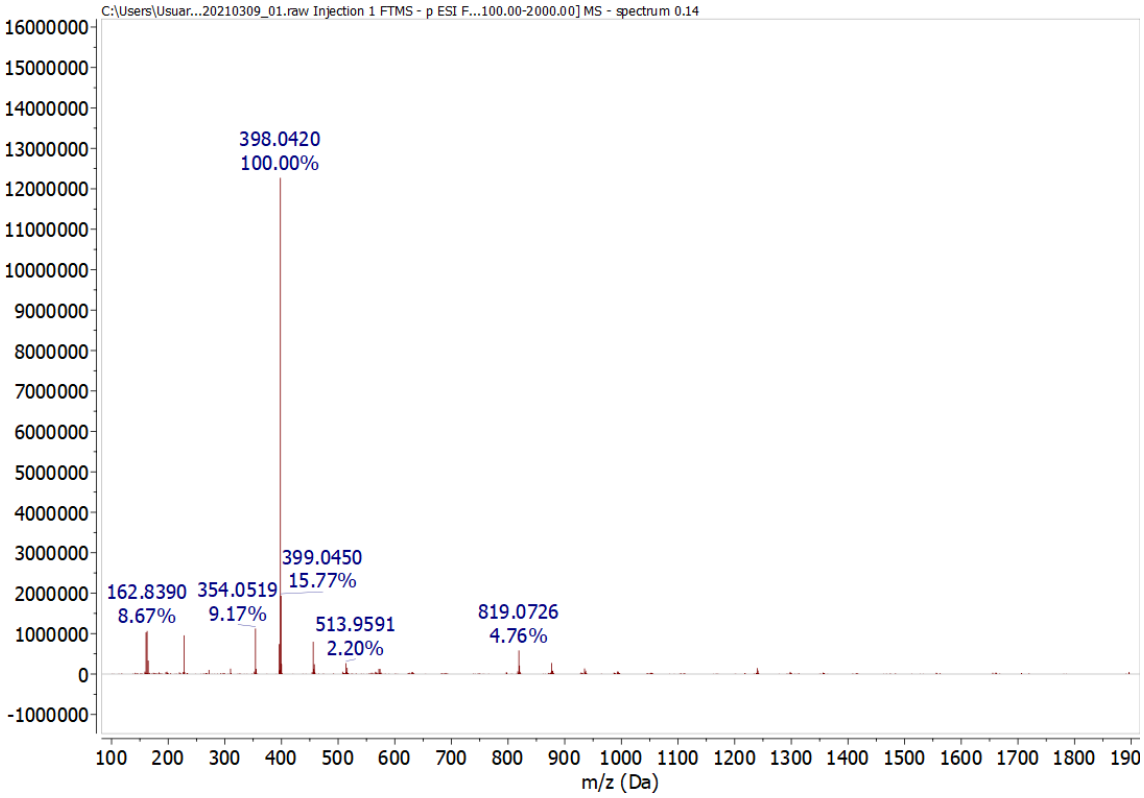


Figure S17: Experimental high resolution mass spectrum (ESI$^+$) of [**Fe(*t*-CDTA)**]$^-$.

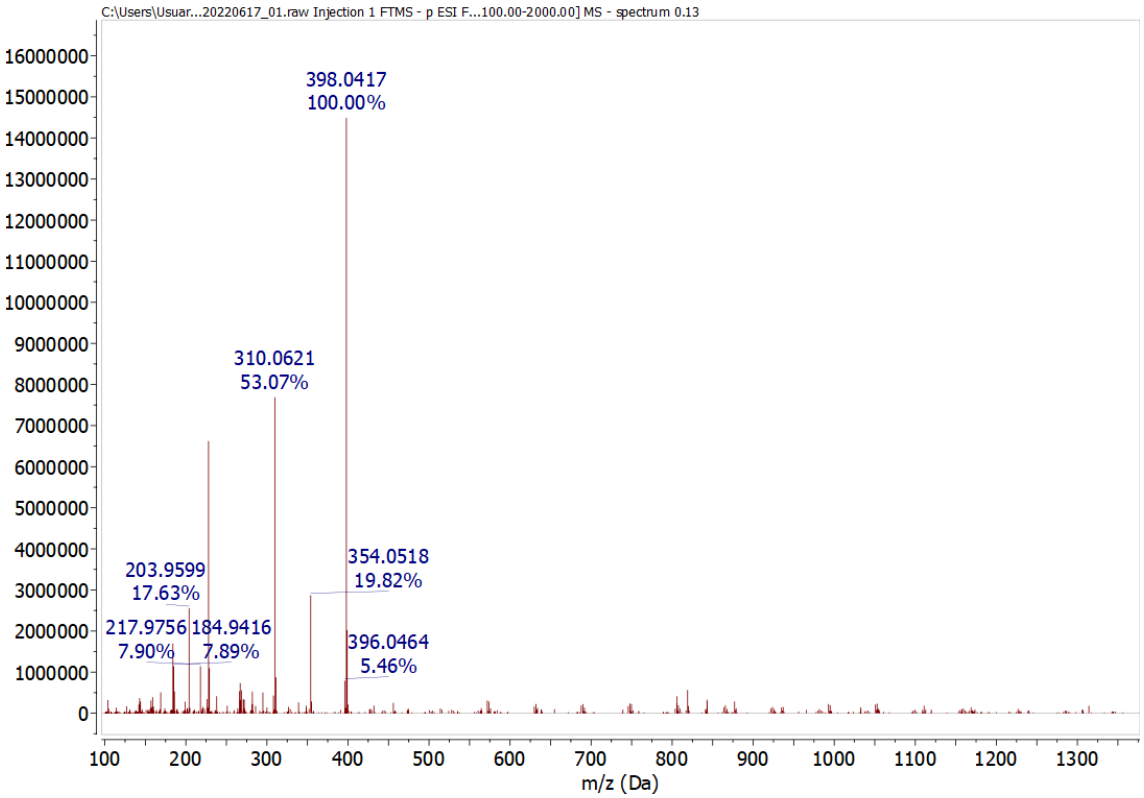


Figure S 18: Experimental high resolution mass spectrum (ESI$^+$) of **[Fe(*c*-CDTA)]**$^-$.

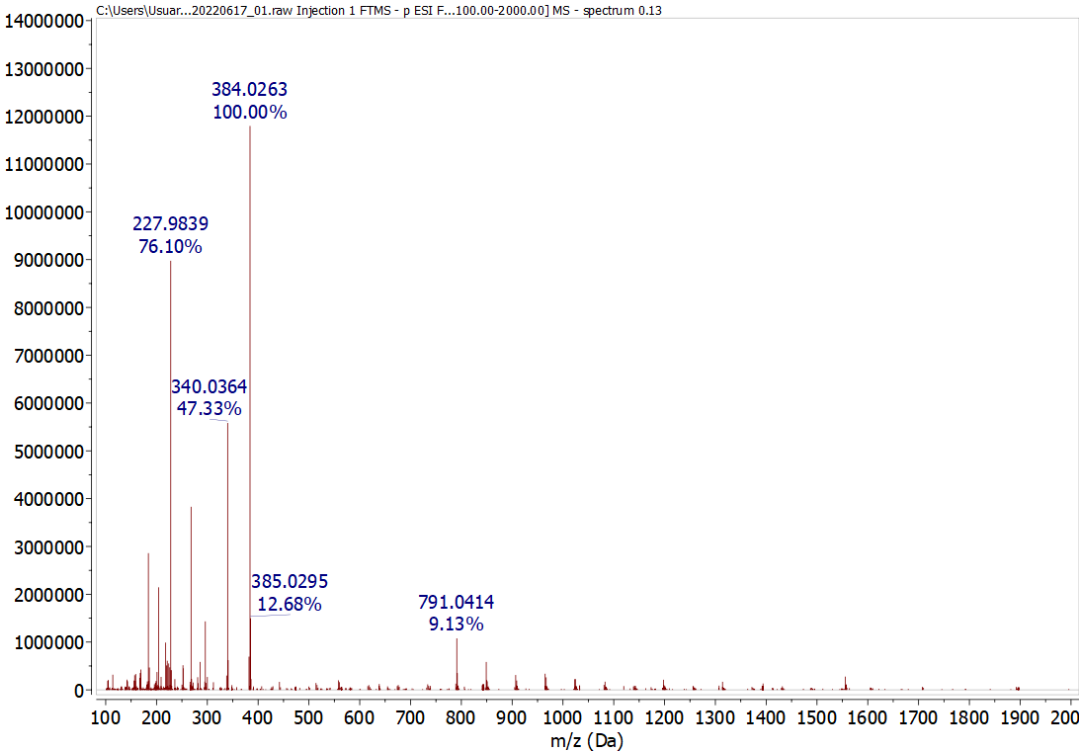


Figure S 19: Experimental high resolution mass spectrum (ESI^+) of **[Fe(CpDTA)]**$^-$.

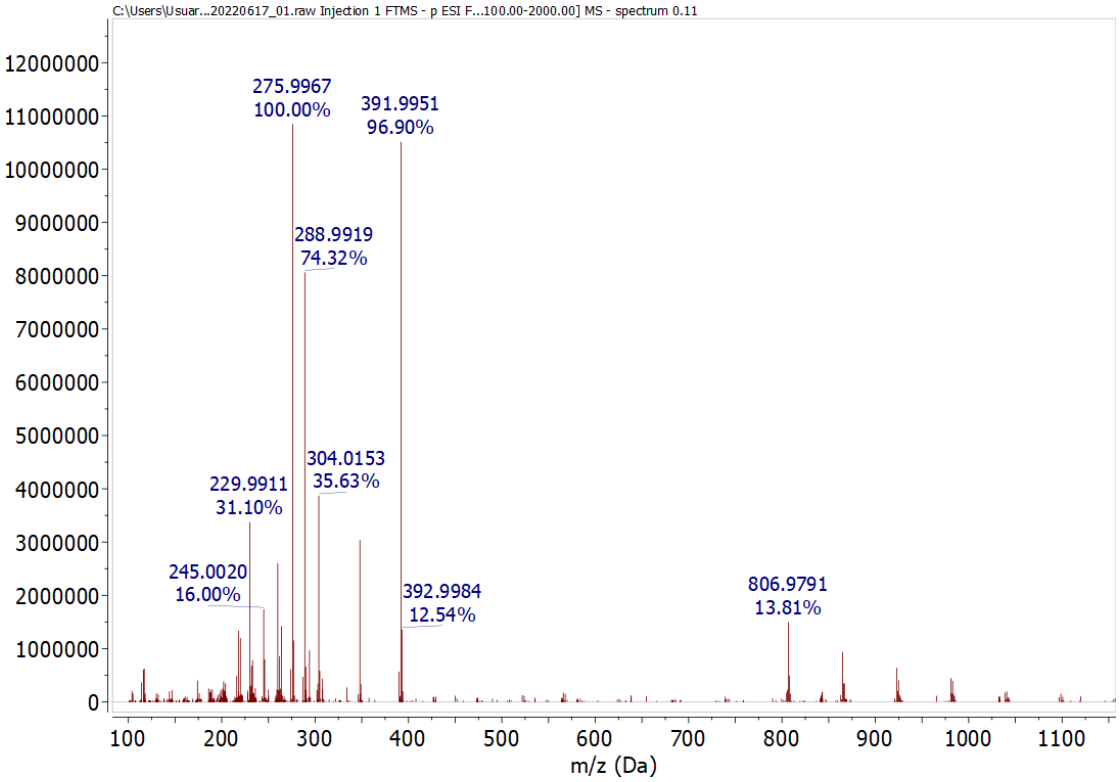


Figure S 20: Experimental high resolution mass spectrum (ESI^+) of **[Fe(PhDTA)]**$^-$.

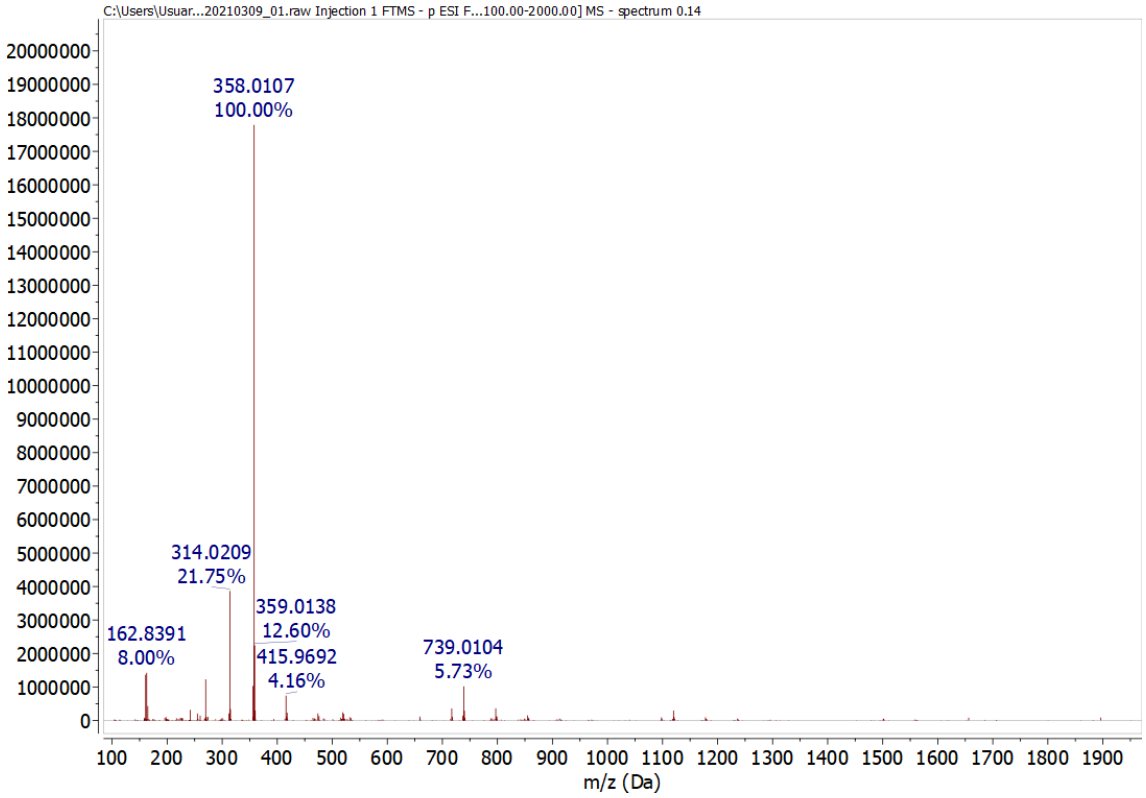


Figure S21: Experimental high resolution mass spectrum (ESI$^+$) of [**Fe(PDTA)**]$^-$.

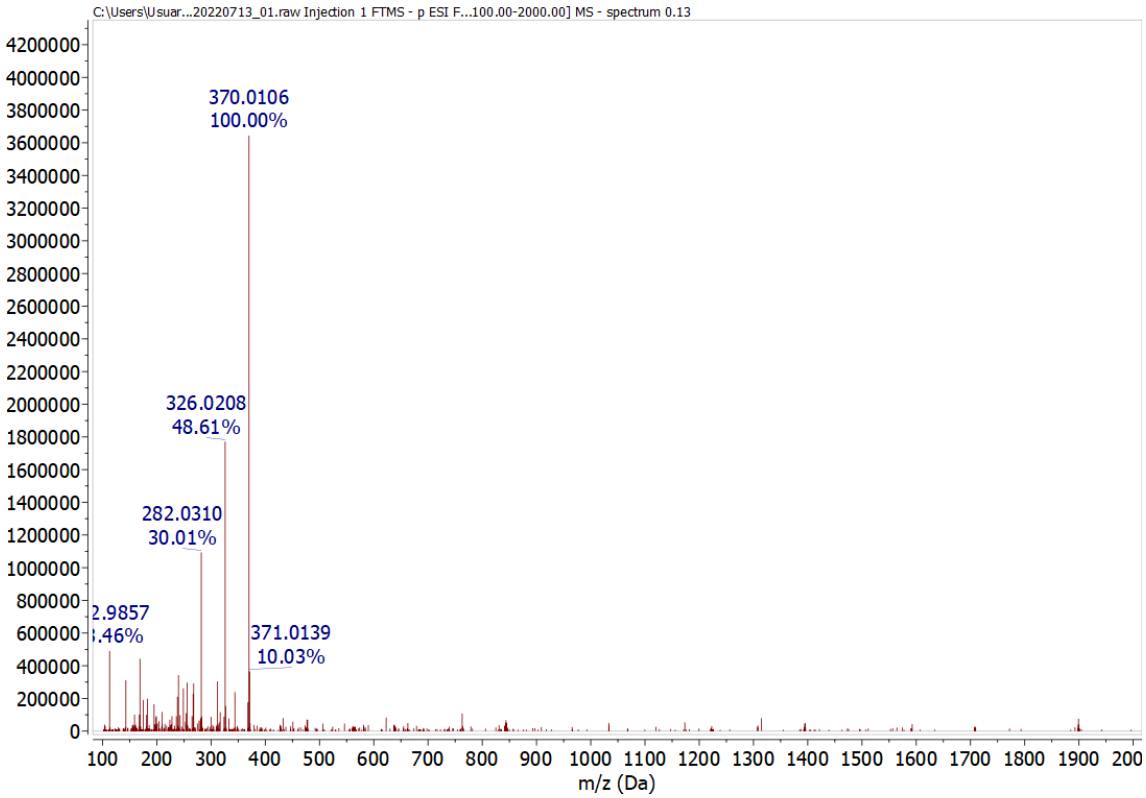


Figure S22: Experimental high resolution mass spectrum (ESI$^+$) of [**Fe(CBuDTA)**]$^-$.

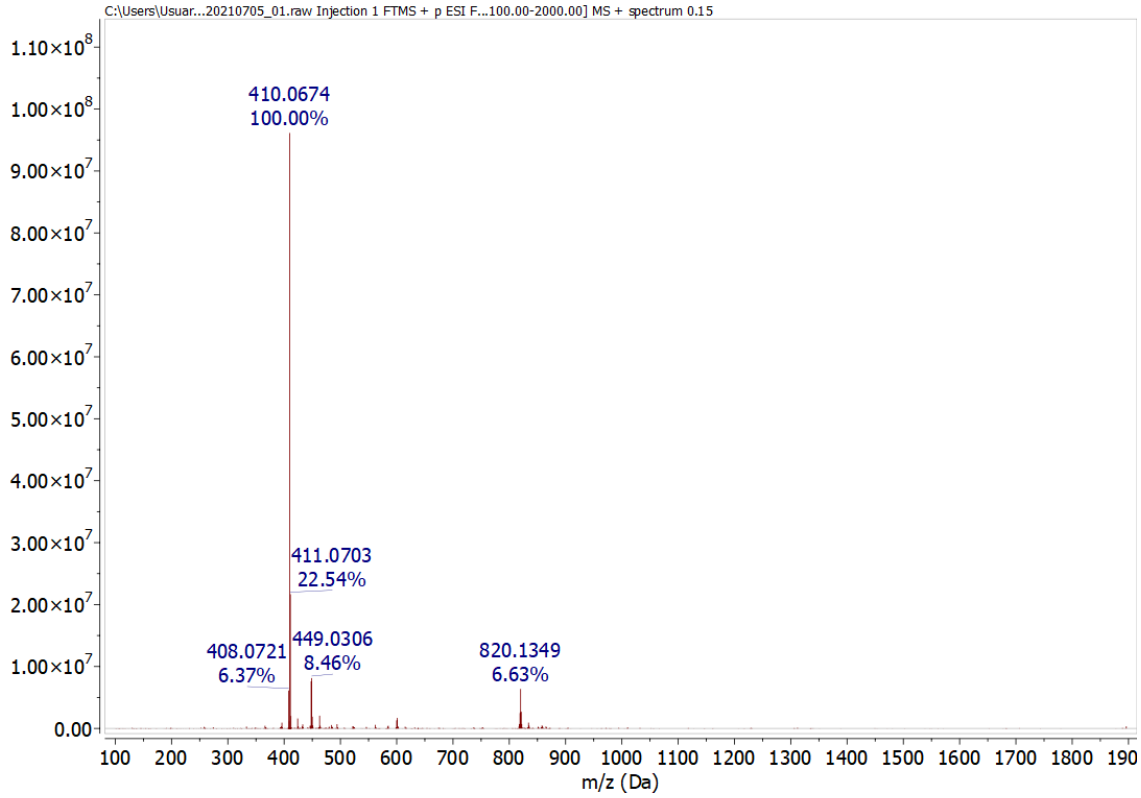


Figure S23: Experimental high resolution mass spectrum (ESI$^+$) of [**Fe(CBuDEDPA)]**$^+$.

Table S1: Crystal Data and Structure Refinement Details. Parameter **[Fe(CBuDEDPA)](PF$_6$)**.

Empirical formula	**[Fe($C_{18}H_{20}N_4O_5$]PF_6**
Molecular weight MW	573.20
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	12.4135(5)
b/Å, β/°	10.9733(4), 93.6190(10)
c/Å	15.5664(6)
Volume (Å^3)	2116.18(14)
Z	4
ρ_{calc} (g/cm^3)	1.799
μ (mm^{-1})	0.883
θ range	2.48º-28.31º
***R*$_{int}$**	0.0310
Measured reflections	43559
Independent reflections / unique (I >2σ (I)	5254 / 4893
Goodness-of-fit on F^2	1.092
R_1	0.0298
wR_2 (all data)	0.0710
Larg. diff. peak and hole (eÅ^{-3})	0.45 and -0.35

Cyclic voltammetry

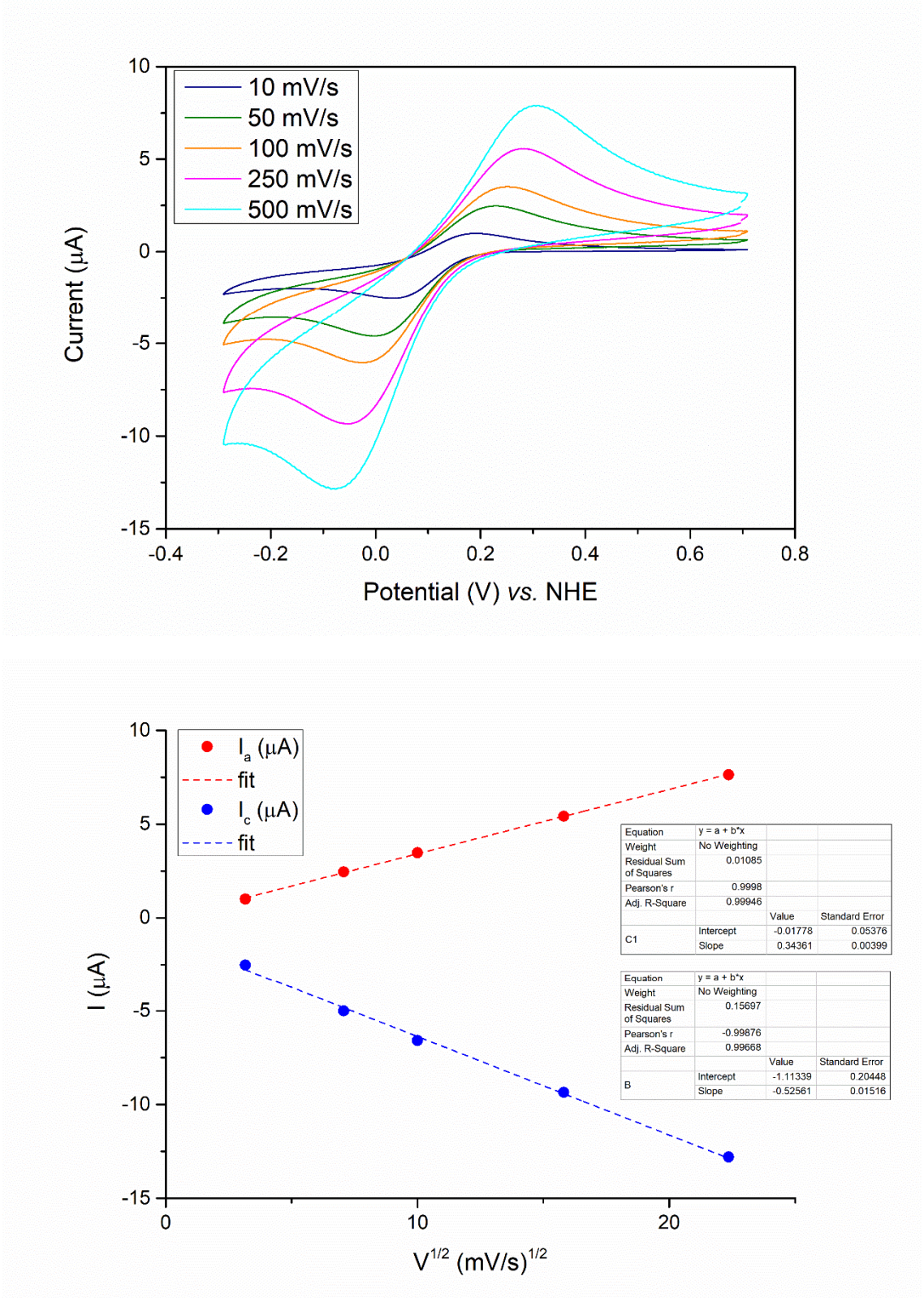


Figure S24: Cyclic voltammogram of **[Fe(EDTA)]**$^{-}$ complex in aqueous solution in 0.15 M NaCl (2.6 mM, pH= 5.5), recorded at 10, 50, 100, 250, and 500 mV·s^{-1} (top); and plots of the linear dependence of anodic and cathodic peak currents with the square root of the scan rate (bottom).

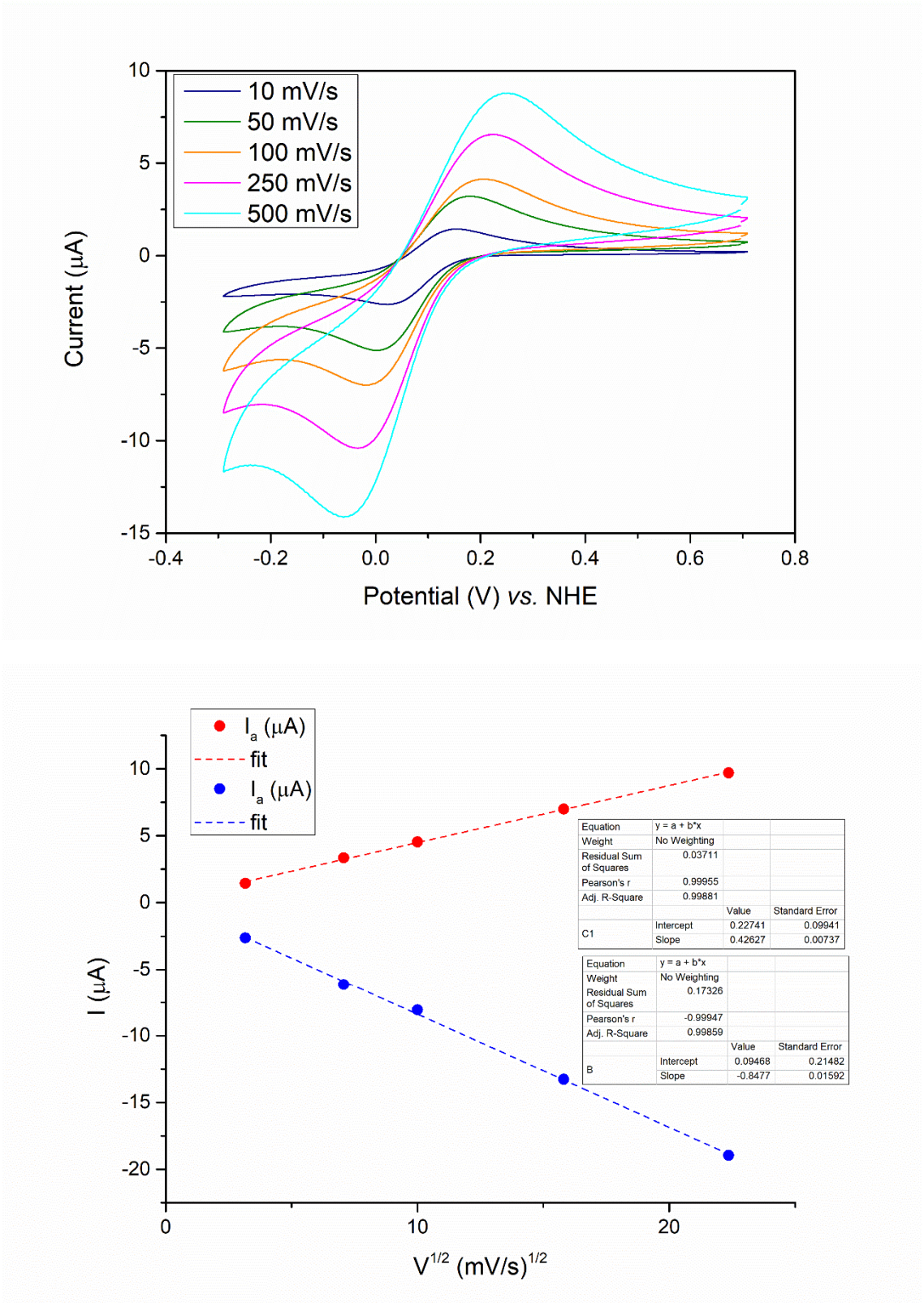


Figure S25: Cyclic voltammogram of **[Fe(*t*-CDTA)]**$^{-}$ complex in aqueous solution in 0.15 M NaCl (2.6 mM, pH= 5.3), recorded at 10, 50, 100, 250, and 500 mV·s^{-1} (top); and plots of the linear dependence of anodic and cathodic peak currents with the square root of the scan rate (bottom).

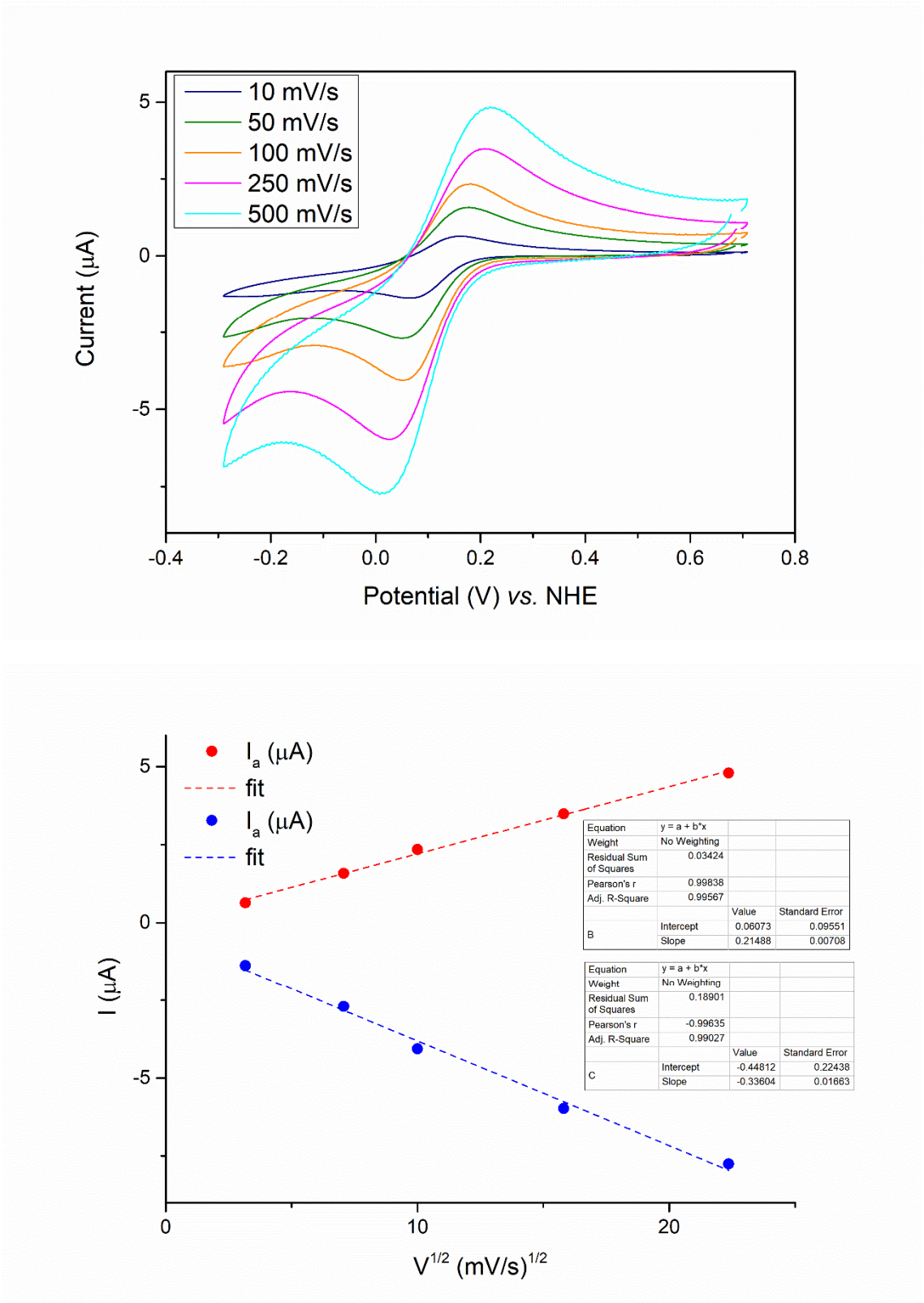


Figure S26: Cyclic voltammogram of **[Fe(*c*-CDTA)]**$^{-}$ complex in aqueous solution in 0.15 M NaCl (2.0 mM, pH= 6.8), recorded at 10, 50, 100, 250, and 500 mV·s^{-1} (top); and plots of the linear dependence of anodic and cathodic peak currents with the square root of the scan rate (bottom).

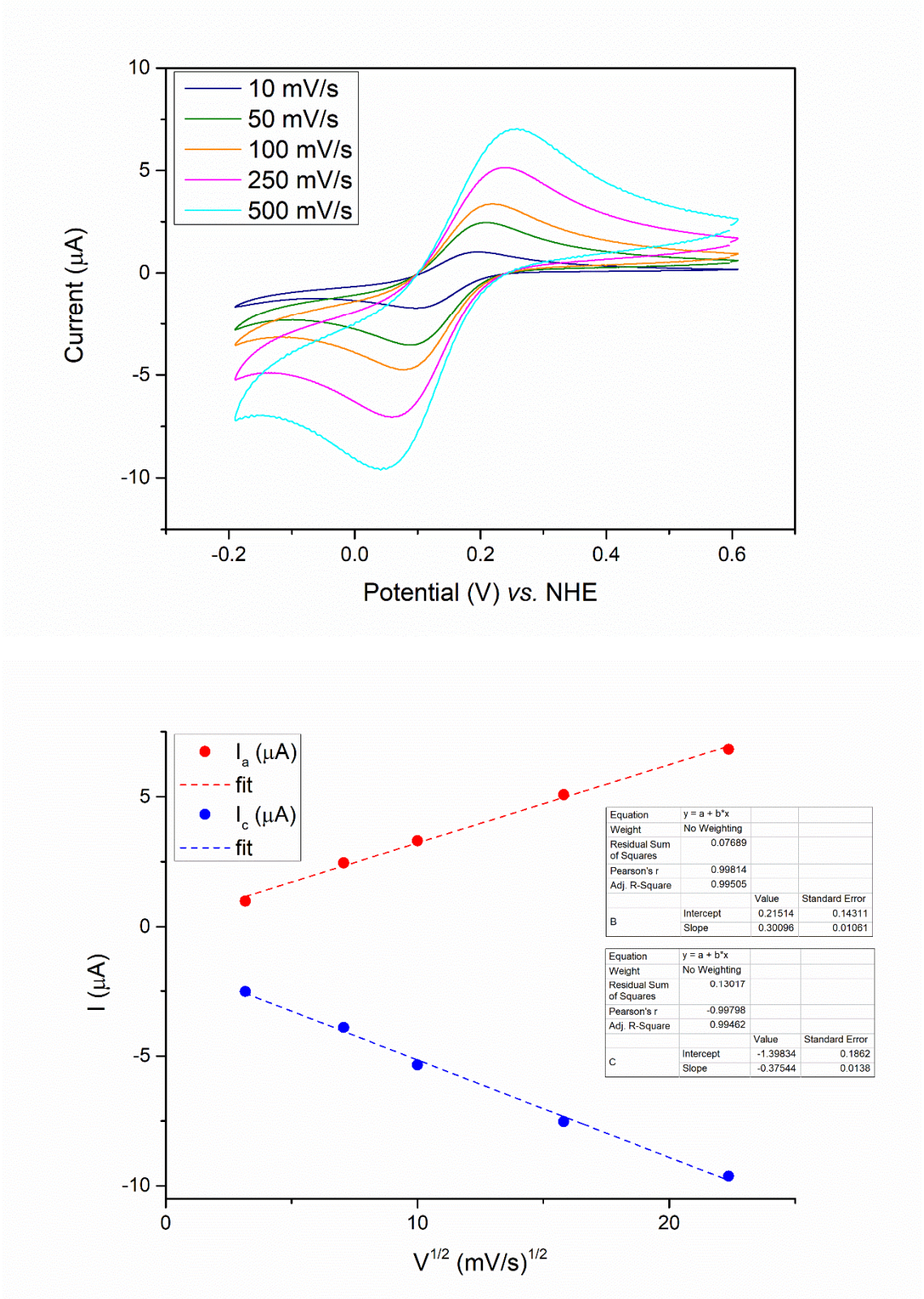


Figure S27: Cyclic voltammogram of **[Fe(CpDTA)]**$^{-}$ complex in aqueous solution in 0.15 M NaCl (2.0 mM, pH= 5.7), recorded at 10, 50, 100, 250, and 500 mV·s^{-1} (top); and plots of the linear dependence of anodic and cathodic peak currents with the square root of the scan rate (bottom).

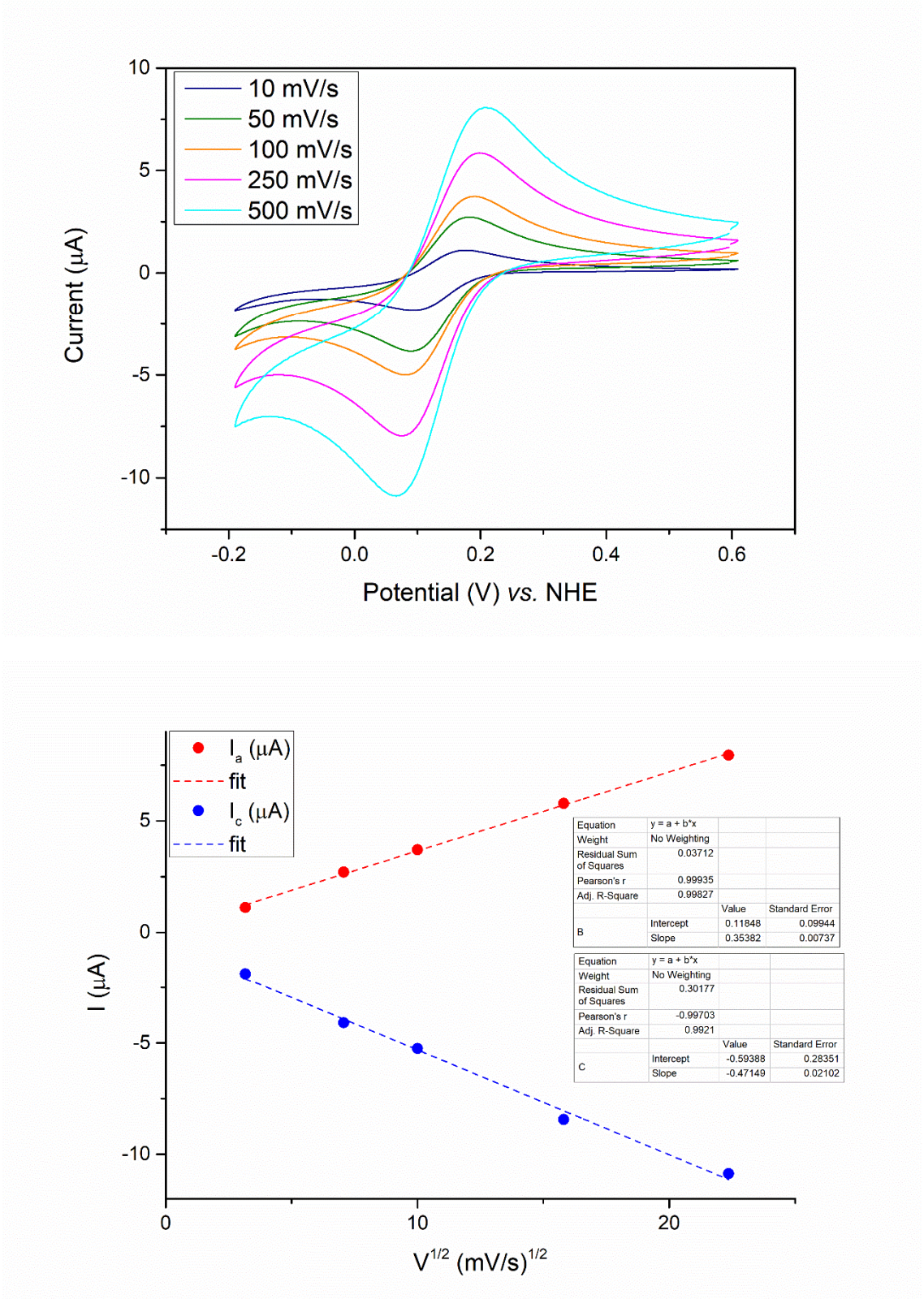


Figure S28: Cyclic voltammogram of **[Fe(PhDTA)]**$^{-}$ complex in aqueous solution in 0.15 M NaCl (2 mM, pH= 5.6), recorded at 10, 50, 100, 250, and 500 mV·s^{-1} (top); and plots of the linear dependence of anodic and cathodic peak currents with the square root of the scan rate (bottom).

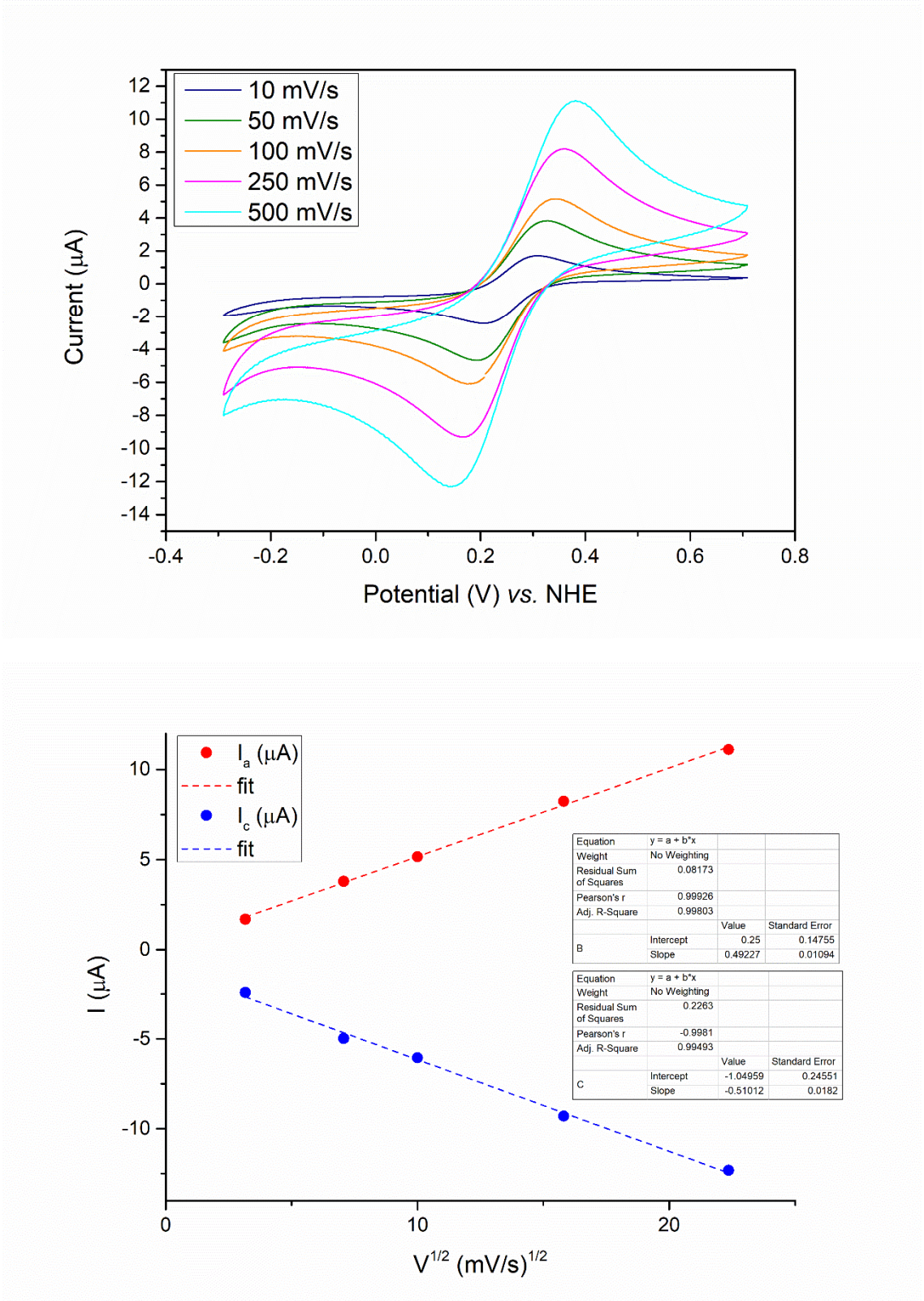


Figure S29: Cyclic voltammogram of **[Fe(PDTA)]**$^{-}$ complex in aqueous solution in 0.15 M NaCl (3.0 mM, pH= 5.9), recorded at 10, 50, 100, 250, and 500 mV·s^{-1} (top); and plots of the linear dependence of anodic and cathodic peak currents with the square root of the scan rate (bottom).

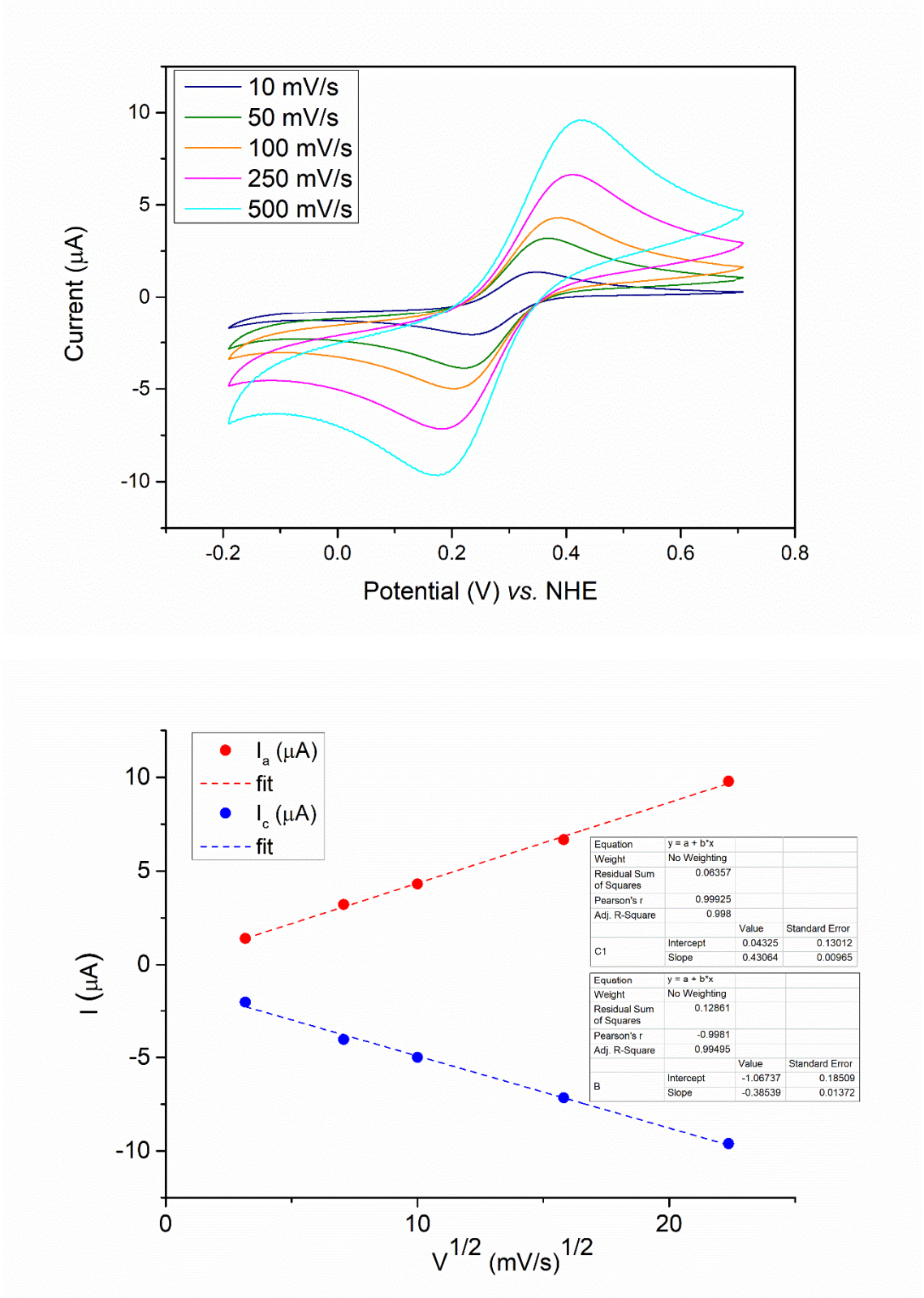


Figure S30: Cyclic voltammogram of **[Fe(CBuDTA)]**$^{-}$ complex in aqueous solution in 0.15 M NaCl (2.3 mM, pH= 5.7), recorded at 10, 50, 100, 250, and 500 mV·s^{-1} (top); and plots of the linear dependence of anodic and cathodic peak currents with the square root of the scan rate (bottom).

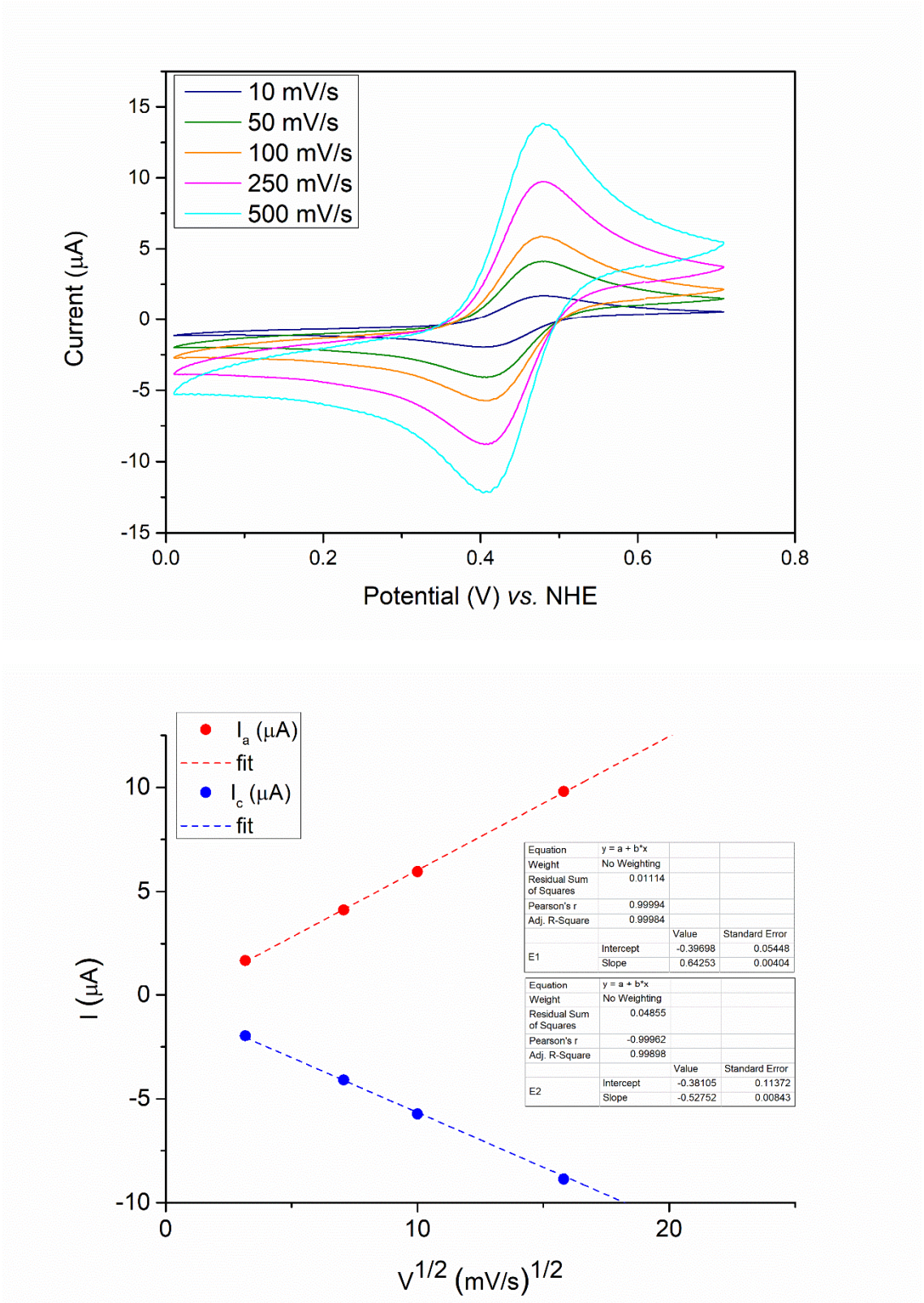


Figure S31: Cyclic voltammogram of **[Fe(CBuDEDPA)]**$^{+}$ complex in aqueous solution in 0.15 M NaCl (1.5 mM, pH= 5.1), recorded at 10, 50, 100, 250, and 500 mV·s^{-1} (top); and plots of the linear dependence of anodic and cathodic peak currents with the square root of the scan rate (bottom).

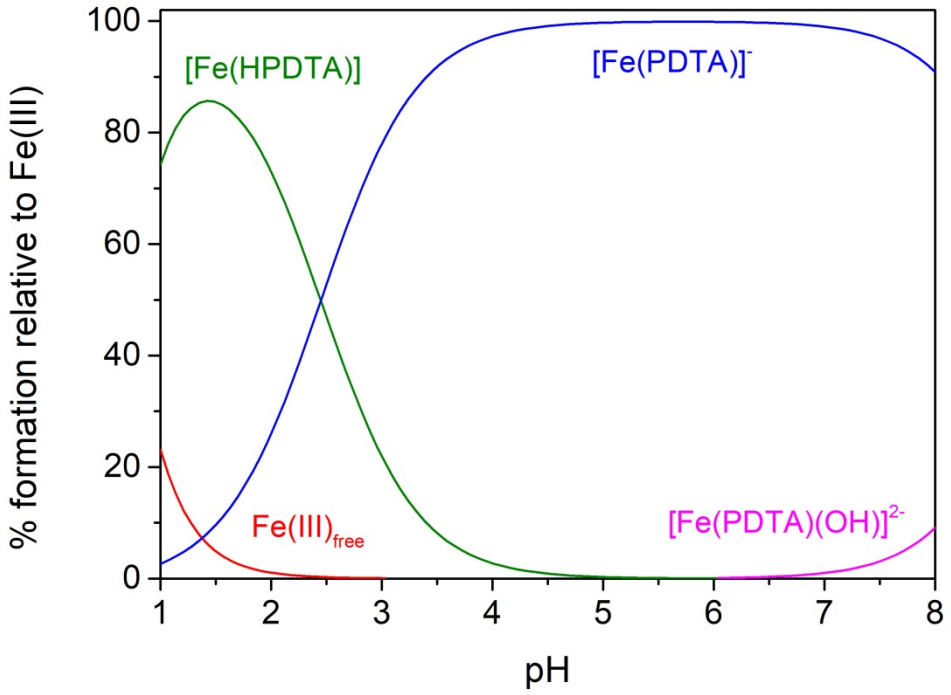


Figure S32: Speciation diagram calculated for the Fe(III)-PDTA^{4-} using the equilibrium data reported in the literature.[1]

Table S2: Optimized Cartesian coordinates (Å) of the **[Fe(EDTA)(δ)(H$_2$O)]$^-$·5H$_2$O** system obtained with DFT calculations (0 Imaginary Frequencies).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8		2.260386	-0.720986	1.364607
2	8		3.749283	-2.381962	1.257905
3	8		2.699927	3.027797	-1.480850
4	8		1.002364	1.892593	-0.576985
5	8		-0.272768	-2.128111	0.635356
6	8		-1.988091	-3.529867	0.377144
7	8		-1.694301	1.014213	0.143891
8	8		-2.736900	2.265112	-1.379147
9	7		-0.827094	-0.766069	-1.631576
10	7		2.057891	-0.496393	-1.283552
11	6		0.128328	-1.424204	-2.524820
12	1		0.306078	-2.429024	-2.124202
13	6		1.445053	-0.666274	-2.603167
14	1		1.270045	0.334653	-3.014102
15	6		2.712607	-1.691415	-0.771657
16	1		2.064953	-2.560203	-0.934401
17	1		3.675199	-1.891724	-1.265565
18	6		2.943438	-1.602963	0.745886
19	6		2.936161	0.668182	-1.260442
20	1		3.591291	0.606205	-0.384418
21	1		3.575407	0.724569	-2.152972
22	6		2.156569	1.984499	-1.113633
23	6		-1.824685	-1.706111	-1.138329
24	1		-2.701659	-1.155845	-0.779452
25	1		-2.173492	-2.393026	-1.923495
26	6		-1.315330	-2.531780	0.053325

27	6	-1.426654	0.445665	-2.166806
28	1	-0.660697	1.053810	-2.658816
29	1	-2.217997	0.242460	-2.904025
30	6	-2.006828	1.314834	-1.043825
31	8	0.077022	0.976794	2.362594
32	1	0.813332	0.891751	2.996708
33	1	-0.081237	1.926332	2.168212
34	8	-0.177393	3.518512	1.337854
35	8	2.350214	0.298596	3.821716
36	1	0.194793	3.097577	0.537631
37	1	-1.118260	3.699833	1.150147
38	1	2.259482	-0.327626	4.543945
39	1	2.463389	-0.219185	2.988964
40	26	0.348452	-0.025323	0.355241
41	8	-3.321749	-0.447054	1.957513
42	1	-2.779214	0.074710	1.343276
43	1	-3.788655	-1.123553	1.441017
44	8	-4.546015	-2.659609	0.602375
45	8	-2.887960	3.942846	0.740950
46	1	-2.914235	3.324891	-0.030163
47	1	-3.165168	4.805736	0.423509
48	1	-5.040118	-2.637915	-0.220708
49	1	-3.692077	-3.112322	0.424353
50	1	-0.288612	-1.549707	-3.536680
51	1	2.128005	-1.180352	-3.297719

Zero-point correction=	0.395443 (Hartree/Particle)
Thermal correction to Energy=	0.429967
Thermal correction to Enthalpy=	0.430911
Thermal correction to Gibbs Free Energy=	0.328274
Sum of electronic and zero-point Energies=	-2822.171259
Sum of electronic and thermal Energies=	-2822.136735
Sum of electronic and thermal Enthalpies=	-2822.135791
Sum of electronic and thermal Free Energies=	-2822.238428

Table S3: Optimized Cartesian coordinates (Å) of the **[Fe(EDTA)(λ)(H_2O)]$^-$·5H_2O** system obtained with DFT calculations (0 Imaginary Frequencies).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8		2.025312	0.170235	1.499139
2	8		3.934835	-0.705839	2.215335
3	8		2.273762	2.321420	-2.527490
4	8		0.870876	1.509959	-1.011310
5	8		-0.091661	-1.666672	0.995398
6	8		-1.389577	-3.460508	0.956583
7	8		-1.669150	0.625846	0.001190
8	8		-3.323395	1.163769	-1.381370
9	7		-0.551892	-1.054510	-1.644222
10	7		2.174180	-0.901860	-0.875139
11	6		0.510663	-1.410592	-2.588380
12	1		0.172870	-2.164704	-3.304481
13	6		1.714562	-1.914195	-1.833701
14	1		2.512044	-2.187205	-2.530097
15	6		3.026926	-1.492594	0.154341
16	1		2.609105	-2.454462	0.451812
17	1		4.046124	-1.663022	-0.197376
18	6		3.035354	-0.618599	1.395081
19	6		2.830906	0.237419	-1.533504
20	1		3.654899	0.586318	-0.910236
21	1		3.262417	-0.052399	-2.492462
22	6		1.935928	1.457554	-1.740364
23	6		-1.211750	-2.226403	-1.054364
24	1		-2.294595	-2.109896	-1.104855
25	1		-0.978936	-3.133766	-1.614219

26	6	-0.879311	-2.486694	0.411152
27	6	-1.518440	-0.132603	-2.229322
28	1	-0.988399	0.620101	-2.812911
29	1	-2.228898	-0.631732	-2.891617
30	6	-2.253201	0.609001	-1.130900
31	8	-0.174015	1.478969	1.817585
32	1	0.527145	1.734414	2.443825
33	1	-0.481644	2.302274	1.377823
34	8	-0.667146	3.642116	0.272781
35	8	1.972415	2.000717	3.512764
36	1	-0.245351	3.150377	-0.442779
37	1	-1.622350	3.658216	0.072303
38	1	1.865163	1.633089	4.390385
39	1	2.279885	1.265070	2.954654
40	26	0.364084	0.093494	0.260504
41	8	-3.406172	-0.101247	2.161926
42	1	-2.803352	0.223875	1.479770
43	1	-3.650969	-0.993020	1.875342
44	8	-4.054190	-2.796678	1.426149
45	8	-3.405111	3.557608	-0.086141
46	1	-3.481602	2.675094	-0.502857
47	1	-3.767893	4.174038	-0.722253
48	1	-4.575818	-2.922105	0.633504
49	1	-3.178858	-3.165362	1.224682
50	1	0.769522	-0.521420	-3.161830
51	1	1.453209	-2.811350	-1.274258

Zero-point correction=	0.394748 (Hartree/Particle)
Thermal correction to Energy=	0.429716
Thermal correction to Enthalpy=	0.430660
Thermal correction to Gibbs Free Energy=	0.325829
Sum of electronic and zero-point Energies=	-2822.171634
Sum of electronic and thermal Energies=	-2822.136666
Sum of electronic and thermal Enthalpies=	-2822.135722
Sum of electronic and thermal Free Energies=	-2822.240552

Table S4: Optimized Cartesian coordinates (Å) of the **[Fe(*t*-CDTA)(δ)(H_2O)]$^{-}$·5H_2O** system obtained with DFT calculations (0 Imaginary Frequencies).

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	8	-0.186053	-2.236125	1.438499
2	8	-1.672776	-2.907648	2.949202
3	8	-0.872021	-2.780407	-2.942684
4	8	0.225805	-1.441606	-1.549676
5	8	0.393909	0.348983	2.018451
6	8	0.799173	2.260032	3.070034
7	8	1.841685	0.548593	-0.693879
8	8	2.174905	1.757605	-2.529111
9	7	-0.508539	1.497323	-0.203773
10	7	-1.899571	-0.959689	-0.026463
11	6	-1.983956	1.509025	-0.084569
12	1	-2.190845	1.546890	0.988163
13	6	-2.572412	0.215599	-0.629643
14	1	-2.344941	0.167342	-1.697698
15	6	-2.365582	-1.316043	1.315097
16	1	-2.443756	-0.419833	1.930497
17	1	-3.340650	-1.804353	1.305338
18	6	-1.352766	-2.238889	1.981375
19	6	-1.970109	-2.108134	-0.939509
20	1	-1.904360	-3.035405	-0.371960
21	1	-2.910771	-2.135840	-1.488863
22	6	-0.804453	-2.125443	-1.918994
23	6	0.100325	2.373449	0.803407
24	1	1.030914	2.794869	0.424736

25	1	-0.543052	3.217023	1.053501
26	6	0.453818	1.622484	2.078679
27	6	0.009947	1.787687	-1.540770
28	1	-0.545013	1.223073	-2.289316
29	1	-0.056563	2.845035	-1.800249
30	6	1.462397	1.342889	-1.617193
31	8	2.257840	-1.596132	0.611613
32	1	2.237972	-2.432225	1.112688
33	1	2.674704	-1.778927	-0.259766
34	8	2.958651	-2.122285	-1.951337
35	8	1.848351	-3.875050	2.126735
36	1	2.030056	-1.905356	-2.119205
37	1	3.465348	-1.365738	-2.301454
38	1	2.144013	-3.784489	3.032925
39	1	0.971448	-3.450388	2.090040
40	26	0.378230	-0.615393	0.273873
41	8	4.075961	1.530419	0.822138
42	1	3.357395	1.133489	0.312828
43	1	3.691664	2.304304	1.258741
44	8	2.996195	3.745222	2.284603
45	8	4.336835	0.112259	-2.855443
46	1	3.615156	0.763396	-2.734077
47	1	4.524146	0.106938	-3.794078
48	1	2.741609	4.544268	1.823352
49	1	2.171998	3.371342	2.641094
50	6	-4.094919	0.200229	-0.472915
51	6	-2.642579	2.725965	-0.738967
52	1	-2.413639	2.729742	-1.807082
53	1	-2.225946	3.642689	-0.320544
54	6	-4.156715	2.700946	-0.567311
55	1	-4.593093	3.569505	-1.060577
56	1	-4.409053	2.776448	0.494178
57	6	-4.735508	1.412765	-1.138092
58	1	-5.815124	1.379232	-0.991772
59	1	-4.558248	1.378536	-2.216764
60	1	-4.501124	-0.721921	-0.889394
61	1	-4.350058	0.211089	0.588944

Zero-point correction=	0.490144 (Hartree/Particle)
Thermal correction to Energy=	0.528063
Thermal correction to Enthalpy=	0.529008
Thermal correction to Gibbs Free Energy=	0.419060
Sum of electronic and zero-point Energies=	-2978.147442
Sum of electronic and thermal Energies=	-2978.109522
Sum of electronic and thermal Enthalpies=	-2978.108578
Sum of electronic and thermal Free Energies=	-2978.218526

Table S5: Optimized Cartesian coordinates (Å) of the **[Fe(*t*-CDTA)(λ)(H_2O)]$^-$·5H_2O** system obtained with DFT calculations (0 Imaginary Frequencies).

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	8	-0.077061	2.509234	-1.044476
2	8	-1.447457	3.746546	-2.275408
3	8	-1.292191	1.767531	3.296168
4	8	0.084848	1.087243	1.695130
5	8	0.329110	-0.129453	-1.980184
6	8	0.652157	-1.993808	-3.130780
7	8	1.951603	-0.629504	0.373811
8	8	2.646992	-2.256705	1.716646
9	7	-0.526417	-1.486265	0.276462
10	7	-1.955823	0.911774	-0.163020
11	6	-1.939957	-1.377184	0.706406
12	6	-2.649544	-0.401158	-0.220184
13	6	-2.292253	1.729804	-1.328688

14	1	-2.334746	1.090466	-2.210926
15	1	-3.258631	2.226582	-1.228963
16	6	-1.214218	2.766535	-1.586699
17	6	-2.156683	1.664494	1.086886
18	1	-2.158520	2.730153	0.855994
19	1	-3.114780	1.453773	1.554027
20	6	-1.061254	1.487802	2.134621
21	6	-0.321025	-2.214276	-0.985204
22	1	0.310433	-3.088266	-0.828590
23	1	-1.261419	-2.597087	-1.378969
24	6	0.283735	-1.399253	-2.122828
25	6	0.312447	-2.026845	1.342146
26	1	0.003620	-1.593096	2.293662
27	1	0.238078	-3.112260	1.429637
28	6	1.759346	-1.631337	1.135473
29	8	2.264436	1.784965	-0.233129
30	1	2.217273	2.726356	-0.477803
31	1	2.645287	1.739545	0.671134
32	8	2.850423	1.668187	2.407306
33	8	1.865048	4.417460	-1.051146
34	1	1.941693	1.362759	2.521353
35	1	3.423932	0.891000	2.547635
36	1	2.243922	4.607211	-1.909825
37	1	1.018504	3.971699	-1.229578
38	26	0.403083	0.685933	-0.204421
39	8	4.115271	-1.097259	-1.437346
40	1	3.445155	-0.838178	-0.790118
41	1	3.769968	-1.913780	-1.826616
42	8	2.980594	-3.426150	-2.668428
43	8	4.549490	-0.507767	2.571260
44	1	3.955114	-1.198909	2.214011
45	1	4.779597	-0.798252	3.453798
46	1	2.819178	-4.165238	-2.082053
47	1	2.105597	-3.054444	-2.870100
48	1	-1.913168	-0.931958	1.703602
49	1	-2.506721	-0.753317	-1.244259
50	6	-4.160019	-0.329372	0.018904
51	1	-4.375817	0.145620	0.976576
52	1	-4.616076	0.289428	-0.754061
53	6	-2.651344	-2.727637	0.839983
54	1	-2.543739	-3.306101	-0.078968
55	1	-2.170516	-3.302950	1.631534
56	6	-4.791092	-1.716289	0.041098
57	1	-5.862734	-1.622343	0.216972
58	1	-4.668470	-2.201683	-0.931592
59	6	-4.139771	-2.566997	1.122507
60	1	-4.287160	-2.092306	2.096885
61	1	-4.605640	-3.551134	1.174561

Zero-point correction=	0.489298 (Hartree/Particle)
Thermal correction to Energy=	0.527759
Thermal correction to Enthalpy=	0.528704
Thermal correction to Gibbs Free Energy=	0.416769
Sum of electronic and zero-point Energies=	-2978.143913
Sum of electronic and thermal Energies=	-2978.105452
Sum of electronic and thermal Enthalpies=	-2978.104507
Sum of electronic and thermal Free Energies=	-2978.216442

Table S6: Optimized Cartesian coordinates (Å) of the **[Fe(*c*-CDTA)(δ)(H_2O)]$^-$·5H_2O** system obtained with DFT calculations (0 Imaginary Frequencies).

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	8	-0.626513	-1.677041	1.798476
2	8	-2.455947	-1.960899	3.028433

3	8	-0.433807	-3.502788	-2.272742
4	8	0.459984	-1.838031	-1.103061
5	8	0.031558	0.979446	1.706985
6	8	0.321114	3.126872	2.189506
7	8	2.026537	0.261699	-0.573401
8	8	2.805249	0.790207	-2.587868
9	7	-0.281897	1.385570	-0.898310
10	7	-1.897561	-0.866491	-0.313889
11	6	-1.737424	1.488514	-1.199122
12	6	-2.304753	0.075727	-1.390485
13	1	-1.819089	-0.331427	-2.277578
14	6	-2.668272	-0.845920	0.931519
15	1	-2.815691	0.175188	1.268524
16	1	-3.648341	-1.312438	0.824008
17	6	-1.887348	-1.559650	2.027482
18	6	-1.864851	-2.235025	-0.855876
19	1	-2.003970	-2.953599	-0.049211
20	1	-2.666078	-2.407236	-1.573767
21	6	-0.525402	-2.573047	-1.492166
22	6	0.255484	2.495464	-0.104118
23	1	1.314804	2.615177	-0.325423
24	1	-0.208826	3.450866	-0.334516
25	6	0.184260	2.207660	1.387040
26	6	0.509885	1.214695	-2.119723
27	1	0.052722	0.462442	-2.760791
28	1	0.580505	2.142269	-2.692370
29	6	1.901658	0.720860	-1.757161
30	8	1.975383	-1.333742	1.404246
31	1	1.784326	-1.969786	2.117993
32	1	2.544579	-1.789053	0.744736
33	8	3.138930	-2.673712	-0.646036
34	8	1.084274	-3.037273	3.394784
35	1	2.287748	-2.500763	-1.074200
36	1	3.772994	-2.084064	-1.095072
37	1	1.174553	-2.675911	4.276866
38	1	0.267748	-2.648374	3.031525
39	26	0.289663	-0.486185	0.376058
40	8	3.925718	1.695138	1.051215
41	1	3.307854	1.160800	0.535715
42	1	3.517410	2.568735	1.137354
43	8	2.748625	4.268881	1.494514
44	8	4.858497	-0.881318	-1.893890
45	1	4.176412	-0.226202	-2.149415
46	1	5.228869	-1.201919	-2.716191
47	1	2.662758	4.876363	0.759824
48	1	1.840149	4.045317	1.759962
49	1	-1.836351	1.977436	-2.175263
50	6	-2.551918	2.350008	-0.231287
51	1	-2.167793	3.366901	-0.227113
52	1	-2.479296	1.990096	0.794959
53	6	-3.807342	0.118922	-1.706102
54	1	-3.895858	0.484979	-2.731543
55	1	-4.212128	-0.893593	-1.713595
56	6	-4.638280	1.023807	-0.799582
57	1	-5.642467	1.108081	-1.216203
58	1	-4.757744	0.585090	0.190608
59	6	-4.011564	2.405361	-0.678096
60	1	-4.059173	2.909246	-1.647935
61	1	-4.577279	3.018896	0.022751

Zero-point correction= 0.490986 (Hartree/Particle)
Thermal correction to Energy= 0.528626
Thermal correction to Enthalpy= 0.529571
Thermal correction to Gibbs Free Energy= 0.421096
Sum of electronic and zero-point Energies= -2978.133845
Sum of electronic and thermal Energies= -2978.096205
Sum of electronic and thermal Enthalpies= -2978.095260
Sum of electronic and thermal Free Energies= -2978.203735

Table S7: Optimized Cartesian coordinates (Å) of the **[Fe(*c*-CDTA)(λ)(H_2O)]$^{-}$·5H_2O** system obtained with DFT calculations (0 Imaginary Frequencies).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8		-0.394635	2.379369	1.241319
2	8		0.820456	3.911431	2.289152
3	8		-0.059487	2.508010	-3.250606
4	8		-0.782958	1.261264	-1.563443
5	8		0.236872	-0.332547	1.824398
6	8		1.028643	-2.188241	2.735869
7	8		-1.766548	-1.071124	-0.224962
8	8		-2.311941	-2.628907	-1.712400
9	7		0.793484	-1.158885	-0.749818
10	7		1.613156	1.494993	-0.195718
11	6		1.988481	-0.595836	-1.424660
12	6		2.653292	0.515710	-0.613661
13	6		1.951448	2.244106	1.014398
14	1		2.272523	1.554556	1.791629
15	1		2.747636	2.972764	0.850353
16	6		0.719362	2.931688	1.568221
17	6		1.296273	2.417773	-1.302352
18	1		1.067317	3.403398	-0.895676
19	1		2.149130	2.546306	-1.969101
20	6		0.074909	2.039383	-2.135848
21	6		1.016241	-2.080059	0.374072
22	1		0.341862	-2.932586	0.285464
23	1		2.015886	-2.498021	0.375281
24	6		0.752348	-1.499402	1.757730
25	6		-0.094760	-1.776654	-1.735401
26	1		-0.136716	-1.151718	-2.627137
27	1		0.238010	-2.770963	-2.039085
28	6		-1.506277	-1.856012	-1.194102
29	8		-2.551730	1.023439	0.884952
30	1		-2.699637	1.904986	1.271054
31	1		-3.113445	0.969067	0.081250
32	8		-3.702555	1.083958	-1.567687
33	8		-2.723050	3.582467	1.988809
34	1		-2.804072	1.083133	-1.920477
35	1		-4.073791	0.200596	-1.753297
36	1		-2.885821	3.589772	2.932362
37	1		-1.768304	3.424323	1.888079
38	26		-0.526381	0.565916	0.259454
39	8		-2.884408	-2.485482	2.008015
40	1		-2.572557	-1.961787	1.258130
41	1		-2.180183	-3.126483	2.181769
42	8		-0.773148	-4.303358	2.697309
43	8		-4.761819	-1.452952	-1.843185
44	1		-3.935376	-1.968242	-1.744018
45	1		-5.103707	-1.680316	-2.707867
46	1		-0.511543	-4.975742	2.068378
47	1		-0.023745	-3.687860	2.752756
48	1		1.570731	-0.115892	-2.309542
49	6		3.031609	-1.600373	-1.948595
50	1		2.524019	-2.465320	-2.376412
51	6		3.586613	-0.006332	0.477192
52	1		3.057390	-0.569067	1.246829
53	6		4.107551	-2.043312	-0.954662
54	1		3.728161	-2.798595	-0.266029
55	1		4.909403	-2.532429	-1.509047
56	1		3.315411	1.030779	-1.318644
57	6		4.673204	-0.869173	-0.165673
58	1		4.072794	0.828909	0.977010
59	1		5.264053	-0.236378	-0.834261

60	1	5.352934	-1.228808	0.606536
61	1	3.529756	-1.102620	-2.783602

Zero-point correction=	0.489949 (Hartree/Particle)
Thermal correction to Energy=	0.528191
Thermal correction to Enthalpy=	0.529135
Thermal correction to Gibbs Free Energy=	0.418318
Sum of electronic and zero-point Energies=	-2978.132192
Sum of electronic and thermal Energies=	-2978.093950
Sum of electronic and thermal Enthalpies=	-2978.093005
Sum of electronic and thermal Free Energies=	-2978.203823

Table S8: Optimized Cartesian coordinates (Å) of the **[Fe(CpDTA)(δ)(H_2O)]$^-$·5H_2O** system obtained with DFT calculations (0 Imaginary Frequencies).

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	8	-0.989101	-1.834115	1.568315
2	8	-2.690666	-1.951264	2.993990
3	8	-1.546916	-2.644907	-2.811489
4	8	-0.222197	-1.496496	-1.446478
5	8	0.271923	0.535237	1.955073
6	8	1.128478	2.353613	2.893306
7	8	1.832187	0.071874	-0.645750
8	8	2.589927	0.974638	-2.529769
9	7	-0.168814	1.678759	-0.400561
10	7	-2.225184	-0.345517	-0.146576
11	6	-1.591863	2.028010	-0.370905
12	1	-1.838069	2.183522	0.682158
13	6	-2.451532	0.897221	-0.893935
14	1	-2.143030	0.686360	-1.920414
15	6	-2.852489	-0.422778	1.169885
16	1	-2.739272	0.526056	1.693955
17	1	-3.918212	-0.650056	1.115919
18	6	-2.151085	-1.490061	2.002937
19	6	-2.550635	-1.512324	-0.972190
20	1	-2.774826	-2.366094	-0.333679
21	1	-3.428286	-1.334598	-1.594423
22	6	-1.372521	-1.928191	-1.843474
23	6	0.589298	2.455307	0.582364
24	1	1.615613	2.594988	0.243943
25	1	0.168081	3.451566	0.722436
26	6	0.670044	1.748179	1.928207
27	6	0.472618	1.695591	-1.711293
28	1	-0.179898	1.242771	-2.457077
29	1	0.718411	2.703307	-2.050311
30	6	1.742020	0.857229	-1.647336
31	8	1.575112	-1.980086	0.855395
32	1	1.304183	-2.722075	1.427913
33	1	1.967598	-2.356662	0.035479
34	8	2.237184	-2.918472	-1.590123
35	8	0.488795	-3.873946	2.542696
36	1	1.412170	-2.481582	-1.846909
37	1	2.947048	-2.360263	-1.959758
38	1	0.765649	-3.772701	3.453694
39	1	-0.235454	-3.234295	2.411949
40	26	0.067649	-0.569115	0.310293
41	8	4.176454	0.558449	0.952154
42	1	3.400696	0.329843	0.423806
43	1	4.003773	1.444412	1.302227
44	8	3.687655	3.109187	2.157725
45	8	4.211496	-1.230530	-2.566330
46	1	3.696067	-0.397641	-2.549255
47	1	4.434215	-1.376967	-3.485629
48	1	3.685869	3.895969	1.612696

49	1	2.776205	3.009619	2.482215
50	6	-3.853691	1.506093	-0.930602
51	1	-4.317233	1.436708	0.052807
52	1	-4.507552	1.000963	-1.637753
53	6	-2.084460	3.234565	-1.167715
54	6	-3.606176	2.990185	-1.298282
55	1	-4.164196	3.641951	-0.629530
56	1	-3.941089	3.207433	-2.310014
57	1	-1.849208	4.181012	-0.686064
58	1	-1.619969	3.241150	-2.153727

Zero-point correction=	0.460375 (Hartree/Particle)
Thermal correction to Energy=	0.497639
Thermal correction to Enthalpy=	0.498583
Thermal correction to Gibbs Free Energy=	0.388979
Sum of electronic and zero-point Energies=	-2938.848257
Sum of electronic and thermal Energies=	-2938.810993
Sum of electronic and thermal Enthalpies=	-2938.810049
Sum of electronic and thermal Free Energies=	-2938.919653

Table S9: Optimized Cartesian coordinates (Å) of the **[Fe(CpDTA)(λ)(H_2O)]$^-$·5H_2O** system obtained with DFT calculations (0 Imaginary Frequencies).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8		0.775798	2.199134	1.247032
2	8		2.447337	3.027728	2.447758
3	8		1.606662	1.809298	-3.218207
4	8		0.210539	1.194884	-1.608000
5	8		-0.103343	-0.419818	1.888926
6	8		-0.624670	-2.310500	2.915194
7	8		-1.942725	-0.251890	-0.383796
8	8		-3.058315	-1.514581	-1.831064
9	7		0.261484	-1.650411	-0.550499
10	7		2.248054	0.390536	0.057031
11	6		1.642358	-1.719993	-1.033774
12	6		2.560398	-1.038994	-0.039703
13	6		2.808457	0.988314	1.265619
14	1		2.762612	0.260261	2.076107
15	1		3.851742	1.283513	1.142383
16	6		1.978303	2.182218	1.702776
17	6		2.563594	1.180671	-1.139396
18	1		2.885268	2.176022	-0.831896
19	1		3.388458	0.756107	-1.708709
20	6		1.389910	1.409811	-2.089632
21	6		-0.027734	-2.467902	0.630800
22	1		-0.906480	-3.088527	0.457251
23	1		0.785340	-3.161685	0.847282
24	6		-0.281513	-1.686038	1.916302
25	6		-0.715423	-1.857747	-1.610011
26	1		-0.355771	-1.384760	-2.524435
27	1		-0.889192	-2.913773	-1.827367
28	6		-2.022716	-1.176299	-1.256655
29	8		-1.698922	2.072139	0.529319
30	1		-1.441778	2.943160	0.882408
31	1		-2.119206	2.225699	-0.345867
32	8		-2.406731	2.427370	-2.053528
33	8		-0.730452	4.439250	1.620457
34	1		-1.592741	1.957353	-2.272982
35	1		-3.141686	1.814576	-2.247226
36	1		-1.022226	4.589955	2.519924
37	1		0.019908	3.823339	1.686639
38	26		-0.127751	0.634046	0.242969
39	8		-3.990832	-0.459150	1.612032
40	1		-3.335869	-0.287046	0.922016

41	1	-3.783580	-1.349683	1.930648
42	8	-3.296190	-3.038412	2.651546
43	8	-4.542779	0.703812	-2.357960
44	1	-4.105798	-0.139263	-2.118899
45	1	-4.866093	0.581231	-3.250527
46	1	-3.387959	-3.774622	2.046813
47	1	-2.340619	-2.923208	2.781487
48	1	1.657716	-1.145437	-1.959707
49	1	2.351226	-1.447807	0.951176
50	6	3.952991	-1.523229	-0.432006
51	1	4.699708	-1.335292	0.336882
52	1	4.291689	-1.053588	-1.356418
53	6	2.290089	-3.093139	-1.313979
54	6	3.691237	-3.017186	-0.665839
55	1	1.704339	-3.916678	-0.908951
56	1	2.357859	-3.255751	-2.387545
57	1	3.686151	-3.536873	0.293181
58	1	4.459027	-3.480322	-1.281277

Zero-point correction= 0.459916 (Hartree/Particle)
Thermal correction to Energy= 0.497395
Thermal correction to Enthalpy= 0.498339
Thermal correction to Gibbs Free Energy= 0.388328
Sum of electronic and zero-point Energies= -2938.847031
Sum of electronic and thermal Energies= -2938.809552
Sum of electronic and thermal Enthalpies= -2938.808608
Sum of electronic and thermal Free Energies= -2938.918619

Table S10: Optimized Cartesian coordinates (Å) of the **[Fe(PhDTA)(H$_2$O)]$^{-}$·5H$_2$O** system obtained with DFT calculations (0 Imaginary Frequencies).

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	8	-0.389426	2.274311	-1.299831
2	8	-1.883537	3.031418	-2.759985
3	8	-1.270698	2.197524	3.162251
4	8	0.017719	1.252420	1.619567
5	8	0.236256	-0.321410	-1.969188
6	8	0.553327	-2.206972	-3.089687
7	8	1.876544	-0.492011	0.553845
8	8	2.507275	-1.766158	2.262967
9	7	-0.476689	-1.558127	0.324763
10	7	-2.055364	0.740513	-0.027313
11	6	-1.905584	-1.644118	0.492941
12	6	-2.682985	-0.512298	0.321085
13	6	-2.514224	1.231168	-1.334312
14	1	-2.525162	0.397499	-2.035760
15	1	-3.519071	1.653925	-1.291267
16	6	-1.545412	2.276010	-1.865140
17	6	-2.233304	1.750790	1.032669
18	1	-2.216495	2.743822	0.583488
19	1	-3.187067	1.639716	1.544795
20	6	-1.100961	1.733821	2.051221
21	6	0.007043	-2.388548	-0.792924
22	1	0.948214	-2.865181	-0.518275
23	1	-0.692384	-3.188234	-1.030752
24	6	0.280503	-1.594896	-2.062017
25	6	0.236077	-1.858907	1.572245
26	1	-0.250988	-1.333841	2.392980
27	1	0.241229	-2.924966	1.805174
28	6	1.661976	-1.348608	1.474098
29	8	2.054755	1.793689	-0.507798
30	1	1.956478	2.667948	-0.928427
31	1	2.460699	1.934387	0.377588
32	8	2.717724	2.172006	2.078810

33	8	1.479263	4.177517	-1.793901
34	1	1.830267	1.840507	2.269925
35	1	3.331460	1.464261	2.353851
36	1	1.799047	4.210101	-2.695882
37	1	0.641237	3.682930	-1.827855
38	26	0.282877	0.627209	-0.243972
39	8	4.043375	-1.183988	-1.202624
40	1	3.348124	-0.884365	-0.602508
41	1	3.686952	-1.973780	-1.634447
42	8	3.000163	-3.442174	-2.624924
43	8	4.447464	0.101915	2.682277
44	1	3.826168	-0.634906	2.508607
45	1	4.690835	0.022140	3.604578
46	1	2.896395	-4.273005	-2.161232
47	1	2.101662	-3.157279	-2.859716
48	6	-4.063935	-0.594622	0.478113
49	6	-2.510406	-2.851234	0.832690
50	6	-4.660923	-1.794533	0.810180
51	1	-5.734296	-1.846441	0.927777
52	6	-3.879671	-2.928329	0.992229
53	1	-4.338446	-3.870755	1.256928
54	1	-1.901736	-3.734879	0.970875
55	1	-4.674338	0.287407	0.337981

Zero-point correction=	0.418465 (Hartree/Particle)
Thermal correction to Energy=	0.455417
Thermal correction to Enthalpy=	0.456361
Thermal correction to Gibbs Free Energy=	0.348203
Sum of electronic and zero-point Energies=	-2974.563079
Sum of electronic and thermal Energies=	-2974.526127
Sum of electronic and thermal Enthalpies=	-2974.525183
Sum of electronic and thermal Free Energies=	-2974.633341

Table S11: Optimized Cartesian coordinates (Å) of the **[Fe(CBuDTA)(H_2O)]$^-$·5H_2O** system obtained with DFT calculations (0 Imaginary Frequencies).

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	8	2.000571	0.434288	1.764372
2	8	3.613501	-0.756986	2.727504
3	8	2.765853	2.757642	-2.012790
4	8	1.095669	1.773591	-0.924763
5	8	-0.581689	-1.426327	1.554053
6	8	-2.119622	-2.995240	1.867670
7	8	-1.831221	0.673898	-0.334106
8	8	-2.917387	1.022713	-2.242468
9	7	-0.699868	-1.506980	-1.089119
10	7	2.383807	-0.513709	-0.602385
11	6	0.401646	-2.379230	-1.514396
12	1	-0.011035	-3.373212	-1.681534
13	6	2.073332	-1.317265	-1.793135
14	1	2.823471	-1.092611	-2.549975
15	6	3.009417	-1.275908	0.476770
16	1	2.482689	-2.219809	0.615648
17	1	4.056408	-1.503514	0.266323
18	6	2.895403	-0.491601	1.779016
19	6	3.188080	0.656748	-0.970516
20	1	3.771806	0.987492	-0.112207
21	1	3.890342	0.424774	-1.771972
22	6	2.307343	1.834863	-1.365152
23	6	-1.716877	-2.268079	-0.358055
24	1	-2.700235	-1.823036	-0.507063
25	1	-1.780502	-3.297908	-0.711870
26	6	-1.461578	-2.254343	1.142192
27	6	-1.295230	-0.722622	-2.168256

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     28          1                   -0.514106   -0.284069   -2.788032
     29          1                   -1.935775   -1.326325   -2.814638
     30          6                   -2.092486    0.421451   -1.557489
     31          8                   -0.474173    1.718936    1.730866
     32          1                    0.106286    1.977960    2.471245
     33          1                   -0.688568    2.529005    1.215476
     34          8                   -0.727250    3.795056    0.016167
     35          8                    1.371339    2.133222    3.736411
     36          1                   -0.171777    3.234638   -0.545239
     37          1                   -1.611694    3.769013   -0.394750
     38          1                    1.102421    1.769204    4.580202
     39          1                    1.742835    1.386618    3.230681
     40         26                    0.260516    0.226672    0.394770
     41          8                   -3.961809    0.677968    1.306388
     42          1                   -3.160448    0.784254    0.777408
     43          1                   -4.158504   -0.270033    1.295631
     44          8                   -4.553655   -2.120099    1.439793
     45          8                   -3.242672    3.593264   -1.148318
     46          1                   -3.131047    2.708043   -1.552320
     47          1                   -3.381314    4.194457   -1.880111
     48          1                   -4.937552   -2.545226    0.673038
     49          1                   -3.688452   -2.543718    1.572043
     50          6                    0.998238   -1.907359   -2.853431
     51          6                    2.185040   -2.822275   -1.486432
     52          1                    2.574338   -3.054907   -0.517293
     53          1                    2.510560   -3.424696   -2.308640
     54          1                    1.376953   -2.698009   -3.466903
     55          1                    0.418327   -1.158720   -3.351569
 ---------------------------------------------------------------------
Zero-point correction=                           0.430168 (Hartree/Particle)
 Thermal correction to Energy=                    0.466168
 Thermal correction to Enthalpy=                  0.467113
 Thermal correction to Gibbs Free Energy=         0.361580
 Sum of electronic and zero-point Energies=          -2899.529010
 Sum of electronic and thermal Energies=             -2899.493010
 Sum of electronic and thermal Enthalpies=           -2899.492066
 Sum of electronic and thermal Free Energies=        -2899.597598
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References

1 J. M. Wilson and R. F. Carbonaro, Capillary electrophoresis study of iron(II) and iron(III) polyaminocarboxylate complex speciation, *Environ. Chem.*, 2011, **8**, 295–303.