Fe_4 Cluster and a Buckled Macrocycle Complex from the Reduction of $[(dmgBF_2)_2Fe(L)_2]$ (L = MeCN, $^tBu^iNC$)

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General Procedures and Reagents. Dimethylglyoxime, iron acetate and BF_3•Et_2O were obtained from Sigma-Aldrich chemical company and used without further purification; *tert*-butyl isocyanide was obtained from TCI Chemicals. $CHCl_3$, MeOH and pyridine were purchased from J.T. Baker and used without further purification, and all other solvents (MeCN, THF, Et_2O) were obtained from a solvent purification system. Deuterated CD_3CN and $CDCl_3$ were purchased from Cambridge Isotopes and used as received. Sodium amalgam reductions were carried out using standard Schlenk technique under inert (N_2) atmosphere

Syntheses. [(dmgBF$_2$)$_2$Fe(MeCN)$_2$] (1). The complex was prepared from [(dmgH)Fe(py)$_2$][1] according to the procedure of Stynes and co-workers.[2] Orange, block-like crystals of **1** suitable for X-ray diffraction were grown from slow evaporation of a $CHCl_3$/MeCN (3:1) solution of the complex, with analytical data (^{1}H NMR, IR) consistent with that reported previously.

[(dmgBF$_2$)$_2$Fe(^{t}Bu^{i}NC)$_2$] (2). A small batch of **1** (0.100 g, 0.218 mmol) was slurried in 10 mL of MeCN. To this stirred solution was added 2 equiv of ^{t}Bu^{i}NC (36 mg, 0.44 mmol) diluted in 3 mL of MeCN. Within 5 min, the orange slurry became clear and developed a dark orange color. After an additional 1 h stirring at room temperature, the solution was filtered and mixed with 3 mL of toluene. Slow evaporation of the MeCN/tol (3:1) mixture over 2 weeks afforded dark orange blocks of **2** suitable for X-ray diffraction. Yield: 65 mg (60%). Selected IR bands in cm^{-1} (KBr disc): 2185 s (ν_{NC}), 1605 w (ν_{CN}), 1206 w, 1157 m, 1087 m, 996 s, 937 w, 818 m. ^{1}H NMR in CD_3CN (δ from TMS): 2.39 s (6 H), 1.31 s (9 H); ^{19}F NMR in CD_3CN (δ from $CFCl_3$): -147.5 s (2 H). UV/Vis in MeCN, λ in nm: 436. Anal. calcd. for $C_{18}H_{30}N_6O_4B_2F_4Fe$: C 39.46, H 5.52, N 15.34; found: C 40.41, H 5.33, N 15.81.

[(dmgBF$_2$)$_2$Fe(glyIm)] (3). A small amount of freshly cut Na (45 mg, 1.98 mmol) was prepared in Hg amalgam and stirred in 15 mL of degassed THF. Separately, a slurry of **1** (0.50 g, 0.94 mmol) was prepared in 15 mL of degassed MeCN, and added to the Na/Hg amalgam under inert atmosphere at room temperature. After 30 min stirring, the solution became a dark green color, which developed into a maroon solution over the next 2 h; the mixture was allowed to stir for an additional 12 h. The next day, the solution was cannulaed onto a Celite filter pad (prepared under inert atmosphere) and filtered to afford a clear dark red solution. Slow vapor diffusion of

degassed Et_2O into this MeCN/THF (1:1) mixture at room temperature over 6 days afforded very small dark red crystals suitable for synchrotron X-ray diffraction analysis. Yield: 65 mg (16%). Selected IR bands in cm^{-1} (KBr disc): 3280 w, 1657 w, 1630 w, 1460 m, 1385 m, 1238 w, 1192 s, 1001 s, 806 w. UV/vis in MeCN, λ in nm: 540. Anal. calcd. for $C_{12}H_{20}N_6O_4B_2F_4Fe$: C 30.94, H 4.33, N 18.04; found: C 30.91, H 4.56, N 17.84.

[((dmg$_2$BF$_2$)(½dmg)Fe)$_3$Fe(O$_6$)] (4). A small amount of freshly cut Na (17 mg, 0.75 mmol) was prepared in Hg amalgam in 10 mL of THF. Separately, a slurry of **1** (0.200 g, 0.375 mmol) was stirred in 10 mL of MeCN open to ambient atmosphere. The solution of **1** was then added to the Na/Hg amalgam at room temperature to generate a dark green solution within 15 minutes. The solution became reddish-violet after several hours, and the reaction was allowed to stir for an additional 12 h. The next day, the mixture was filtered through Celite (in air) to afford a violet solution. Vapor diffusion of Et_2O into this THF/MeCN mixture at room temperature over two days afforded violet block-like crystals of the Fe_4-cluster (along with a substantial amount of intractable brown powder); these crystals were suitable for X-ray diffraction analysis. Yield: 26 mg (14%). Selected IR bands in cm^{-1} (KBr disc): 3283 m, 1465 w, 1384 w, 1144 m, 1083 m, 1006 m. UV/vis in MeCN, λ in nm: 460, 520, 690. Anal. calcd. for $C_{36}H_{54}N_{18}O_{12}B_3F_6Fe_4$: C 33.24, H 4.18, N 19.39; found: C 34.76, H 4.93, N 18.14.

X-ray crystallography. For complexes **1**, **2** and **4**, diffraction intensity data were collected at 100 K on a Bruker Kappa APEX II diffractometer equipped with a MoKα X-ray source and data were collected using APEX2 v2009.7-0; the data reduction program SAINT-plus v7.66A was used. In the case of **3**, diffraction intensity data were collected at 150 K on a D8 goniostat equipped with a Bruker APEX II CCD detector at Beamline 11.3.1 at the Advanced Light Source (Lawrence Berkeley National Laboratory) using synchrotron radiation tuned to λ = 0.7749 Å. The data frames were collected using the program APEX2 and processed using the program SAINT routine within APEX2.[3] The data were corrected for absorption and beam corrections based on the multi-scan technique as implemented in SADABS.

Physical Measurements. The ^1H and ^{19}F NMR spectra of **1** and **2** were recorded on a Varian Mercury 300 MHz spectrometer and chemical shifts were referenced to TMS or $CFCl_3$,

respectively. The EPR spectrum of **4** was recorded on a Bruker EMX Biospin spectrometer at 77 K using a Gunn diode microwave source. Cyclic voltammograms were taken in MeCN containing 0.1 M TBAP on a CHI660 potentiostat using a freshly polished glassy carbon electrode, 0.01 M $Ag/AgNO_3$ in MeCN as reference electrode, and a Pt wire counter-electrode. All potentials were referenced to the Fc/Fc^+ couple and are plotted versus SCE. The magnetic moment of **4** was determined at 298 K with a magnetic susceptability balance from Johnson Matthey (model MSB1).

DFT calculations. Geometry optimization and orbital calculations on the crystal structure coordinates of **4** was performed in the Firefly software package[4] (which is partially based on the GAMESS (US) source code[5]) using the 6-31G* basis set and the pure functional PW91[6,7] which has been shown to be accurate for Fe systems.[8-14] Orbitals were visualized using MacMolPlt,[15] and spin density plots were generated using gOpenMol.[16,17]

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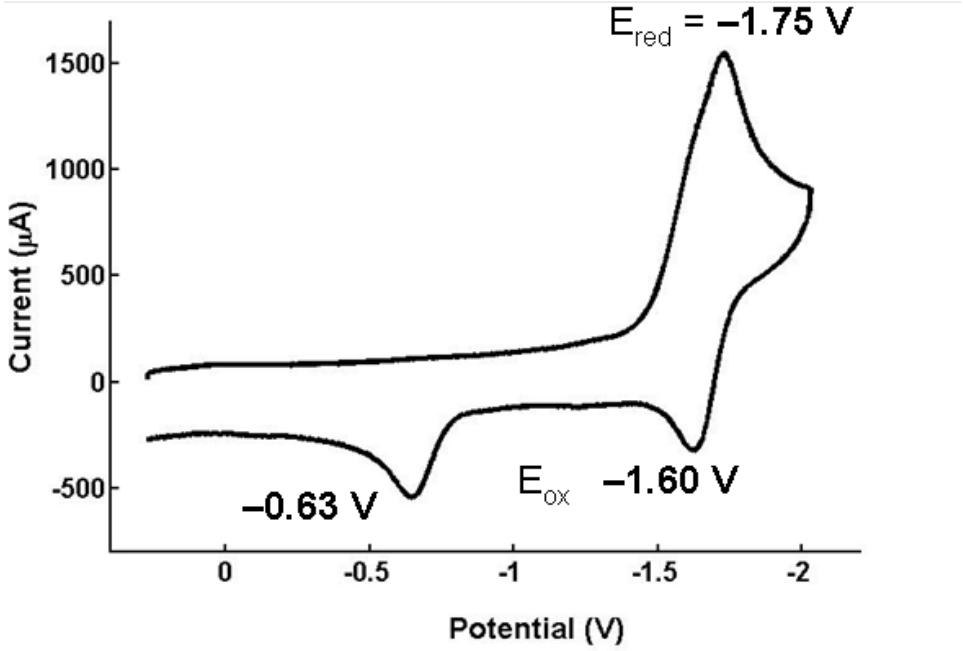

Figure S1. Cyclic voltammogram (potential vs SCE) of **1** in MeCN containing 0.1 M TBAP (scan rate = 100 mV/s).

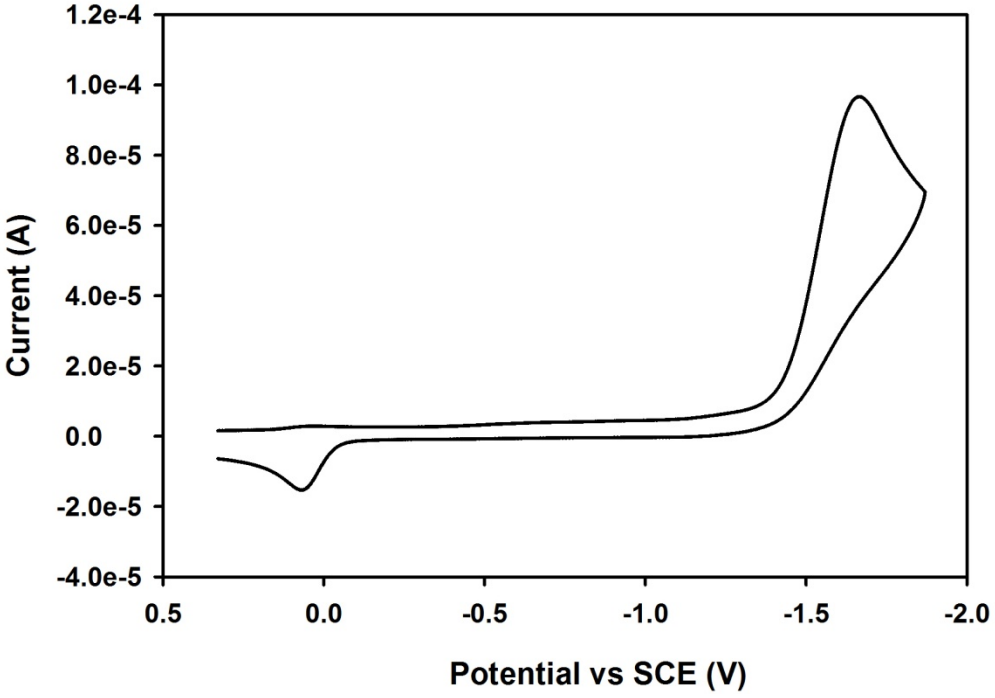

Figure S2. Cyclic voltammogram of **2** in MeCN containing 0.1 M TBAP (scan rate = 100 mV/s).

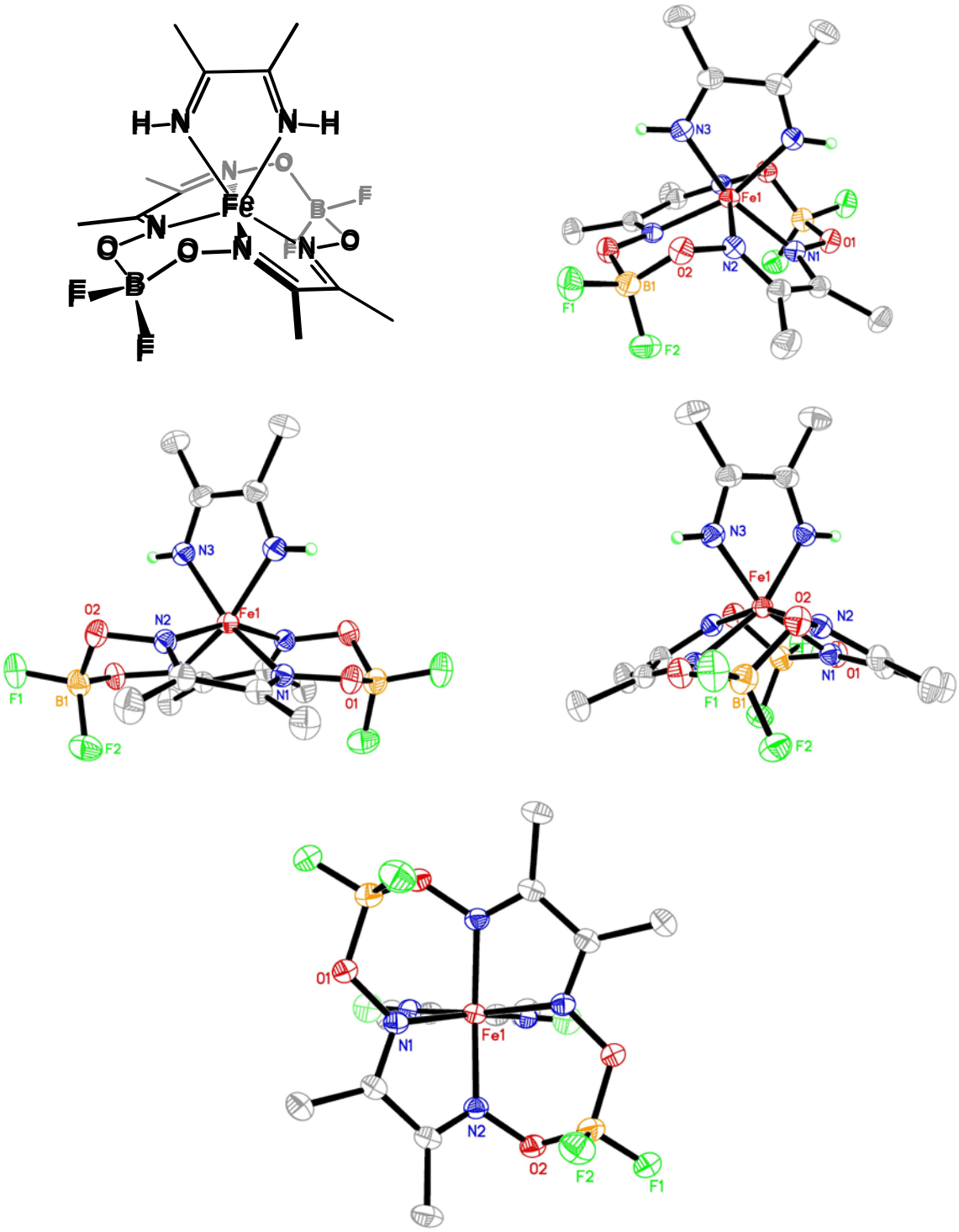

Figure S3. Chemical structure and ORTEP diagrams (50% ellipsoids) for [(dmgBF$_2$)$_2$Fe(glyIm)] (**3**) shown in additional orientations. All H(C) atoms have been omitted for sake of clarity.

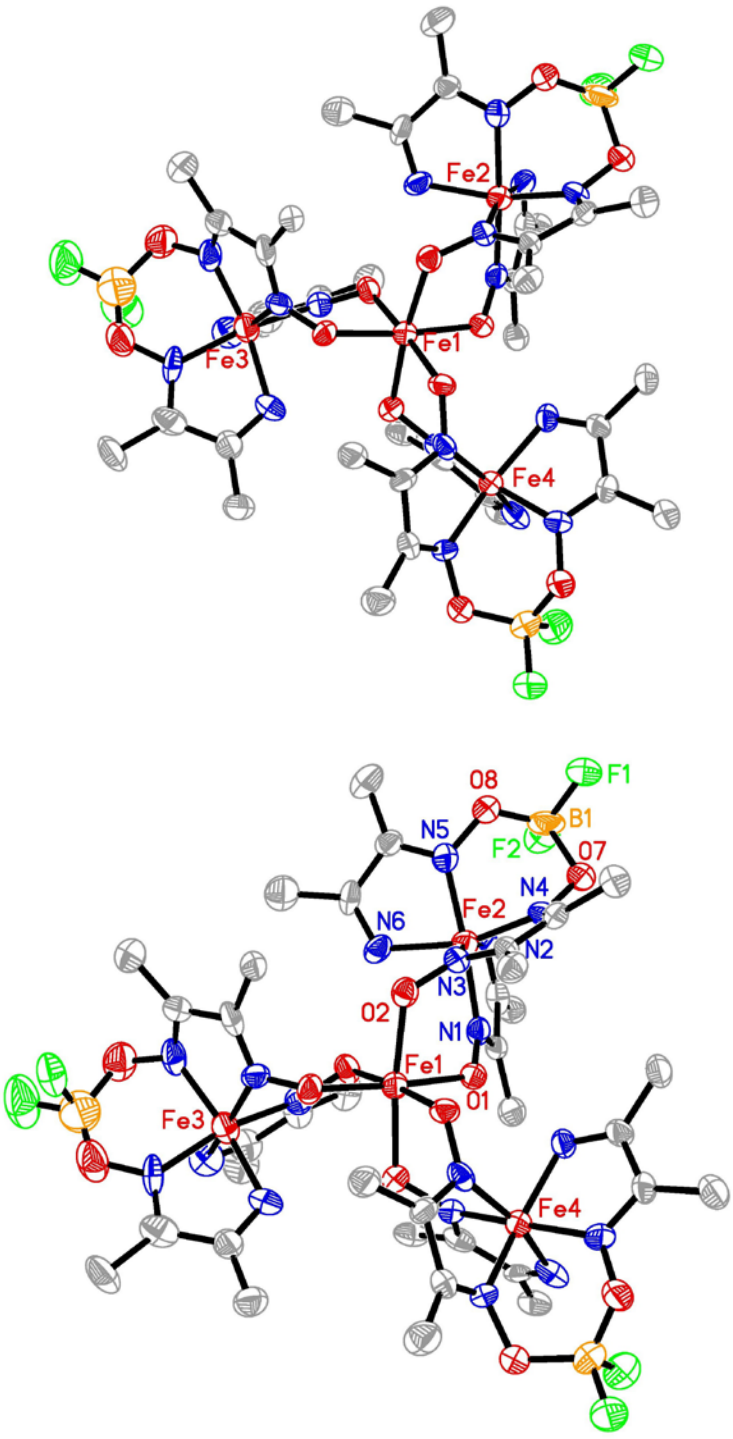

Figure S4. ORTEP diagram (50% ellipsoids) for $[(dmg_2BF_2)_3Fe_3(½dmg)_3Fe(O)_6]$ (**4**) shown in additional orientations. H atoms have been omitted for sake of clarity.

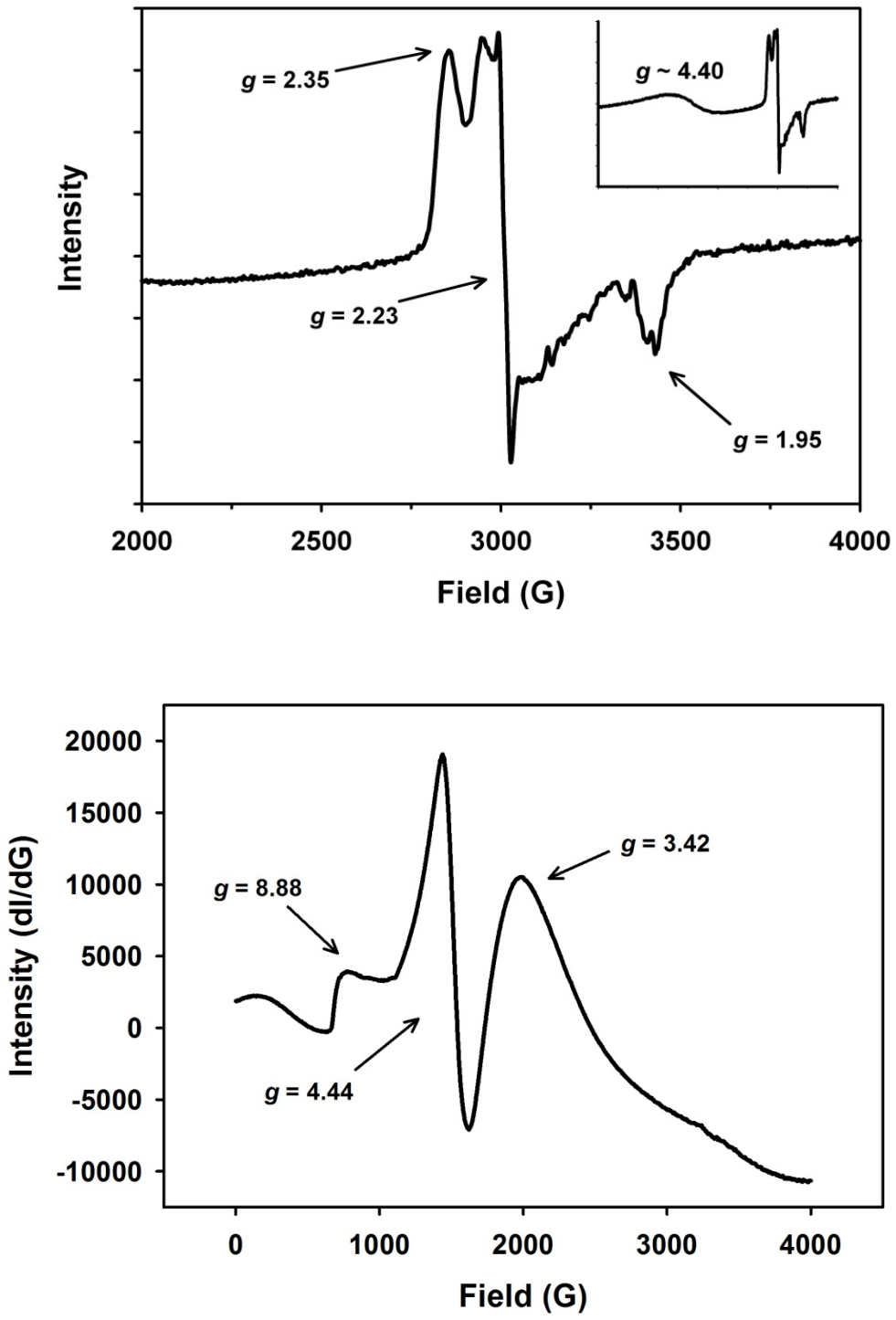

Figure S5. (Top) X-band EPR spectrum of **4** in MeCN/tol glass recorded at 77 K. (Bottom) X-band EPR spectrum of [$Fe^{III}(acac)_3$] in MeCN/tol glass recorded at 77 K. Instrument parameters: Instrument parameters: microwave frequency, 9.45 GHz; microwave power, 5 mW; frequency modulation, 100 kHz; field resolution, 5 G.

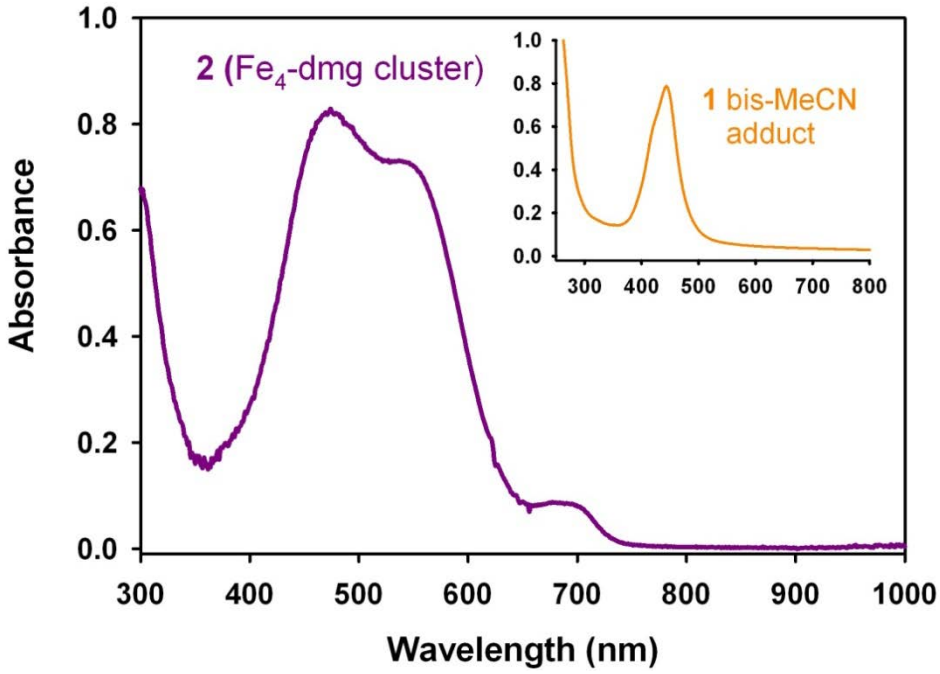

Figure S6. Electronic absorption spectrum of **4** in MeCN at 298 K (inset: spectrum of **1**).

Table S1. X-ray data collection and refinement parameters for complexes **1**-**4**.

	1 [(dmgBF$_2$)Fe(MeCN)$_2$]	**2** [(dmgBF$_2$)Fe(^{t}Bu^{i}NC)$_2$]	**3** [(dmgBF$_2$)Fe(glyIm)]	**4** Fe$_4$ cluster
empirical formula	$C_{12}H_{18}N_6O_4B_2F_4Fe$	$C_{18}H_{30}N_6O_4B_2F_4Fe$	$C_{12}H_{20}N_6O_4B_2F_4Fe$	$C_{36}H_{54}N_{18}O_{12}B_3F_6Fe_4$
Fw	463.79	547.95	465.81	1300.80
color	red-orange	red-orange	dark red	violet
habit	blade	block	rectangular block	triangular prism
size (mm)	0.12 × 0.12 × 0.07	0.17 × 0.17 × 0.15	0.09 × 0.09 × 0.03	0.15 × 0.15 × 0.14
T (K)	100(2)	100(2)	150(2)	100(2)
wavelength (Å)	0.71073	0.71073	0.7749	0.71073
lattice system	monoclinic	triclinic	orthorhombic	rhombohedral
space group	$P2_1/c$	$P\bar{1}$	P*bcn*	R-3
a (Å)	8.6038(4)	9.9760(6)	15.448(3)	35.6736(7)
b (Å)	11.6895(6)	11.1614(7)	8.5409(17)	35.6736(7)
c (Å)	9.4407(4)	13.0925(8)	13.9490(3)	32.5160(9)
α (deg)	90	70.193(3)	90	90
β (deg)	112.894(2)	71.497(3)	90	90
γ (deg)	90	68.000(3)	90	120
V (Å^3)	874.69(7)	1241.02(13)	1840.4(6)	35836.1(14)
Z	2	2	4	1
d_{calc} (g/cm^3)	1.761	1.466	1.681	1.085
μ (mm^{-1})	0.939	0.674	0.893	0.778
GOF on F^2	1.787	2.078	2.440	3.091
final R indices	$R1$ = 0.0264	$R1$ = 0.0398	$R1$ = 0.0327	$R1$ = 0.0886
[I>2σ(I)]	w$R2$ = 0.0476	w$R2$ = 0.0552	w$R2$ = 0.0735	w$R2$ = 0.1183
R indices	$R1$ = 0.0354	$R1$ = 0.0569	$R1$ = 0.0400	$R1$ = 0.1438
all data	w$R2$ = 0.0481	w$R2$ = 0.0559	w$R2$ = 0.0743	w$R2$ = 0.1197

Table S2. Selected bond distances (Å) and bond angles (deg) for the X-ray structures of complexes **1**-**4**. Also included for comparison are DFT-optimized (6-31G*/PW91) bond distances for the Fe_4-cluster **4**. (Note: DFT bond distances for **4** are given as the average ± standard deviation.)

	1	**2**	**3**	**4**	**4** **6-31G*** *S* = 1/2	**4** **TZV** *S* = 1/2	**4** **6-31G*** *S* = 5/2
Fe–N1$_{dmgBF2}$	1.8918(5)	1.8905(7)	1.925(1)	1.903(4) 1.876(9)	1.912(5) 1.890(3)	1.919(4) 1.90(1)	1.917(4) 1.897(2)
Fe–N2$_{dmgBF2}$	1.8918(5)	1.886(7)	1.886(2)	1.912(5) 1.911(20)	1.916(2) 1.89(1)	1.895(3) 1.918(2)	1.894(3) 1.906(3)
Fe–N$_{MeCN/N2H2}$	1.9387(4)	—	1.916(2)	1.923(6) 1.92(1)	1.934(5) 1.901(2)	1.932(5) 1.914(2)	1.917(7) 1.897(2)
Fe–C$_{t\text{Bu}i\text{NC}}$	—	1.9064(9)	—	—	—	—	—
Fe–O	—	—	—	2.01(4)	1.93(1)*	1.95(1)*	2.02(4)
L$_{ax}$–Fe–**L**$_{ax}$	180.0	180.0	78.50(9)	—	—	—	—

*Denotes a difference of greater than 0.05 Å between the experimental and DFT calculated bond distance.

Table S3. DFT optimized (6-31G*/PW91) coordinates for the Fe_4 dmg-type cluster **4**.

Atom	X	Y	Z
Fe	20.7675	-1.908	7.9882
Fe	20.1473	4.5554	7.6675
Fe	15.009	0.83	7.9643
Fe	18.6796	1.1408	7.2662
O	19.7329	0.0653	6.112
O	20.3697	-4.8035	7.9094
O	18.3544	-0.2503	8.4727
O	22.6483	-4.0405	7.1571
O	18.9674	2.5139	5.9772
O	22.7838	5.7687	7.4032
O	20.1648	1.6461	8.2554
O	20.9074	7.2023	6.575
O	17.2357	0.6395	6.1424
O	12.6608	2.541	7.7625
O	17.6012	2.2171	8.3418
O	12.2798	0.1662	7.0588
N	19.8224	-1.306	6.4884
B	21.8726	-5.0341	8.0017
B	22.1546	7.1564	7.4329
B	11.7556	1.3194	7.8898
N	20.0318	-3.4983	7.4019
N	19.4079	-1.0707	8.9879
N	21.098	-2.6368	9.6889
N	21.8254	-0.3701	7.8743
N	22.3897	-2.6588	7.4382
N	20.0667	3.3764	6.2254
N	21.8487	4.7575	6.9829
N	20.2406	3.004	8.7143
N	20.6088	5.29	9.335
N	18.2777	4.651	7.6621
N	19.8857	6.2856	6.9907
N	15.988	1.251	6.4389
N	13.9697	2.189	7.2759
N	16.3977	1.6856	8.9075
N	14.2301	0.9653	9.6681
N	15.8432	-0.8423	8.0253

N	13.5887	-0.2778	7.4505
F	22.1474	-6.299	7.515
F	21.7969	7.5309	8.777
F	23.0681	8.0406	6.888
F	11.6656	0.8949	9.2637
F	10.5149	1.6642	7.3856
F	22.3148	-4.9001	9.3667
C	14.3195	2.7748	6.1247
C	16.2272	1.9624	10.2168
C	22.1993	4.1045	5.8677
C	20.5341	3.1017	10.0234
C	20.7125	4.4805	10.382
C	14.9459	1.4879	10.6545
C	19.2836	-1.3677	10.2992
C	19.2588	-3.5106	6.3094
C	21.155	3.2064	5.4578
C	15.5784	2.2628	5.6552
C	21.225	2.171	4.3798
C	17.6924	5.7376	7.1836
C	18.6442	6.7387	6.7703
C	16.3398	2.7667	4.4677
C	17.2014	2.7311	11.0564
C	23.0797	-0.4929	7.4632
C	14.4833	1.5671	12.0852
C	12.7007	-2.5623	6.9558
C	23.9961	0.6801	7.2198
C	16.1952	5.8759	7.0576
C	13.7743	-1.6009	7.3606
C	23.4879	4.3906	5.16
C	15.1399	-1.9174	7.7042
C	23.4491	-1.8671	7.2295
C	18.7611	-4.7757	5.6836
C	18.1561	-0.9189	11.1783
C	20.4713	-2.7978	12.1014
C	15.7172	-3.3099	7.697
C	18.1905	-1.806	4.6469
C	19.0733	-2.1829	5.796
C	13.4364	3.7582	5.4215
C	18.3764	8.0897	6.1853
C	20.7176	1.901	10.894
C	20.9824	4.9538	11.7873
C	20.3205	-2.2745	10.6951
C	24.7928	-2.3984	6.8433

H	21.7421	-3.4503	9.8158
H	21.3964	0.5831	8.0015
H	20.9218	6.281	9.4104
H	17.7139	3.7957	7.9179
H	13.213	0.7777	9.8061
H	16.8813	-0.9026	8.2022
H	21.1107	1.1703	4.8366
H	22.1698	2.2388	3.8231
H	20.3759	2.288	3.6852
H	17.1596	2.0657	4.2642
H	16.8011	3.7461	4.6854
H	15.681	2.8709	3.589
H	16.6819	3.5083	11.6418
H	17.9488	3.194	10.3999
H	17.7261	2.0679	11.7674
H	14.6063	2.5824	12.4978
H	15.0782	0.8767	12.7127
H	13.4248	1.2744	12.1659
H	12.3366	-3.1406	7.8244
H	13.0749	-3.2723	6.2014
H	11.8606	-1.9864	6.5443
H	24.7886	0.7292	7.9869
H	23.4186	1.6194	7.2515
H	24.4838	0.603	6.2329
H	15.7125	5.7193	8.0378
H	15.8037	5.1041	6.373
H	15.9072	6.8648	6.6758
H	24.3406	3.9653	5.7187
H	23.6412	5.4813	5.1336
H	23.4811	3.9788	4.1417
H	18.5657	-5.5197	6.4666
H	19.5366	-5.2047	5.0253
H	17.8532	-4.5901	5.0906
H	18.5168	-0.2844	12.008
H	17.6494	-1.7921	11.6265
H	17.4368	-0.3492	10.5761
H	20.4621	-1.9695	12.8305
H	21.4251	-3.3393	12.2028
H	19.6501	-3.4886	12.3616
H	15.7726	-3.7039	8.7282
H	16.7441	-3.2922	7.2933
H	15.106	-4.0012	7.0986
H	17.387	-2.5468	4.5092

H	18.7744	-1.7498	3.7093
H	17.7494	-0.8172	4.8538
H	12.3881	3.4813	5.6103
H	13.6492	3.7791	4.3435
H	13.5783	4.776	5.83
H	17.3815	8.1302	5.7215
H	19.1516	8.3158	5.4377
H	18.4393	8.8746	6.962
H	20.6728	2.1718	11.9587
H	21.6935	1.4181	10.695
H	19.9492	1.1532	10.6489
H	20.9262	6.0525	11.8335
H	21.9779	4.6367	12.1422
H	20.2263	4.542	12.4794
H	25.3038	-2.8307	7.7251
H	25.4245	-1.6038	6.4248
H	24.6709	-3.2149	6.1151

Table S4. DFT calculated (6-31G*/PW91) gradient parameters for the Fe_4 dmg-type cluster **4**.

Atom	E = -9023.8551153260 X	Gmax = 0.0017431 Y	Grms = 0.0003531 Z
FE	-0.000185997809560	-0.000188015922110	0.000033521495094
FE	0.000163447972190	-0.000041223038346	-0.000078369211332
FE	0.000048641720096	0.000272130273370	-0.000092513903294
FE	0.000005238164439	-0.000154100287420	-0.000001355018198
O	-0.000156585736020	0.000506350902180	-0.000219672031550
O	-0.000065689975575	-0.000341121658610	0.000243634637540
O	-0.000734046456090	0.000003486114315	0.000033511450061
O	0.000310669559510	-0.000468751378390	0.000340488600180
O	-0.000240884887660	-0.000464636235150	-0.000085475809855
O	0.000307530304420	0.000261864460390	0.000314799161000
O	0.000397626256390	-0.000900067967300	-0.000194199880790
O	0.000264862426220	0.000638961277790	0.000177564403810
O	0.000656599614610	-0.000025397910322	-0.000197968738470
O	-0.000312872689280	0.000189172774270	0.000362974872720
O	0.000699073683550	0.000771213916220	-0.000126347349150
O	-0.000616371388540	-0.000007359548552	0.000175182070160
N	-0.000218079428530	-0.000277349463580	-0.000068060842589
B	-0.000239356614020	0.000424191473170	-0.000412816883590
B	-0.000342232410160	-0.000425600588680	-0.000275839356010
B	0.000559233218830	-0.000091845481230	-0.000271735489750
N	0.000214645249590	-0.000079194304652	0.000366617783130
N	0.000134289629460	0.000235875853430	0.000260133374260
N	0.001134638472000	-0.001031356185900	-0.000288932177640
N	-0.000399741675490	0.001400990162200	0.000115865201590
N	0.000045397353365	-0.000217679358160	0.000008094094897
N	0.000452173357850	0.000047471896256	-0.000149243128560
N	-0.000044927436199	0.000187755201630	0.000271605988690
N	-0.000158832180130	0.000417971043430	-0.000313735531570
N	0.000117729015180	-0.000254177404350	0.000436847158200
N	-0.000720971771580	-0.000124039975610	-0.000121440785340
N	0.000118849620780	-0.000087714517540	0.000039781198727
N	-0.000222166538630	0.000369587501280	0.000040519597322
N	0.000013309846739	-0.000051653147905	0.000202207603540
N	-0.000197271589830	-0.000416538178860	-0.000241636711030
N	-0.000275539780470	-0.000077043550987	-0.000043993188633
N	0.000954823723220	-0.000339399505900	0.000050324695262
N	0.000125923212330	0.000203323332500	0.000007088768890
F	0.000218729922700	-0.000073712848863	0.000313157669440
F	-0.000510763130330	-0.000437746651390	0.000527611047870
F	-0.000165232728820	0.000382639328070	0.000384697524610
F	0.000702974548170	-0.000148481993660	0.000439454941330
F	-0.000153692337260	-0.000293019550790	0.000360289853680

F	-0.000283334169640	0.000518384644190	0.000582226652960
C	-0.000225402460730	0.000289204558840	-0.000154455369290
C	-0.000202010299460	-0.000448236067210	0.000094969757431
C	0.000340284151850	0.000081685187588	-0.000253753014930
C	-0.000155091464960	0.000622238871150	0.000130913194380
C	-0.000169080450070	0.000024647657494	-0.000631222740980
C	0.000045946610026	0.000018087538549	0.000210583057870
C	0.000620648984660	-0.000279383701930	-0.000166046116230
C	-0.000322693909120	-0.000467505483850	-0.000413331247440
C	0.000016383352541	-0.000095493310371	-0.000055849516815
C	0.000072381838784	0.000178256760470	-0.000043567850466
C	0.000364757693070	-0.000173093592930	-0.000106122792350
C	0.000376944512260	-0.000467965093630	0.000078504106972
C	-0.000393719480110	0.000375769171870	-0.000238936398550
C	-0.000083484582522	0.000665459698430	-0.000426408969770
C	0.000679963329950	0.001743072528500	0.000085034269637
C	0.000000015118879	-0.000215471578130	-0.000129720860330
C	-0.000002229769012	-0.000280865392030	-0.000229570108630
C	0.000115796792490	-0.000161214407670	0.000074796908581
C	0.000037128231185	0.000271900400970	-0.000232073322750
C	-0.000310100189110	0.000258072671720	-0.000326831584790
C	-0.000113619475590	-0.000515219289330	-0.000171470138760
C	0.000379524554110	-0.000018225872521	-0.000256188846550
C	0.000004736105682	0.000235195840840	-0.000088941314693
C	0.000490110373830	-0.000151771123460	-0.000148564951230
C	-0.000193857213250	-0.000158395834430	-0.000128717380290
C	0.000289594704910	-0.000018711707527	0.000956751587970
C	0.000583987453760	-0.001091646181000	-0.000679805162320
C	0.000039504467086	-0.000264698659170	-0.000204177738460
C	-0.000477593263080	-0.000094329830599	-0.000287717897340
C	-0.000109738818560	0.000075729471103	0.000046726450750
C	-0.000105054163240	0.000412259264820	-0.000085678912650
C	-0.000139036308580	0.000050841193169	0.000057415110896
C	0.000439792814140	-0.000883081653270	0.000365277832210
C	-0.000288424253400	0.000237690798250	0.000078062266185
C	-0.000961153544200	0.000716893611640	0.000787509745130
C	0.000139192278180	0.000111814265690	0.000258516724260
H	-0.000311426910490	0.000517541089910	0.000203984013330
H	0.000110215094340	-0.000650937166420	-0.000210460154480
H	-0.000148303323400	0.000226423896210	0.000383353042250
H	0.000081398288906	-0.000052155521606	-0.000141874079430
H	0.000206616466370	-0.000153451526140	0.000319514011190
H	-0.000133332120830	0.000125692522400	-0.000138784575040
H	0.000260730105860	0.000064458077770	0.000287912922920
H	0.000355006165600	0.000136749139740	-0.000249630568950
H	-0.000125415814450	0.000123288573380	0.000147022589180
H	0.000042999279578	-0.000055894557497	0.000313656529820
H	-0.000034744684514	0.000248445148760	0.000120731561780

H	-0.000062345395693	0.000253664088720	-0.000086337929464
H	0.000407956004970	-0.000848259356890	-0.000550222748290
H	-0.000469104851500	-0.000391077575830	0.000189385055470
H	0.000355162647260	-0.000553042750100	-0.000183837666820
H	0.000166368785850	-0.000132823653820	0.000137915249160
H	0.000291375386720	-0.000675516228270	-0.000075410011455
H	0.000236910442010	-0.000358488269410	-0.000224145001160
H	0.000015950300740	0.000291336235500	0.000182647350870
H	0.000257989151080	0.000072105134367	0.000011233845213
H	-0.000143566165940	0.000138453453590	-0.000154613361630
H	-0.000377026992100	-0.000008064270471	0.000316037688800
H	-0.000771487115170	-0.000251279419290	-0.000239697083420
H	-0.000176530352570	-0.000269708368100	-0.000278045451410
H	0.000386846791220	-0.000221613223370	0.000252062995760
H	0.000358902834860	-0.000634608318500	-0.000189205209350
H	0.000352414919580	-0.000215138880900	-0.000266832301990
H	0.000255552281690	0.000104635272840	0.000150758510290
H	0.000465264202990	0.000198474923170	0.000075114358478
H	0.000304294078910	0.000084592675395	-0.000024637714220
H	-0.000108201177260	-0.000361637868310	0.000118519646360
H	-0.000361744970760	-0.000391630804570	-0.000140913271610
H	-0.000467798134050	-0.000038309333375	0.000208444112120
H	-0.000087678322238	0.000129830645650	-0.000847376458910
H	0.000186366349950	0.000054752605206	-0.000138007379840
H	-0.000573271479740	0.000258593111230	-0.000536269553040
H	0.000078777112951	0.000945397546250	0.000512562520210
H	-0.000150930677620	0.000523961667360	-0.000206726567150
H	0.000401362756630	-0.000088652331993	-0.000082618548028
H	0.000444909832070	0.000620335342830	0.000415619605570
H	0.000258885068700	0.000578608654470	-0.000462869316370
H	-0.000164895223880	0.000209543376560	0.000162738592880
H	-0.000346874607670	-0.000220596890230	0.000171717340940
H	-0.000181681645300	-0.000163768415470	0.000033952552754
H	-0.000033251268252	-0.000004634913878	0.000469089248140
H	-0.000282239196250	0.000600319747900	0.000300188198300
H	-0.000299152947440	0.000266157765740	-0.000107780528020
H	0.000096099588651	0.000351428932800	0.000126649652430
H	-0.000101546959990	-0.000406102564380	-0.000156910743460
H	0.000221351670950	0.000189705962870	0.000031057819405
H	-0.000124232639550	-0.000113433829110	0.000090807366992
H	-0.000435977314870	-0.000048471540065	-0.000580600935480
H	-0.000513253719840	0.000066538220392	-0.000198599256620
H	-0.000344160581770	-0.000000051870039	-0.000394868393620
H	-0.000682085986800	-0.000140285819600	-0.000185886758180
H	-0.000122048784000	0.000193583776130	0.000078705434198
H	-0.000592965298210	-0.000232794605910	-0.000040596068029
H	-0.000026315117835	0.000114283992900	0.000355267117490
H	-0.000181575554610	0.000119415451130	-0.000022134918290

H	0.000149206136390	-0.000523544269330	0.000278464458360

Table S5. DFT calculated (6-31G* basis set unless otherwise noted) Mulliken and Lowdin populations and charges for the Fe_4 dmg-type cluster **4** (*S* = 1/2 calculations).

	Mulliken pop	**Mulliken charge**	**Lowdin pop**	**Lowdin charge**
		PW91		
Fe1	24.973446	1.026554	25.808855	0.191145
Fe2	25.139204	0.860796	26.071038	-0.071038
Fe3	25.132813	0.867187	26.055118	-0.055118
Fe4	25.137731	0.862269	26.066423	-0.066423
		B3PW91		
Fe1	24.769385	1.230615	25.692478	0.307522
Fe2	25.01044	0.989556	26.046931	-0.046931
Fe3	25.005389	0.994611	26.035622	-0.035622
Fe4	25.012077	0.987923	26.052389	-0.052389
		B3LYP		
Fe1	24.805106	1.194894	25.692152	0.307848
Fe2	25.081768	0.918232	26.045112	-0.045112
Fe3	25.075451	0.924549	26.033612	-0.033612
Fe4	25.083426	0.916574	26.050377	-0.050377
		PW91 (TZV basis set)		
Fe1	25.379748	0.620252	26.558440	-0.558440
Fe2	24.996410	1.003590	26.822711	-0.822711
Fe3	24.998145	1.001855	26.797212	-0.797212
Fe4	25.024660	0.975340	26.828786	-0.828786