Supporting Information

Controlled generation of highly saddled (porphyrinato) iron(III) iodide, tri-iodide and one-electron oxidized complex

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Instrumentation.

UV-vis spectra were recorded on a PerkinElmer UV/vis spectrometer. Electron paramagnetic resonance (EPR) spectra were obtained on a Bruker EMX EPR spectrometer. Infrared spectra were recorded in the range of 4000-400 cm^{-1} on a Vertex 70 Bruker spectrophotometer on KBr pellets. ^{1}H NMR spectra were recorded on a JEOL 500 MHz instrument. The spectra for paramagnetic molecules were recorded over a 100- kHz bandwidth with 64 K data points and a 5-ms 90° pulse. For a typical spectrum between 2000 and 3000 transients were accumulated with a 50-μs delay time. The residual ^{1}H resonances of the solvents were used as a secondary reference. ^{57}Fe Mössbauer spectra were recorded using a Wissel 1200 spectrometer and a proportional counter. $^{57}Co(Rh)$ in a constant acceleration mode was used as the radioactive source. Isomer shifts (δ) are given related to α-iron foil at room temperature. Magnetic susceptibility data were collected using a Quantum Design MPMS SQUID magnetometer over the temperature range 5 to 300K.

X-ray Structure Solution and Refinement.

Single-crystal X-ray data were collected at 100 K on a Bruker SMART APEX CCD diffractometer equipped with CRYO Industries low temperature apparatus and intensity data were collected using graphite-monochromated MoKα radiation (λ= 0.71073 Å). The data integration and reduction were processed with SAINT software.[1] An absorption correction was applied.[2] The structure was solved by the direct method using SHELXS-97 and was refined on F2 by full-matrix least-squares technique using the SHELXL-2014 program package.[3] Non-hydrogen atoms were refined anisotropically. In the refinement, hydrogens were treated as riding atoms using SHELXL default parameters. Crystal data and data collection parameters are given in Table S1.

Computational Details.

Calculations were initiated from the crystal structure of **3** coordinates reported in this paper. Calculations for **4** molecule were initiated from the crystal structure but failed to report due to highly disordered nature of the complex.Complex **3** represents [Fe^{III}(TDMOETPP)I_3] in complex where I_3 is axially co-ordinated. After adding the hydrogen atoms to crystal structure **3**, we were therefore left with a system that has the molecular formula $C_{68}H_{76}N_4FeI_3$ and an atom count of 152. The crystal structure **4** has both iodine and tri-iodide; both are axially coordinated and therefore has the molecular formula $C_{68}H_{76}N_4FeI_4$ with a total atom count of 153. All structures were optimized using the Jaguar 8.4 software package.[4] Analytical frequencies were also carried out on all optimised structures using the Gaussian-09 software package.[5] Free energies were taken from the Gaussian frequencies and contain, zero-point, thermal and entropic corrections to the energy at 298.15 K and 1 atm.

Initial geometry optimisations were carried out on the quartet and sextet spin states for each structure using both the unrestricted hybrid density functional method B3LYP.[6] A basis set containing the 6-31g* basis set on all atoms except for the iron were LACVP* basis set, that includes an effective core potential, was used (basis set BS1). Such a hybrid Jaguar/Gaussian protocol has been used very successfully before on iron dependent ligand systems.[7,8]

Experimental Section:

Materials:

Porphyrin free base 3,5-dimethyl-2,3,7,8,12,13,17,18-octaethyl-5,10,l5,20-tetraphenylporphyrin was prepared from 3,5-dimethyl benzaldehyde and the diethyl pyrrole using a literature procedure.[9] Reagents and solvents were purchased from commercial sources and purified by standard procedures before use.

Synthesis of 2:

3,5-Dimethyl-2,3,7,8,12,13,17,18-octaethyl-5,10,l5,20-tetraphenylporphyrin (100 mg, 0.105 mmol) was dissolved in 100 mL N, N-dimethylformamide. Excess FeI_2 (65 mg, 0.21 mmol) was added and refluxed for 1 hour under nitrogen. The resulting solution was then cooled to room temperature and transferred into a separatory funnel. 100 mL chloroform was added to the solution which was then washed well with 1% HI solution. Organic layer was separated and dried over anhydrous Na_2SO_4. The resulting solution was evaporated to dryness and purified by column chromatography using silica gel. The major fraction eluted with chloroform was collected and vacuum dried to obtain brown solid. Yield: 85 mg (71%). UV-vis (chloroform) [λ_{max}, nm (ε, M^{-1} cm^{-1})]: 416 (3.2×10^4), 575(2.0×10^1); ^{1}H NMR ($CDCl_3$, 295 K): o-*H*, 12.46,11.59; p-*H*, 9.22; -CH_2-, 48.81, 32.15, 30.15 and 15.06 ppm. EPR data: in solid (77 K), $g_\perp$ = 4.24 and g_{II} = 1.99; in toluene (77 K), $g_\perp$=4.26 and g_{II}=1.99.

Synthesis of 3:

3,5-Dimethyl-2,3,7,8,12,13,17,18-octaethyl-5,10,l5,20-tetraphenylporphyrin (100 mg, 0.105 mmol) was dissolved in 100 mL N, N-dimethylformamide. Excess FeI_2 (65 mg, 0.21 mmol) was added and refluxed for 1 hour under nitrogen. The resulting solution was then cooled to room temperature and dissolved in 100 ml chloroform solution. This solution was then washed well with mixture of 5 % HI solution (95 ml water) and solid iodine (27 mg, 0.105 mmol). Organic layer was separated and dried over anhydrous Na_2SO_4. The resulting solution was evaporated to dryness and purified by column chromatography using silica gel. The major fraction eluted with chloroform-methanol (98:2) was collected and vacuum dried to obtain brown solid. Yield: 80 mg (55%). UV-vis (chloroform) [λ_{max}, nm (ε, M^{-1} cm^{-1})]: 413 (2.8×10^4), 440(1.2 $\times10^4$), 573(2.0×10^1); ^{1}H NMR ($CDCl_3$, 295K): o-*H*, 11.07 (2-H); p-*H*, 7.89, -CH_2-, 42.25, 14.09, 12.85 and 9.45 ppm. EPR data: in solid (77 K), $g_\perp$ = 4.05 and g_{II} = 2.01; in toluene (77 K), $g_\perp$=4.06 and g_{II}=2.01.

Synthesis of 4:

Compound **2** (100 mg, 0.088 mmol) was dissolved in chloroform (20 mL); solid iodine (113 mg, 0.44 mmol) was added to it and the mixture was stirred for 6 hours under nitrogen atmosphere. The resulting solution was then carefully washed with n-hexane to remove the excess iodine from the complex several times. The solid was then dissolved into the minimum volume of chloroform and carefully layered with hexane which was then kept for slow diffusion in air at room temperature. On standing for 6–8 days, highly crystalline solid was separated out, which was collected by filtration, washed thoroughly with the mother liquor, and dried under vacuum. Yield: 70 mg (55%). UV-vis (chloroform) [λ_{max}, nm (ε, M^{-1} cm^{-1})]: 408 (2.4×10^4), 442(1.8 $\times 10^4$), 578(2.0×10^1);. ^{1}H NMR ($CDCl_3$, 295 K): o-*H*, 30.29, 28.09; p-*H*, 36.65; -CH_2-, 87.06, 14.07, 10.28 and 10.28 ppm.

References:

[1] SAINT+, 6.02 ed., Bruker AXS, Madison, WI, **1999**.

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[4] Jaguar, *Jaguar* 8.4. Schrodinger, LLC.: New York, 2007.

[5] M. J. Frisch et al Gaussian 09, revision C.01; Gaussian, Inc., Wallingford, CT, 2010.

[6] P. J. Hay, W. R. Wadt, *J. Chem. Phys*. **1985**, *82*, 270–283.

[7] M. G. Quesne, S. P. de Visser, *J. Biol. Inorg. Chem*. **2012**, *17*, 841-852.

[8] D. Sahoo, M. G. Quesne, S. P. de Visser ,S. P. Rath, *Angew.Chem.Int. Ed.*, **2015**, *54*, 4796-4800.

[9] K. M. Barkigia, M. Dolores Berber, J. Fajer, C. J. Medforth, M. W. Renner, K. M. Smith, *J. Am. Chem. Soc.* **1990**, *112*, 8851-8857.

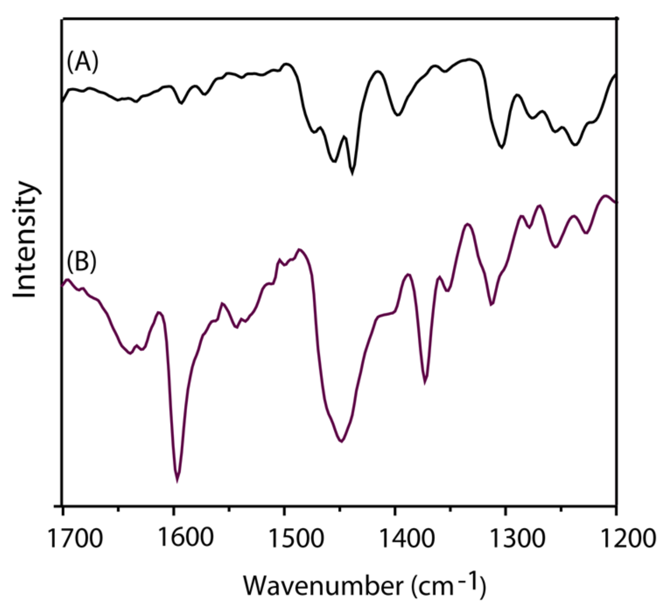


Figure S1. IR spectra of (A) **2**, and (B) **4** in solid at 295 K.

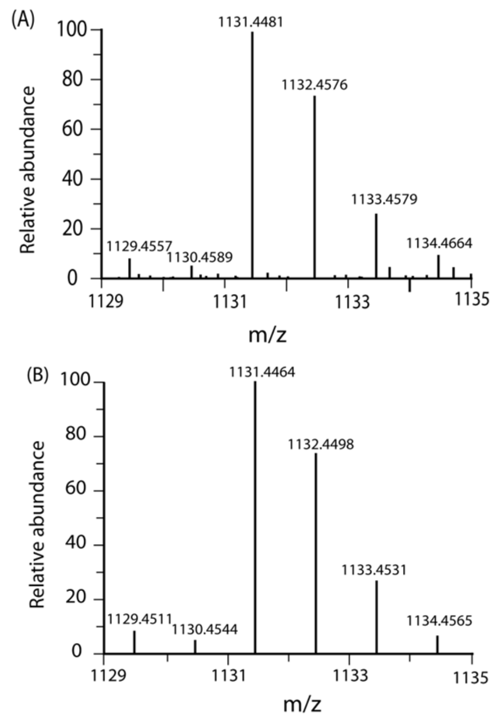


Figure S2. Isotopic distribution pattern of (A) experimental and (B) simulated ESI-MS spectrum (positive ion mode) of [**2**]$^{+}$.

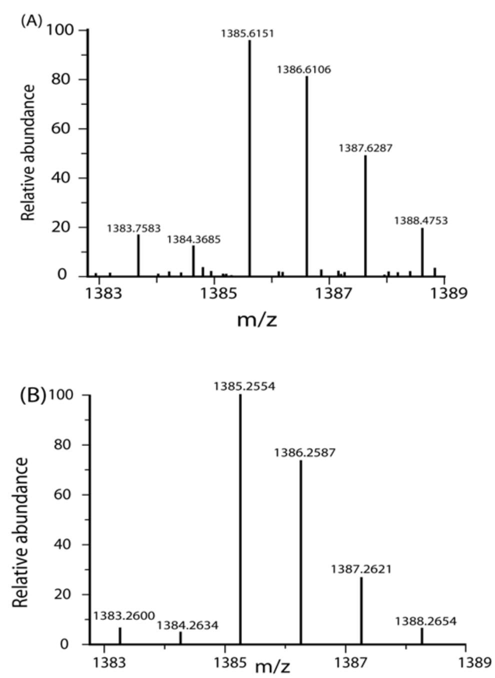


Figure S3. Isotopic distribution pattern of (A) experimental and (B) simulated ESI-MS spectrum (positive ion mode) of [**3**]$^{+}$.

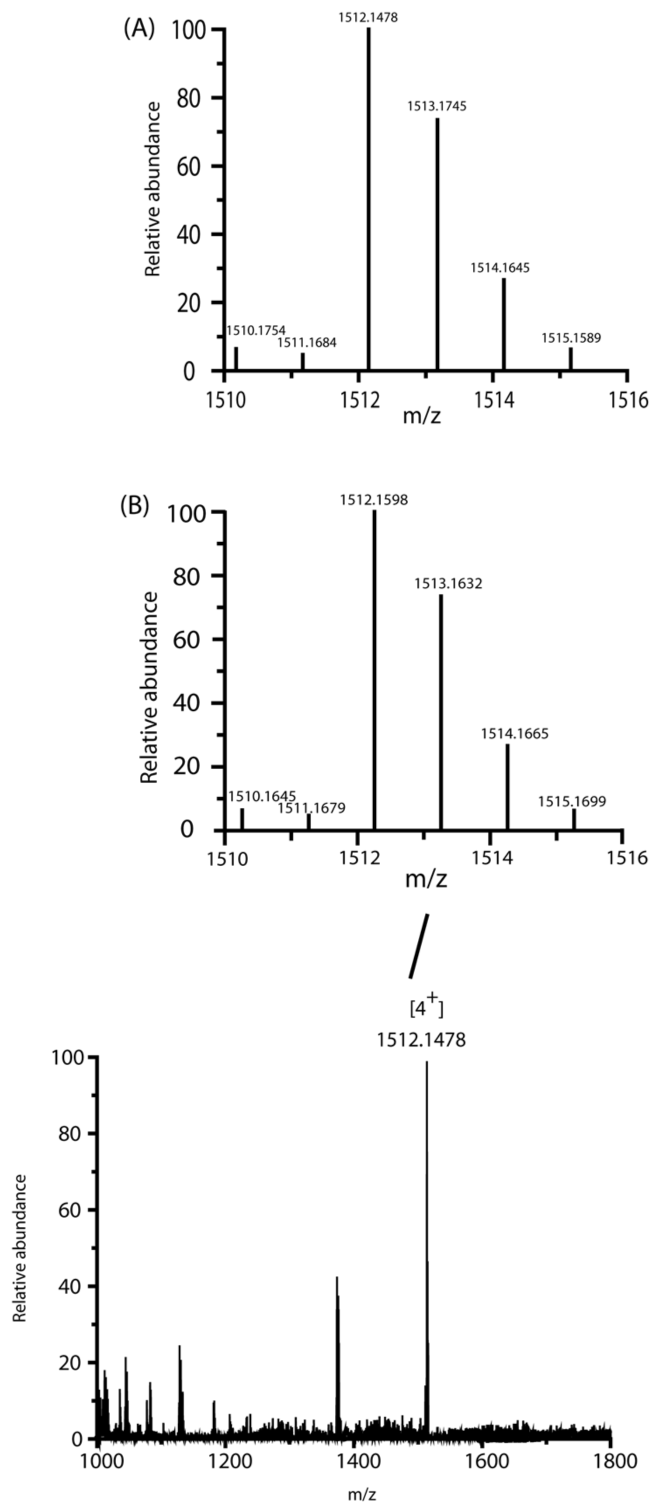


Figure S4. ESI-MS spectrum (positive ion mode) of [**4**]$^{+}$**.** Inset shows the isotopic distribution patterns: (A) experimental and (B) simulated.

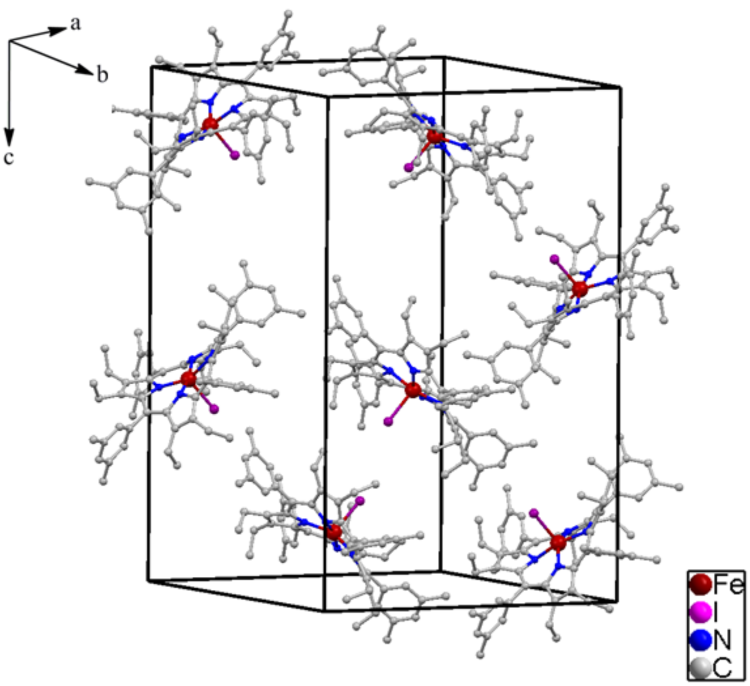


Figure S5. Diagram illustrating the packing of complex **2** in the unit cell (H atoms have been omitted for clarity).

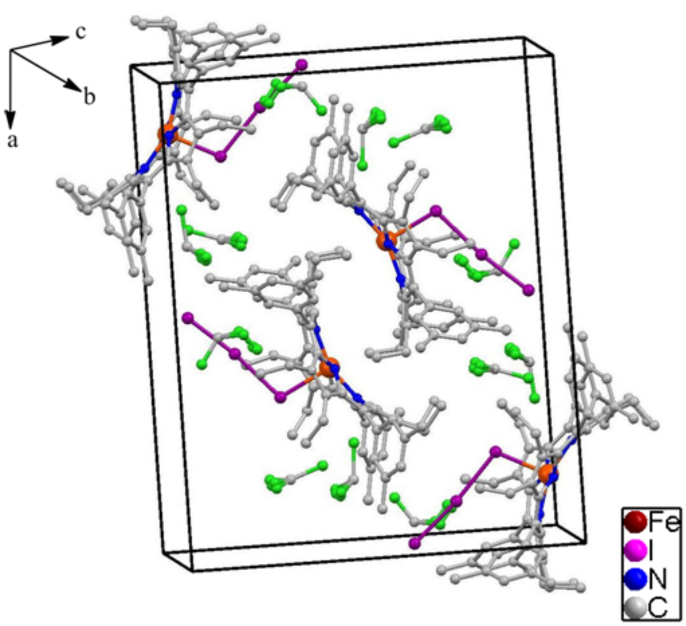


Figure S6. Diagram illustrating the packing of complex **3** in the unit cell (H atoms have been omitted for clarity).

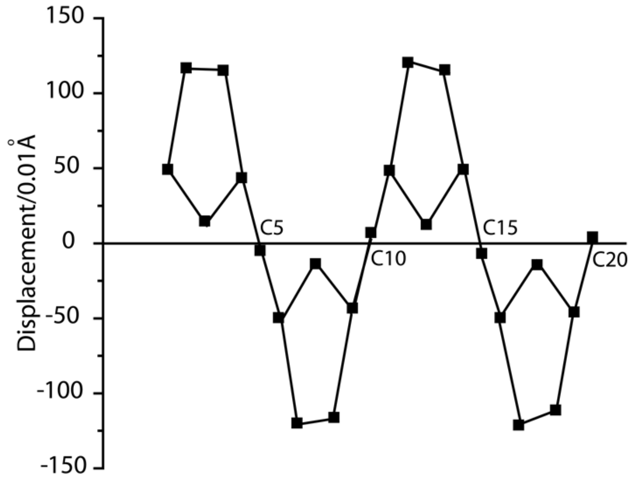


Figure S7. Atom deviations (in units of 0.01 Å) from the least-squares plane of the $C_{20}N_4$ porphyrinato core of **2**. The horizontal axis represents the atom number in the macrocycle showing the bond connectivity between atoms.

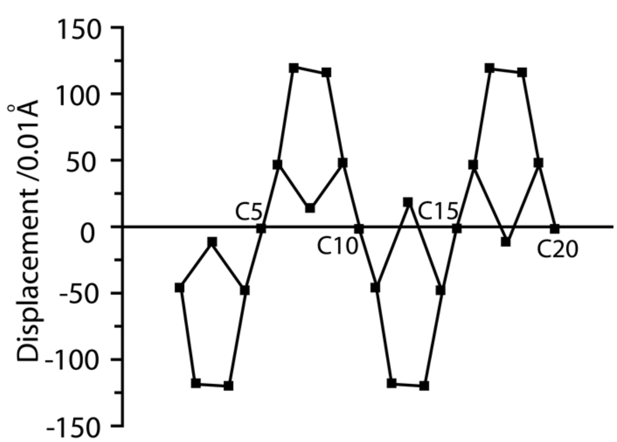


Figure S8. Atom deviations (in units of 0.01 Å) from the least-squares plane of the $C_{20}N_4$ porphyrinato core of **3**. The horizontal axis represents the atom number in the macrocycle showing the bond connectivity between atoms.

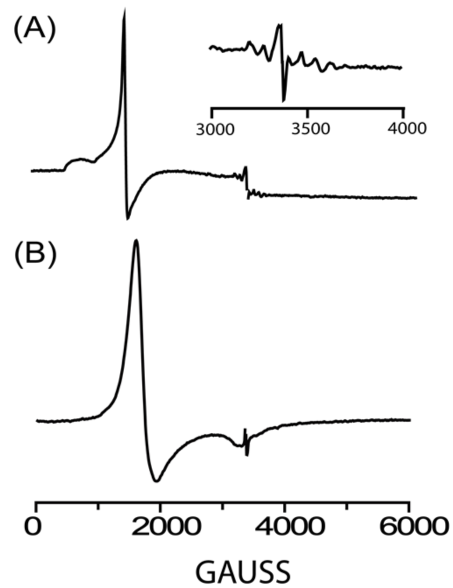


Figure S9. EPR spectra of (A) **2**, and (B) **3** in solid at 77 K.

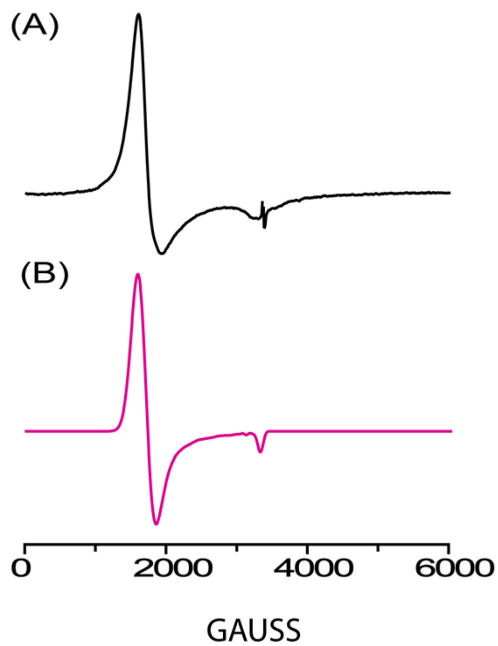


Figure S10. X-band EPR spectra in solid at 77 K of (A) **3**, and (B) the simulated spectra.

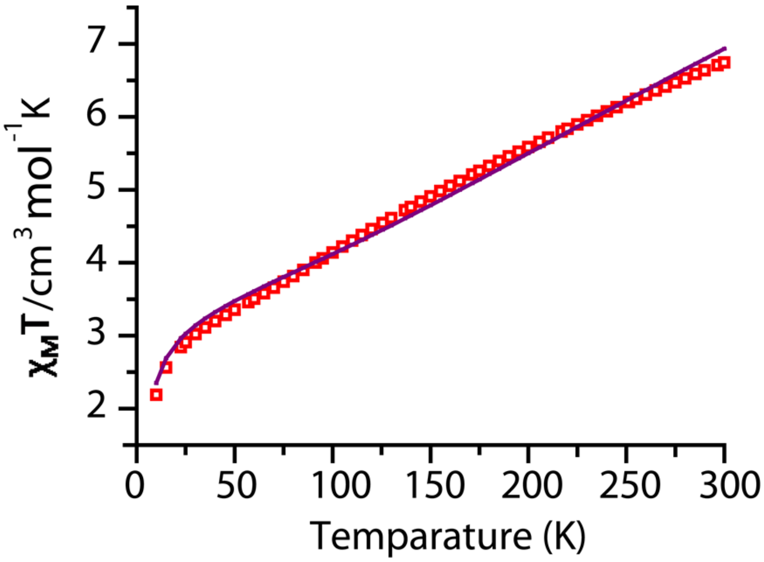
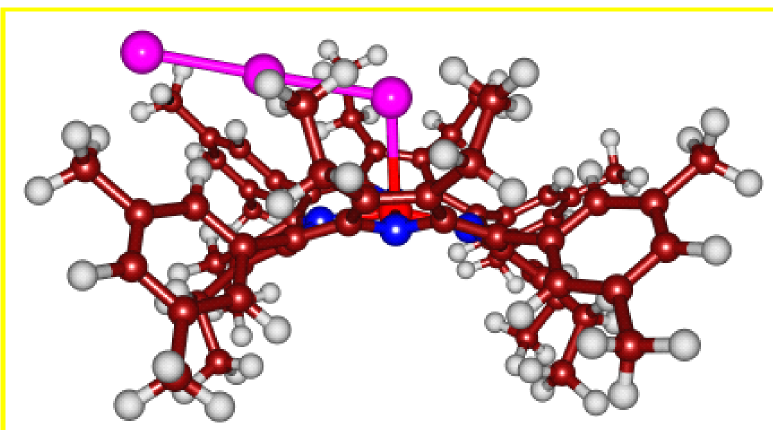


Figure S11. $\chi_M T$ versus T plots for **4**. The solid line is the best fit calculated by using the values given. The value of g was kept fixed at 2.00. The fitting parameters for **4** are $J_{\text{Fe-r}}$ = - 62.8 cm^{-1}, p = 0.002, D =10.37 and TIP =11.2×10^{-4} cm^3mol^{-1}.



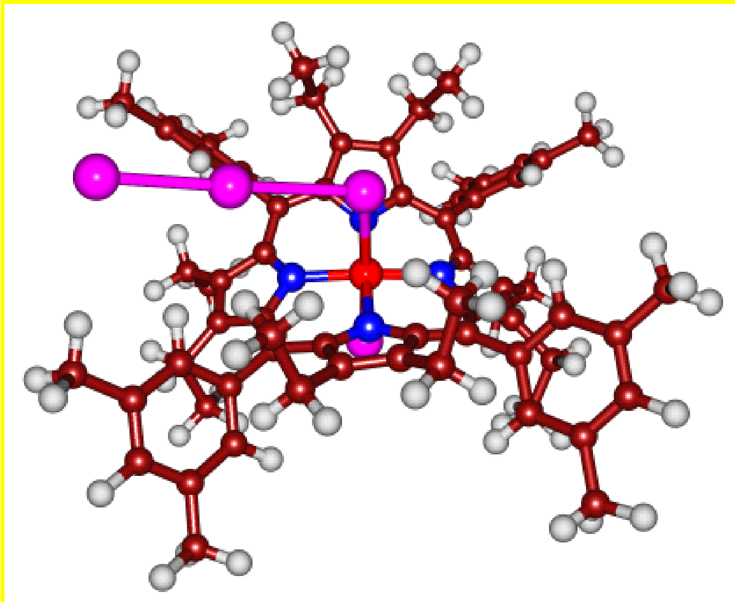
$r_{\text{Fe-I}}$ = 2.951 [2.877]

$r_{\text{Fe-Nav}}$ = 1.970 [2.062]

Δ_{24}^{Fe} = 0.22 [0.42]

^{4}3 [^{6}3]

Figure S12. Bonding data of the complex ^{4,6}**3** calculated at B3LYP/BS1. Bond lengths (r) are shown in Å. Δ_{24}^{Fe} is the average displacement in Å of the metal from the least-square plane of the $C_{20}N_4$ porphyrinato core.



$r_{\text{Fe-I}}$ = 2.730 [2.869]

$r_{\text{Fe-I3}}$=2.911 [3.777]

$r_{\text{Fe-Nav}}$ = 1.975 [2.070]

Δ_{24}^{Fe}= 0.035 [0.035]

^{3}4 [^{5}4]

Figure S13. Bonding data of the complex ^{3,5}**4** calculated at B3LYP/BS1. Bond lengths (*r*) are shown in Å. Δ_{24}^{Fe} is the average displacement in Å of the metal from the least-square plane of the $C_{20}N_4$ porphyrinato core.

Table S1. Crystal data and data collection parameters.

	2	**3**
Formula	$C_{68.25}\,H_{76.50}\,Cl_{0.50}\,Fe\,I\,N_4$	$C_{280}\,H_{312}\,Cl_{24}\,Fe_{24}\,I_{12}\,N_{16}$
T, (K)	100(2)	100(2)
Formula weight	1153.30	6498.44
Crystal system	Orthorhombic	Orthorhombic
Space group	P b c a	P n m a
a, Å	19.736(5)	23.387(5)
b, Å	24.456(5)	17.301(4)
c, Å	31.304(5)	18.913(4)
α , deg	90.000(5)	90
β, deg	90.000(5)	90

γ, deg	90.000(5)	90
V, Å^3	15109(5)	7653(3)
Radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)
Z	8	1
d_{calcd}, g.cm^{-3}	1.014	1.410
F(000)	4812	3252
μ, mm^{-1}	0.660	1.656
No. of unique data	13271	7359
No. of parameters, refined	684	437
GOF on F^2	1.034	1.046
$R1^a$ [$I > 2\sigma(I)$]	0.0888	0.0740
$R1^a$ (all data)	0.1214	0.1252
$wR2^b$ (all data)	0. 2583	0.2379

^{a} $R1 = \frac{\sum ||Fo| - |Fc||}{\sum |Fo|}$; ^{b} $wR2 = \sqrt{\frac{\sum [w(Fo^2 - Fc^2)^2]}{\sum [w(Fo^2)^2]}}$

Table S2. Selected Bond Distance (Å) and Angles (°) for **2** and **3**.

	2	**3**
Fe1-N1	1.977(4)	1.932(6)
Fe1-N2	1.999(4)	1.975(10)
Fe1-N3	1.976(4)	1.951(9)
Fe1-N4	2.001(4)	
Fe(1)-I(1)	2.5236(10)	2.7503(19)
N(1)-Fe(1)-N(2)	88.08(16)	89.53(19)
N(1)-Fe(1)-N(4)	88.36(16)	
N(2)-Fe(1)-N(4)	151.14(17)	
N(3)-Fe(1)-N(1)	167.06(17)	89.42(19)
N(3)-Fe(1)-N(2)	88.36(17)	158.3(4)
N(3)-Fe(1)-N(4)	88.76(17)	
N(1)-Fe(1)- I(1)	96.26(12)	92.8(2)
N(2)-Fe(1)- I(1)	105.51(12)	101.4(3)
N(3)-Fe(1)- I(1)	96.69(12)	100.4(3)
N(4)-Fe(1)-I(1)	103.35(12)	
I(3)-I(2)-I(1)		173.87(5)

Table S3. Selected structural parameters and magnetic properties for five coordinated [Fe^{III}(por)I] complexes.

Complex	Fe-N_p[a]	Fe-I_1	Δ^{Fe}_{4N}[b]	Δ^{Fe}_{24}[c]	Δ_{24}[d]	g⊥	g_{II}	S=3/2(%)	Ref
2	1.988(4)	2.5236(10)	0.36	0.36	0.58	4.24	1.99	88	tw
3	1.947(8)	2.7503(19)	0.23	0.21	0.58	4.05	2.01	98	tw
[Fe^{III}(TPP)I]	2.07	2.55	0.46	0.51	0.51				10
[Fe^{III}(EtioP)I]	2.061(7)	2.617(1)	0.47	0.43	0.56	5.82	1.98	9	12
[Fe^{III}(OEP)I]	2.068(2)	2.610(1)	0.49	0.06	0.01	5.80	1.96	10	13

[a]Average value in Å. [b]Displacement of iron from mean plane containing four porphyrinic nitrogen. [c]Displacement of iron from mean plane containing $C_{20}N_4$ porphyrinic core. [d]Average displacement of the 24 atoms from the least-squares plane of the porphyrin.

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[12] Y. Ohgo, S. Neya, T. Ikeue, M. Takahashi, M. Takeda, N. Funasaki, and M. Nakamura *Inorg. Chem.*, **2002**, *41*, 4627-4629.
[13] Y. Ohgo, S. Neya, M. Takahashi, M. Takeda, N. Funasaki, and M. Nakamura, *Chem. Lett.*, **2003**, *32*, 526-527.

Table S4. Absolute and Relative energies B3LYP/BS1 optimised

	E[au] [B3LYP/BS1]	ZPE[au] [B3LYP/BS1]	G[au] [B3LYP/BS1]	ΔE [BS1]	ΔE+ZPE [BS1]	ΔG [BS1]
^{4}**3**	-3013.776383	1.275331	-3012.632738	0.00	0.00	0.00
^{6}**3**	-3013.759493	1.273591	-3012.622436	10.60	9.51	6.46
^{3}**4**	-3025.134973	1.276286	-3023.994173	0.00	0.00	0.00
^{5}**4**	-3025.145652	1.273811	-3024.011391	-6.70	-8.25	-10.80

Cartesians

^{6}3{B3LYP}$_{optBS1}$

26	10.237041	7.770889	18.377213
53	12.336441	7.408246	20.311221
53	14.123489	5.030423	18.851783
53	15.776898	2.892989	17.533761
7	11.162902	9.235026	17.255599
7	10.840418	6.404272	16.974194
7	8.903452	6.354197	19.058415
7	8.897799	9.215407	19.024610
6	11.274585	10.515185	17.764573
6	12.619035	11.017307	17.515711
6	13.267054	10.063413	16.753994
6	12.325331	8.960526	16.571512
6	12.450372	7.805842	15.761914
6	11.605470	6.672224	15.857555
6	11.517764	5.543316	14.938990
6	10.798809	4.556626	15.586377
6	10.435596	5.088015	16.894158
6	9.876693	4.393918	17.995465
6	9.290370	5.031179	19.113704
6	8.837692	4.446419	20.370770
6	8.088208	5.417970	21.010375
6	8.101584	6.592261	20.149777
6	7.342204	7.784358	20.264117
6	7.648615	8.976238	19.569093
6	6.824981	10.166273	19.412851
6	7.638380	11.146138	18.872764
6	8.950564	10.544587	18.680780
6	10.157293	11.192082	18.294481
6	13.281753	12.241262	18.102251
1	14.210156	12.436198	17.555613
1	12.663699	13.131022	17.975093
6	13.621711	12.077438	19.597782
1	14.131980	12.973253	19.971463
1	14.274893	11.214798	19.764953
1	12.717933	11.929263	20.196728
6	14.715903	10.161315	16.334930
1	14.871350	9.712193	15.356390
1	14.975888	11.220217	16.221020
6	15.690987	9.517125	17.339885
1	16.723308	9.615659	16.983024
1	15.478113	8.450908	17.470994
1	15.625001	9.991502	18.324769
6	11.957691	5.474118	13.495809
1	12.978772	5.834348	13.372556
1	11.970663	4.426103	13.179880
6	11.028133	6.259721	12.549270
1	11.372456	6.168526	11.511907
1	11.008473	7.324132	12.806126
1	9.999315	5.885349	12.600273
6	10.369411	3.255602	14.952349
1	10.452493	2.428826	15.655836
1	11.054771	3.017904	14.132161
6	8.932548	3.300921	14.397092
1	8.669454	2.340137	13.938627
1	8.822910	4.082080	13.636531
1	8.208111	3.504972	15.192615
6	9.212575	3.116775	20.982972
1	9.174233	2.316156	20.244963
1	8.467361	2.856828	21.743068
6	10.605571	3.123093	21.642903
1	10.820623	2.142202	22.084071
1	10.668463	3.875017	22.436972
1	11.391403	3.347176	20.913864
6	7.525675	5.292786	22.406687
1	7.452154	4.231121	22.664855
1	6.508860	5.683829	22.460370
6	8.391431	5.996232	23.471024
1	7.956600	5.860046	24.468826
1	8.463517	7.071472	23.276282
1	9.409937	5.593887	23.484853
6	5.333618	10.304657	19.610534
1	5.013876	9.867477	20.556040
1	5.079138	11.368060	19.670282
6	4.518692	9.669083	18.466425
1	3.444665	9.809123	18.637452
1	4.711581	8.593810	18.394911
1	4.771192	10.119318	17.500008
6	7.156934	12.502997	18.416284
1	6.225839	12.744084	18.939995
1	7.862643	13.286365	18.690768
6	6.897385	12.568655	16.897881
1	6.542889	13.566186	16.610654
1	6.140236	11.837957	16.592016
1	7.810339	12.357603	16.330815
6	13.569137	7.751304	14.772101
6	13.540361	8.543003	13.616857
1	12.695698	9.207438	13.447232
6	14.579331	8.487754	12.680125
6	15.657995	7.631444	12.930396
1	16.473452	7.582645	12.209318
6	15.717277	6.831369	14.079440
6	14.658465	6.897164	14.991514
6	9.863987	2.899469	17.966680
6	11.039354	2.158948	18.125202
1	11.981609	2.681053	18.265261
6	11.015163	0.756908	18.108447
6	9.789944	0.112563	17.911441
1	9.762386	-0.975943	17.884862
6	8.595100	0.827629	17.747600
6	8.647117	2.223107	17.784562
1	7.732291	2.800321	17.669458
6	6.123872	7.732963	21.129929
6	5.050306	6.914086	20.741808
1	5.130912	6.342297	19.820229
6	3.892668	6.821886	21.515101
6	3.829974	7.557742	22.708544
1	2.935881	7.488058	23.326767
6	4.884313	8.373810	23.128652
6	6.028695	8.459389	22.320941
1	6.857781	9.094838	22.625102
6	10.228166	12.673174	18.479258
6	10.206496	13.209987	19.776511
1	10.147891	12.533698	20.626173
6	10.261060	14.588267	19.990145
6	10.319588	15.434265	18.872070
1	10.353622	16.512151	19.025030
6	10.334985	14.932081	17.567448
6	10.298217	13.542200	17.385418
1	10.318235	13.129018	16.379169
6	14.552916	9.352323	11.439183
1	15.000877	8.836776	10.582075
1	15.119018	10.281206	11.590053
1	13.529822	9.633682	11.167985
6	16.893044	5.910042	14.315248
1	17.844662	6.447682	14.221565
1	16.910574	5.096624	13.578118
1	16.853992	5.451585	15.307508
6	12.291922	-0.028735	18.304870
1	12.126703	-1.102462	18.168578
1	12.695183	0.121582	19.314240
1	13.072320	0.293173	17.605274
6	7.281296	0.100858	17.564074
1	7.423106	-0.860568	17.058010
1	6.572530	0.693104	16.975221
1	6.805838	-0.109371	18.531615
6	2.734358	5.946371	21.090624
1	2.517279	5.178737	21.844268
1	2.944354	5.435607	20.145395
1	1.817000	6.533701	20.956883
6	4.801452	9.150354	24.424504
1	3.843107	8.986935	24.928092
1	4.910103	10.228723	24.252806
1	5.598373	8.854137	25.118276
6	10.243100	15.164389	21.388550
1	11.080600	15.854891	21.547032
1	10.309501	14.377395	22.146453
1	9.320711	15.729815	21.574867
6	10.395371	15.858910	16.373143
1	10.331589	16.908760	16.677098
1	9.574130	15.661702	15.673032
1	11.331184	15.729984	15.814151
1	14.675171	6.279828	15.885693

^{4}3{B3LYP}$_{optBS1}$

26	1.019120	-0.054334	0.328165
53	0.119458	0.009359	-2.481495
53	-3.123925	0.200957	-2.162810
53	-6.144038	0.309706	-1.890634
7	1.027139	1.906541	0.451210
7	-0.782751	-0.094102	1.114521
7	1.055059	-2.016630	0.373648
7	3.001263	-0.042938	0.227624
6	1.990558	2.659516	-0.213547
6	1.370373	3.831626	-0.800530
6	0.058851	3.854087	-0.362169
6	-0.135375	2.663789	0.446519
6	-1.251503	2.300500	1.221271
6	-1.435512	0.984539	1.689017
6	-2.437116	0.499860	2.620100
6	-2.476129	-0.876374	2.484138
6	-1.480418	-1.228510	1.489491
6	-1.288089	-2.469198	0.845826
6	-0.098402	-2.765352	0.161933
6	0.219129	-3.925817	-0.650544
6	1.594183	-3.933175	-0.812731
6	2.106414	-2.769131	-0.120330
6	3.445776	-2.441049	0.173929
6	3.817618	-1.130343	0.514946
6	5.097137	-0.655535	1.005553
6	5.091929	0.721652	0.865849
6	3.791864	1.085000	0.337260
6	3.355573	2.349866	-0.117185
6	1.946211	4.772650	-1.831929
1	1.278171	5.634082	-1.931898
1	2.911405	5.172153	-1.516846
6	2.104306	4.114837	-3.217823
1	2.477231	4.847533	-3.943463
1	1.149336	3.723129	-3.582898
1	2.812477	3.281377	-3.183701
6	-0.962974	4.881092	-0.790164
1	-1.657601	5.100301	0.017967
1	-0.444995	5.823616	-1.000429
6	-1.762637	4.460524	-2.039045
1	-2.482668	5.242559	-2.308599
1	-2.317999	3.534202	-1.862445
1	-1.104721	4.292650	-2.898525
6	-3.180668	1.286305	3.672954
1	-3.639621	2.181010	3.252226
1	-2.857326	2.235581	5.611059
1	-1.462399	2.344530	4.522510
1	-1.829741	0.814811	5.334757
6	-3.301242	-1.803916	3.342714
1	-3.747675	-2.597988	2.745549
1	-4.139413	-1.241797	3.767103
6	-2.491640	-2.431562	4.494794
1	-3.130264	-3.085607	5.100886
1	-2.072232	-1.661617	5.152688
1	-1.660238	-3.032679	4.110972
6	-0.725927	-4.892464	-1.324464
1	-1.558709	-5.147281	-0.672106
1	-0.194391	-5.832048	-1.513696
6	-1.286454	-4.359858	-2.658612
1	-1.950906	-5.104891	-3.112826
1	-0.485724	-4.136627	-3.371712
1	-1.860156	-3.439428	-2.507333
6	2.355407	-4.894608	-1.694386
1	1.725157	-5.768382	-1.889764
1	3.247040	-5.272984	-1.191567
6	2.763560	-4.274648	-3.045957
1	3.279803	-5.017663	-3.666027
1	3.437486	-3.423423	-2.904499
1	1.889014	-3.915867	-3.598935
6	6.174011	-1.452824	1.701164
1	6.452162	-2.336079	1.124811
1	7.079181	-0.841104	1.773690
6	5.761950	-1.892173	3.120255
1	6.580710	-2.436616	3.605372
1	4.888910	-2.552157	3.090529
1	5.509125	-1.028187	3.745418
6	6.188339	1.644120	1.342157
1	7.124328	1.078898	1.407602
1	6.371229	2.441732	0.621468
6	5.890147	2.268686	2.719515
1	6.713925	2.921359	3.033232
1	5.757539	1.496215	3.485762
1	4.974493	2.869317	2.689858
6	-2.306015	3.315255	1.513029
6	-2.033130	4.375952	2.388300
1	-1.045353	4.453668	2.836531
6	-3.008369	5.329691	2.695378
6	-4.265916	5.211296	2.090184
1	-5.034079	5.950604	2.316015
6	-4.566405	4.169004	1.203464
6	-3.577047	3.215510	0.931338
6	-2.376961	-3.487778	0.919636
6	-3.592834	-3.267521	0.258464
1	-3.726951	-2.357347	-0.320879
6	-4.625428	-4.212589	0.319885
6	-4.425560	-5.370711	1.081175
1	-5.226896	-6.106361	1.144618
6	-3.225021	-5.611173	1.762651
6	-2.201381	-4.663969	1.663633
1	-1.255561	-4.836845	2.171414
6	4.460895	-3.535371	0.129411
6	4.353759	-4.603566	1.034847
1	3.539944	-4.602317	1.756325
6	5.266068	-5.660307	1.022114
6	6.292135	-5.641340	0.066100
1	7.005674	-6.464022	0.038266
6	6.420624	-4.598094	-0.856389
6	5.501388	-3.541304	-0.805142
1	5.590857	-2.714514	-1.505748
6	4.390036	3.350693	-0.517965
6	5.223400	3.078756	-1.615064
1	5.090019	2.148327	-2.161343
6	6.210931	3.980212	-2.016315
6	6.371831	5.163693	-1.280828
1	7.146646	5.869754	-1.576666
6	5.563586	5.462788	-0.180095
6	4.568226	4.545814	0.187221
1	3.922546	4.761656	1.035337
6	-2.715213	6.467080	3.649297
1	-3.438029	6.494026	4.474354
1	-2.771104	7.438865	3.141839
1	-1.714620	6.376554	4.084764
6	-5.926402	4.084523	0.547791
1	-6.051584	4.877620	-0.201180
1	-6.731367	4.206863	1.282749
1	-6.069217	3.125842	0.040128
6	-5.919174	-3.995380	-0.432954
1	-5.923373	-4.556383	-1.377443
1	-6.069400	-2.939787	-0.680434
1	-6.782431	-4.338424	0.149467
6	-3.054036	-6.859695	2.599184
1	-3.590598	-6.775541	3.553769
1	-2.000073	-7.046561	2.829958
1	-3.449577	-7.743700	2.085267
6	5.155596	-6.801721	2.008667
1	5.115441	-7.770629	1.495443
1	4.255363	-6.712082	2.625151
1	6.020368	-6.831280	2.684014
6	7.509207	-4.616866	-1.906246
1	8.315203	-5.306915	-1.636037
1	7.947375	-3.622313	-2.048422
1	7.114219	-4.936964	-2.879678
6	7.081651	3.698685	-3.220098
1	6.811469	4.345778	-4.064886
1	6.979590	2.661143	-3.553805
1	8.140555	3.881349	-3.001040
6	5.755387	6.742601	0.603987
1	6.556502	7.355627	0.178224

^{5}4{B3LYP}$_{optBS1}$

53	-6.239681	0.700223	-1.299775
53	-0.266839	0.178109	-3.049264
53	-3.305052	0.408056	-2.236989
26	0.933234	-0.080802	0.522796
7	0.914018	-2.111487	0.277796
7	-1.036371	-0.144189	0.994745
7	0.837067	1.964220	0.368498
7	2.890543	-0.032871	-0.096037
6	1.953262	-2.805756	-0.208981
6	1.483637	-3.988150	-0.929651
6	0.108756	-3.998333	-0.818416
6	-0.249503	-2.842151	0.011612
6	-1.451707	-2.522293	0.632341
6	-1.679424	-1.268070	1.337588
6	-2.653280	-0.994598	2.405158
6	-2.610508	0.359570	2.637914
6	-1.630759	0.914780	1.694499
6	-1.392268	2.233525	1.337124
6	-0.298188	2.671176	0.478852
6	-0.204254	3.912847	-0.302443
6	1.047190	3.920958	-0.876863
6	1.740883	2.721464	-0.392488
6	3.082387	2.375057	-0.471197
6	3.612047	1.091793	-0.018575
6	4.953631	0.808371	0.505498
6	5.018500	-0.551559	0.710437
6	3.728949	-1.102406	0.271957
6	3.330039	-2.416475	0.080757
6	2.310605	-4.942981	-1.752981
1	3.188771	-5.274096	-1.194204
1	1.721070	-5.844481	-1.949063
6	2.760323	-4.342928	-3.098828
1	3.341025	-5.076741	-3.669983
1	1.899324	-4.040313	-3.704022
1	3.387192	-3.456865	-2.950578
6	-0.810238	-4.930594	-1.568068
1	-1.610403	-5.299955	-0.926685
1	-0.239314	-5.811476	-1.880453
6	-1.430576	-4.269185	-2.816066
1	-2.054930	-4.992849	-3.352999
1	-2.057196	-3.413711	-2.544950
1	-0.657424	-3.905217	-3.500942
6	-3.443539	-1.993071	3.212564
1	-3.918333	-2.729897	2.564463
1	-4.261250	-1.468775	3.717210
6	-2.590173	-2.718075	4.272049
1	-3.210130	-3.418113	4.844824
1	-1.776152	-3.286191	3.809303
1	-2.138153	-2.007844	4.972297
6	-3.307851	1.060452	3.778286
1	-4.136888	0.433604	4.121840
1	-3.756423	1.998694	3.453461
6	-2.366477	1.334290	4.969942
1	-2.920080	1.822374	5.781329
1	-1.933087	0.406710	5.358247
1	-1.536786	1.986938	4.681281
6	-1.272762	4.948615	-0.559103
1	-1.873835	5.114846	0.333564
1	-0.782952	5.906598	-0.768566
6	-2.201113	4.589735	-1.735587
1	-2.953526	5.374907	-1.875082
1	-1.639672	4.484779	-2.670050
1	-2.724672	3.645045	-1.560321
6	1.490851	4.899896	-1.936227
1	2.467729	5.328413	-1.706408
1	0.785711	5.736400	-1.949865
6	1.534625	4.272821	-3.344549
1	1.775601	5.040996	-4.088453
1	2.294363	3.488456	-3.408883
1	0.573412	3.820513	-3.607845
6	6.008562	1.807053	0.910867
1	6.965223	1.286085	1.022786
1	6.162789	2.551668	0.127296
6	5.678479	2.521407	2.236708
1	6.478659	3.223608	2.499819
1	4.741562	3.083770	2.166199
1	5.566673	1.803792	3.055712
6	6.146568	-1.263086	1.416929
1	6.398039	-2.199553	0.918923
1	7.045560	-0.640044	1.360775
6	5.836105	-1.552169	2.900631
1	6.690446	-2.054015	3.371105
1	5.629665	-0.629272	3.451671
1	4.957452	-2.195168	3.006343
6	-2.587014	-3.484723	0.614548
6	-2.470230	-4.725021	1.256213
1	-1.533716	-4.986426	1.743213
6	-3.546964	-5.619008	1.292927
6	-4.734662	-5.253639	0.651023
1	-5.577609	-5.943123	0.667832
6	-4.878952	-4.022544	-0.006003
6	-3.798710	-3.135435	-0.000930
1	-3.893581	-2.167017	-0.485244
6	-2.309213	3.289778	1.853945
6	-3.640152	3.340763	1.410675
1	-3.999225	2.597752	0.703068
6	-4.506129	4.339478	1.863686
6	-4.018544	5.275023	2.788898
1	-4.005321	0.676692	4.055648
6	-2.277556	1.692780	4.854812
6	4.351299	4.554835	-0.451831
1	3.790069	4.853313	0.430153
6	5.340749	5.402205	-0.968256
6	6.045584	4.988371	-2.102646
1	6.812926	5.641532	-2.515693
6	5.799761	3.752410	-2.719513
6	4.826197	2.917937	-2.168805
1	4.625776	1.949514	-2.621433
6	4.303280	-3.538508	0.220448
6	5.380617	-3.678512	-0.666239
1	5.517820	-2.943516	-1.455377
6	6.271417	-4.749028	-0.551063
6	6.078404	-5.667915	0.489785
1	6.774902	-6.498035	0.596579
6	5.018479	-5.550700	1.396028
6	4.124462	-4.483849	1.239464
1	3.290372	-4.371821	1.928965
6	-3.426292	-6.936250	2.026668
1	-4.282930	-7.586608	1.822983
1	-2.516657	-7.476180	1.737227
1	-3.377493	-6.783045	3.112648
6	-6.169382	-3.671495	-0.709641
1	-6.262476	-2.592638	-0.867550
1	-6.220775	-4.154779	-1.694615
1	-7.039483	-4.012331	-0.136368
6	-5.933927	4.410359	1.371039
1	-6.107132	5.328913	0.795643
1	-6.177230	3.560595	0.726009
1	-6.642159	4.417464	2.209089
6	-2.211118	6.232122	4.287402
1	-2.828797	7.136252	4.297359
1	-2.241307	5.802438	5.297736
1	-1.174228	6.530836	4.095822
6	5.645311	6.722271	-0.295949
1	6.295360	7.346875	-0.916775
1	4.729179	7.288444	-0.090462
1	6.151596	6.569668	0.666074
6	6.567212	3.345629	-3.956490
1	6.421386	2.285787	-4.187401
1	6.241041	3.922615	-4.831453
1	7.642631	3.522212	-3.835901
6	7.406223	-4.919908	-1.536132
1	8.215698	-5.523399	-1.112215
1	7.065652	-5.424687	-2.450205
1	7.825374	-3.953456	-1.837614
6	4.837125	-6.543595	2.522511
1	5.572228	-7.352856	2.465926
1	4.948524	-6.058637	3.500578
1	3.837426	-6.994622	2.500565
53	1.740631	-0.169790	3.274227

^{3}4{B3LYP}$_{optBS1}$

53	-6.234206	0.739084	-1.919725
53	0.028903	0.030009	-2.340430
53	-3.215697	0.443584	-2.106849
26	0.856670	-0.035948	0.449815
7	0.841220	-2.014550	0.262498
7	-1.023002	-0.077260	1.051252
7	0.809717	1.952485	0.347314
7	2.804285	-0.020247	0.028664
6	1.869693	-2.760405	-0.208288
6	1.361568	-3.954933	-0.881155
6	-0.007250	-3.934808	-0.737074
6	-0.322461	-2.751202	0.061773
6	-1.506792	-2.441982	0.723994
6	-1.720307	-1.189796	1.383704
6	-2.740237	-0.865051	2.381858
6	-2.680793	0.495358	2.574479
6	-1.650902	0.999158	1.667367
6	-1.427183	2.310106	1.257941
6	-0.314208	2.702857	0.445466
6	-0.163817	3.941080	-0.328194
6	1.102218	3.915547	-0.865104
6	1.745178	2.701454	-0.365989
6	3.093826	2.362684	-0.392330
6	3.580178	1.088660	0.048535
6	4.935494	0.752485	0.479499
6	4.959695	-0.610458	0.671592
6	3.636646	-1.104078	0.302441
6	3.236508	-2.408786	0.032499
6	2.126234	-4.946507	-1.725692
1	3.047509	-5.259699	-1.233948
1	1.522248	-5.853655	-1.833253
6	2.459377	-4.411026	-3.132246
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1	1.550174	-4.145508	-3.681555
1	3.085981	-3.514603	-3.078767
6	-0.960093	-4.880692	-1.429254
1	-1.765913	-5.192966	-0.766889
1	-0.418239	-5.794186	-1.694481
6	-1.572735	-4.279764	-2.711221
1	-2.236266	-5.009930	-3.190179
1	-2.158838	-3.382099	-2.490400
1	-0.797121	-3.998364	-3.431398
6	-3.605375	-1.812454	3.176240
1	-4.048697	-2.572417	2.534151
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1	-2.004855	-3.088772	3.957778
1	6.013018	6.535847	1.650513
1	4.839785	7.347333	0.612280
1	-3.790494	2.390832	0.256434
6	-2.564634	1.579935	4.866630
1	-3.157405	2.111325	5.621140
1	-2.163437	0.668961	5.323481
1	-1.714357	2.212552	4.592622
6	-1.189398	5.009366	-0.635203
1	-1.814786	5.216906	0.230636
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6	-2.090099	4.673490	-1.839373
1	-2.815268	5.479018	-2.005510
1	-1.503087	4.550570	-2.755789
1	-2.645952	3.745396	-1.678457
6	1.612105	4.889347	-1.901002
1	2.617785	5.239029	-1.667993
1	0.972415	5.777285	-1.890128
6	1.604664	4.301534	-3.327116
1	1.939598	5.057490	-4.047423
1	2.272523	3.438756	-3.406329
1	0.601854	3.971291	-3.616043
6	6.065869	1.693769	0.817863
1	7.003594	1.127768	0.821632
1	6.184804	2.459002	0.050174
6	5.893707	2.371581	2.191442
1	6.737102	3.042602	2.395604
1	4.971671	2.960928	2.232162
1	5.843975	1.629680	2.995571
6	6.091434	-1.375811	1.313025
1	6.306642	-2.298925	0.775638
1	7.003777	-0.773062	1.255134
6	5.812531	-1.711303	2.792450
1	6.666403	-2.245875	3.226314
1	5.638185	-0.804104	3.380336
1	4.924790	-2.343275	2.894742
6	-2.613343	-3.442752	0.747410
6	-2.497914	-4.627551	1.483676
1	-1.582068	-4.827424	2.035418
6	-3.552665	-5.550785	1.520496
6	-4.712131	-5.268400	0.791316
1	-5.535105	-5.981757	0.810597
6	-4.850400	-4.093789	0.037304
6	-3.793512	-3.180622	0.037211
1	-3.878474	-2.248708	-0.514087
6	-2.420715	3.353324	1.631518
6	-3.694926	3.350703	1.045000
1	-3.950746	2.571131	0.333114
6	-4.628451	4.343198	1.352652
6	-4.268085	5.332839	2.279224
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6	-2.086358	4.354585	2.548965
1	-1.094569	4.361302	2.996216
6	4.107981	3.319491	-0.926626
6	4.426795	4.505900	-0.258514
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6	5.407532	5.373796	-0.760541
6	6.049835	5.034009	-1.954929
1	6.809712	5.703453	-2.355805
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6	4.778991	3.000593	-2.117663
1	4.533580	2.073971	-2.631425
6	4.255252	-3.498783	-0.023884
6	5.212386	-3.524153	-1.047329
1	5.211776	-2.732533	-1.792560
6	6.161321	-4.548642	-1.121228
6	6.146455	-5.541570	-0.133133
1	6.886331	-6.339260	-0.175046
6	5.206985	-5.540543	0.905354
6	4.256609	-4.513328	0.941946
1	3.510155	-4.494496	1.732617
6	-3.433035	-6.822099	2.331762
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1	-2.579441	-7.428211	2.002460
1	-3.280939	-6.603921	3.396425
6	-6.104455	-3.830062	-0.764843
1	-6.175905	-2.780532	-1.067331
1	-6.121911	-4.439651	-1.678286
1	-7.005026	-4.082034	-0.192198
6	-5.999575	4.344563	0.715767
1	-6.263853	5.341488	0.342597
1	-6.054970	3.639235	-0.118926
1	-6.771569	4.058463	1.442353
6	-2.655038	6.409468	3.910090
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1	-2.708784	6.012030	4.932239
1	-1.634122	6.780129	3.762155
6	5.756407	6.645948	-0.019730
1	6.521558	7.220928	-0.551315
1	4.877373	7.291201	0.102378
1	6.138406	6.430093	0.986051
6	6.446270	3.526286	-3.950360
1	6.192253	2.520357	-4.298938
1	6.165573	4.232518	-4.742304
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1	7.698425	-3.623075	-2.339415
6	5.208166	-6.623362	1.961505
1	6.034912	-7.325767	1.813875
1	5.303939	-6.198702	2.968339
1	4.273673	-7.198512	1.943340

1	-4.687339	6.053558	3.154151
6	-2.700977	5.238255	3.257988
6	-1.844806	4.244159	2.766041
1	-0.812083	4.203333	3.106690
6	4.086821	3.314619	-1.042754

1	-2.446721	-1.759692	5.034272
6	-3.437312	1.253365	3.637973
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