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ELECTRONIC SUPPLEMENTARY INFORMATION

New insights into the Chemistry of Di- and Trimetallic Iron Dithiolene Derivatives. Structural, Mössbauer, Magnetic, Electrochemical and Theoretical Studies.

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Table S1. Comparison between DFT optimized and X-ray selected geometries (distances in Å and angles in º).

		DFT (OPBE)	X-Ray
Compound **1**	Fe-Fe	2.468	2.480
	Fe-S	2.241	2.254
	C-S	1.778	1.758
	C-C	1.396	1.427
Compound **3**	Fe(1)-Fe(2)	2.675	2.715
	Fe(2)-Fe(2)	3.142	3.219
	Fe(1)-S	2.150	2.190
	Fe(2)-S	2.302	2.305
	C-S	1.767	1.778
	C-C	1.400	1.402
	Fe(2)-Fe(1)-Fe(3)	72.0	72.7
Compound **4**	Fe(1)-Fe(2)	2.504	2.538
	Fe(2)-Fe(3)	2.524	2.565
	Fe(1)-S(4)	2.237/2.235	2.263/2.252
	Fe(2)-S(4)	2.208/2.206	2.241/2.235
	Fe(2)-S(6)	2.177/2.184	2.215/2.215
	Fe(3)-S(6)	2.215/2.216	2.238/2.237
	Fe(1)-C(18)	2.472	2.576
	Fe(2)-C(18)	1.721	1.764
	Fe(1)-Fe(2)-Fe(3)	155.0	151.7

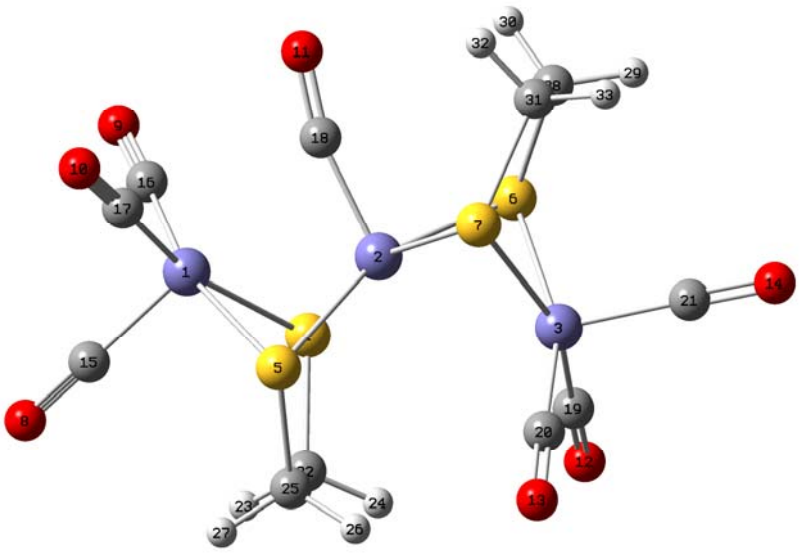

Figure S1. Atom labeling of structure **4**.

Table S2. List of Cartesian coordinates (in Å) of OPBE/TZP optimized structures **1**, **3** and **4**.

Compound **1**

1.C	1.660.665	0.697864	-0.000519
2.C	1.660.748	-0.697806	0.000231
3.C	2.857.919	-1.400.800	0.001583
4.C	4.067.499	-0.690658	0.001384
5.C	4.067.375	0.691311	-0.000021
6.C	2.857.654	1.401.164	-0.001214
7.H	5.005.980	-1.239.424	0.002457
8.H	5.005.744	1.240.275	-0.000046
9.Cl	2.896.145	-3.121.833	0.003249
10.Cl	2.895.489	3.122.209	-0.002081
11.S	0.048563	1.447.998	0.000459
12.S	0.048692	-1.448.264	-0.001068
13.Fe	-1.136.220	-0.000871	1.233.757
14.Fe	-1.136.263	0.000406	-1.234.175
15.C	-0.285183	-0.000877	-2.767.640
16.C	-2.310.646	1.238.912	-1.625.751
17.C	-2.312.815	-1.235.239	-1.628.044
18.C	-2.311.192	-1.238.711	1.625.607
19.C	-0.285331	0.000253	2.767.396
20.C	-2.312.225	1.235.237	1.627.498
21.O	0.233079	-0.003097	-3.801.557
22.O	-3.090.647	2.044.142	-1.912.675
23.O	-3.093.545	2.038.326	1.916.879
24.O	0.232559	0.002463	3.801.513
25.O	-3.091.784	-2.043.232	1.912.914
26.O	-3.094.638	-2.037.856	-1.917.497

Compound **3**

1.C	2.250.847	2.045.872	-1.334.903
2.C	2.958.424	3.232.855	-1.566.101
3.C	4.327.817	3.189.164	-1.813.248
4.H	4.867.447	4.113.619	-2.000.206
5.C	4.999.711	1.973.865	-1.817.854
6.H	6.068.897	1.940.345	-2.008.700
7.C	4.309.169	0.789749	-1.574.430
8.C	2.928.443	0.820500	-1.337.998
9.C	0.000000	0.000000	1.152.207
10.C	-1.788.932	0.670081	-3.950.992
11.C	-1.619.729	2.887.048	-2.760.716
12.C	0.381746	1.920.644	-3.934.103
13.Cl	2.160.190	4.759.421	-1.562.182
14.Cl	5.177.224	-0.698131	-1.582.393

15.Fe	0.000000	0.000000	-0.552947
16.Fe	-0.758941	1.375.572	-2.717.424
17.O	0.000000	0.000000	2.316.484
18.O	-2.498.357	0.372890	-4.814.313
19.O	-2.190.610	3.889.184	-2.836.788
20.O	1.010.403	2.391.785	-4.782.451
21.S	0.529312	2.047.586	-0.933342
22.S	2.016.587	-0.638773	-0.936094
23.C	-2.250.847	-2.045.872	-1.334.903
24.C	-2.958.424	-3.232.855	-1.566.101
25.C	-4.327.817	-3.189.164	-1.813.248
26.H	-4.867.447	-4.113.619	-2.000.206
27.C	-4.999.711	-1.973.865	-1.817.854
28.H	-6.068.897	-1.940.345	-2.008.700
29.C	-4.309.169	-0.789749	-1.574.430
30.C	-2.928.443	-0.820500	-1.337.998
31.C	1.788.932	-0.670081	-3.950.992
32.C	1.619.729	-2.887.048	-2.760.716
33.C	-0.381746	-1.920.644	-3.934.103
34.Cl	-2.160.190	-4.759.421	-1.562.182
35.Cl	-5.177.224	0.698131	-1.582.393
36.Fe	0.758941	-1.375.572	-2.717.424
37.O	2.498.357	-0.372890	-4.814.313
38.O	2.190.610	-3.889.184	-2.836.788
39.O	-1.010.403	-2.391.785	-4.782.451
40.S	-0.529312	-2.047.586	-0.933342
41.S	-2.016.587	0.638773	-0.936094

Compound **4**

1.Fe	4.012.096	1.856.235	2.253.319
2.Fe	3.551.319	1.238.784	4.636.037
3.Fe	3.502.967	-0.307334	6.630.897
4.S	5.552.638	1.140.316	3.708.373
5.S	3.054.280	-0.050649	2.916.833
6.S	4.254.298	1.776.292	6.625.705
7.S	1.748.337	0.729500	5.759.468
8.O	5.184.953	0.920074	-0.226006
9.O	5.295.683	4.465.855	2.026.631
10.O	1.565.195	2.753.870	0.940259
11.O	2.539.220	3.910.020	4.316.445
12.O	6.201.498	-1.363.191	6.892.474
13.O	2.552.562	-2.887.592	5.678.843
14.O	2.735.752	-0.719070	9.402.759

15.C	4.722.738	1.278.752	0.773743
16.C	4.776.973	3.441.657	2.154.252
17.C	2.516.783	2.401.416	1.491.933
18.C	2.999.313	2.830.719	4.287.066
19.C	5.136.038	-0.919391	6.768.104
20.C	2.922.201	-1.843.920	6.027.005
21.C	3.033.888	-0.535822	8.295.850
22.C	5.762.840	-0.590765	3.180.225
23.H	6.485.560	-0.580354	2.356.853
24.H	6.224.242	-1.111.893	4.024.164
25.C	4.445.917	-1.220.092	2.770.675
26.H	4.185.892	-2.076.959	3.398.433
27.H	4.459.538	-1.558.638	1.728.732
28.C	2.857.151	2.684.334	7.373.349
29.H	2.989.145	2.604.470	8.457.430
30.H	2.984.512	3.734.004	7.088.534
31.C	1.524.548	2.127.923	6.912.253
32.H	0.930814	2.876.274	6.377.112
33.H	0.923954	1.743.889	7.743.363

Table S3. Table of OPBE/TZP energies, $<S^2>$ values and electron density at the Fe nucleus ($\rho(0)$) employed for the calculation of Mossbauer isomer shift using the Universal fit parameters (α = -0.287, C = 0.594 and A = 11820) obtained by Noodleman.[a]

Compound	bond energy (a.u.)	$<S^2>$	$\rho(0)$	$\rho(0)$
1	-6.88928	0	11821.61802	
2	-11.26037	2.47	11821.43534	
3	-10.51134	0	11821.43534	11821.23326
4	-8.15066	0	11821.66067	11821.11405

[a] G. M. Sandala, K. H. Hopmann, A. Ghosh, L. Noodleman, J. Chem. Theor. Comput. 2011, 7, 3232-3247.

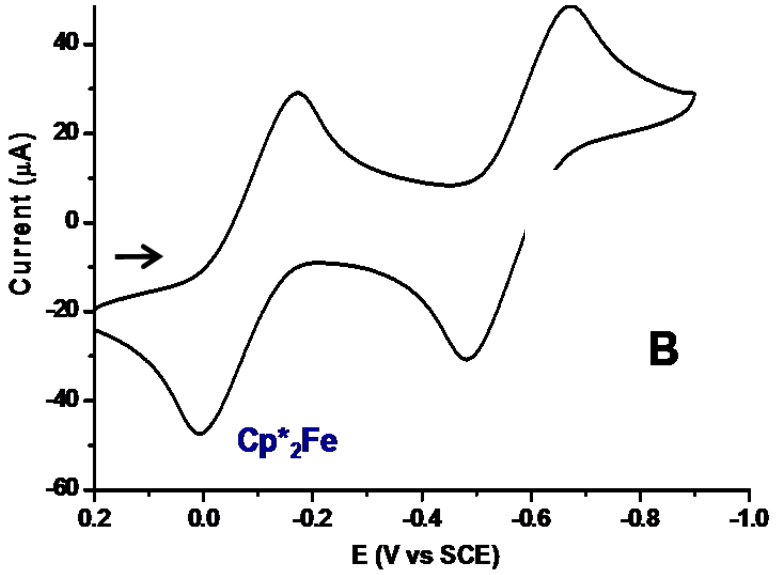

Figure S2. Cyclic voltammetric response, on glassy-carbon working electrode at a scan rate of 0.1 V s^{-1}, of trinuclear cluster $[Fe_3(CO)_7(\mu_3\text{-}SC_6H_2Cl_2S)_2]$ (**3**) recorded in CH_2Cl_2 containing 0.1 M [*n*-Bu_4N][PF_6], in the presence of Cp^*_2Fe added as an internal standard.

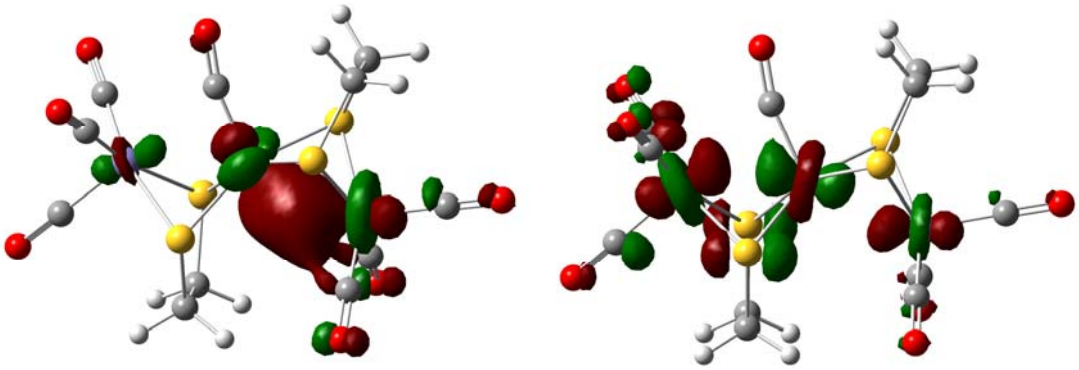

Figure S3. HOMO (left) and LUMO (right) orbitals of compound **4**.

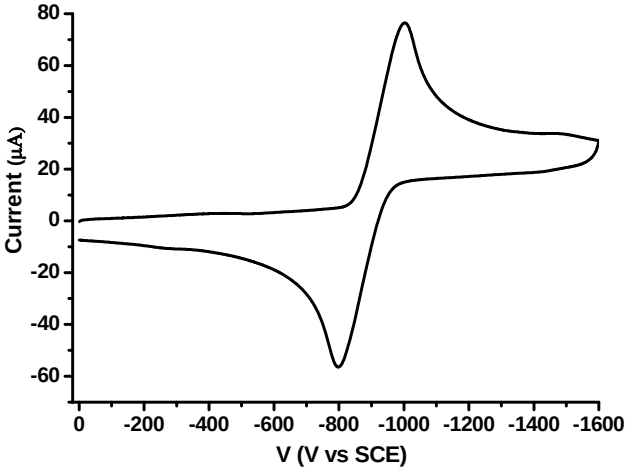

Figure S4. Cyclic voltammogram of bimetallic $[Fe_2(CO)_6(\mu\text{-}SC_6H_2Cl_2S)]$ (**1**), recorded on glassy-carbon working electrode at a scan rate of 0.1 V s^{-1}, in CH_2Cl_2 solution containing 0.1 M [*n*-Bu_4N][

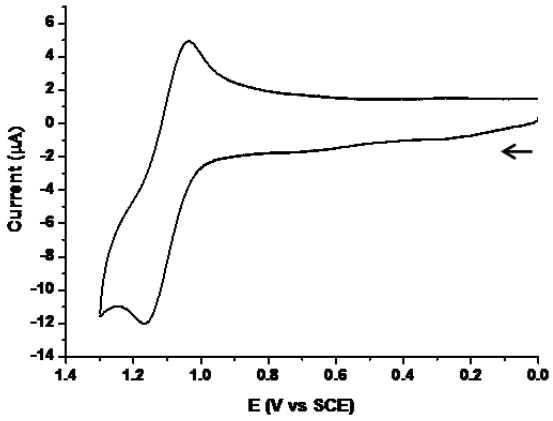

Figure S5. Cyclic voltammetric response, on glassy-carbon working electrode, of trinuclear cluster $[Fe_3(CO)_7(\mu_3\text{-}SC_6H_2Cl_2S)_2]$ **3** in the anodic region, recorded in CH_2Cl_2 containing 0.1 M [n-Bu_4N][PF_6]. CVs are at a scan rate of 0.1 V s^{-1}.