

Supplementary Information

Effect of Lewis Acid on the Structure of a Diiron Dithiolate Complex Based on the Active Site of [FeFe]- Hydrogenase Assessed by Density Functional Theory

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Cartesian coordinates and total energies (in a.u.) of all molecules from DFT calculations

1		19.S	-1.836	0.776	-1.088		
E ($\epsilon = 1$) = -6.3839		20.C	-3.372	0.504	-0.112		
E ($\epsilon = 4$) = -6.3933		21.H	-3.321	1.192	0.740		
E ($\epsilon = 10$) = -6.3959		22.H	-4.244	0.744	-0.733		
E ($\epsilon = 40$) = -6.3973		23.H	-3.415	-0.528	0.251		
1.Fe	-0.005	-0.010	0.008	24.H	-2.122	-0.177	-2.022
2.Fe	2.546	-0.003	0.006	25.C	-0.473	-1.714	0.206
3.S	1.271	1.937	0.018	26.O	-0.782	-2.828	0.352
4.C	1.315	2.723	-1.705	27.C	-0.448	0.356	1.696
5.N	1.947	2.003	-2.768	28.O	-0.731	0.578	2.803
6.C	1.344	0.756	-3.124				
7.S	1.266	-0.627	-1.826	1*			
8.H	0.303	0.928	-3.441	E ($\epsilon = 1$) = -6.3737			
9.H	1.897	0.304	-3.958	E ($\epsilon = 4$) = -6.3855			
10.H	2.950	1.892	-2.595	E ($\epsilon = 10$) = -6.3887			
11.H	0.264	2.923	-1.964	E ($\epsilon = 40$) = -6.3905			
12.H	1.832	3.680	-1.551	1.Fe	-0.001	-0.003	0.001
13.C	2.883	0.344	1.738	2.Fe	2.617	-0.002	0.006
14.O	3.105	0.556	2.855	3.S	1.341	1.963	-0.002
15.C	4.127	0.498	-0.693	4.C	1.387	2.685	-1.753
16.O	5.164	0.807	-1.120	5.N	2.039	1.919	-2.773
17.C	2.878	-1.757	0.234	6.C	1.403	0.689	-3.128
18.O	3.099	-2.885	0.382	7.S	1.350	-0.701	-1.833

8.H	0.368	0.893	-3.442	2.F	3.243	-0.274	0.988
9.H	1.938	0.221	-3.965	3.F	1.956	1.847	-0.351
10.H	3.028	1.768	-2.544	4.O	1.400	1.274	2.345
11.H	0.346	2.882	-2.048	5.C	1.721	1.164	3.489
12.H	1.907	3.643	-1.619	6.Al	1.807	0.511	0.607
13.C	3.798	0.811	1.049	7.Fe	2.037	1.002	5.191
14.O	4.573	1.346	1.731	8.Fe	3.425	0.233	7.197
15.C	1.636	-0.799	1.312	9.S	2.685	-1.201	5.524
16.O	1.553	-1.417	2.309	10.C	4.107	-1.644	4.326
17.C	3.717	-1.365	-0.286	11.N	4.686	-0.612	3.548
18.O	4.440	-2.256	-0.472	12.C	5.312	0.454	4.234
19.S	-1.637	0.842	-1.413	13.S	4.284	1.508	5.461
20.C	-3.303	0.650	-0.661	14.H	6.148	0.085	4.850
21.H	-3.362	1.381	0.153	15.H	5.691	1.192	3.516
22.H	-4.064	0.878	-1.417	16.H	4.135	-0.347	2.725
23.H	-3.434	-0.361	-0.260	17.H	4.859	-2.115	4.980
24.H	-1.795	-0.152	-2.333	18.H	3.667	-2.405	3.669
25.C	-0.717	-1.634	0.109	19.S	5.298	-0.896	7.803
26.O	-1.202	-2.687	0.186	20.C	5.259	-1.344	9.587
27.C	-0.754	0.575	1.515	21.H	4.497	-2.130	9.692
28.O	-1.252	0.959	2.491	22.H	6.243	-1.738	9.881
				23.H	4.980	-0.474	10.197
1/AlF₃				24.H	6.256	0.065	7.942
E (ε = 1) = -7.1625				25.C	3.584	1.645	8.272
1.F	0.491	-0.454	0.417	26.O	3.675	2.562	8.983

27.C	2.236	-0.534	8.288	17.Al	-1.400	2.339	-3.605
28.O	1.453	-1.016	9.000	18.F	-2.039	3.866	-3.395
29.C	0.399	0.439	5.720	19.F	-2.409	1.059	-3.207
30.O	-0.650	0.087	6.047	20.F	-0.444	2.060	-4.945
31.C	1.725	2.685	5.797	21.C	1.038	3.904	0.339
32.O	1.513	3.758	6.170	22.O	0.694	4.996	0.512
1*/AlF₃				23.S	-0.260	-1.824	1.233
E (ε = 1) = -7.1587				24.C	-1.330	-3.032	0.352
1.Fe	0.012	0.121	-0.096	25.H	-0.720	-3.460	-0.451
2.S	2.424	0.040	0.006	26.H	-1.619	-3.822	1.054
3.Fe	1.578	2.223	0.082	27.H	-2.210	-2.537	-0.072
4.S	0.198	1.547	1.846	28.H	-1.207	-1.433	2.133
5.C	1.280	0.656	3.135	29.C	-1.758	0.416	-0.117
6.N	2.656	0.438	2.830	30.O	-2.902	0.573	-0.073
7.C	2.931	-0.469	1.761	31.C	0.055	-0.808	-1.631
8.H	2.450	-1.437	1.966	32.O	0.097	-1.414	-2.615
9.H	4.014	-0.624	1.671	1/AlCl₃			
10.H	3.162	1.322	2.715	E (ε = 1) = -6.9066			
11.H	0.800	-0.306	3.361	E (ε = 4) = -6.9198			
12.H	1.188	1.306	4.015	E (ε = 10) = -6.9231			
13.C	2.843	2.734	-1.062	E (ε = 40) = -6.9249			
14.O	3.670	3.071	-1.802	1.Fe	0.110	0.032	-0.116
15.C	0.324	1.790	-1.152	2.Fe	2.663	-0.073	0.108
16.O	-0.147	2.264	-2.168	3.S	1.411	1.786	0.700

4.C	1.687	3.139	-0.611	29.Al	6.786	1.038	-1.692
5.N	2.373	2.805	-1.810	30.Cl	7.938	2.484	-0.832
6.C	1.788	1.811	-2.636	31.Cl	5.487	1.847	-3.182
7.S	1.547	0.056	-1.923	32.Cl	7.598	-0.842	-2.164
8.H	0.782	2.122	-2.961				
9.H	2.422	1.641	-3.514	1*/AlCl₃			
10.H	3.381	2.662	-1.695	E (ε = 1) = -6.9085			
11.H	0.674	3.506	-0.838	E (ε = 4) = -6.9285			
12.H	2.238	3.917	-0.067	E (ε = 10) = -6.9338			
13.C	2.722	-0.416	1.886	E (ε = 40) = -6.9365			
14.O	2.785	-0.639	3.017				
15.C	4.309	0.435	-0.160	1.Fe	-0.016	0.131	-0.076
16.O	5.493	0.554	-0.291	2.S	2.395	-0.016	-0.028
17.C	2.889	-1.822	-0.299	3.Fe	1.601	2.184	0.041
18.O	3.046	-2.938	-0.554	4.S	0.250	1.566	1.847
19.S	-1.589	1.249	-1.001	5.C	1.341	0.664	3.121
20.C	-3.224	0.642	-0.417	6.N	2.703	0.404	2.785
21.H	-3.294	0.912	0.643	7.C	2.925	-0.523	1.721
22.H	-4.016	1.150	-0.982	8.H	2.421	-1.473	1.948
23.H	-3.292	-0.445	-0.528	9.H	4.002	-0.711	1.608
24.H	-1.731	0.765	-2.269	10.H	3.229	1.272	2.647
25.C	-0.413	-1.598	-0.612	11.H	0.841	-0.282	3.374
26.O	-0.756	-2.663	-0.930	12.H	1.290	1.329	3.994
27.C	-0.525	-0.198	1.539	13.C	2.852	2.646	-1.140
28.O	-0.930	-0.367	2.616	14.O	3.670	2.952	-1.901

15.C	0.297	1.799	-1.152	5.O	3.117	-1.013	-1.725
16.O	-0.193	2.296	-2.152	6.C	3.092	-1.147	-2.910
17.Al	-1.423	2.435	-3.616	7.Fe	2.983	-1.484	-4.618
18.Cl	-2.505	4.187	-3.103	8.Fe	2.707	-0.830	-7.080
19.Cl	-2.557	0.623	-3.508	9.S	1.196	-0.241	-5.413
20.Cl	-0.123	2.561	-5.288	10.C	1.409	1.581	-4.902
21.C	1.141	3.886	0.310	11.N	2.638	1.993	-4.323
22.O	0.853	4.995	0.485	12.C	3.815	1.836	-5.095
23.S	-0.317	-1.782	1.292	13.S	4.311	0.089	-5.689
24.C	-1.449	-2.969	0.460	14.H	3.749	2.425	-6.024
25.H	-0.874	-3.432	-0.350	15.H	4.687	2.170	-4.519
26.H	-1.747	-3.736	1.185	16.H	2.744	1.735	-3.336
27.H	-2.323	-2.453	0.047	17.H	1.212	2.140	-5.831
28.H	-1.228	-1.342	2.206	18.H	0.588	1.752	-4.194
29.C	-1.779	0.460	-0.059	19.S	2.377	0.932	-8.472
30.O	-2.918	0.642	0.023	20.C	1.917	0.381	-10.167
31.C	0.017	-0.844	-1.584	21.H	0.897	-0.023	-10.096
32.O	0.091	-1.506	-2.528	22.H	1.926	1.250	-10.841
1/AlBr₃				23.H	2.603	-0.401	-10.518
E = -6.8320				24.H	3.632	1.342	-8.819
1.Br	0.055	-0.597	-0.454	25.C	4.009	-1.660	-7.972
2.Al	2.275	-0.082	-0.175	26.O	4.851	-2.210	-8.557
3.Br	2.849	2.102	-0.712	27.C	1.476	-1.956	-7.723
4.Br	3.384	-1.007	1.597	28.O	0.690	-2.704	-8.140
				29.C	1.808	-2.861	-4.558

30.O	1.067	-3.745	-4.509
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31.C	4.382	-2.619	-4.846
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32.O	5.270	-3.346	-4.974
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1*/AlBr₃**E = -6.8305**

1.Br	0.006	0.024	-0.008
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2.Al	2.313	0.002	-0.000
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3.Br	3.295	2.105	-0.011
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4.Br	3.327	-1.528	1.387
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5.O	2.705	-0.700	-1.740
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6.C	2.870	-0.699	-2.949
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7.Fe	2.723	-1.851	-4.336
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8.Fe	3.469	0.662	-4.303
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9.S	4.792	-1.157	-5.182
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10.C	4.694	-1.126	-7.078
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11.N	3.432	-1.402	-7.689
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12.C	2.399	-0.444	-7.465
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13.S	1.718	-0.237	-5.697
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14.H	2.739	0.544	-7.806
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15.H	1.502	-0.721	-8.035
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16.H	3.115	-2.356	-7.491
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17.H	5.053	-0.137	-7.400
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18.H	5.429	-1.885	-7.376
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19.S	4.158	2.192	-5.984
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20.C	4.712	3.763	-5.201
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21.H	5.689	3.558	-4.742
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22.H	4.826	4.525	-5.986
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23.H	4.000	4.091	-4.431
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24.H	2.968	2.680	-6.436
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25.C	2.307	1.856	-3.636
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26.O	1.548	2.648	-3.272
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27.C	4.855	1.085	-3.241
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28.O	5.785	1.339	-2.603
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29.C	3.539	-3.231	-3.558
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30.O	4.070	-4.131	-3.058
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31.C	1.107	-2.483	-3.916
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32.O	0.061	-2.905	-3.653
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2**E (ε = 1) = -6.7715****E (ε = 4) = -6.8617****E (ε = 10) = -6.8826****E (ε = 40) = -6.8936**

1.Fe	-0.003	0.006	0.013
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2.S	2.400	-0.024	-0.004
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3.Fe	1.498	2.139	0.028
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4.S	0.193	1.513	1.871
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5.C	1.309	0.783	3.131
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6.N	2.741	0.676	2.676
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7.C	2.997	-0.427	1.675	32.C	0.035	-0.996	-1.491
8.H	2.536	-1.340	2.079	33.O	0.136	-1.679	-2.412
9.H	4.087	-0.559	1.615				
10.H	2.996	1.581	2.215	3			
11.H	3.359	0.549	3.496	E ($\epsilon = 1$) = -6.9915			
12.H	0.999	-0.223	3.446	E ($\epsilon = 4$) = -7.0285			
13.H	1.293	1.456	4.000	E ($\epsilon = 10$) = -7.0385			
14.C	2.716	2.662	-1.174	E ($\epsilon = 40$) = -7.0439			
15.O	3.502	3.000	-1.946	1.Fe	-0.035	-0.014	-0.021
16.C	0.200	1.679	-1.163	2.S	2.350	-0.078	-0.065
17.O	-0.320	2.090	-2.166	3.Fe	1.481	2.135	0.008
18.Al	-1.667	2.071	-3.657	4.S	0.129	1.485	1.857
19.Cl	-2.765	3.792	-3.141	5.C	1.398	0.947	3.083
20.Cl	-2.618	0.198	-3.253	6.N	2.766	0.934	2.466
21.Cl	-0.365	2.099	-5.307	7.C	3.049	-0.279	1.622
22.C	0.981	3.840	0.246	8.H	2.645	-1.158	2.145
23.O	0.652	4.936	0.384	9.H	4.140	-0.365	1.530
24.S	-0.220	-1.880	1.408	10.H	2.769	1.778	1.759
25.C	-1.063	-3.274	0.552	11.H	3.497	1.061	3.183
26.H	-0.340	-3.691	-0.158	12.H	1.202	-0.052	3.494
27.H	-1.320	-4.028	1.305	13.H	1.411	1.688	3.895
28.H	-1.955	-2.919	0.025	14.C	2.801	2.657	-1.049
29.H	-1.272	-1.540	2.206	15.O	3.669	3.003	-1.742
30.C	-1.794	0.251	0.031	16.C	0.169	1.687	-1.197
31.O	-2.932	0.372	0.149	17.O	-0.390	2.064	-2.208

18.Al	-1.635	2.111	-3.650	4.S	0.092	1.508	1.870
19.Cl	-2.766	3.860	-3.211	5.C	1.445	1.100	3.084
20.Cl	-2.719	0.277	-3.463	6.N	2.759	1.166	2.425
21.Cl	-0.356	2.217	-5.347	7.C	3.129	-0.043	1.670
22.C	1.075	3.825	0.347	8.H	2.814	-0.952	2.203
23.O	0.814	4.937	0.570	9.H	4.218	-0.053	1.527
24.S	-0.147	-2.021	1.662	10.H	2.533	2.056	1.436
25.C	-0.908	-3.479	0.842	11.H	3.502	1.473	3.064
26.H	-0.156	-3.870	0.146	12.H	1.281	0.109	3.530
27.H	-1.153	-4.243	1.589	13.H	1.402	1.870	3.865
28.H	-1.799	-3.176	0.280	14.C	0.154	1.698	-1.218
29.H	-1.236	-1.668	2.396	15.O	-0.410	1.994	-2.244
30.C	-1.814	0.141	0.025	16.Al	-1.610	1.979	-3.754
31.O	-2.967	0.222	0.119	17.Cl	-2.729	3.756	-3.442
32.C	-0.053	-1.090	-1.445	18.Cl	-2.701	0.162	-3.497
33.O	-0.020	-1.814	-2.350	19.Cl	-0.246	1.988	-5.382
TS 3-4				20.C	2.761	2.720	-1.005
E ($\epsilon = 1$) = -6.9875				21.O	3.632	3.099	-1.672
E ($\epsilon = 4$) = -7.0159				22.C	0.986	3.847	0.391
E ($\epsilon = 10$) = -7.0236				23.O	0.718	4.952	0.627
E ($\epsilon = 40$) = -7.0278				24.S	-0.071	-1.955	1.693
1.Fe	-0.002	-0.015	0.026	25.C	-0.736	-3.474	0.898
2.S	2.374	0.002	-0.030	26.H	0.052	-3.846	0.233
3.Fe	1.435	2.167	0.033	27.H	-0.956	-4.227	1.664
				28.H	-1.629	-3.239	0.308

29.H -1.192 -1.650 2.400
30.C -1.787 0.129 0.040
31.O -2.941 0.210 0.108
32.C 0.021 -1.104 -1.393
33.O 0.074 -1.838 -2.288

4

E ($\epsilon = 1$) = -7.0121

E ($\epsilon = 4$) = -7.0318

E ($\epsilon = 10$) = -7.0404

E ($\epsilon = 40$) = -7.0452

1.Fe 0.012 0.035 -0.010
2.S 2.388 -0.011 0.012
3.Fe 1.560 2.181 0.053
4.S 0.193 1.510 1.839
5.C 1.383 0.793 3.145
6.N 2.751 0.611 2.785
7.C 3.021 -0.356 1.772
8.H 2.605 -1.332 2.061
9.H 4.106 -0.455 1.635
10.H 3.176 1.513 2.538
11.H 0.951 -0.165 3.469
12.H 1.308 1.512 3.971
13.C 2.736 2.615 -1.224
14.O 3.512 2.923 -2.022

15.C 0.178 1.645 -1.172
16.O -0.381 2.025 -2.179
17.Al -1.658 2.063 -3.630
18.Cl -2.787 3.784 -3.123
19.Cl -2.682 0.203 -3.420
20.Cl -0.381 2.198 -5.317
21.C 0.947 3.855 0.234
22.O 0.592 4.947 0.349
23.H 2.683 2.704 0.980
24.S -0.190 -1.975 1.487
25.C -1.186 -3.277 0.656
26.H -0.541 -3.716 -0.114
27.H -1.457 -4.046 1.388
28.H -2.078 -2.846 0.187
29.H -1.168 -1.564 2.341
30.C -1.779 0.237 0.043
31.O -2.926 0.344 0.136
32.C 0.072 -1.019 -1.472
33.O 0.151 -1.718 -2.389

5

E ($\epsilon = 1$) = -6.8852

E ($\epsilon = 4$) = -6.9576

E ($\epsilon = 10$) = -6.9865

E ($\epsilon = 40$) = -6.9964

1.Fe	-0.001	0.031	0.008	26.C	-0.939	-3.426	0.569
2.S	2.367	-0.061	0.008	27.H	-0.140	-3.800	-0.081
3.Fe	1.581	2.162	0.089	28.H	-1.205	-4.194	1.305
4.S	0.154	1.502	1.858	29.H	-1.809	-3.134	-0.028
5.C	1.324	0.861	3.131	30.H	-1.380	-1.676	2.171
6.N	2.732	0.786	2.628	31.C	-1.806	0.253	0.030
7.C	3.012	-0.358	1.704	32.O	-2.946	0.369	0.122
8.H	2.588	-1.276	2.135	33.C	0.020	-1.012	-1.481
9.H	4.103	-0.458	1.623	34.O	0.092	-1.707	-2.393
10.H	2.858	1.689	2.011				
11.H	3.400	0.790	3.415	6			
12.H	1.023	-0.132	3.490	E ($\epsilon = 1$) = -7.1451			
13.H	1.308	1.575	3.966	E ($\epsilon = 4$) = -7.1668			
14.C	2.719	2.589	-1.239	E ($\epsilon = 10$) = -7.1724			
15.O	3.457	2.880	-2.070	E ($\epsilon = 40$) = -7.1755			
16.C	0.178	1.642	-1.153	1.Fe	-0.024	-0.002	-0.038
17.O	-0.347	2.052	-2.147	2.S	2.378	-0.005	-0.027
18.Al	-1.685	2.093	-3.678	3.Fe	1.634	2.272	0.057
19.Cl	-2.752	3.815	-3.102	4.S	0.162	1.532	1.802
20.Cl	-2.639	0.220	-3.327	5.C	1.280	0.752	3.083
21.Cl	-0.330	2.175	-5.284	6.N	2.661	0.633	2.676
22.C	0.954	3.847	0.223	7.C	2.943	-0.406	1.710
23.O	0.582	4.931	0.306	8.H	2.482	-1.378	1.966
24.H	2.731	2.695	1.035	9.H	4.031	-0.534	1.632
25.S	-0.252	-1.976	1.469	10.H	2.849	2.308	1.496

11.H	3.291	0.585	3.479
12.H	0.820	-0.218	3.351
13.H	1.223	1.418	3.956
14.C	2.670	2.664	-1.347
15.O	3.324	2.922	-2.264
16.C	0.233	1.575	-1.051
17.O	-0.268	2.067	-2.064
18.Al	-1.532	2.067	-3.489
19.Cl	-2.714	3.774	-3.017
20.Cl	-2.586	0.209	-3.359
21.Cl	-0.271	2.237	-5.195
22.C	0.889	3.898	0.115
23.O	0.401	4.945	0.135
24.H	2.962	2.980	1.068
25.S	-0.213	-2.035	1.495
26.C	-1.335	-3.232	0.663
27.H	-0.752	-3.692	-0.143
28.H	-1.637	-4.002	1.381
29.H	-2.208	-2.722	0.240
30.H	-1.126	-1.579	2.396
31.C	-1.804	0.153	0.032
32.O	-2.953	0.224	0.158
33.C	0.024	-1.079	-1.467
34.O	0.110	-1.812	-2.359

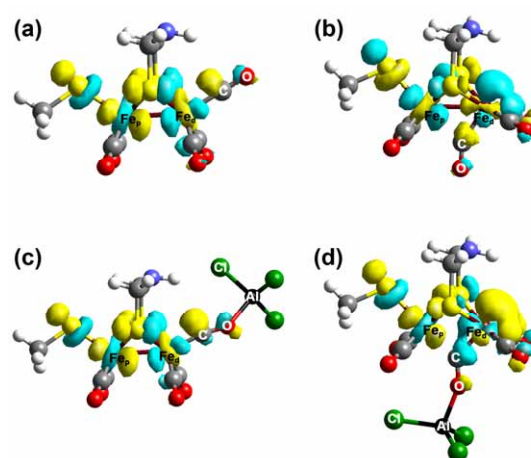


Figure S1. The lowest unoccupied molecular orbitals (LUMOs) of **1** (a), **1*** (b), **1/AlCl₃** (c), and **1*/AlCl₃** (d).