Electronic supplementary information (ESI):

Evidences of crystal packing effects in stabilizing high or low spin state of iron(II) complexes with functionalized 2,6-bis(pyrazol-1-yl)pyridine ligands

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Experimental section (continue)

General information

Citrazinic acid, tetramethylammonium chloride, phosphorous oxychloride, K_2CO_3, Na_2CO_3, pyrazole, NaH (80% in mineral oil), HCl 37% *w*/*w* in water, thionyl chloride, anhydrous Na_2SO_4, tris(hydroxymethyl)aminomethane were of reagent grade and used as received. Commercial solvents were used as received, including diglyme. Methanol was distilled over magnesium methoxide prior to use, DMSO was treated with alumina and then distilled over CaH_2 at reduced pressure (10 mmHg). Elemental analyses were recorded using a Carlo Erba EA1110 CHNS-O automatic analyser. ^{1}H NMR spectra were recorded on a 200 MHz Bruker FT-DPX200 spectrometer, while ^{13}C NMR spectra were recorded on a 400 MHz Bruker FT-NMR Advance400 spectrometer at room temperature. Proton chemical shifts are given in parts per million (ppm) versus external TMS, and were determined by reference to the solvent residual signals (3.31 for CD_2HOD, 7.26 for $CHCl_3$, and 2.50 ppm for protio impurities in DMSO-d_6); coupling constants are given in Hz. IR spectra were recorded as KBr discs using a Jasco FTIR-4700LE spectrophotometer with a 2 cm^{-1} resolution.

Synthesis of methyl 2,6-dichloroisonicotinate.[1] Tetramethylammonium chloride was dried in vacuum for 2 h prior to use. Citrazinic acid (2.00 g, 12.9 mmol) and tetramethylammonium chloride (2.56 g, 15.5 mmol) were placed under nitrogen atmosphere before careful addition of phosphorous oxychloride (6.00 g, 3.65 mL, 39.1 mmol). The mixture was slowly heated to 80 °C for 30 min, enabling dissolution of the solids to give a homogeneous dark red solution (*Caution: vigorous evolution of gaseous HCl!*). The reaction mixture was then heated to 140 °C overnight. After cooling down to room temperature, 30 mL of cold distilled methanol were added cautiously. The solution was poured in 200 mL of saturated aqueous K_2CO_3 solution, producing a light grey precipitate that was filtered and washed with distilled water, then dried in vacuum for several hours. Yield: 2.28 g, 85.8%. Anal Calc for $C_7H_5Cl_2NO_2$ (206.03): C 40.80, H 2.45, N 6.80. Found: C 40.40, H 2.64, N 6.66%. IR (KBr): 1733s (νC=O ester), 1585m+1546s+1441s (νC=C,C=N), 1363s (δCH_3), 738 (νC–Cl) cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz, 293 K): δ 7.81 (s, 2H, Hpy), 3.98 (s, 3H, OCH_3) ppm.

Synthesis of bpp-COOH.[2] Pyrazole (1.25 g, 18.4 mmol) was solubilized in diglyme (50 mL) under nitrogen atmosphere. NaH (80% in mineral oil, 0.92 g, 31 mmol) was added in four portions (*Caution: evolution of H_2!*) and the white turbid solution was stirred for 1 h. Methyl 2,6-dichloroisonicotinate (1.26 g, 6.12 mmol) was added in one portion and the solution was heated to 140 °C for 5 days, producing a light grey precipitate. The mixture was poured in cold distilled water (30 mL), and few drops of aqueous HCl 37% *w*/*w* were added to reprotonate the compound,

producing the appearance of a white precipitate which was filtered and washed with a small amount of cold water, then dried in vacuum. Yield: 1.30 g, 83.3%. Anal Calc for $C_{12}H_9N_5O_2$ (255.23): C 56.47, H 3.55, N 27.44. Found: C 55.82, H 4.02, N 26.85%. IR (KBr): 3000br (νO–H), 1726s (νC=O acid), 1576s+1466s+1399s (νC=C,C=N,C–H) cm^{-1}. ^1H NMR (200 MHz, 293 K, CD_3OD): δ 8.79 (dd, 2H, J_1 = 2.7 Hz, J_2 = 0.5 Hz, H^5-pz), 8.32 (s, 2H, $H^{3/5}$-py), 7.82 (dd, 2H, J_2 = 0.5 Hz, J_3 = 1.6 Hz, H^3-pz), 6.60 (dd, J_1 = 2.7 Hz, J_3 = 1.6 Hz, H^4-pz) ppm.

Synthesis of bpp-COOMe. bpp-COOH (1.29 g, 5.05 mmol) was placed in distilled methanol (60 mL) under nitrogen atmosphere. Thionyl chloride (0.73 mL, 10 mmol) was added, and the solution was stirred for 5 h at room temperature. Solvent was removed under reduced pressure and distilled water (30 mL) was added, before extracting the compound with ethyl acetate (3 × 40 mL). The organic layer was washed with aqueous Na_2CO_3, dried with Na_2SO_4 and the solvent evaporated to give a white precipitate which was dried on vacuum. Yield: 1.12 g, 82.3%. Anal Calc for $C_{13}H_{11}N_5O_2$ (269.26): C 57.99, H 4.12, N 26.01%. Found: C 58.36, H 4.23, N 25.87%. IR (KBr): 1740s (νC=O ester), 1575s+1466s+1398s (νC=C,C=N,C–H) cm^{-1}. ^1H NMR (200 MHz, 293 K, DMSO-d_6): δ 8.99 (d, 2H, J_1 = 2.6 Hz, H^5-pz), 8.18 (s, 2H, $H^{3/5}$-py), 7.92 (d, 2H, J_2 = 1.2 Hz, H^3-pz), 6.67 (dd, J_1 = 2.6 Hz, J_2 = 1.2 Hz, H^4-pz), 3.98 (s, 3H, OCH_3) ppm.

Synthesis of bpp-triolH_3.[3] Tris(hydroxymethyl)aminomethane was dried for 1 h in an oven prior to use. K_2CO_3 and the glassware were dried in an oven overnight. Tris(hydroxymethyl)amino-methane (180 mg, 1.49 mmol) was solubilized in distilled DMSO (10 mL) and K_2CO_3 (205 mg, 1.48 mmol) was added, followed by bpp-COOMe (400 mg, 1.49 mmol). The reaction mixture was stirred at room temperature for 3 h, and then the excess of K_2CO_3 was filtered off on paper. The solvent was removed under reduced pressure, leaving approx. 1 mL of solution. The remaining oil was dissolved in $CHCl_3$ and the solvent was evaporated again to a few milliliters. Addition of *n*-hexane produced the appearance of a white precipitate which was filtered and dried in vacuum. Yield: 459 mg, 86.0%. Anal Calc for $C_{16}H_{18}N_6O_4$ (358.35): C 53.63, H 5.06, N 23.45. Found: C 53.36, H 4.80, N 23.05%. IR (KBr): 3389br (νO–H), 1671s (νC=O amide), 1618s+1571s+1518s+1402s (νC=N), 1465s (δC–H), 1052s (νC–O), 759s (δ aromatic ring) cm^{-1}. ^1H NMR (400 MHz, 293 K, DMSO-d_6): δ 8.98 (d, 2H, J_1 = 2.6 Hz, H^5-pz), 8.12 (s, 2H, $H^{3/5}$-py), 7.91 (d, 2H, J_2 = 1.1 Hz, H^3-pz), 7.82 broad (s, 1H, N*H*), 6.66 (dd, J_1 = 2.6 Hz, J_2 = 1.1 Hz, H^4-pz), 4.69 (t, 3H, O*H*), 3.74 (s, 6H, CCH_2OH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, 293 K, DMSO-d_6): δ 60.1 (CH_2), 63.8 (CNH(CH_2)$_3$), 107.6, 109.2, 128.8, 143.4, 149.7, 150.3, 165.0 (*C*O) ppm.

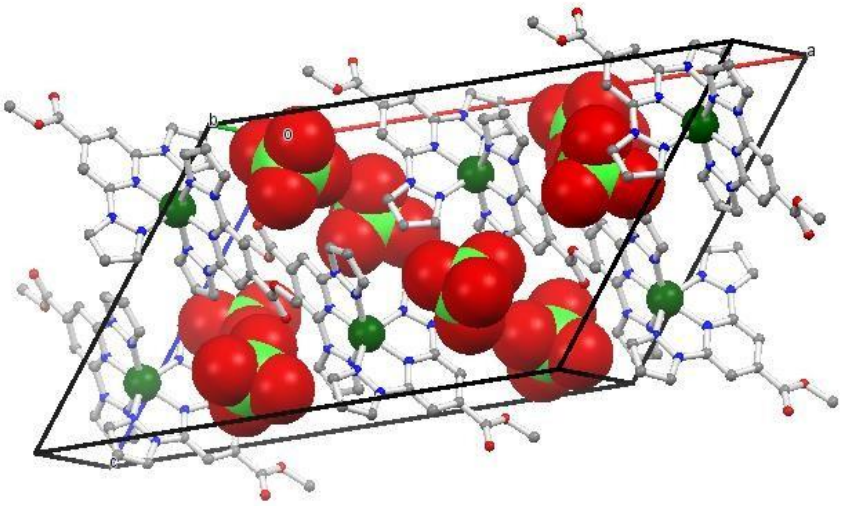


Fig. S1 Crystal packing in **1** with perchlorate ions drawn using a space-filling model. Colour code: Fe = dark green, Cl = light green, O = red, N = blue, C = grey, H omitted for clarity.

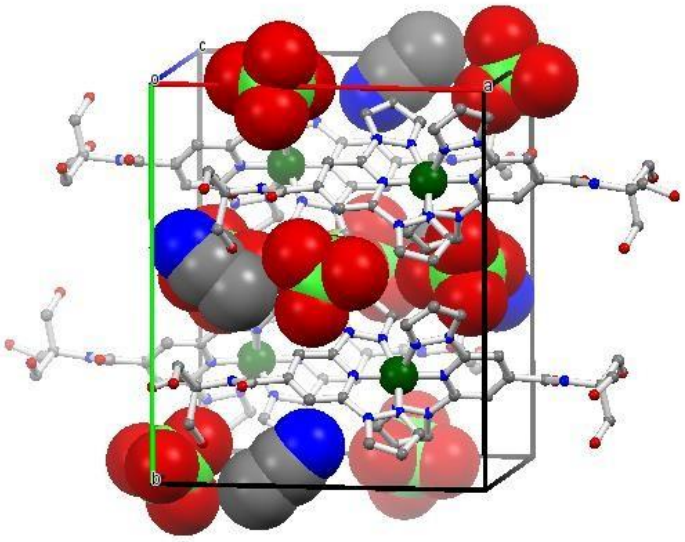


Fig. S2 Crystal packing in **2**·MeCN with perchlorate and acetonitrile molecules drawn using a space-filling model. Colour code: Fe = dark green, Cl = light green, O = red, N = blue, C = grey, H omitted for clarity.

Table S1 Hydrogen bonds in **1** (Å and °).

D–H···A	***d*(D–H)**	***d*(H···A)**	***d*(D···A)**	**<(DHA)**
C1–H1···O1#1	0.914(18)	2.427(18)	3.2704(15)	153.4(15)
C2–H2···O3#2	0.92(2)	2.53(2)	3.4033(17)	157.3(16)
C3–H3···O4#3	0.938(19)	2.276(19)	3.2117(16)	175.2(15)
C5–H5···O4#3	0.964(18)	2.480(18)	3.4044(16)	160.5(14)
C7–H7···O5#4	0.95(2)	2.486(19)	3.2875(16)	141.6(15)
C9–H9···O5#4	0.92(2)	2.41(2)	3.3081(17)	164.4(16)
C10–H10···O3#5	0.917(19)	2.644(19)	3.1520(16)	115.7(14)
C11–H11···O6#5	0.94(2)	2.53(2)	3.4001(19)	155.5(16)

Symmetry transformations used to generate equivalent atoms: #1 = x+1/2,–y+1/2,z+1/2; #2 = –x,y,–z+1/2; #3 = x–1/2,y–1/2,z; #4 = x–1/2,–y+1/2,z+1/2; #5 = x,y–1,z+1

Table S2 Hydrogen bonds in **2**·MeCN (Å and °).

D–H···A	***d*(D–H)**	***d*(H···A)**	***d*(D···A)**	**<(DHA)**
N11–H11A···O8A#1	0.88	2.03	2.846(7)	154.2
O2–H2A···O1	0.84	2.16	2.770(5)	129.8
O3–H3A···O11#1	0.84	2.12	2.902(10)	155.4
O4A–H4A···O7#2	0.84	1.86	2.671(7)	163.0
O4B–H4B···O3	0.84	1.83	2.441(13)	128.7
N12–H12A···O4B#3	0.88	2.15	2.940(10)	148.4
O6–H6···O12	0.84	1.94	2.769(7)	171.1
O7–H7A···O5	0.84	2.04	2.747(5)	141.3
O8A–H8A···O6	0.84	1.96	2.658(8)	140.4
O8C–H8C···O2#4	0.84	1.81	2.63(2)	163.5

Symmetry transformations used to generate equivalent atoms: #1 = x+1,y,z; #2 = x+3/2,–y+1/2,z+1/2; #3 = x–1,y,z; #4 = x–3/2,–y+1/2,z–1/2

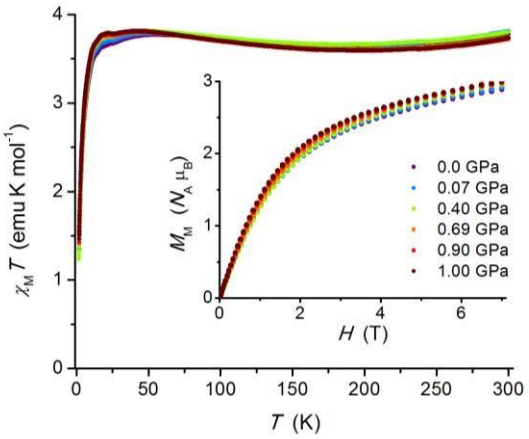


Fig. S3 Temperature dependence of the $\chi_M T$ product in the 1.8 – 300 K range measured at H_{DC} = 0.1 T and different external pressures of **1**; inset: isothermal field dependence of the magnetization at T = 1.8 K under different external pressures.

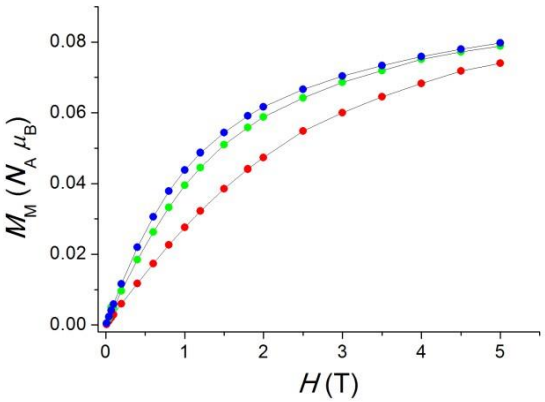


Fig. S4 Isothermal field dependence of the magnetization, M_M, at 1.8 (blue), 2.5 (green) and 4.5 (red) K of **2** (grey lines are a guide for the eye).

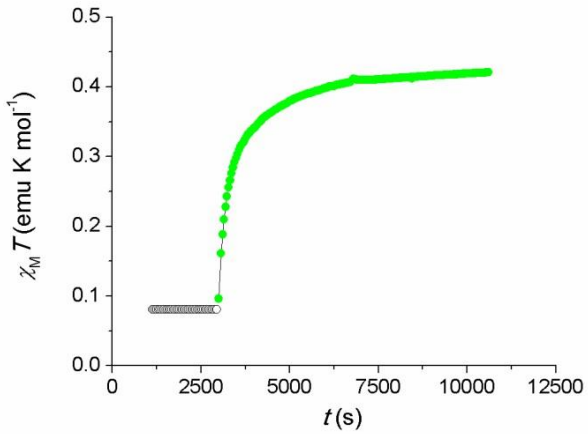
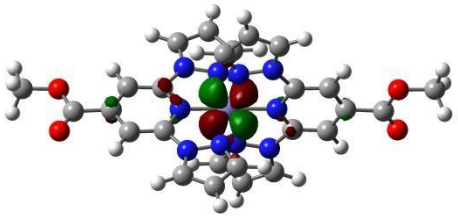
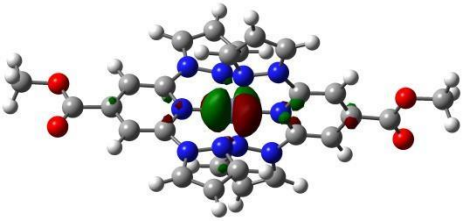


Fig. S5 Time dependence of the $\chi_M T$ product of **2** under 532 nm light irradiation at 10 K (green points).

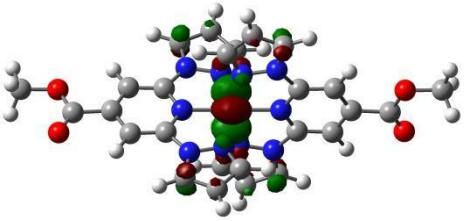
a) $[Fe(bpp\text{-}COOMe)_2]^{2+}$ in its LS configuration ($S = 0$)



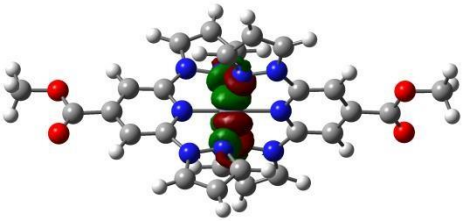
HOMO–2, E = –0.45372 a.u., d_{Fe} = 0.80



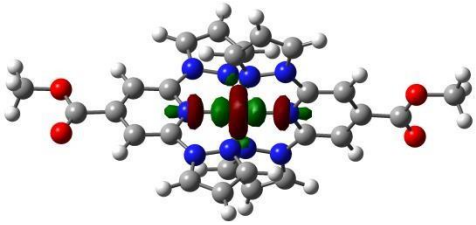
HOMO–1, E = –0.45370 a.u., d_{Fe} = 0.80



HOMO, E = –0.44144 a.u., d_{Fe} = 0.72

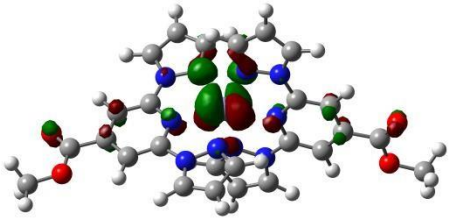


LUMO+6, E = –0.22636 a.u., d_{Fe} = 0.71

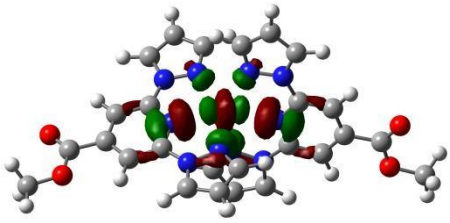


LUMO+8, E = –0.22088 a.u., d_{Fe} = 0.45

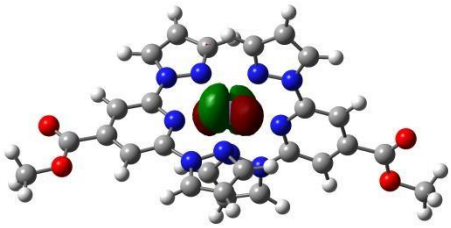
b) $[Fe(bpp\text{-}COOMe)_2]^{2+}$ in its HS configuration (S = 2)



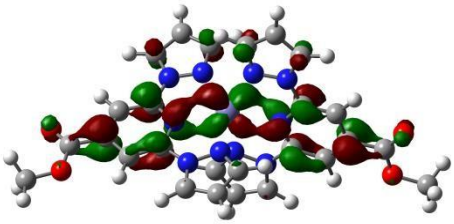
HOMO(α)–18, E = –0.55690 a.u., d_{Fe} = 0.52



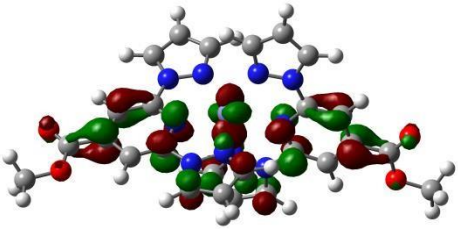
HOMO(α)–2, E = –0.48192 a.u., d_{Fe} = 0.37



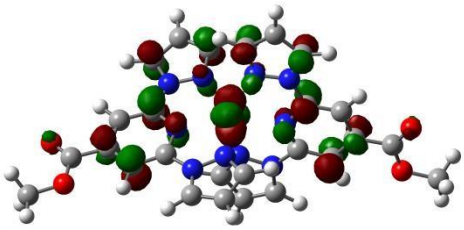
HOMO(β), E = –0.41396 a.u., d_{Fe} = 0.87



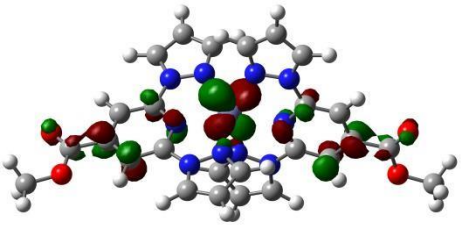
LUMO(β), E = –0.29878 a.u., d_{Fe} = 0.22



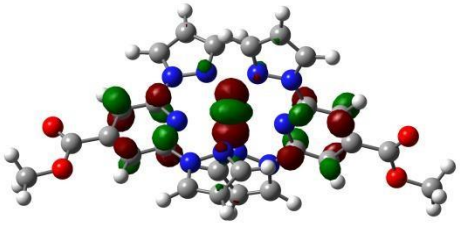
LUMO(β+1), E = –0.28642 a.u., d_{Fe} = 0.20



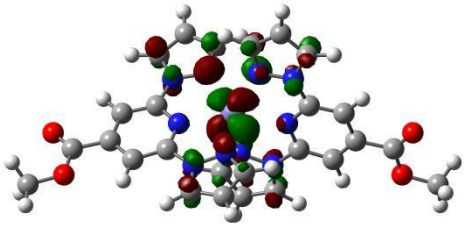
LUMO(β+2), E = –0.27697 a.u., d_{Fe} = 0.22



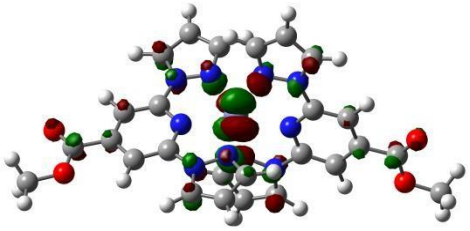
LUMO(β+4), E = –0.25534 a.u., d_{Fe} = 0.55



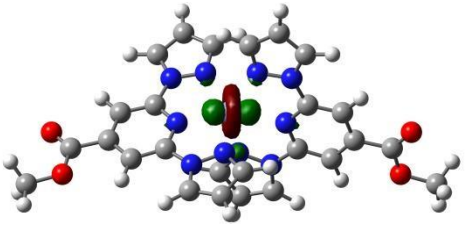
LUMO(β+5), E = –0.25290 a.u., d_{Fe} = 0.46



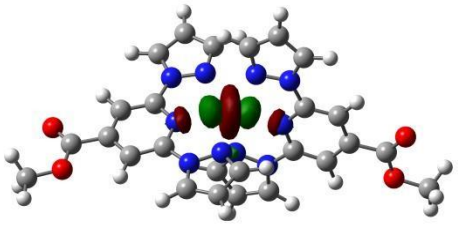
LUMO(β+6), E = –0.23010 a.u., d_{Fe} = 0.49



LUMO(β+8), E = –0.22092 a.u., d_{Fe} = 0.41

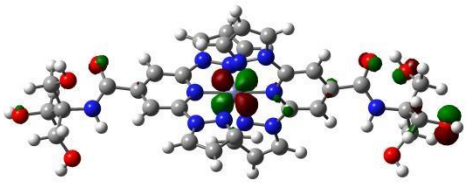


LUMO(β+9), E = –0.21810 a.u., d_{Fe} = 0.26

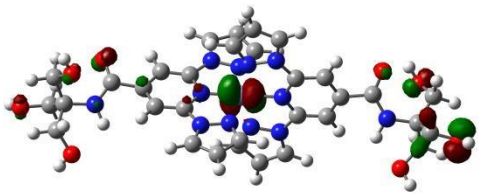


LUMO(β+10), E = –0.21055 a.u., d_{Fe} = 0.52

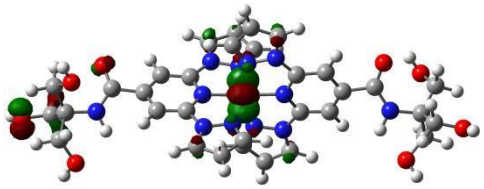
c) $[Fe(bpp\text{-}triolH_3)_2]^{2+}$ in its LS configuration ($S = 0$)



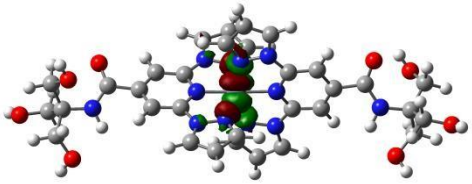
HOMO–8, E = –0.44158 a.u., d_{Fe} = 0.63



HOMO–7, E = –0.44137 a.u., d_{Fe} = 0.63



HOMO–2, E = –0.42997 a.u., d_{Fe} = 0.59



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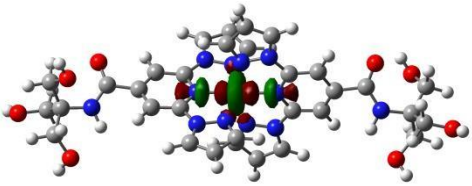
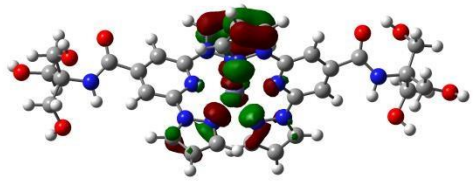
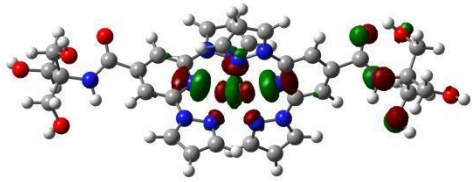


LUMO+8, E = –0.21148 a.u., d_{Fe} = 0.56

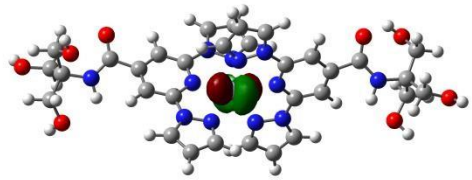
d) $[Fe(bpp\text{-}triolH_3)_2]^{2+}$ in its HS configuration ($S = 2$)



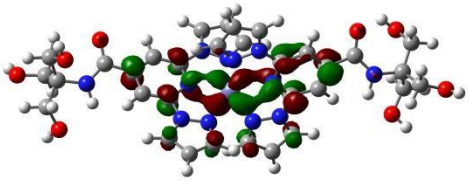
HOMO(α)–16, E = –0.48537 a.u., d_{Fe} = 0.16



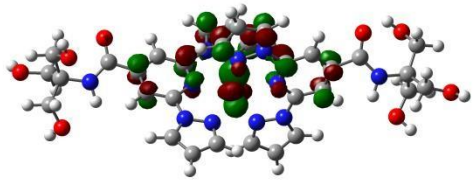
HOMO(α)–11, E = –0.46935 a.u., d_{Fe} = 0.28



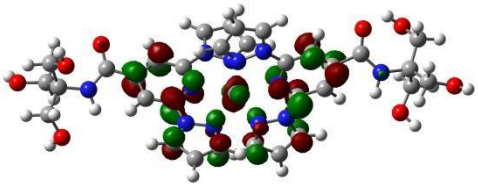
HOMO(β), E = –0.40279 a.u., d_{Fe} = 0.87



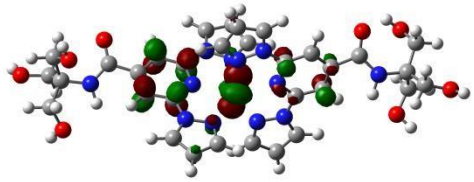
LUMO(β), E = –0.28495 a.u., d_{Fe} = 0.28



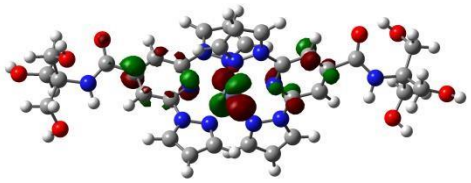
LUMO(β)+1, E = –0.27232 a.u., d_{Fe} = 0.31



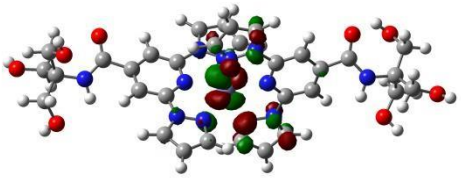
LUMO(β)+2, E = –0.26358 a.u., d_{Fe} = 0.11



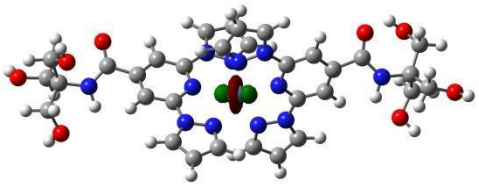
LUMO(β)+4, E = –0.24170 a.u., d_{Fe} = 0.46



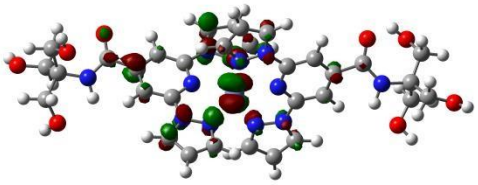
LUMO(β)+5, E = –0.24040 a.u., d_{Fe} = 0.56



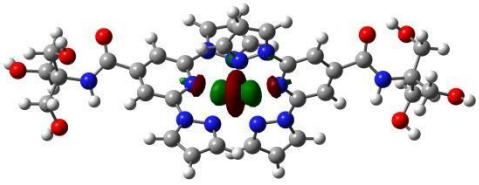
LUMO(β)+6, E = –0.21905 a.u., d_{Fe} = 0.53



LUMO(β)+8, E = –0.20937 a.u., d_{Fe} = 0.15



LUMO(β)+9, E = –0.20779 a.u., d_{Fe} = 0.30

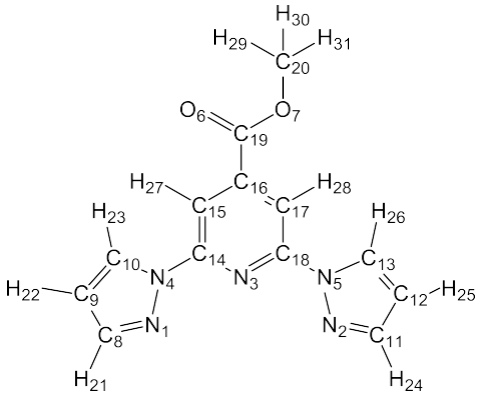


LUMO(β)+10, E = –0.19919 a.u., d_{Fe} = 0.63

Fig. S6 Plots of the (U)M06/6-311+G(d) frontier orbitals mainly localized on the iron(II) centre of the $[Fe(bpp\text{-}R)_2]^{2+}$ cations (R = COOMe, triolH_3) in both HS (S = 2) and LS (S = 0) configurations, using an isosurface value of 0.04, together with the corresponding energies (in atomic units, a.u.) and the *d*-orbital contributions.

Table S3. Cartesian coordinates, electronic energies (a.u.) and NBO charges (e) of the modelled bpp-R free ligands and $[Fe(bpp\text{-}R)_2]^{2+}$ cations (R = COOMe, triolH_3) in both spin configurations $S = 2$ and $S = 0$.

a) bpp-COOMe at the M06/6-311+G(d) level of theory



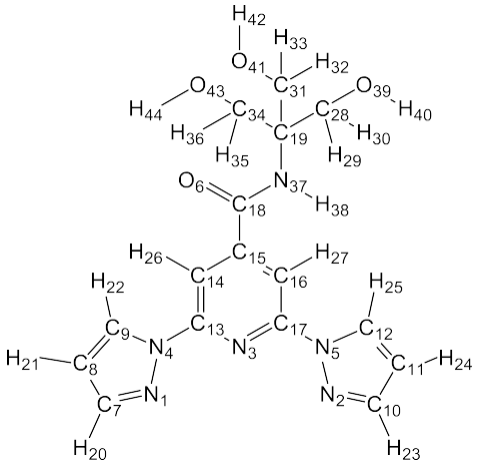
E(RM06) = -925.771255248 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	3.458819	0.557852	0.471134
2	7	0	-0.364995	3.375939	0.484695
3	7	0	0.769953	0.906452	-0.033242
4	7	0	2.679367	-0.422653	-0.028911
5	7	0	-1.058242	2.345886	-0.039903
6	8	0	-1.270791	-3.663092	0.050185
7	8	0	-3.020170	-2.264582	0.114535
8	6	0	4.689845	0.127180	0.291866
9	6	0	4.729323	-1.138024	-0.335621
10	6	0	3.416222	-1.461479	-0.524930
11	6	0	-1.131918	4.427931	0.287081
12	6	0	-2.333888	4.097318	-0.377317
13	6	0	-2.251917	2.747451	-0.570063
14	6	0	1.273722	-0.313354	-0.011236
15	6	0	0.499595	-1.469014	0.011786
16	6	0	-0.877493	-1.315172	0.014767
17	6	0	-1.426706	-0.041971	0.014559
18	6	0	-0.542459	1.032756	-0.013876
19	6	0	-1.715365	-2.547101	0.060589
20	6	0	-3.889649	-3.391526	0.171703
21	1	0	5.519745	0.739628	0.624025
22	1	0	5.594348	-1.721401	-0.618219
23	1	0	2.950622	-2.315298	-0.997719
24	1	0	-0.799293	5.398985	0.634276
25	1	0	-3.136203	4.754609	-0.682049
26	1	0	-2.915568	2.053935	-1.068078
27	1	0	0.930222	-2.463770	0.065409
28	1	0	-2.500154	0.098970	0.072397
29	1	0	-3.661969	-4.006982	1.045543
30	1	0	-4.899128	-2.988468	0.242448
31	1	0	-3.785111	-4.003109	-0.728064

Atom	No	Natural Charge	Natural Population Core	Valence	Rydberg	Total
N	1	-0.25909	1.99945	5.23816	0.02148	7.25909
N	2	-0.25811	1.99945	5.23721	0.02145	7.25811
N	3	-0.42348	1.99921	5.40803	0.01623	7.42348
N	4	-0.24623	1.99922	5.22052	0.02650	7.24623
N	5	-0.24608	1.99922	5.22020	0.02666	7.24608
O	6	-0.59627	1.99975	6.58491	0.01161	8.59627
O	7	-0.56247	1.99972	6.54823	0.01453	8.56247
C	8	0.00252	1.99932	3.97081	0.02735	5.99748
C	9	-0.31058	1.99912	4.29576	0.01570	6.31058

C	10	-0.00580	1.99916	3.98805	0.01859	6.00580
C	11	0.00145	1.99932	3.97190	0.02734	5.99855
C	12	-0.31117	1.99912	4.29632	0.01572	6.31117
C	13	-0.00779	1.99916	3.98999	0.01864	6.00779
C	14	0.42970	1.99900	3.54448	0.02681	5.57030
C	15	-0.22733	1.99898	4.21351	0.01484	6.22733
C	16	-0.09569	1.99891	4.07795	0.01884	6.09569
C	17	-0.23410	1.99898	4.22078	0.01435	6.23410
C	18	0.42950	1.99900	3.54448	0.02703	5.57050
C	19	0.82617	1.99927	3.12668	0.04788	5.17383
C	20	-0.19945	1.99926	4.18387	0.01633	6.19945
H	21	0.19942	0.00000	0.80005	0.00054	0.80058
H	22	0.22032	0.00000	0.77902	0.00067	0.77968
H	23	0.21148	0.00000	0.78772	0.00080	0.78852
H	24	0.19968	0.00000	0.79978	0.00053	0.80032
H	25	0.21995	0.00000	0.77938	0.00067	0.78005
H	26	0.20950	0.00000	0.78969	0.00081	0.79050
H	27	0.23914	0.00000	0.75971	0.00115	0.76086
H	28	0.23406	0.00000	0.76478	0.00116	0.76594
H	29	0.18798	0.00000	0.81101	0.00101	0.81202
H	30	0.18667	0.00000	0.81288	0.00045	0.81333
H	31	0.18611	0.00000	0.81289	0.00100	0.81389
* Total *		0.00000	39.98458	99.57876	0.43666	140.00000

b) bpp-triolH_3 at the M06/6-311+G(d) level of theory

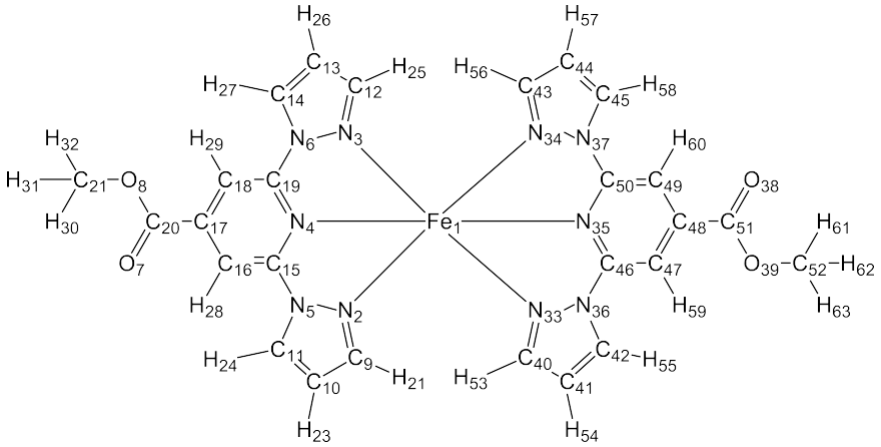


E(RM06) = -1249.38127080 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-4.568968	-1.810100	-0.692693
2	7	0	-3.547516	2.859874	-0.594580
3	7	0	-2.848719	0.234732	-0.010304
4	7	0	-3.389740	-2.026976	-0.074218
5	7	0	-2.434532	2.522382	0.086564
6	8	0	1.615302	-1.756889	0.932440
7	6	0	-5.218790	-2.948673	-0.576110
8	6	0	-4.474774	-3.921389	0.129228
9	6	0	-3.302019	-3.292911	0.434807
10	6	0	-3.696886	4.148925	-0.369925
11	6	0	-2.685817	4.666959	0.469361
12	6	0	-1.889698	3.590550	0.741636
13	6	0	-2.415574	-1.012863	0.011722
14	6	0	-1.075093	-1.364391	0.137872
15	6	0	-0.144409	-0.342572	0.224069
16	6	0	-0.581403	0.974463	0.189227
17	6	0	-1.951984	1.196070	0.079740
18	6	0	1.300039	-0.732177	0.361688
19	6	0	3.648346	-0.015469	-0.167054
20	1	0	-6.208080	-3.041431	-1.008414
21	1	0	-4.762021	-4.931309	0.386071
22	1	0	-2.439540	-3.622863	0.997322
23	1	0	-4.528846	4.673656	-0.824307
24	1	0	-2.567422	5.677549	0.834382
25	1	0	-1.018976	3.485471	1.374589
26	1	0	-0.740448	-2.396616	0.142614
27	1	0	0.109279	1.810729	0.251182
28	6	0	4.177160	1.175185	-0.984097
29	1	0	3.714422	2.095768	-0.597344
30	1	0	3.836129	1.051138	-2.030568
31	6	0	4.042226	-1.333680	-0.855694
32	1	0	3.717512	-2.190081	-0.253698
33	1	0	3.521051	-1.382179	-1.820188
34	6	0	4.130541	0.050329	1.288553
35	1	0	3.366200	-0.392573	1.938341
36	1	0	4.270000	1.105081	1.572838
37	7	0	2.190502	0.143286	-0.180992
38	1	0	1.819149	0.877214	-0.771253
39	8	0	5.550811	1.364510	-0.907138
40	1	0	5.969372	0.545301	-1.213342
41	8	0	5.425027	-1.396554	-1.133097
42	1	0	5.864586	-1.516411	-0.277934
43	8	0	5.343718	-0.669137	1.423949
44	1	0	5.620403	-0.676401	2.343895

			Natural Population			
		Natural				
Atom	No	Charge	Core	Valence	Rydberg	Total
N	1	-0.25945	1.99945	5.23855	0.02146	7.25945
N	2	-0.25761	1.99945	5.23677	0.02140	7.25761
N	3	-0.42765	1.99921	5.41216	0.01627	7.42765
N	4	-0.24707	1.99921	5.22140	0.02646	7.24707
N	5	-0.24754	1.99922	5.22148	0.02684	7.24754
O	6	-0.62895	1.99976	6.61763	0.01156	8.62895
C	7	0.00390	1.99932	3.96947	0.02731	5.99610
C	8	-0.30939	1.99912	4.29461	0.01566	6.30939
C	9	-0.00537	1.99916	3.98762	0.01858	6.00537
C	10	0.00150	1.99932	3.97191	0.02727	5.99850
C	11	-0.31005	1.99912	4.29519	0.01574	6.31005
C	12	-0.01060	1.99916	3.99276	0.01868	6.01060
C	13	0.43570	1.99900	3.53831	0.02700	5.56430
C	14	-0.23056	1.99896	4.21677	0.01483	6.23056
C	15	-0.06612	1.99893	4.04809	0.01910	6.06612
C	16	-0.26472	1.99897	4.25230	0.01345	6.26472
C	17	0.43599	1.99900	3.53778	0.02723	5.56401
C	18	0.69789	1.99924	3.25820	0.04467	5.30211
C	19	0.07583	1.99908	3.90271	0.02238	5.92417
H	20	0.19986	0.00000	0.79961	0.00053	0.80014
H	21	0.22083	0.00000	0.77851	0.00066	0.77917
H	22	0.21298	0.00000	0.78623	0.00079	0.78702
H	23	0.20060	0.00000	0.79887	0.00053	0.79940
H	24	0.22087	0.00000	0.77846	0.00067	0.77913
H	25	0.20842	0.00000	0.79077	0.00081	0.79158
H	26	0.23657	0.00000	0.76223	0.00120	0.76343
H	27	0.21401	0.00000	0.78479	0.00120	0.78599
C	28	-0.00956	1.99909	3.97940	0.03107	6.00956
H	29	0.16902	0.00000	0.82997	0.00101	0.83098
H	30	0.15435	0.00000	0.84440	0.00124	0.84565
C	31	-0.03077	1.99907	4.00202	0.02968	6.03077
H	32	0.19607	0.00000	0.80286	0.00107	0.80393
H	33	0.17823	0.00000	0.82096	0.00081	0.82177
C	34	-0.01555	1.99906	3.99124	0.02526	6.01555
H	35	0.18282	0.00000	0.81604	0.00115	0.81718
H	36	0.16586	0.00000	0.83295	0.00119	0.83414
N	37	-0.66946	1.99928	5.64506	0.02512	7.66946
H	38	0.39849	0.00000	0.60044	0.00107	0.60151
O	39	-0.74105	1.99979	6.72686	0.01440	8.74105
H	40	0.48817	0.00000	0.50976	0.00207	0.51183
O	41	-0.76754	1.99979	6.75382	0.01393	8.76754
H	42	0.49582	0.00000	0.50272	0.00146	0.50418
O	43	-0.77573	1.99976	6.76296	0.01300	8.77573
H	44	0.48097	0.00000	0.51792	0.00111	0.51903
* Total *		0.00000	51.98051	135.43255	0.58694	188.00000

c) $[Fe(bpp\text{-}COOMe)_2]^{2+}$ in its HS configuration (S = 2) at the UM06/6-311+G(d) level of theory



E(UM06) = -3114.85552836 a.u.

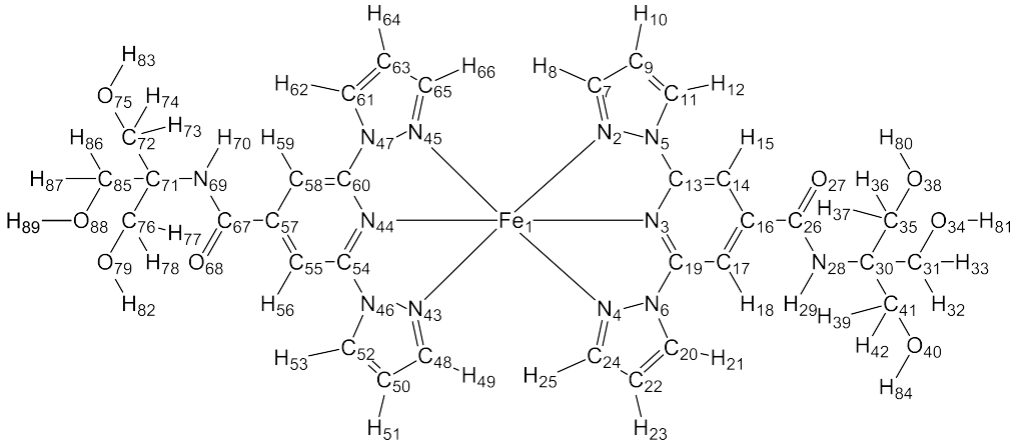
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	26	0	0.000013	0.633009	0.000042
2	7	0	1.003565	2.167708	1.168427
3	7	0	0.268220	-0.932701	-1.522268
4	7	0	2.107551	0.230952	-0.131498
5	7	0	2.337008	1.952864	1.348711
6	7	0	1.545579	-1.385316	-1.642848
7	8	0	6.967605	-0.131586	0.699520
8	8	0	6.552185	-1.756730	-0.798225
9	6	0	0.712737	3.221764	1.914969
10	6	0	1.847888	3.702530	2.587211
11	6	0	2.865620	2.874664	2.199359
12	6	0	-0.443690	-1.660050	-2.367300
13	6	0	0.359223	-2.588234	-3.049712
14	6	0	1.621489	-2.385444	-2.562765
15	6	0	2.953431	0.917453	0.629467
16	6	0	4.301595	0.623357	0.690611
17	6	0	4.755262	-0.436282	-0.086925
18	6	0	3.881637	-1.158241	-0.893129
19	6	0	2.552873	-0.771426	-0.879593
20	6	0	6.225421	-0.749755	-0.008639
21	6	0	7.943981	-2.128229	-0.798783
22	1	0	-0.302781	3.598242	1.940450
23	1	0	1.912995	4.545413	3.259707
24	1	0	3.915495	2.874162	2.459416
25	1	0	-1.510772	-1.490727	-2.456709
26	1	0	0.056011	-3.306204	-3.797701
27	1	0	2.558223	-2.869483	-2.803336
28	1	0	5.012140	1.170932	1.302700
29	1	0	4.248422	-1.980557	-1.497527
30	1	0	8.240828	-2.458887	0.198265
31	1	0	8.033615	-2.939406	-1.517736
32	1	0	8.556274	-1.275485	-1.097212
33	7	0	-1.003482	2.167699	-1.168403
34	7	0	-0.268276	-0.932717	1.522404
35	7	0	-2.107538	0.230982	0.131526
36	7	0	-2.336920	1.952866	-1.348731
37	7	0	-1.545660	-1.385279	1.642935
38	8	0	-6.967566	-0.131512	-0.699679
39	8	0	-6.552217	-1.756657	0.798085
40	6	0	-0.712617	3.221740	-1.914951
41	6	0	-1.847739	3.702505	-2.587244
42	6	0	-2.865493	2.874659	-2.199411
43	6	0	0.443562	-1.660066	2.367497
44	6	0	-0.359427	-2.588173	3.049924
45	6	0	-1.621651	-2.385382	2.562873
46	6	0	-2.953380	0.917474	-0.629492
47	6	0	-4.301544	0.623388	-0.690692
48	6	0	-4.755253	-0.436233	0.086842
49	6	0	-3.881671	-1.158184	0.893100
50	6	0	-2.552902	-0.771379	0.879620
51	6	0	-6.225411	-0.749700	0.008494
52	6	0	-7.944021	-2.128128	0.798613

53	1	0	0.302906	3.598207	-1.940403
54	1	0	-1.912814	4.545377	-3.259756
55	1	0	-3.915359	2.874164	-2.459503
56	1	0	1.510644	-1.490784	2.456970
57	1	0	-0.056284	-3.306110	3.797974
58	1	0	-2.558414	-2.869383	2.803407
59	1	0	-5.012056	1.170956	-1.302824
60	1	0	-4.248490	-1.980487	1.497493
61	1	0	-8.240852	-2.458783	-0.198442
62	1	0	-8.033688	-2.939300	1.517565
63	1	0	-8.556303	-1.275370	1.097025

			Natural Population			
Atom	No	Natural Charge	Core	Valence	Rydberg	Total
Fe	1	0.91370	17.99509	7.03144	0.05976	25.08630
N	2	-0.35540	1.99943	5.31107	0.04489	7.35540
N	3	-0.34615	1.99944	5.30167	0.04504	7.34615
N	4	-0.61141	1.99938	5.54876	0.06327	7.61141
N	5	-0.25737	1.99929	5.22517	0.03291	7.25737
N	6	-0.25400	1.99929	5.22184	0.03287	7.25400
O	7	-0.56265	1.99975	6.55135	0.01155	8.56265
O	8	-0.55203	1.99971	6.53852	0.01380	8.55203
C	9	0.08536	1.99924	3.89176	0.02364	5.91464
C	10	-0.27382	1.99913	4.25962	0.01507	6.27382
C	11	0.05807	1.99917	3.92397	0.01879	5.94193
C	12	0.07571	1.99923	3.89978	0.02528	5.92429
C	13	-0.27518	1.99912	4.26025	0.01581	6.27518
C	14	0.05611	1.99917	3.92594	0.01879	5.94389
C	15	0.58419	1.99900	3.38606	0.03075	5.41581
C	16	-0.25886	1.99906	4.22623	0.03358	6.25886
C	17	-0.03567	1.99894	4.01256	0.02416	6.03567
C	18	-0.26574	1.99908	4.23254	0.03411	6.26574
C	19	0.58783	1.99900	3.38200	0.03117	5.41217
C	20	0.81305	1.99928	3.13931	0.04836	5.18695
C	21	-0.20239	1.99924	4.18793	0.01521	6.20239
H	22	0.22550	0.00000	0.77388	0.00061	0.77450
H	23	0.25620	0.00000	0.74328	0.00053	0.74380
H	24	0.24036	0.00000	0.75895	0.00070	0.75964
H	25	0.21682	0.00000	0.78227	0.00091	0.78318
H	26	0.25456	0.00000	0.74489	0.00055	0.74544
H	27	0.23734	0.00000	0.76199	0.00067	0.76266
H	28	0.26472	0.00000	0.73392	0.00136	0.73528
H	29	0.25668	0.00000	0.74212	0.00120	0.74332
H	30	0.19923	0.00000	0.79998	0.00079	0.80077
H	31	0.20141	0.00000	0.79817	0.00042	0.79859
H	32	0.20089	0.00000	0.79830	0.00080	0.79911
N	33	-0.35540	1.99943	5.31107	0.04489	7.35540
N	34	-0.34615	1.99944	5.30167	0.04504	7.34615
N	35	-0.61142	1.99938	5.54877	0.06327	7.61142
N	36	-0.25737	1.99929	5.22517	0.03291	7.25737
N	37	-0.25400	1.99929	5.22184	0.03287	7.25400
O	38	-0.56265	1.99975	6.55135	0.01155	8.56265
O	39	-0.55203	1.99971	6.53852	0.01380	8.55203
C	40	0.08537	1.99924	3.89176	0.02364	5.91463
C	41	-0.27382	1.99913	4.25962	0.01507	6.27382
C	42	0.05807	1.99917	3.92397	0.01879	5.94193
C	43	0.07571	1.99923	3.89978	0.02528	5.92429
C	44	-0.27518	1.99912	4.26025	0.01581	6.27518
C	45	0.05610	1.99917	3.92594	0.01879	5.94390
C	46	0.58419	1.99900	3.38606	0.03075	5.41581
C	47	-0.25887	1.99906	4.22623	0.03358	6.25887
C	48	-0.03567	1.99894	4.01256	0.02416	6.03567
C	49	-0.26574	1.99908	4.23254	0.03411	6.26574
C	50	0.58783	1.99900	3.38200	0.03117	5.41217
C	51	0.81305	1.99928	3.13931	0.04836	5.18695
C	52	-0.20239	1.99924	4.18793	0.01521	6.20239
H	53	0.22550	0.00000	0.77388	0.00061	0.77450
H	54	0.25620	0.00000	0.74328	0.00053	0.74380
H	55	0.24036	0.00000	0.75895	0.00070	0.75964
H	56	0.21682	0.00000	0.78227	0.00091	0.78318
H	57	0.25456	0.00000	0.74489	0.00055	0.74544
H	58	0.23734	0.00000	0.76199	0.00067	0.76266
H	59	0.26472	0.00000	0.73392	0.00136	0.73528
H	60	0.25668	0.00000	0.74212	0.00120	0.74332

H	61	0.19923	0.00000	0.79998	0.00079	0.80077
H	62	0.20141	0.00000	0.79817	0.00042	0.79859
H	63	0.20089	0.00000	0.79830	0.00080	0.79911
* Total *		2.04040	97.96500	204.75965	1.23496	303.95960

d) $[Fe(bpp\text{-}triolH_3)_2]^{2+}$ in its LS configuration (S = 0) at the M06/6-311+G(d) level of theory



E(RM06) = -3762.07272452 a.u.

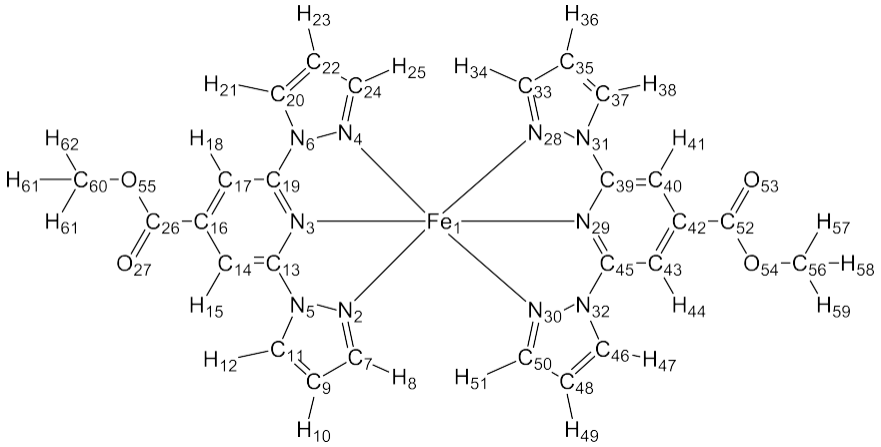
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	26	0	0.004026	0.232686	0.005342
2	7	0	-0.499985	-1.088562	1.415995
3	7	0	-1.902722	0.248309	-0.178173
4	7	0	-0.195644	1.559977	-1.473142
5	7	0	-1.856019	-1.252766	1.504550
6	7	0	-1.508794	1.786303	-1.783672
7	6	0	0.014499	-1.885354	2.334381
8	1	0	1.089050	-1.936032	2.463487
9	6	0	-0.994002	-2.576501	3.030877
10	1	0	-0.871749	-3.292342	3.830455
11	6	0	-2.169903	-2.151227	2.478887
12	1	0	-3.195837	-2.414367	2.698747
13	6	0	-2.648907	-0.504327	0.626249
14	6	0	-4.029898	-0.491725	0.567331
15	1	0	-4.633880	-1.077682	1.253753
16	6	0	-4.620947	0.353072	-0.371657
17	6	0	-3.838889	1.161055	-1.195843
18	1	0	-4.331593	1.846558	-1.879666
19	6	0	-2.470589	1.067286	-1.064549
20	6	0	-1.617064	2.713688	-2.774636
21	1	0	-2.580167	3.025618	-3.155667
22	6	0	-0.348140	3.094226	-3.112525
23	1	0	-0.063075	3.815533	-3.864305
24	6	0	0.499545	2.348196	-2.273171
25	1	0	1.582012	2.357310	-2.219119
26	6	0	-6.122794	0.529804	-0.490252
27	8	0	-6.545835	1.598600	-0.879252
28	7	0	-6.846512	-0.539288	-0.124062
29	1	0	-6.406972	-1.449815	-0.028792
30	6	0	-8.301331	-0.584273	0.039198
31	6	0	-8.818512	0.632371	0.797112
32	1	0	-8.797015	1.516821	0.147128
33	1	0	-9.865917	0.433757	1.065633
34	8	0	-8.012150	0.814044	1.940573
35	6	0	-8.576260	-1.839986	0.873092
36	1	0	-8.272878	-1.649357	1.907258
37	1	0	-9.650483	-2.049403	0.858137
38	8	0	-7.815538	-2.940436	0.406722
39	1	0	-8.498012	-1.528116	-1.883788
40	8	0	-10.327274	-0.859408	-1.147976
41	6	0	-8.948164	-0.680232	-1.338931
42	1	0	-8.723789	0.236565	-1.904966
43	7	0	0.506172	-1.213727	-1.278016
44	7	0	1.910760	0.264524	0.186364
45	7	0	0.204546	1.691188	1.352617
46	7	0	1.862698	-1.383763	-1.352782
47	7	0	1.518101	1.947453	1.639043
48	6	0	-0.008260	-2.097265	-2.112786
49	1	0	-1.082926	-2.161943	-2.234738
50	6	0	1.000490	-2.852070	-2.740416
51	1	0	0.877716	-3.640903	-3.468009
52	6	0	2.176640	-2.373375	-2.235268

53	1	0	3.202754	-2.655616	-2.429807
54	6	0	2.655473	-0.556386	-0.549676
55	6	0	4.036915	-0.533814	-0.498924
56	1	0	4.636175	-1.185688	-1.129001
57	6	0	4.629149	0.402808	0.348553
58	6	0	3.848160	1.283048	1.096156
59	1	0	4.339388	2.036669	1.705059
60	6	0	2.478970	1.167967	0.986252
61	6	0	1.625262	2.957529	2.546578
62	1	0	2.587861	3.302880	2.899000
63	6	0	0.356050	3.362366	2.852081
64	1	0	0.070265	4.145909	3.538496
65	6	0	-0.491243	2.543762	2.082227
66	1	0	-1.573829	2.544041	2.029447
67	6	0	6.130655	0.603543	0.427134
68	8	0	6.546431	1.720591	0.675984
69	7	0	6.853900	-0.495269	0.186048
70	1	0	6.389900	-1.393881	0.088736
71	6	0	8.303812	-0.620338	-0.000776
72	6	0	8.466356	-1.702187	-1.071650
73	1	0	8.193436	-1.277845	-2.044126
74	1	0	9.514157	-2.015464	-1.109552
75	8	0	7.597277	-2.797119	-0.813762
76	6	0	8.966970	0.666416	-0.500464
77	1	0	9.079162	1.376497	0.326956
78	1	0	9.976657	0.399403	-0.833657
79	8	0	8.279018	1.233980	-1.583794
80	1	0	-8.354582	-3.510357	-0.149471
81	1	0	-8.398229	1.496529	2.497710
82	1	0	7.757836	1.974071	-1.254203
83	1	0	8.096661	-3.553161	-0.492320
84	1	0	-10.804987	-0.748986	-1.975620
85	6	0	8.906211	-1.050185	1.332386
86	1	0	8.753931	-0.237904	2.062721
87	1	0	8.369104	-1.938364	1.708964
88	8	0	10.264050	-1.319967	1.114472
89	1	0	10.730323	-1.441031	1.947250

			Natural Population			
Atom	No	Natural Charge	Core	Valence	Rydberg	Total
Fe	1	0.07667	17.99091	7.86172	0.07070	25.92333
N	2	-0.20526	1.99927	5.16086	0.04513	7.20526
N	3	-0.47162	1.99915	5.42060	0.05188	7.47162
N	4	-0.20758	1.99927	5.16340	0.04491	7.20758
N	5	-0.25396	1.99929	5.22294	0.03173	7.25396
N	6	-0.25222	1.99929	5.22133	0.03161	7.25222
C	7	0.07382	1.99921	3.90407	0.02290	5.92618
H	8	0.22011	0.00000	0.77914	0.00075	0.77989
C	9	-0.27220	1.99913	4.25785	0.01521	6.27220
H	10	0.25373	0.00000	0.74575	0.00052	0.74627
C	11	0.04913	1.99917	3.93301	0.01870	5.95087
H	12	0.23967	0.00000	0.75969	0.00064	0.76033
C	13	0.57650	1.99900	3.39440	0.03010	5.42350
C	14	-0.28423	1.99908	4.24946	0.03570	6.28423
H	15	0.24743	0.00000	0.75134	0.00123	0.75257
C	16	-0.00391	1.99898	3.97965	0.02528	6.00391
C	17	-0.25896	1.99905	4.22396	0.03595	6.25896
H	18	0.26525	0.00000	0.73332	0.00143	0.73475
C	19	0.57199	1.99899	3.39972	0.02930	5.42801
C	20	0.05134	1.99917	3.93077	0.01872	5.94866
H	21	0.24160	0.00000	0.75776	0.00064	0.75840
C	22	-0.27196	1.99913	4.25747	0.01536	6.27196
H	23	0.25441	0.00000	0.74507	0.00052	0.74559
C	24	0.07245	1.99920	3.90537	0.02298	5.92755
H	25	0.22066	0.00000	0.77859	0.00075	0.77934
C	26	0.68328	1.99924	3.27174	0.04575	5.31672
O	27	-0.61274	1.99976	6.60165	0.01134	8.61274
N	28	-0.64856	1.99926	5.62589	0.02341	7.64856
H	29	0.41731	0.00000	0.58113	0.00155	0.58269
C	30	0.08590	1.99907	3.88746	0.02757	5.91410
C	31	-0.03189	1.99904	4.00874	0.02411	6.03189
H	32	0.18945	0.00000	0.80935	0.00120	0.81055
H	33	0.19008	0.00000	0.80899	0.00093	0.80992

O	34	-0.75947	1.99978	6.74779	0.01189	8.75947
C	35	-0.03451	1.99904	4.00925	0.02622	6.03451
H	36	0.19671	0.00000	0.80231	0.00097	0.80329
H	37	0.20741	0.00000	0.79172	0.00087	0.79259
O	38	-0.77161	1.99979	6.75955	0.01227	8.77161
H	39	0.15694	0.00000	0.84172	0.00133	0.84306
O	40	-0.75195	1.99977	6.74033	0.01184	8.75195
C	41	-0.02103	1.99905	3.99655	0.02543	6.02103
H	42	0.18139	0.00000	0.81741	0.00120	0.81861
N	43	-0.20468	1.99927	5.16026	0.04515	7.20468
N	44	-0.47047	1.99915	5.41939	0.05193	7.47047
N	45	-0.20650	1.99926	5.16229	0.04494	7.20650
N	46	-0.25486	1.99929	5.22379	0.03178	7.25486
N	47	-0.25316	1.99929	5.22222	0.03166	7.25316
C	48	0.07520	1.99921	3.90272	0.02287	5.92480
H	49	0.22094	0.00000	0.77832	0.00075	0.77906
C	50	-0.27122	1.99913	4.25688	0.01521	6.27122
H	51	0.25408	0.00000	0.74540	0.00052	0.74592
C	52	0.04835	1.99917	3.93378	0.01870	5.95165
H	53	0.24021	0.00000	0.75913	0.00067	0.75979
C	54	0.57889	1.99900	3.39238	0.02973	5.42111
C	55	-0.28737	1.99908	4.25276	0.03553	6.28737
H	56	0.24678	0.00000	0.75192	0.00130	0.75322
C	57	-0.00750	1.99898	3.98325	0.02527	6.00750
C	58	-0.26017	1.99905	4.22525	0.03586	6.26017
H	59	0.26484	0.00000	0.73377	0.00139	0.73516
C	60	0.57355	1.99900	3.39788	0.02958	5.42645
C	61	0.05069	1.99917	3.93144	0.01871	5.94931
H	62	0.24128	0.00000	0.75808	0.00064	0.75872
C	63	-0.27126	1.99913	4.25681	0.01533	6.27126
H	64	0.25445	0.00000	0.74503	0.00052	0.74555
C	65	0.07364	1.99920	3.90417	0.02298	5.92636
H	66	0.22185	0.00000	0.77741	0.00075	0.77815
C	67	0.68069	1.99923	3.27354	0.04654	5.31931
O	68	-0.63993	1.99976	6.62782	0.01235	8.63993
N	69	-0.64300	1.99925	5.61812	0.02562	7.64300
H	70	0.41620	0.00000	0.58111	0.00270	0.58380
C	71	0.08354	1.99906	3.89147	0.02593	5.91646
C	72	-0.03506	1.99903	4.01054	0.02549	6.03506
H	73	0.19696	0.00000	0.80204	0.00100	0.80304
H	74	0.20853	0.00000	0.79055	0.00092	0.79147
O	75	-0.78118	1.99979	6.76929	0.01210	8.78118
C	76	-0.03049	1.99905	4.00286	0.02859	6.03049
H	77	0.18925	0.00000	0.80978	0.00097	0.81075
H	78	0.20282	0.00000	0.79639	0.00079	0.79718
O	79	-0.74727	1.99979	6.73453	0.01295	8.74727
H	80	0.48562	0.00000	0.51345	0.00093	0.51438
H	81	0.47912	0.00000	0.51976	0.00112	0.52088
H	82	0.47996	0.00000	0.51878	0.00126	0.52004
H	83	0.48881	0.00000	0.51028	0.00090	0.51119
H	84	0.48345	0.00000	0.51542	0.00113	0.51655
C	85	-0.01552	1.99906	3.99110	0.02536	6.01552
H	86	0.17141	0.00000	0.82746	0.00113	0.82859
H	87	0.15701	0.00000	0.84169	0.00129	0.84299
O	88	-0.74927	1.99977	6.73751	0.01199	8.74927
H	89	0.48373	0.00000	0.51512	0.00115	0.51627
* Total *		2.03253	121.95122	276.51171	1.50454	399.96747

e) $[Fe(bpp\text{-}COOMe)_2]^{2+}$ in its LS configuration ($S = 0$) at the M06/6-311+G(d) level of theory



E(RM06) = -3114.83445217 a.u.

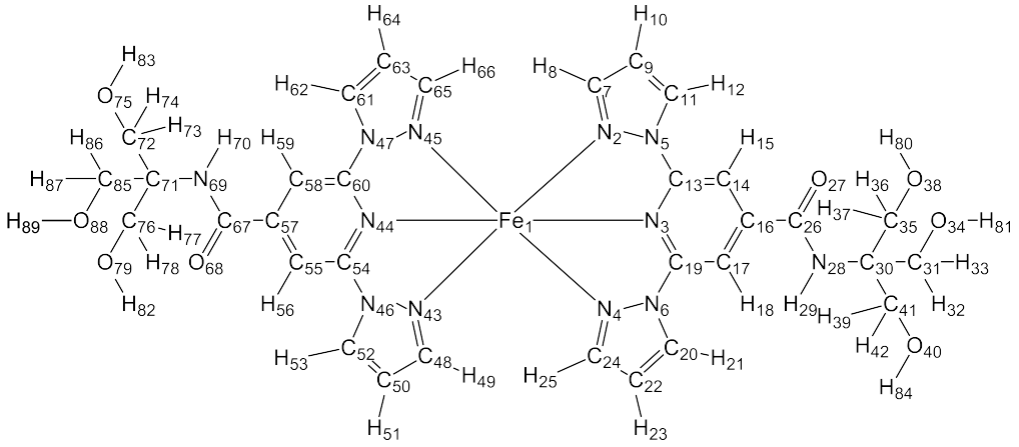
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	26	0	0.000001	-0.030660	0.001954
2	7	0	-0.405593	1.396464	-1.333647
3	7	0	-1.913109	-0.038226	0.070657
4	7	0	-0.294651	-1.457081	1.366351
5	7	0	-1.752796	1.589512	-1.484020
6	7	0	-1.625749	-1.670759	1.604183
7	6	0	0.169767	2.254619	-2.155233
8	1	0	1.250376	2.298339	-2.222486
9	6	0	-0.789382	3.016009	-2.849312
10	1	0	-0.613264	3.789285	-3.582693
11	6	0	-1.999572	2.568369	-2.399331
12	1	0	-3.008044	2.864939	-2.654257
13	6	0	-2.602728	0.794791	-0.707315
14	6	0	-3.984881	0.822922	-0.702096
15	1	0	-4.559684	1.496127	-1.328944
16	6	0	-4.630432	-0.064592	0.156595
17	6	0	-3.912244	-0.939258	0.968612
18	1	0	-4.450708	-1.618230	1.623668
19	6	0	-2.535932	-0.887528	0.887749
20	6	0	-1.798350	-2.651274	2.534422
21	1	0	-2.783688	-2.962330	2.854755
22	6	0	-0.554639	-3.079565	2.904899
23	1	0	-0.319806	-3.849776	3.624931
24	6	0	0.346031	-2.305479	2.149289
25	1	0	1.429371	-2.334246	2.145074
26	6	0	-6.130729	-0.132681	0.257573
27	8	0	-6.682220	-0.907147	0.985951
28	7	0	0.410162	1.320057	1.413630
29	7	0	1.912968	-0.037832	-0.069544
30	7	0	0.290162	-1.380965	-1.438802
31	7	0	1.757829	1.507694	1.567230
32	7	0	1.620599	-1.585672	-1.687761
33	6	0	-0.162096	2.123162	2.291150
34	1	0	-1.242339	2.159327	2.367756
35	6	0	0.799459	2.842553	3.025490
36	1	0	0.625886	3.568834	3.806011
37	6	0	2.007897	2.427439	2.541090
38	1	0	3.017226	2.709552	2.808692
39	6	0	2.605121	0.755856	0.746372
40	6	0	3.987205	0.785956	0.736650
41	1	0	4.564073	1.428508	1.393073
42	6	0	4.630029	-0.058546	-0.166286
43	6	0	3.909221	-0.892095	-1.018264
44	1	0	4.445570	-1.538252	-1.707363
45	6	0	2.533161	-0.843389	-0.931732
46	6	0	1.790218	-2.511641	-2.672823
47	1	0	2.774550	-2.807294	-3.010344
48	6	0	0.545188	-2.913547	-3.067717
49	1	0	0.308066	-3.640228	-3.830942
50	6	0	-0.353153	-2.180719	-2.269379
51	1	0	-1.436593	-2.205992	-2.267284
52	6	0	6.130032	-0.122408	-0.274113

53	8	0	6.679277	-0.861045	-1.040401
54	8	0	6.714418	0.717433	0.560976
55	8	0	-6.712713	0.747479	-0.536694
56	6	0	8.154719	0.732179	0.532452
57	1	0	8.504748	0.979105	-0.471323
58	1	0	8.456611	1.495070	1.246458
59	1	0	8.542076	-0.245808	0.823946
60	6	0	-8.153086	0.761669	-0.510712
61	1	0	-8.452915	1.561090	-1.184507
62	1	0	-8.539923	-0.199736	-0.853611
63	1	0	-8.505420	0.955924	0.503803

			Natural Population			
Atom	No	Natural Charge	Core	Valence	Rydberg	Total
Fe	1	0.07572	17.99091	7.86297	0.07040	25.92428
N	2	-0.20612	1.99927	5.16179	0.04507	7.20612
N	3	-0.46486	1.99915	5.41435	0.05136	7.46486
N	4	-0.20723	1.99926	5.16298	0.04498	7.20723
N	5	-0.25460	1.99929	5.22358	0.03172	7.25460
N	6	-0.25396	1.99929	5.22302	0.03164	7.25396
C	7	0.07625	1.99921	3.90170	0.02284	5.92375
H	8	0.22151	0.00000	0.77776	0.00074	0.77849
C	9	-0.26928	1.99913	4.25489	0.01526	6.26928
H	10	0.25605	0.00000	0.74343	0.00052	0.74395
C	11	0.05017	1.99917	3.93198	0.01868	5.94983
H	12	0.23984	0.00000	0.75954	0.00062	0.76016
C	13	0.57435	1.99900	3.39751	0.02914	5.42565
C	14	-0.26217	1.99909	4.22793	0.03515	6.26217
H	15	0.26037	0.00000	0.73846	0.00117	0.73963
C	16	-0.04165	1.99895	4.01883	0.02387	6.04165
C	17	-0.25418	1.99907	4.22048	0.03464	6.25418
H	18	0.26811	0.00000	0.73061	0.00128	0.73189
C	19	0.57425	1.99900	3.39813	0.02862	5.42575
C	20	0.05188	1.99917	3.93028	0.01867	5.94812
H	21	0.24272	0.00000	0.75664	0.00064	0.75728
C	22	-0.26947	1.99913	4.25504	0.01529	6.26947
H	23	0.25629	0.00000	0.74320	0.00051	0.74371
C	24	0.07596	1.99921	3.90198	0.02286	5.92404
H	25	0.22105	0.00000	0.77822	0.00073	0.77895
C	26	0.81300	1.99928	3.13939	0.04833	5.18700
O	27	-0.56287	1.99975	6.55157	0.01155	8.56287
N	28	-0.20615	1.99927	5.16182	0.04506	7.20615
N	29	-0.46484	1.99915	5.41433	0.05136	7.46484
N	30	-0.20722	1.99926	5.16297	0.04498	7.20722
N	31	-0.25468	1.99929	5.22366	0.03172	7.25468
N	32	-0.25387	1.99929	5.22293	0.03164	7.25387
C	33	0.07639	1.99921	3.90158	0.02283	5.92361
H	34	0.22157	0.00000	0.77770	0.00073	0.77843
C	35	-0.26929	1.99913	4.25491	0.01525	6.26929
H	36	0.25606	0.00000	0.74343	0.00052	0.74394
C	37	0.05014	1.99917	3.93201	0.01868	5.94986
H	38	0.23983	0.00000	0.75954	0.00062	0.76017
C	39	0.57431	1.99900	3.39756	0.02913	5.42569
C	40	-0.26221	1.99909	4.22796	0.03516	6.26221
H	41	0.26037	0.00000	0.73845	0.00117	0.73963
C	42	-0.04164	1.99895	4.01882	0.02387	6.04164
C	43	-0.25416	1.99907	4.22047	0.03463	6.25416
H	44	0.26810	0.00000	0.73062	0.00128	0.73190
C	45	0.57428	1.99900	3.39809	0.02863	5.42572
C	46	0.05191	1.99917	3.93026	0.01867	5.94809
H	47	0.24272	0.00000	0.75664	0.00064	0.75728
C	48	-0.26946	1.99913	4.25504	0.01530	6.26946
H	49	0.25628	0.00000	0.74320	0.00051	0.74372
C	50	0.07583	1.99921	3.90211	0.02286	5.92417
H	51	0.22100	0.00000	0.77827	0.00073	0.77900
C	52	0.81301	1.99928	3.13938	0.04833	5.18699
O	53	-0.56283	1.99975	6.55154	0.01155	8.56283
O	54	-0.55263	1.99971	6.53914	0.01379	8.55263
O	55	-0.55264	1.99971	6.53914	0.01379	8.55264
C	56	-0.20224	1.99924	4.18781	0.01518	6.20224
H	57	0.20054	0.00000	0.79867	0.00080	0.79946
H	58	0.20158	0.00000	0.79801	0.00041	0.79842
H	59	0.19983	0.00000	0.79939	0.00078	0.80017

C	60	-0.20223	1.99924	4.18780	0.01518	6.20223
H	61	0.20160	0.00000	0.79799	0.00041	0.79840
H	62	0.19982	0.00000	0.79940	0.00078	0.80018
H	63	0.20056	0.00000	0.79864	0.00080	0.79944
* Total *		2.04079	97.95961	204.79554	1.20406	303.95921

f) $[Fe(bpp\text{-}triolH_3)_2]^{2+}$ in its HS configuration (S = 2) at the UM06/6-311+G(d) level of theory



E(UM06) = -3762.09459632 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	26	0	0.010418	-0.529539	0.197546
2	7	0	-1.109135	-2.054664	1.275360
3	7	0	-2.066812	-0.139675	-0.165268
4	7	0	-0.090476	1.061574	-1.320869
5	7	0	-2.454479	-1.842966	1.302042
6	7	0	-1.350800	1.487395	-1.601299
7	6	0	-0.900584	-3.098680	2.062099
8	1	0	0.106761	-3.471484	2.203207
9	6	0	-2.102254	-3.576673	2.608087
10	1	0	-2.240519	-4.410748	3.280416
11	6	0	-3.072100	-2.756925	2.098236
12	1	0	-4.144509	-2.758026	2.238362
13	6	0	-2.991093	-0.821545	0.498737
14	6	0	-4.342380	-0.541375	0.399186
15	1	0	-5.083454	-1.086857	0.975326
16	6	0	-4.716748	0.508420	-0.435197
17	6	0	-3.751010	1.236445	-1.123692
18	1	0	-4.063656	2.080223	-1.731892
19	6	0	-2.434147	0.860239	-0.961716
20	6	0	-1.331687	2.499152	-2.509855
21	1	0	-2.242306	2.964960	-2.861367
22	6	0	-0.021361	2.737643	-2.826260
23	1	0	0.359002	3.474239	-3.518781
24	6	0	0.708335	1.817507	-2.057096
25	1	0	1.782271	1.676421	-2.004487
26	6	0	-6.151085	0.980866	-0.568684
27	8	0	-6.350013	2.157667	-0.788460
28	7	0	-7.075402	0.021988	-0.404387
29	1	0	-6.810378	-0.957619	-0.444705
30	6	0	-8.522061	0.223413	-0.294806
31	6	0	-8.855632	1.379647	0.639806
32	1	0	-8.626919	2.335161	0.149690
33	1	0	-9.936949	1.346702	0.834358
34	8	0	-8.107336	1.217476	1.825502
35	6	0	-9.067158	-1.075493	0.308102
36	1	0	-8.795763	-1.111619	1.367674
37	1	0	-10.158771	-1.075283	0.227810
38	8	0	-8.489977	-2.210166	-0.312082
39	1	0	-8.772244	-0.348217	-2.354171
40	8	0	-10.489245	0.529962	-1.569846
41	6	0	-9.091348	0.471916	-1.687911
42	1	0	-8.670344	1.407411	-2.086340
43	7	0	1.064726	-2.059286	-0.941131
44	7	0	2.108279	-0.181973	0.487635
45	7	0	0.199743	0.994416	1.773904
46	7	0	2.406862	-1.848837	-1.041058
47	7	0	1.474703	1.418901	1.987845
48	6	0	0.809165	-3.087234	-1.734174
49	1	0	-0.205686	-3.455482	-1.824893
50	6	0	1.976786	-3.555823	-2.358217
51	1	0	2.074268	-4.377246	-3.052942
52	6	0	2.976342	-2.747311	-1.890588

53	1	0	4.039069	-2.747722	-2.093468
54	6	0	2.986937	-0.835675	-0.260540
55	6	0	4.335527	-0.525211	-0.270321
56	1	0	5.035856	-1.051176	-0.914659
57	6	0	4.751997	0.531671	0.536024
58	6	0	3.832523	1.233164	1.309521
59	1	0	4.169575	2.087190	1.889353
60	6	0	2.516282	0.820752	1.260282
61	6	0	1.509483	2.399375	2.930671
62	1	0	2.439103	2.856484	3.241641
63	6	0	0.221948	2.617126	3.338544
64	1	0	-0.116929	3.326239	4.079579
65	6	0	-0.552307	1.719266	2.585773
66	1	0	-1.626328	1.573749	2.602652
67	6	0	6.175993	1.051820	0.506338
68	8	0	6.345225	2.249463	0.643757
69	7	0	7.100851	0.103057	0.305201
70	1	0	6.780165	-0.858491	0.242214
71	6	0	8.498600	0.198847	-0.151940
72	6	0	8.536484	-0.606804	-1.453042
73	1	0	7.963294	-0.068001	-2.213605
74	1	0	9.569887	-0.699345	-1.800306
75	8	0	7.929144	-1.879412	-1.270597
76	6	0	8.970629	1.625593	-0.415187
77	1	0	8.975428	2.193544	0.524639
78	1	0	10.010957	1.553309	-0.754156
79	8	0	8.232974	2.275303	-1.411790
80	1	0	-9.081014	-2.564578	-0.982977
81	1	0	-8.399124	1.862050	2.477065
82	1	0	7.543505	2.793435	-0.978604
83	1	0	8.611816	-2.542150	-1.123401
84	1	0	-10.888215	0.855580	-2.382394
85	6	0	9.362598	-0.450574	0.928361
86	1	0	9.432098	0.234909	1.788104
87	1	0	8.874092	-1.373080	1.286187
88	8	0	10.617047	-0.727352	0.366040
89	1	0	11.266091	-0.920754	1.049406

			Natural Population			
Atom	No	Natural Charge	Core	Valence	Rydberg	Total
Fe	1	0.91143	17.99510	7.03367	0.05980	25.08857
N	2	-0.35206	1.99943	5.30768	0.04495	7.35206
N	3	-0.61867	1.99938	5.55601	0.06328	7.61867
N	4	-0.34835	1.99944	5.30398	0.04493	7.34835
N	5	-0.25673	1.99929	5.22452	0.03292	7.25673
N	6	-0.25188	1.99929	5.21986	0.03273	7.25188
C	7	0.08167	1.99924	3.89536	0.02372	5.91833
H	8	0.22404	0.00000	0.77535	0.00060	0.77596
C	9	-0.27635	1.99913	4.26213	0.01509	6.27635
H	10	0.25381	0.00000	0.74566	0.00053	0.74619
C	11	0.05517	1.99917	3.92686	0.01881	5.94483
H	12	0.23754	0.00000	0.76178	0.00068	0.76246
C	13	0.58671	1.99900	3.38153	0.03277	5.41329
C	14	-0.28817	1.99907	4.25450	0.03459	6.28817
H	15	0.24431	0.00000	0.75442	0.00128	0.75569
C	16	0.00304	1.99897	3.97220	0.02579	5.99696
C	17	-0.26160	1.99904	4.22810	0.03445	6.26160
H	18	0.26045	0.00000	0.73806	0.00149	0.73955
C	19	0.58493	1.99899	3.38517	0.03091	5.41507
C	20	0.05748	1.99917	3.92451	0.01884	5.94252
H	21	0.23902	0.00000	0.76029	0.00069	0.76098
C	22	-0.27723	1.99913	4.26223	0.01588	6.27723
H	23	0.25342	0.00000	0.74603	0.00055	0.74658
C	24	0.07333	1.99923	3.90217	0.02527	5.92667
H	25	0.21586	0.00000	0.78322	0.00092	0.78414
C	26	0.68258	1.99924	3.27232	0.04587	5.31742
O	27	-0.61211	1.99976	6.60101	0.01134	8.61211
N	28	-0.64864	1.99926	5.62597	0.02342	7.64864
H	29	0.41799	0.00000	0.58049	0.00152	0.58201
C	30	0.08556	1.99907	3.88785	0.02753	5.91444
C	31	-0.03211	1.99904	4.00896	0.02411	6.03211
H	32	0.18957	0.00000	0.80922	0.00121	0.81043
H	33	0.19027	0.00000	0.80881	0.00093	0.80973
O	34	-0.75995	1.99978	6.74827	0.01191	8.75995

C	35	-0.03440	1.99904	4.00907	0.02630	6.03440
H	36	0.19666	0.00000	0.80237	0.00097	0.80334
H	37	0.20705	0.00000	0.79208	0.00087	0.79295
O	38	-0.77048	1.99979	6.75840	0.01229	8.77048
H	39	0.15728	0.00000	0.84137	0.00135	0.84272
O	40	-0.75217	1.99978	6.74056	0.01184	8.75217
C	41	-0.02123	1.99906	3.99676	0.02542	6.02123
H	42	0.18146	0.00000	0.81734	0.00120	0.81854
N	43	-0.35073	1.99943	5.30632	0.04497	7.35073
N	44	-0.61662	1.99938	5.55339	0.06385	7.61662
N	45	-0.34635	1.99944	5.30182	0.04509	7.34635
N	46	-0.25786	1.99929	5.22528	0.03329	7.25786
N	47	-0.25396	1.99929	5.22180	0.03287	7.25396
C	48	0.08304	1.99924	3.89389	0.02383	5.91696
H	49	0.22393	0.00000	0.77546	0.00062	0.77607
C	50	-0.27556	1.99913	4.26132	0.01511	6.27556
H	51	0.25396	0.00000	0.74551	0.00053	0.74604
C	52	0.05435	1.99917	3.92768	0.01880	5.94565
H	53	0.24011	0.00000	0.75908	0.00082	0.75989
C	54	0.58885	1.99900	3.37822	0.03394	5.41115
C	55	-0.29704	1.99907	4.26332	0.03465	6.29704
H	56	0.24669	0.00000	0.75176	0.00155	0.75331
C	57	-0.00208	1.99897	3.97768	0.02543	6.00208
C	58	-0.26338	1.99904	4.22971	0.03463	6.26338
H	59	0.25962	0.00000	0.73895	0.00144	0.74038
C	60	0.58698	1.99899	3.38260	0.03143	5.41302
C	61	0.05631	1.99917	3.92571	0.01881	5.94369
H	62	0.23843	0.00000	0.76086	0.00070	0.76157
C	63	-0.27635	1.99913	4.26148	0.01574	6.27635
H	64	0.25334	0.00000	0.74612	0.00055	0.74666
C	65	0.07662	1.99924	3.89898	0.02516	5.92338
H	66	0.21812	0.00000	0.78095	0.00093	0.78188
C	67	0.68311	1.99922	3.27106	0.04661	5.31689
O	68	-0.63854	1.99975	6.62671	0.01208	8.63854
N	69	-0.64344	1.99926	5.61806	0.02612	7.64344
H	70	0.41045	0.00000	0.58780	0.00175	0.58955
C	71	0.08481	1.99904	3.89086	0.02529	5.91519
C	72	-0.03582	1.99902	4.01039	0.02641	6.03582
H	73	0.19780	0.00000	0.80114	0.00106	0.80220
H	74	0.21004	0.00000	0.78910	0.00086	0.78996
O	75	-0.78146	1.99979	6.76939	0.01228	8.78146
C	76	-0.03485	1.99904	4.00694	0.02888	6.03485
H	77	0.18460	0.00000	0.81432	0.00108	0.81540
H	78	0.20696	0.00000	0.79217	0.00087	0.79304
O	79	-0.74769	1.99979	6.73470	0.01321	8.74769
H	80	0.48526	0.00000	0.51380	0.00093	0.51474
H	81	0.47885	0.00000	0.52002	0.00112	0.52115
H	82	0.48469	0.00000	0.51386	0.00145	0.51531
H	83	0.48673	0.00000	0.51225	0.00102	0.51327
H	84	0.48332	0.00000	0.51555	0.00113	0.51668
C	85	-0.01600	1.99906	3.99081	0.02613	6.01600
H	86	0.17460	0.00000	0.82413	0.00127	0.82540
H	87	0.15703	0.00000	0.84178	0.00118	0.84297
O	88	-0.75253	1.99977	6.74045	0.01231	8.75253
H	89	0.48545	0.00000	0.51345	0.00110	0.51455
* Total *		2.03228	121.95657	276.47276	1.53839	399.96772

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