Supporting Information

1. Figure S1
2. Figure S2
3. Figure S3
4. Table S1 of absolute energies
5. XYZ Files

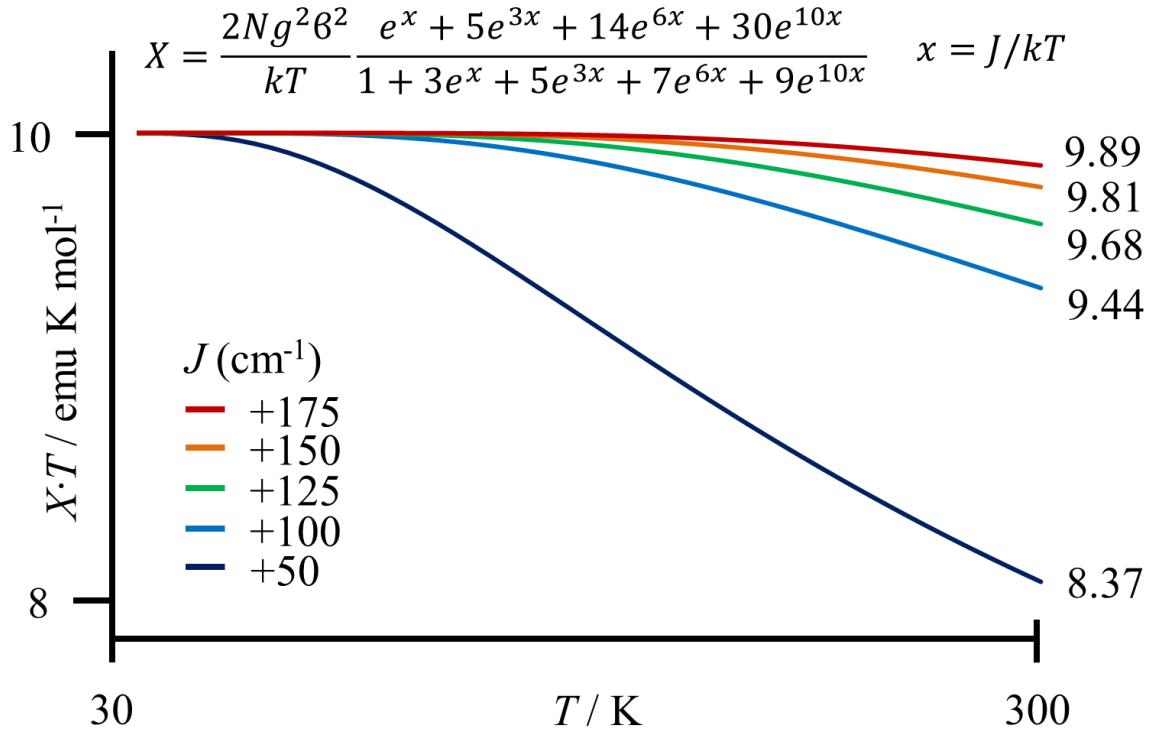

Figure S1 Various values for *J*, (each value has a different color) from 30 K to room temperature (300 K). A *J* value of +125 cm^{-1} (green line), reproduces the $\chi{\cdot}$T value of 9.68 emu K mol^{-1} measured for **1**.

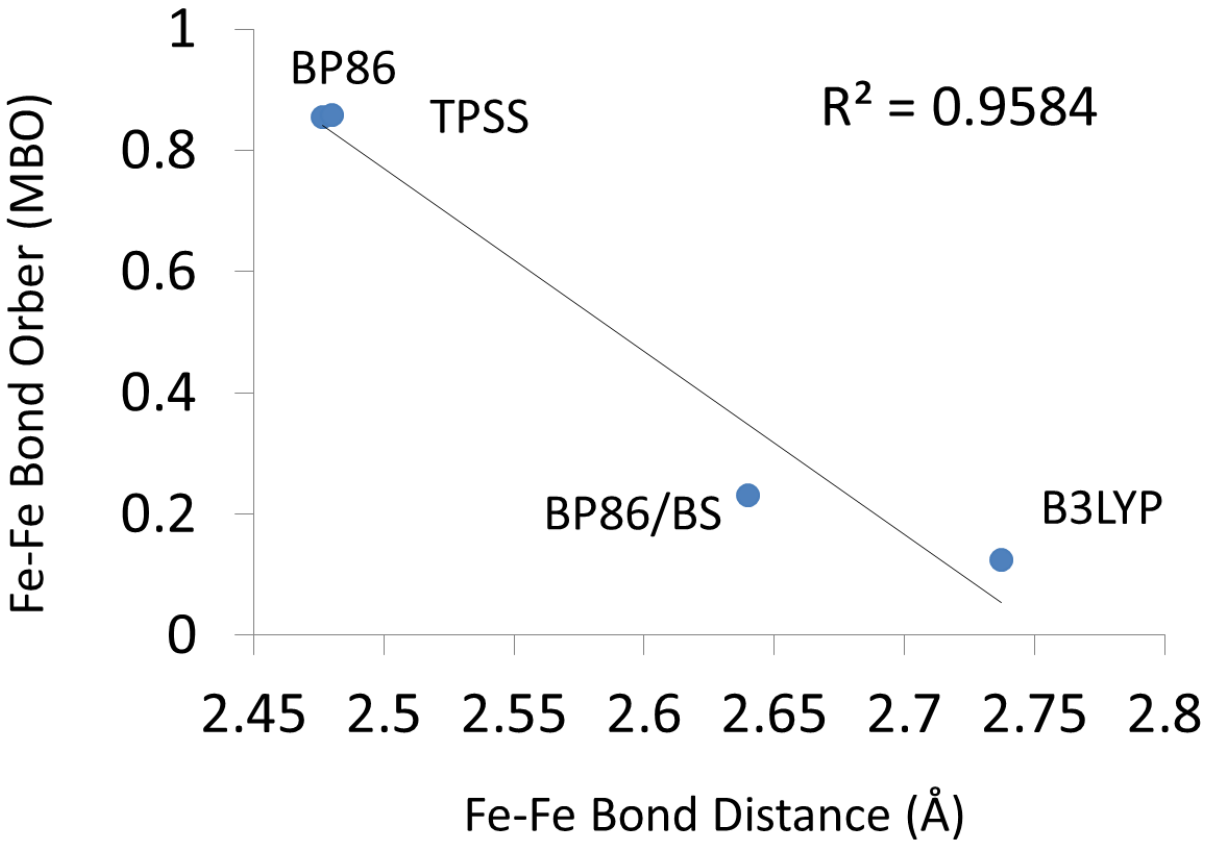

Figure S2 The correlation between Fe-Fe bond distance and MBO from geometry optimizations of $Fe_2(TNC)_4$ with BP86, TPSS, BP/broken symmetry surface, and B3LYP.

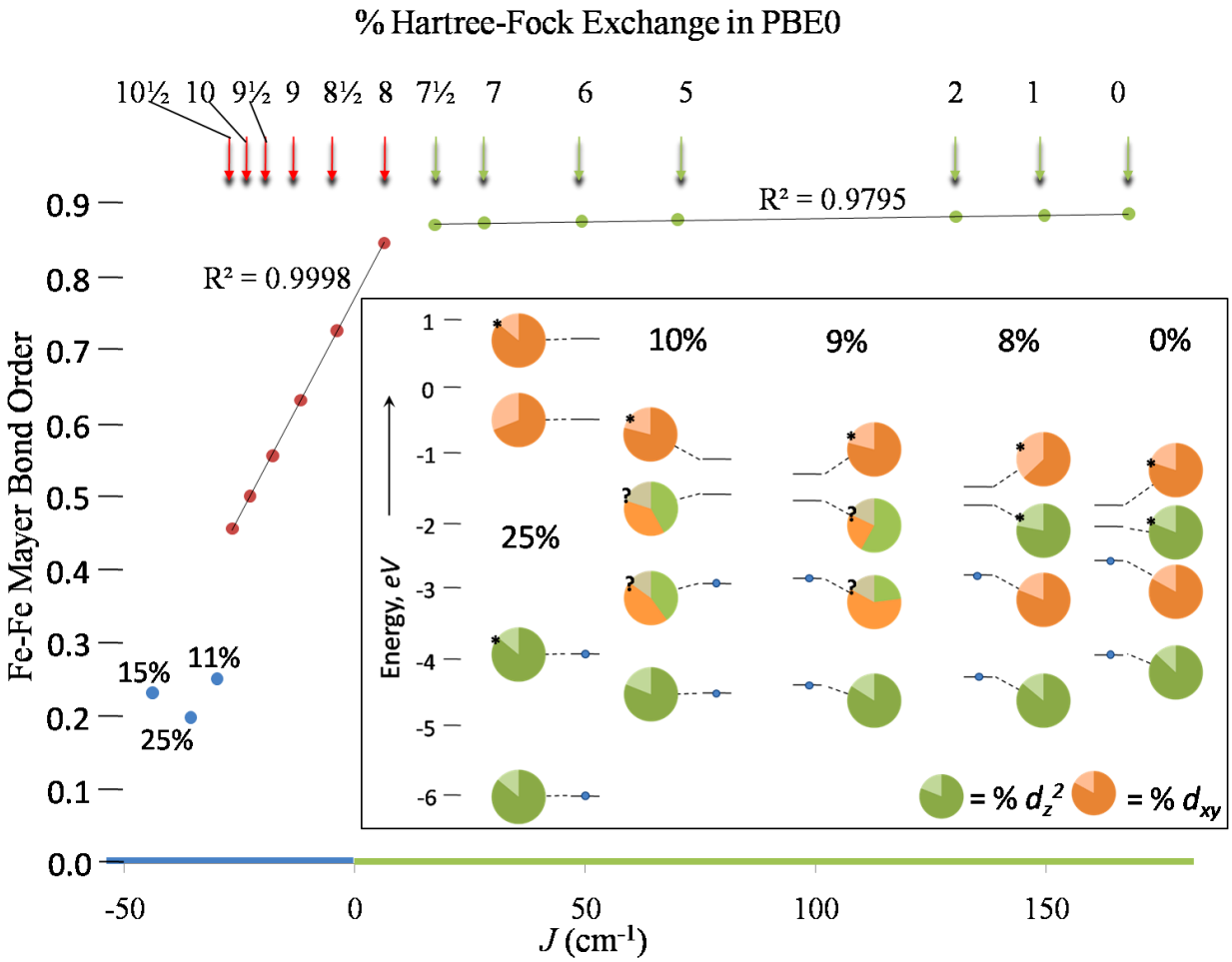

Figure S3 The correlation between MBO of the HS calculation that precedes the BS calculation and the associated *J* value have been extensively studied using the **1m**(D_{2d}) model. Here the PBE0 functional has been used scaling the HF from 0% (PBE) to 25% (PBE0). The orbitals at bottom right show the effect of HF exchange on the singly-occupied sigma and delta beta spin Fe-Fe bonding and antibonding orbitals. As HF increases the sigma* drops in energy while the delta orbital rises. At ~10% HF exchange, the occupancies switch, breaking the Fe-Fe bond, while the exchange coupling constant switches from ferromagnetic coupling to antiferromagnetic.

Table S1 Absolute energies in hartrees for relevant **1**(D_2) and **1**(D_4) HS and BS calculations corresponding to Figure 3 and Table 2 of the main text.				
Functional	**1**$(D_2)^{HS}$	**1**$(D_2)^{BS}$	**1**$(D_4)^{HS}$	**1**$(D_2)^{BS}$
BP86	-5004.915103	-5004.897118	-5004.910843	-5004.885972
B3LYP	-5002.798039	-5002.800212	-5002.792688	-5002.782877
LSD	-4977.796957	-4977.770539	--	--
BLYP	-5003.654026	-5003.636156	--	--
PBE	-5000.951465	-5000.932679	--	--
B3LYP(5%)	-5003.083024	-5003.071425	--	--
B3LYP(10%)	-5002.979022	-5002.974920	--	--
B3LYP(15%)	-5002.883161	-5002.883994	--	--
B3LYP(25%)	-5002.715038	-5002.717414	--	--
PBE0	-5001.096353	-5001.098842	--	--
TPPS	-5004.989914	-5004.977558	--	--
TPSSh	-5004.644253	-5004.645127	--	--
TPSS0	-5004.175604	-5004.178029	--	--

XYZ Files

1(D_2)

Fe	-0.00108	-0.00135	-1.23061
Fe	0.00312	0.01135	1.22852
N	-2.10699	0.08788	-0.56268
N	0.06111	1.93922	-1.74285
N	2.10319	-0.08330	-0.58897
N	-0.07629	2.10755	0.58223
N	-1.92980	-0.06862	1.76002
N	1.94527	0.06317	1.73651
N	0.08317	-2.10156	0.56779
N	-0.08492	-1.93540	-1.75448
C	-2.65775	0.05544	0.64625
C	0.04423	-2.65860	-0.63793
C	-0.05122	2.66268	-0.62560
C	2.66324	-0.06010	0.61658
C	2.00439	-0.20394	4.14517
C	2.59780	0.28369	2.96637
C	-3.74011	-0.79596	5.51603
C	-4.33589	-1.29141	4.35129
C	2.59394	0.02747	5.38725
C	-2.55241	-0.06108	5.41542
C	3.79214	1.02719	3.07094
C	-2.97630	0.47688	-1.62233
C	2.96218	-0.47020	-1.65780
C	-3.73528	1.66047	-1.54273
C	-3.75618	-1.05940	3.10164
C	3.04528	0.32028	-2.81663
C	-3.07495	-0.31373	-2.77978
C	3.72526	-1.65177	-1.58693
C	-4.57510	2.03847	-2.59223
C	-3.91251	0.07283	-3.82924
C	3.87149	-0.06449	-3.87574
C	-4.66516	1.24876	-3.74329
C	4.55381	-2.02786	-2.64598
C	-2.57061	-0.30246	2.99316
C	-1.97432	0.18460	4.17074
C	4.62841	-1.23824	-3.79820
C	3.79035	0.74853	5.48383
C	4.38310	1.24488	4.31792

C	0.07420	-3.89294	3.84254
C	-0.21459	1.99885	-4.15099
C	-1.62800	3.74641	1.57858
C	-0.31450	-3.06018	2.79005
C	-1.07492	-3.76955	-3.08679
C	-1.99376	4.58196	2.63577
C	1.25075	-4.64478	3.75828
C	-1.31133	-4.35248	-4.33411
C	0.02273	2.58247	-5.39475
C	-0.45286	2.97345	1.64924
C	-1.20052	4.65348	3.78583
C	0.47437	-2.96576	1.63107
C	0.28717	2.58581	-2.97494
C	0.34106	3.05339	2.80585
C	-0.03354	3.88641	3.86318
C	2.03892	-4.55876	2.60593
C	-0.32328	-2.58000	-2.98483
C	1.65843	-3.72413	1.55310
C	0.76378	3.76627	-5.49570
C	-0.82597	-3.75627	-5.50289
C	1.04998	3.76745	-3.08387
C	1.27373	4.35264	-4.33250
C	-0.09671	-2.56463	-5.40862
C	0.15354	-1.98328	-4.16636
H	0.13962	-3.75137	-0.72020
H	-0.14229	3.75580	-0.70693
H	3.75567	-0.16186	0.69467
H	-3.75009	0.15155	0.73367
H	1.08470	-0.78672	4.06942
H	2.11818	-0.36737	6.28644
H	-3.64603	2.28771	-0.65446
H	2.48182	1.25147	-2.86764
H	-2.51485	-1.24659	-2.83685
H	3.64786	-2.27956	-0.69799
H	-5.15314	2.96088	-2.51427
H	-3.98321	-0.55960	-4.71525
H	-4.19092	-0.98752	6.49078
H	3.92985	0.56754	-4.76292
H	4.23730	1.46346	2.17566
H	-5.31637	1.54838	-4.56588
H	5.13475	-2.94904	-2.57475
H	-5.25119	-1.88248	4.41421
H	5.27052	-1.53651	-4.62834
H	-2.07473	0.33317	6.31381
H	4.25032	0.92870	6.45648
H	5.30537	1.82537	4.37808

H	-4.20295	-1.49493	2.20675
H	-1.06149	0.77761	4.09189
H	-0.81253	1.08925	-4.07155
H	-2.25880	3.67142	0.69153
H	-2.90973	5.17108	2.56486
H	-1.50303	-4.21730	-2.18883
H	-0.38305	2.11218	-6.29186
H	-1.49085	5.30133	4.61439
H	-0.55685	-3.96049	4.72975
H	-1.89786	-5.27106	-4.39197
H	1.26735	2.48194	2.85641
H	0.60136	3.94219	4.74848
H	-1.24760	-2.50043	2.84625
H	1.55209	-5.29200	4.58337
H	0.94869	4.22146	-6.46970
H	-1.02082	-4.20990	-6.47573
H	2.96194	-5.13602	2.52934
H	1.86956	5.26479	-4.39601
H	1.49654	4.20681	-2.19077
H	2.28428	-3.63844	0.66359
H	0.28978	-2.08634	-6.31008
H	0.74221	-1.06719	-4.09276

$\mathbf{1}(D_4)$

Fe	0.00000	0.00000	-1.16178
Fe	0.00000	0.00000	1.16178
N	-0.37997	-2.08395	-1.10258
N	-2.08395	0.37997	-1.10258
N	2.08395	-0.37997	-1.10258
N	0.37997	2.08395	-1.10258
N	-2.08395	-0.37997	1.10258
N	0.37997	-2.08395	1.10258
N	-0.37997	2.08395	1.10258
N	2.08395	0.37997	1.10258
C	0.00000	-2.72547	0.00000
C	2.72547	0.00000	0.00000
C	-2.72547	0.00000	0.00000
C	0.00000	2.72547	0.00000
C	2.53319	0.81311	3.45156
C	2.80836	1.06983	2.09503
C	-4.17719	-2.45829	4.13752
C	-4.45794	-2.72225	2.79259
C	3.20968	1.49904	4.45928
C	-3.20968	-1.49904	4.45928

C	3.77795	2.04380	1.77892
C	-2.80836	1.06983	-2.09503
C	2.80836	-1.06983	-2.09503
C	-3.77795	2.04380	-1.77892
C	-3.77795	-2.04380	1.77892
C	2.53319	-0.81311	-3.45156
C	-2.53319	0.81311	-3.45156
C	3.77795	-2.04380	-1.77892
C	-4.45794	2.72225	-2.79259
C	-3.20968	1.49904	-4.45928
C	3.20968	-1.49904	-4.45928
C	-4.17719	2.45829	-4.13752
C	4.45794	-2.72225	-2.79259
C	-2.53319	-0.81311	3.45156
C	4.17719	-2.45829	-4.13752
C	4.17719	2.45829	4.13752
C	4.45794	2.72225	2.79259
C	-2.80836	-1.06983	2.09503
C	-0.81311	-2.53319	-3.45156
C	2.04380	3.77795	-1.77892
C	2.72225	4.45794	-2.79259
C	-1.49904	-3.20968	-4.45928
C	-1.49904	3.20968	4.45928
C	-0.81311	2.53319	3.45156
C	-2.45829	4.17719	4.13752
C	2.04380	-3.77795	1.77892
C	2.45829	4.17719	-4.13752
C	2.72225	-4.45794	2.79259
C	-1.06983	2.80836	2.09503
C	1.06983	2.80836	-2.09503
C	-2.45829	-4.17719	-4.13752
C	1.06983	-2.80836	2.09503
C	-2.72225	4.45794	2.79259
C	-1.06983	-2.80836	-2.09503
C	2.45829	-4.17719	4.13752
C	-2.04380	3.77795	1.77892
C	0.81311	-2.53319	3.45156
C	1.49904	-3.20968	4.45928
C	1.49904	3.20968	-4.45928
C	-2.72225	-4.45794	-2.79259
C	0.81311	2.53319	-3.45156
C	-2.04380	-3.77795	-1.77892
H	3.82683	0.00000	0.00000
H	-3.82683	0.00000	0.00000
H	0.00000	3.82683	0.00000
H	0.00000	-3.82683	0.00000

H	1.81679	0.02775	3.70014
H	2.98896	1.27536	5.50438
H	-3.97344	2.28179	-0.73196
H	1.81679	-0.02775	-3.70014
H	-1.81679	0.02775	-3.70014
H	3.97344	-2.28179	-0.73196
H	-5.20214	3.47552	-2.52816
H	-2.98896	1.27536	-5.50438
H	-4.70348	-2.99684	4.92665
H	2.98896	-1.27536	-5.50438
H	3.97344	2.28179	0.73196
H	-4.70348	2.99684	-4.92665
H	5.20214	-3.47552	-2.52816
H	-5.20214	-3.47552	2.52816
H	4.70348	-2.99684	-4.92665
H	-2.98896	-1.27536	5.50438
H	4.70348	2.99684	4.92665
H	5.20214	3.47552	2.52816
H	-3.97344	-2.28179	0.73196
H	-1.81679	-0.02775	3.70014
H	-0.02775	-1.81679	-3.70014
H	-1.27536	-2.98896	-5.50438
H	2.28179	3.97344	-0.73196
H	2.28179	-3.97344	0.73196
H	3.47552	5.20214	-2.52816
H	3.47552	-5.20214	2.52816
H	-2.99684	-4.70348	-4.92665
H	2.99684	-4.70348	4.92665
H	-1.27536	2.98896	5.50438
H	0.02775	-1.81679	3.70014
H	2.99684	4.70348	-4.92665
H	-0.02775	1.81679	3.70014
H	1.27536	-2.98896	5.50438
H	-2.99684	4.70348	4.92665
H	-3.47552	5.20214	2.52816
H	-3.47552	-5.20214	-2.52816
H	1.27536	2.98896	-5.50438
H	-2.28179	-3.97344	-0.73196
H	-2.28179	3.97344	0.73196
H	0.02775	1.81679	-3.70014

1m(D_{4h})

Fe	0.000000	0.000000	-1.213642
Fe	0.000000	0.000000	1.213642

N	0.000000	-2.114186	-1.164396
N	-2.114186	0.000000	-1.164396
N	2.114186	0.000000	-1.164396
N	0.000000	2.114186	-1.164396
N	-2.114186	0.000000	1.164396
N	0.000000	-2.114186	1.164396
N	0.000000	2.114186	1.164396
N	2.114186	0.000000	1.164396
C	0.000000	-2.747975	0.000000
C	2.747975	0.000000	0.000000
C	-2.747975	0.000000	0.000000
C	0.000000	2.747975	0.000000
H	0.000000	-2.754224	-1.958071
H	-2.754224	0.000000	-1.958071
H	2.754224	0.000000	-1.958071
H	0.000000	2.754224	-1.958071
H	2.754224	0.000000	1.958071
H	0.000000	2.754224	1.958071
H	0.000000	-2.754224	1.958071
H	-2.754224	0.000000	1.958071
H	3.852971	0.000000	0.000000
H	-3.852971	0.000000	0.000000
H	0.000000	3.852971	0.000000
H	0.000000	-3.852971	0.000000

1m(D_{2d})

Fe	-0.00464	-0.00429	-1.24518
Fe	0.00464	0.00429	1.24518
N	-2.03781	-0.00834	-0.54890
N	-0.01272	1.93597	-1.76724
N	-0.00040	-1.94810	-1.75391
N	2.03366	0.00451	-0.56412
N	-0.00438	2.03765	0.54952
N	-1.93547	-0.00007	1.76783
N	1.94859	0.01219	1.75332
N	0.00853	-2.03382	0.56349
C	-2.63779	-0.00619	0.63284
C	0.00605	-2.64226	-0.61391
C	-0.01069	2.63797	-0.63203
C	2.64244	0.01048	0.61311
H	-2.71265	-0.01311	-1.31596
H	-0.01767	2.51147	-2.60637
H	-0.00169	-2.52936	-2.58907
H	2.70277	0.00398	-1.33620
H	0.01352	-2.70315	1.33537

H	2.53009	0.01690	2.58830
H	-2.51073	0.00099	2.60714
H	-0.00364	2.71228	1.31679
H	0.00937	-3.74453	-0.65599
H	-0.01435	3.73993	-0.68168
H	3.74472	0.01412	0.65485
H	-3.73973	-0.00951	0.68282

XYZ of $Fe_2(TNC)_4$ BP86 geometry optimization with Fe-Fe distance of 2.48 Å.

Fe	-0.001488	0.011217	-1.239760
Fe	0.009574	-0.003965	1.241589
N	-0.039387	-2.016850	-0.575440
N	-1.930539	0.051883	-1.738995
N	1.922535	-0.022758	-1.757555
N	0.041564	2.031172	-0.550751
N	-2.017357	0.040357	0.572801
N	-0.025024	-1.933874	1.736516
N	0.049846	1.919576	1.759929
N	2.030716	-0.040546	0.553161
C	-0.046697	-2.627842	0.599478
C	2.628983	-0.045816	-0.628331
C	-2.626442	0.060296	-0.602977
C	0.059543	2.627626	0.631483
H	-0.061090	-2.679704	-1.352411
H	-2.505256	0.070280	-2.578052
H	2.489351	-0.030034	-2.602140
H	0.052749	2.703562	-1.319698
H	2.701873	-0.063218	1.322942
H	0.067112	2.485267	2.605120
H	-0.034407	-2.510058	2.574715
H	-2.681554	0.051954	1.348849
H	3.732006	-0.070336	-0.681850
H	-3.729933	0.084765	-0.645891
H	0.083366	3.730586	0.686480
H	-0.071864	-3.731371	0.640910

XYZ $Fe_2(TNC)_4$ TPSS geometry optimization with Fe-Fe distance of 2.48 Å.

Fe	-0.001401	0.011366	-1.237524
Fe	0.009729	-0.003897	1.238686
N	-0.038374	-2.003744	-0.568754
N	-1.928317	0.051909	-1.740509
N	1.920489	-0.022903	-1.759625
N	0.040853	2.018282	-0.544254
N	-2.004382	0.039460	0.566433

N	-0.025235	-1.931635	1.738359
N	0.049642	1.917429	1.761715
N	2.017670	-0.039713	0.546452
C	-0.046700	-2.622040	0.601035
C	2.623283	-0.045908	-0.629953
C	-2.620714	0.060161	-0.604271
C	0.059311	2.622004	0.632983
H	-0.059449	-2.664381	-1.345207
H	-2.504813	0.071322	-2.575783
H	2.489275	-0.031287	-2.600341
H	0.052095	2.688464	-1.312673
H	2.686595	-0.061895	1.315739
H	0.067306	2.484934	2.603157
H	-0.035597	-2.509639	2.572748
H	-2.666378	0.050369	1.341936
H	3.721093	-0.070735	-0.677607
H	-3.718934	0.084783	-0.641533
H	0.083180	3.719760	0.682219
H	-0.072048	-3.720296	0.636691

XYZ $Fe_2(TNC)_4$ BP/broken symmetry surface geometry optimization with Fe-Fe distance of 2.64 Å.

Fe	-0.002338	0.011992	-1.320416
Fe	0.010423	-0.004620	1.320205
N	-0.038691	-2.026384	-0.635763
N	-1.961590	0.052457	-1.695553
N	1.953311	-0.023943	-1.713887
N	0.040064	2.041747	-0.611279
N	-2.026917	0.038818	0.633063
N	-0.026300	-1.964424	1.692957
N	0.050133	1.950421	1.716514
N	2.041226	-0.039891	0.614018
C	-0.047059	-2.632019	0.540705
C	2.633666	-0.046377	-0.569177
C	-2.630861	0.060051	-0.544077
C	0.059299	2.632475	0.572615
H	-0.059382	-2.700944	-1.403241
H	-2.564791	0.073180	-2.514868
H	2.548647	-0.033865	-2.539149
H	0.051625	2.726016	-1.370314
H	2.724358	-0.061569	1.373854
H	0.069508	2.544527	2.542493
H	-0.037550	-2.568822	2.511579
H	-2.702595	0.049761	1.399759
H	3.738204	-0.071865	-0.612868

H	-3.735791	0.085461	-0.576656
H	0.084314	3.736971	0.617650
H	-0.072730	-3.736984	0.571957

XYZ $Fe_2(TNC)_4$ B3LYP geometry optimization with Fe-Fe distance of 2.73 Å.

Fe	-0.001488	0.011217	-1.239760
Fe	0.009574	-0.003965	1.241589
N	-0.039387	-2.016850	-0.575440
N	-1.930539	0.051883	-1.738995
N	1.922535	-0.022758	-1.757555
N	0.041564	2.031172	-0.550751
N	-2.017357	0.040357	0.572801
N	-0.025024	-1.933874	1.736516
N	0.049846	1.919576	1.759929
N	2.030716	-0.040546	0.553161
C	-0.046697	-2.627842	0.599478
C	2.628983	-0.045816	-0.628331
C	-2.626442	0.060296	-0.602977
C	0.059543	2.627626	0.631483
H	-0.061090	-2.679704	-1.352411
H	-2.505256	0.070280	-2.578052
H	2.489351	-0.030034	-2.602140
H	0.052749	2.703562	-1.319698
H	2.701873	-0.063218	1.322942
H	0.067112	2.485267	2.605120
H	-0.034407	-2.510058	2.574715
H	-2.681554	0.051954	1.348849
H	3.732006	-0.070336	-0.681850
H	-3.729933	0.084765	-0.645891
H	0.083366	3.730586	0.686480
H	-0.071864	-3.731371	0.640910