Supplementary Information for

Evaluation of CH_4 Oxidation Activity of High-Valent Iron-Oxo Species of A μ-Nitrido-Bridged Heterodimer of An Iron Porphycene and An Iron Phthalocyanine

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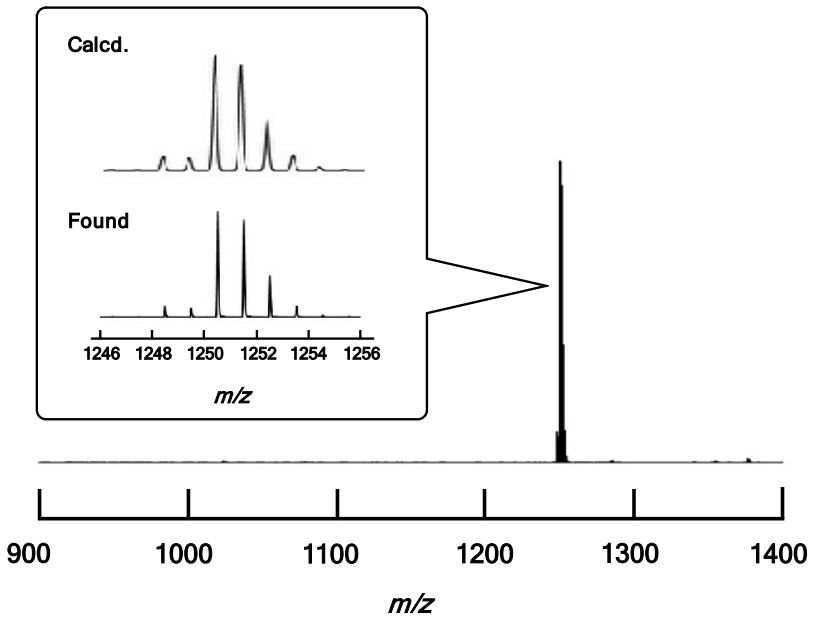

Figure S1. MALDI–TOF MS spectrum of $\mathbf{4}^{+}\cdot I_3^{-}$. Inset: Comparison of the calculated (top) and observed (bottom) spectrum of $\mathbf{4}^{+}$.

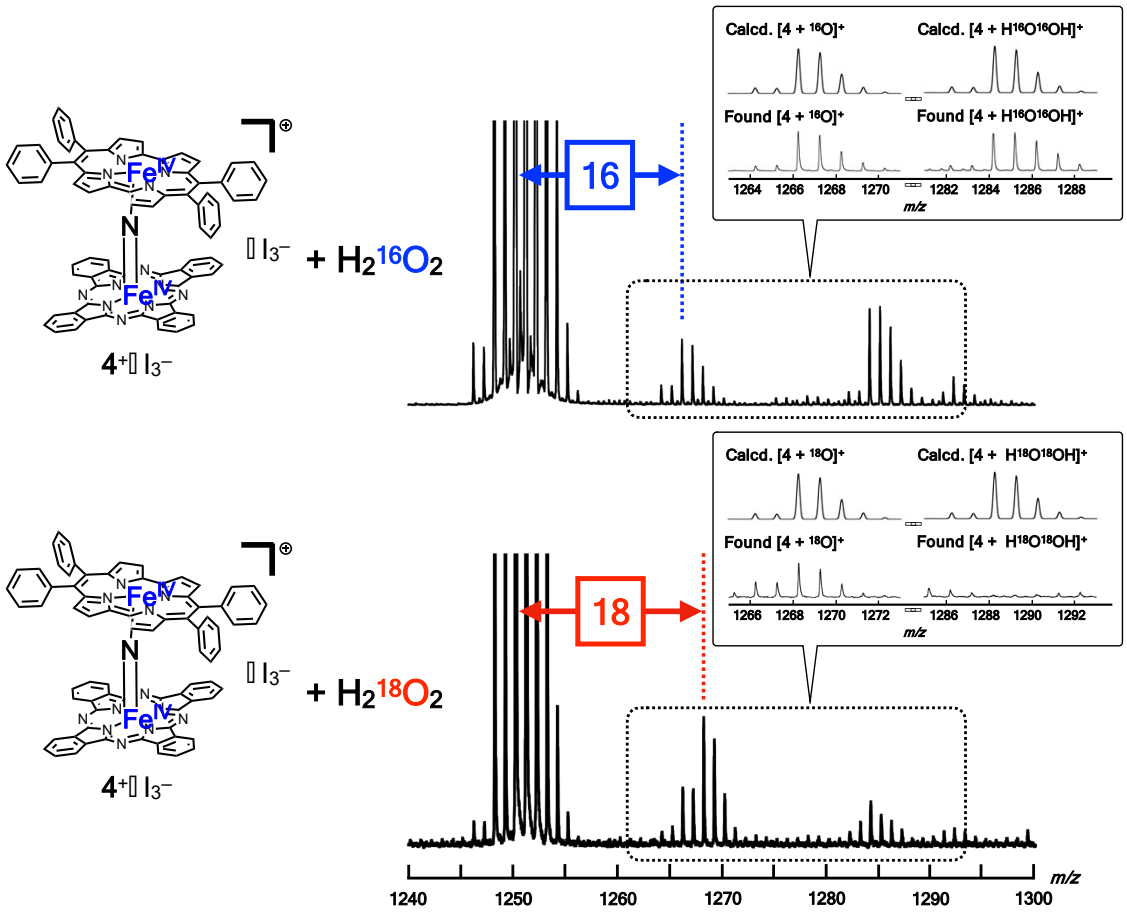

Figure S2. Comparison of ESI–TOF MS spectrum of $\mathbf{4}^{+}\cdot I_3^{-}$ in the presence of (a) $H_2{}^{16}O_2$ and (b) that in the presence of $H_2{}^{18}O_2$ in CH_3CN.

In the case of $H_2{}^{18}O_2$ experiment, to a solution of $\mathbf{4}^{+}\cdot I_3^{-}$ in CH_3CN (1.0 μM, 20 μL) was added 3% aqueous $H_2{}^{18}O_2$ (10 μL, 116 μmol). After addition, the resulting mixture was subjected to ESI-TOF MS measurement immediately.

DFT Calculation.

Table S1. Average bond lengths (in Angstrom) and spin population of **4**, **4**$^{+}$, and **4**$^{-}$, calculated with BP86.

	Bond length				Spin population				
	Fe1–N(Pc)	Fe1–N(Ppc)	Fe1–N(μ)	Fe1–N(μ)	Fe1	Fe1	N(μ)	Pc	Ppc
[Fe(Pc)–N–Fe(Ppc)]$^{+}$	1.948	1.939	1.607	1.582	0.00	0.00	0.00	0.00	0.00
[Fe(Pc)–N–Fe(Ppc)]$^{2+}$	1.946	1.938	1.612	1.578	0.04	0.06	−0.01	0.76	0.15
[Fe(Pc)–N–Fe(Ppc)]	1.950	1.973	1.649	1.600	0.52	0.46	−0.07	0.04	0.05

Table S2. Average bond lengths (in Angstrom) and spin population of **4**, **4**$^{+}$, and **4**$^{-}$, calculated with B3LYP.

	Bond length				Spin population				
	Fe1–N(Pc)	Fe1–N(Ppc)	Fe1–N(μ)	Fe1–N(μ)	Fe1	Fe1	N(μ)	Pc	Ppc
[Fe(Pc)–N–Fe(Ppc)]$^{+}$	1.951	1.938	1.616	1.602	0.85	−1.00	0.10	−0.02	0.07
[Fe(Pc)–N–Fe(Ppc)]$^{2+}$	1.948	1.940	1.626	1.616	−0.65	1.36	−0.29	0.94	−0.37
[Fe(Pc)–N–Fe(Ppc)]	1.966	1.972	1.719	1.605	1.91	−0.59	−0.30	−0.04	0.02

Table S3. Average bond lengths (in Angstrom) of the oxo species, calculated with BP86.

	Fe1–N(Pc)	Fe2–N(Ppc)	Fe1–N(μ)	Fe2–N(μ)	Fe–O
O=Fe(Pc)–N=Fe(Ppc)					
$Fe^{IV}Fe^{V}$	1.964	1.964	1.755	1.579	1.706
$Fe^{IV}Fe^{IV}(P^{\bullet+})$	1.957	1.963	1.769	1.579	1.702
O=Fe(Ppc)–N=Fe(Pc)					
$Fe^{IV}Fe^{V}$	1.947	1.966	1.598	1.726	1.684
$Fe^{IV}Fe^{IV}(P^{\bullet+})$	1.938	1.968	1.645	1.689	1.692

Table S4. Spin populations in the oxo species, calculated with BP86.

	Fe1	Fe2	N(μ)	O	Macrocycles
O=Fe(Pc)–N=Fe(Ppc)					
$Fe^{IV}Fe^{V}$	0.38	0.04	−0.11	0.69	0.01
$Fe^{IV}Fe^{IV}(P^{\bullet+})$	0.41	−0.24	−0.21	0.45	−1.41
O=Fe(Ppc)–N=Fe(Pc)					
$Fe^{IV}Fe^{V}$	0.09	0.31	−0.07	0.64	0.04
$Fe^{IV}Fe^{IV}(P^{\bullet+})$	0.10	0.19	−0.25	0.31	−1.26

Table S5. Relative energies (in kcal mol^{-1}) $\Delta E = E_{Fe(Pc)\text{-}oxo} - E_{Fe(Ppc)\text{-}oxo}$ and Gibbs free energies between the two oxo isomers. Both doublet states $Fe^{IV}Fe^{V}$ and $Fe^{IV}Fe^{IV}(P^{\bullet+})$ were considered.

	ΔE(gas)	$\Delta G^{\ominus}_{298}$(gas)	$\Delta G^{\ominus}_{298}$(pyridine)
$Fe^{IV}Fe^{V}$	−4.6	−4.3	−3.5
$Fe^{IV}Fe^{IV}(P^{\bullet+})$	−2.1	−2.4	−1.9

Table S6. Relative energies (in kcal mol^{-1}) $\Delta E = E_{Fe(Pc)\text{-}OOH} - E_{Fe(Ppc)\text{-}OOH}$ and Gibbs free energies between the two isomers.

	ΔE(gas)	$\Delta G^{\ominus}_{298}$(gas)	$\Delta G^{\ominus}_{298}$(pyridine)
BP86	−3.4	−3.4	−3.0

B3LYP[a]	−3.2	−3.2	−2.8

[a]Thermal corrections taken from BP86 results.

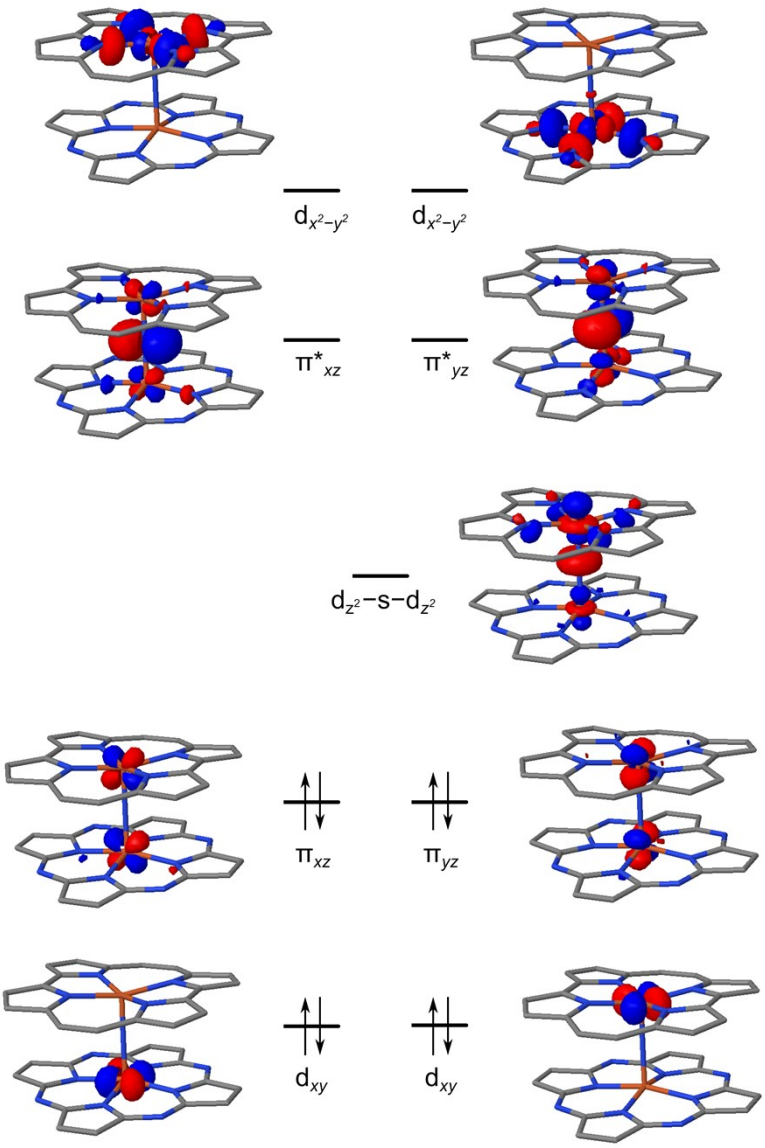

Figure S3. Important natural orbitals in $[Fe(Pc)–N–Fe(Ppc)]^+$.

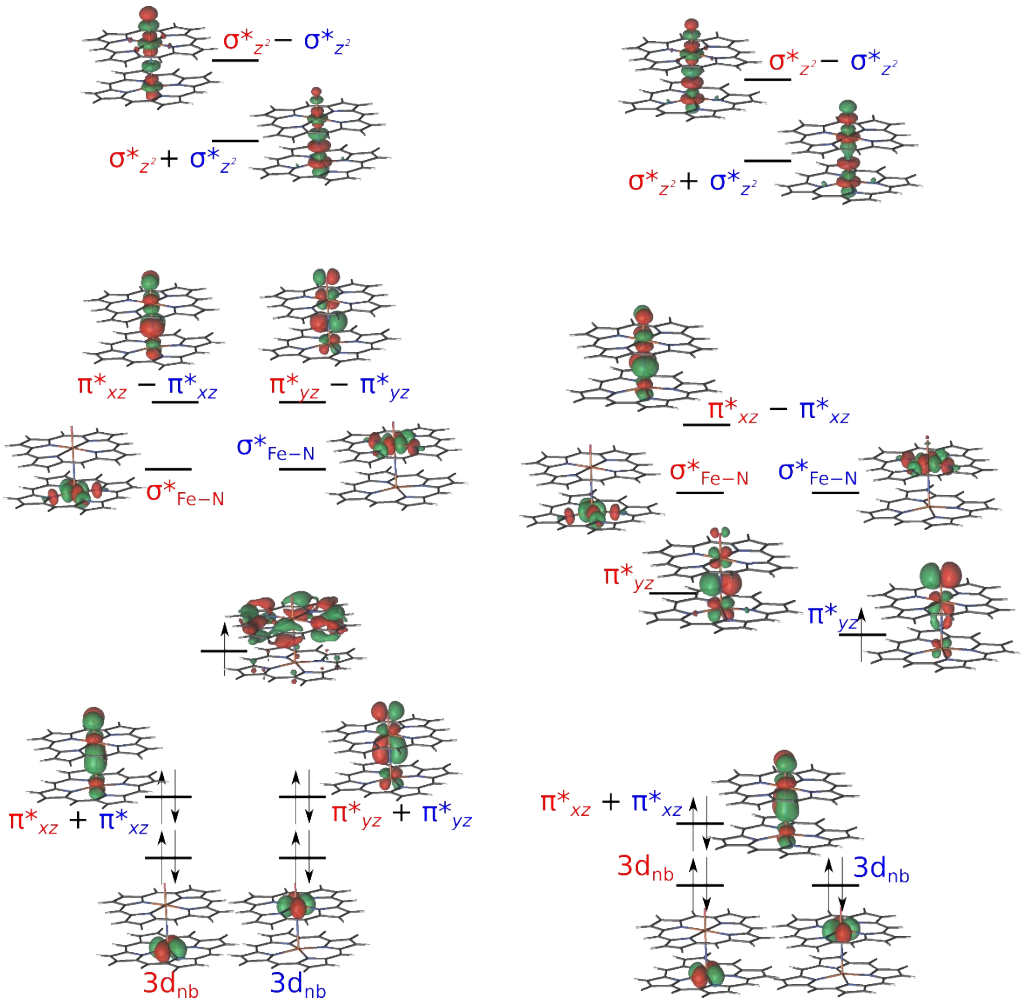

Figure S4. The electronic structure of two relevant doublet states of oxo, denoted as $Fe^{IV}Fe^{IV}(P^{\bullet+})$ and $Fe^{IV}Fe^{V}$.

Cartesian coordinates of the complexes, calculated with BP86-D3(BJ)/def2-TZVP

4^{+}

Fe	-0.0000000	0.0000000	1.8902979
N	1.6898058	-0.9542147	2.0808075
N	-1.6898058	0.9542147	2.0808075
N	-3.2404150	-0.8996384	1.8430212
N	0.8949264	-3.2333556	2.2870970
N	-0.8949264	3.2333556	2.2870970
N	-0.9602358	-1.6712438	2.1512175
N	0.9602358	1.6712438	2.1512175
N	3.2404150	0.8996384	1.8430212
C	3.2315075	-2.6641897	1.8411928
C	-2.3304718	-1.8383453	2.0555859
C	2.9392712	-0.3849158	1.8495095
C	-2.9392712	0.3849158	1.8495095
C	-1.8408712	2.3265059	2.0904996
C	0.3867071	2.9246609	2.3380495
C	-5.2812276	1.4160658	1.3724484
H	-5.8055855	0.4688224	1.2500211
C	-2.6603877	-3.2401806	2.2598331
C	-3.9185828	1.4435167	1.6714822
C	1.8408712	-2.3265059	2.0904996
C	-3.8486167	-5.2826124	2.5980944
H	-4.7819477	-5.8439790	2.6394160
C	2.6603877	3.2401806	2.2598331
C	2.3304718	1.8383453	2.0555859
C	-3.2315075	2.6641897	1.8411928
C	-0.3867071	-2.9246609	2.3380495
C	5.2812276	-1.4160658	1.3724484
H	5.8055855	-0.4688224	1.2500211
C	3.9185828	-1.4435167	1.6714822
C	-1.4410984	-3.9139427	2.4874864

C	1.4410984	3.9139427	2.4874864
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H	4.8153077	3.3941394	2.1158270
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H	-3.3517155	4.8276916	1.8391068
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H	-4.8153077	-3.3941394	2.1158270
C	-2.6348044	-5.9498008	2.8506504
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H	-0.4708444	-5.7886578	2.9811898
C	3.8486167	5.2826124	2.5980944
H	4.7819477	5.8439790	2.6394160
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H	0.4708444	5.7886578	2.9811898
C	5.9347727	-2.6415427	1.2306029
H	6.9980002	-2.6605572	0.9901169
C	2.6348044	5.9498008	2.8506504
H	2.6511356	7.0128717	3.0909798
C	3.8880124	-3.8881797	1.7124452
H	3.3517155	-4.8276916	1.8391068
C	5.2474779	-3.8600867	1.3976645
H	5.7918772	-4.7971920	1.2800261
C	-5.2474779	3.8600867	1.3976645
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N	1.1591837	-1.5300522	-1.5844420
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C	2.4827378	-1.1563468	-1.6386459
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C	2.5050045	-3.3858088	-1.4880706
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C	3.9143993	0.9976973	-1.6453121
H	4.9288190	0.6129953	-1.6530883
C	2.2131933	4.7682273	-1.7009851
C	2.7250232	0.2163885	-1.6620363
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H	4.1387616	3.1877815	-1.5672852
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4^{2+}

Fe	-0.0000000	0.0000000	1.8736062
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N	-1.7078840	0.9196841	2.0619462
N	-3.2244697	-0.9595060	1.8301611
N	0.9540103	-3.2159130	2.2478549
N	-0.9540103	3.2159130	2.2478549
N	-0.9266514	-1.6897449	2.1164153
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C	-2.3006239	-1.8792320	2.0514618
C	2.9429920	-0.3327480	1.8208916
C	-2.9429920	0.3327480	1.8208916
C	-1.8826476	2.2934609	2.0561161
C	0.3352557	2.9290523	2.3057234
C	-5.3037954	1.3191228	1.3377442
H	-5.8145139	0.3639959	1.2195523
C	-2.6051925	-3.2842725	2.2900667
C	-3.9432121	1.3743333	1.6276531
C	1.8826476	-2.2934609	2.0561161
C	-3.7514921	-5.3365424	2.7040093
H	-4.6760274	-5.9065763	2.7912615
C	2.6051925	3.2842725	2.2900667
C	2.3006239	1.8792320	2.0514618
C	-3.2798226	2.6065040	1.7977913

C	-0.3352557	-2.9290523	2.3057234
C	5.3037954	-1.3191228	1.3377442
H	5.8145139	-0.3639959	1.2195523
C	3.9432121	-1.3743333	1.6276531
C	-1.3711604	-3.9358915	2.4925377
C	1.3711604	3.9358915	2.4925377
C	3.8109617	3.9744063	2.3818001
H	4.7618609	3.4693599	2.2172105
C	-3.9576739	3.8177008	1.6856678
H	-3.4423724	4.7670453	1.8245374
C	-3.8109617	-3.9744063	2.3818001
H	-4.7618609	-3.4693599	2.2172105
C	-2.5243043	-5.9804326	2.9266764
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H	-4.9329844	-0.5643788	-1.6770486
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C	1.1040214	-2.9302596	-1.4880795
C	2.4677117	-1.1815088	-1.6700887
C	-2.0802031	-2.3224160	-1.5885643
C	2.4721951	-3.4120253	-1.5433280
H	2.7511262	-4.4584919	-1.5307850
C	-1.1040214	2.9302596	-1.4880795
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H	4.9329844	0.5643788	-1.6770486
C	2.2649791	4.7476497	-1.6741742
C	2.7238159	0.1925612	-1.6887576
C	3.3092194	-2.3323129	-1.6553894
H	4.3916004	-2.3334572	-1.7306462
C	3.5320815	2.2710291	-1.5854282
H	4.1724068	3.1431884	-1.5304325
C	-2.4677117	1.1815088	-1.6700887
C	-0.3917776	5.2514118	-1.2691002
C	-0.8536967	5.7182642	-0.0300582
H	-0.9522960	5.0204185	0.8022096
C	1.1658138	-7.0682763	0.1397702
H	1.5086178	-7.4276004	1.1109173
C	-2.4721951	3.4120253	-1.5433280
H	-2.7511262	4.4584919	-1.5307850

C	-1.0449683	7.9566316	-0.9304769
H	-1.2912157	9.0102286	-0.7990198
C	0.3917776	-5.2514118	-1.2691002
C	3.8603517	7.0266960	-2.0185653
H	4.4723764	7.9184179	-2.1531964
C	1.3836986	3.5437544	-1.5379562
C	-0.0083836	3.8085937	-1.4210421
C	0.8536967	-5.7182642	-0.0300582
H	0.9522960	-5.0204185	0.8022096
C	-3.3092194	2.3323129	-1.6553894
H	-4.3916004	2.3334572	-1.7306462
C	0.0083836	-3.8085937	-1.4210421
C	-1.1658138	7.0682763	0.1397702
H	-1.5086178	7.4276004	1.1109173
C	1.0449683	-7.9566316	-0.9304769
H	1.2912157	-9.0102286	-0.7990198
C	-1.3836986	-3.5437544	-1.5379562
C	-2.4844698	-5.6240739	-0.6056148
H	-2.0154494	-5.4260050	0.3546089
C	3.6475394	6.1556719	-3.0893553
H	4.0921211	6.3642355	-4.0624867
C	-3.8603517	-7.0266960	-2.0185653
H	-4.4723764	-7.9184179	-2.1531964
C	-2.8632778	-5.0143048	-2.9165316
H	-2.6903421	-4.3357410	-3.7530528
C	3.2846420	6.7513982	-0.7737451
H	3.4524371	7.4239379	0.0676477
C	2.4844698	5.6240739	-0.6056148
H	2.0154494	5.4260050	0.3546089
C	-0.6184053	7.4871866	-2.1769320
H	-0.5421949	8.1714974	-3.0218471
C	-0.2875449	6.1440839	-2.3451335
H	0.0543126	5.7849274	-3.3152547

C	0.2875449	-6.1440839	-2.3451335
H	-0.0543126	-5.7849274	-3.3152547
C	0.6184053	-7.4871866	-2.1769320
H	0.5421949	-8.1714974	-3.0218471
C	2.8632778	5.0143048	-2.9165316
H	2.6903421	4.3357410	-3.7530528
C	-3.6475394	-6.1556719	-3.0893553
H	-4.0921211	-6.3642355	-4.0624867
C	-3.2846420	-6.7513982	-0.7737451
H	-3.4524371	-7.4239379	0.0676477
N	-0.0000000	0.0000000	0.2620565

4

Fe	-0.0000000	0.0000000	1.9295025
N	1.6985325	-0.9471682	2.0942958
N	-1.6985325	0.9471682	2.0942958
N	-3.2377785	-0.9180617	1.9097159
N	0.9142650	-3.2319540	2.2785199
N	-0.9142650	3.2319540	2.2785199
N	-0.9491030	-1.6804944	2.1837240
N	0.9491030	1.6804944	2.1837240
N	3.2377785	0.9180617	1.9097159
C	3.2442768	-2.6470701	1.8112666
C	-2.3206347	-1.8483957	2.1224765
C	2.9368188	-0.3704728	1.8791341
C	-2.9368188	0.3704728	1.8791341
C	-1.8532977	2.3177123	2.0838112
C	0.3706552	2.9239696	2.3558807
C	-5.2798292	1.3788967	1.3411449
H	-5.7939914	0.4246828	1.2275568
C	-2.6436613	-3.2530164	2.3354179
C	-3.9237110	1.4190244	1.6640885
C	1.8532977	-2.3177123	2.0838112

C	-3.8149291	-5.3065500	2.6812352
H	-4.7451484	-5.8726188	2.7373681
C	2.6436613	3.2530164	2.3354179
C	2.3206347	1.8483957	2.1224765
C	-3.2442768	2.6470701	1.8112666
C	-0.3706552	-2.9239696	2.3558807
C	5.2798292	-1.3788967	1.3411449
H	5.7939914	-0.4246828	1.2275568
C	3.9237110	-1.4190244	1.6640885
C	-1.4159417	-3.9239408	2.5230138
C	1.4159417	3.9239408	2.5230138
C	3.8564038	3.9390540	2.3999395
H	4.7983393	3.4159822	2.2377316
C	-3.9048741	3.8629319	1.6380806
H	-3.3709378	4.8071690	1.7397343
C	-3.8564038	-3.9390540	2.3999395
H	-4.7983393	-3.4159822	2.2377316
C	-2.5923421	-5.9711327	2.8927113
H	-2.5962856	-7.0386377	3.1150613
C	-5.9385563	2.5970842	1.1577615
H	-6.9971489	2.6034581	0.8950947
C	-1.3757684	-5.2895338	2.8087551
H	-0.4253991	-5.7998944	2.9600318
C	3.8149291	5.3065500	2.6812352
H	4.7451484	5.8726188	2.7373681
C	1.3757684	5.2895338	2.8087551
H	0.4253991	5.7998944	2.9600318
C	5.9385563	-2.5970842	1.1577615
H	6.9971489	-2.6034581	0.8950947
C	2.5923421	5.9711327	2.8927113
H	2.5962856	7.0386377	3.1150613
C	3.9048741	-3.8629319	1.6380806
H	3.3709378	-4.8071690	1.7397343

C	5.2600741	-3.8222503	1.3047624
H	5.8046118	-4.7543919	1.1501019
C	-5.2600741	3.8222503	1.3047624
H	-5.8046118	4.7543919	1.1501019
Fe	-0.0000000	0.0000000	-1.3193067
N	-1.1919707	1.5432599	-1.6197829
N	1.6533958	1.0186536	-1.6592950
N	1.1919707	-1.5432599	-1.6197829
N	-1.6533958	-1.0186536	-1.6592950
C	-3.9572463	-0.9919464	-1.6656904
H	-4.9736464	-0.6117130	-1.6657602
C	2.0917182	2.3244245	-1.6164370
C	-3.5459271	-2.3012922	-1.6178332
H	-4.1745290	-3.1828622	-1.5761568
C	-2.7701244	-0.2039503	-1.6904696
C	1.1459450	-2.9164337	-1.5163524
C	2.5218211	-1.1733169	-1.6784517
C	-2.0917182	-2.3244245	-1.6164370
C	2.5150279	-3.4066595	-1.5453023
H	2.7959464	-4.4522171	-1.5051519
C	-1.1459450	2.9164337	-1.5163524
C	-2.2262234	-4.7553239	-1.6841217
C	3.9572463	0.9919464	-1.6656904
H	4.9736464	0.6117130	-1.6657602
C	2.2262234	4.7553239	-1.6841217
C	2.7701244	0.2039503	-1.6904696
C	3.3580601	-2.3281518	-1.6488387
H	4.4425890	-2.3331952	-1.6777202
C	3.5459271	2.3012922	-1.6178332
H	4.1745290	3.1828622	-1.5761568
C	-2.5218211	1.1733169	-1.6784517
C	-0.4179742	5.2314262	-1.2907440
C	-0.8274956	5.6910508	-0.0323492

H	-0.8769828	4.9890647	0.8020714
C	1.1626605	-7.0335891	0.1535148
H	1.4702567	-7.3811019	1.1413199
C	-2.5150279	3.4066595	-1.5453023
H	-2.7959464	4.4522171	-1.5051519
C	-1.1027101	7.9289742	-0.9163535
H	-1.3591741	8.9789947	-0.7701117
C	0.4179742	-5.2314262	-1.2907440
C	3.8059342	7.0582493	-1.9836094
H	4.4129146	7.9569338	-2.1002846
C	1.3549328	3.5347414	-1.5652111
C	-0.0294713	3.7866945	-1.4597542
C	0.8274956	-5.6910508	-0.0323492
H	0.8769828	-4.9890647	0.8020714
C	-3.3580601	2.3281518	-1.6488387
H	-4.4425890	2.3331952	-1.6777202
C	0.0294713	-3.7866945	-1.4597542
C	-1.1626605	7.0335891	0.1535148
H	-1.4702567	7.3811019	1.1413199
C	1.1027101	-7.9289742	-0.9163535
H	1.3591741	-8.9789947	-0.7701117
C	-1.3549328	-3.5347414	-1.5652111
C	-2.4955456	-5.5781625	-0.5865095
H	-2.0767510	-5.3264224	0.3842661
C	3.5522594	6.2349348	-3.0834902
H	3.9617666	6.4861218	-4.0628588
C	-3.8059342	-7.0582493	-1.9836094
H	-4.4129146	-7.9569338	-2.1002846
C	-2.7713326	-5.0878344	-2.9324610
H	-2.5687219	-4.4437888	-3.7896214
C	3.2800815	6.7210260	-0.7338780
H	3.4773000	7.3498870	0.1349615
C	2.4955456	5.5781625	-0.5865095

H	2.0767510	5.3264224	0.3842661
C	-0.7171594	7.4699328	-2.1790471
H	-0.6765586	8.1593725	-3.0232303
C	-0.3793188	6.1294731	-2.3649010
H	-0.0702651	5.7750261	-3.3482280
C	0.3793188	-6.1294731	-2.3649010
H	0.0702651	-5.7750261	-3.3482280
C	0.7171594	-7.4699328	-2.1790471
H	0.6765586	-8.1593725	-3.0232303
C	2.7713326	5.0878344	-2.9324610
H	2.5687219	4.4437888	-3.7896214
C	-3.5522594	-6.2349348	-3.0834902
H	-3.9617666	-6.4861218	-4.0628588
C	-3.2800815	-6.7210260	-0.7338780
H	-3.4773000	-7.3498870	0.1349615
N	-0.0000000	0.0000000	0.2807195

O=Fe(Pc)-N-Fe(Ppc) $Fe^{IV}Fe^{V}$

Fe	-0.0000000	0.0000000	2.0876326
N	-0.6183733	-1.8607786	2.0223950
N	0.6183733	1.8607786	2.0223950
N	-1.5159404	3.0025860	1.8374313
N	-3.0088532	-1.5113380	2.2248846
N	3.0088532	1.5113380	2.2248846
N	-1.8649519	0.6185889	2.1004619
N	1.8649519	-0.6185889	2.1004619
N	1.5159404	-3.0025860	1.8374313
C	-1.9879732	-3.6968254	1.7789130
C	-2.2690760	1.9285060	2.0300689
C	0.1916154	-2.9536261	1.8190197
C	-0.1916154	2.9536261	1.8190197
C	1.9320842	2.2616662	2.0327903
C	2.9610093	0.1870171	2.2789766

C	0.3549768	5.4558428	1.3195256
H	-0.6798361	5.7790795	1.2063436
C	-3.7163164	1.9846627	2.2256784
C	0.6522369	4.1290859	1.6269802
C	-1.9320842	-2.2616662	2.0327903
C	-5.9518564	2.7540477	2.5774451
H	-6.6804228	3.5633834	2.6333356
C	3.7163164	-1.9846627	2.2256784
C	2.2690760	-1.9285060	2.0300689
C	1.9879732	3.6968254	1.7789130
C	-2.9610093	-0.1870171	2.2789766
C	-0.3549768	-5.4558428	1.3195256
H	0.6798361	-5.7790795	1.2063436
C	-0.6522369	-4.1290859	1.6269802
C	-4.1454960	0.6534574	2.4276800
C	4.1454960	-0.6534574	2.4276800
C	4.6172750	-3.0465609	2.2818914
H	4.2797098	-4.0687015	2.1124915
C	3.0537457	4.5823624	1.6272745
H	4.0823680	4.2403890	1.7376066
C	-4.6172750	3.0465609	2.2818914
H	-4.2797098	4.0687015	2.1124915
C	-6.3731712	1.4326617	2.8111227
H	-7.4191740	1.2397905	3.0516876
C	1.4245714	6.3406837	1.1565345
H	1.2280054	7.3849047	0.9100029
C	-5.4760140	0.3634457	2.7295806
H	-5.7976039	-0.6630066	2.9020663
C	5.9518564	-2.7540477	2.5774451
H	6.6804228	-3.5633834	2.6333356
C	5.4760140	-0.3634457	2.7295806
H	5.7976039	0.6630066	2.9020663
C	-1.4245714	-6.3406837	1.1565345

H	-1.2280054	-7.3849047	0.9100029
C	6.3731712	-1.4326617	2.8111227
H	7.4191740	-1.2397905	3.0516876
C	-3.0537457	-4.5823624	1.6272745
H	-4.0823680	-4.2403890	1.7376066
C	-2.7558081	-5.9095210	1.3091056
H	-3.5667722	-6.6263400	1.1752690
C	2.7558081	5.9095210	1.3091056
H	3.5667722	6.6263400	1.1752690
Fe	0.0000000	0.0000000	-1.2455410
N	1.2627280	1.4616578	-1.5664183
N	1.3333693	-1.4155471	-1.5561295
N	-1.2627280	-1.4616578	-1.5664183
N	-1.3333693	1.4155471	-1.5561295
C	-1.7656297	3.6781794	-1.6046978
H	-1.5937477	4.7494102	-1.6186755
C	2.7036607	-1.5877292	-1.5417624
C	-2.9675670	3.0162499	-1.5639550
H	-3.9572167	3.4563142	-1.5409963
C	-0.7584140	2.6718125	-1.6055290
C	-2.6264308	-1.6892387	-1.4820784
C	-0.6387611	-2.6977169	-1.6166497
C	-2.7036607	1.5877292	-1.5417624
C	-2.8316468	-3.1248024	-1.5275318
H	-3.8014825	-3.6063171	-1.5031923
C	2.6264308	1.6892387	-1.4820784
C	-5.1080615	1.2352173	-1.6979332
C	1.7656297	-3.6781794	-1.6046978
H	1.5937477	-4.7494102	-1.6186755
C	5.1080615	-1.2352173	-1.6979332
C	0.7584140	-2.6718125	-1.6055290
C	-1.6064579	-3.7395338	-1.6136559
H	-1.3985899	-4.8038510	-1.6426712

C	2.9675670	-3.0162499	-1.5639550
H	3.9572167	-3.4563142	-1.5409963
C	0.6387611	2.6977169	-1.6166497
C	5.0456204	1.4546783	-1.2944586
C	5.4386751	1.9478278	-0.0437151
H	4.7576904	1.8554524	0.8047456
C	-6.6909096	-2.5447800	0.1142788
H	-6.9909410	-2.9155800	1.0957802
C	2.8316468	3.1248024	-1.5275318
H	3.8014825	3.6063171	-1.5031923
C	7.5568913	2.6646839	-0.9744890
H	8.5372582	3.1258652	-0.8490985
C	-5.0456204	-1.4546783	-1.2944586
C	7.6659111	-2.3180234	-2.1039179
H	8.6623255	-2.7324413	-2.2617659
C	3.7426725	-0.6289271	-1.5264035
C	3.7075440	0.7789313	-1.4326552
C	-5.4386751	-1.9478278	-0.0437151
H	-4.7576904	-1.8554524	0.8047456
C	1.6064579	3.7395338	-1.6136559
H	1.3985899	4.8038510	-1.6426712
C	-3.7075440	-0.7789313	-1.4326552
C	6.6909096	2.5447800	0.1142788
H	6.9909410	2.9155800	1.0957802
C	-7.5568913	-2.6646839	-0.9744890
H	-8.5372582	-3.1258652	-0.8490985
C	-3.7426725	0.6289271	-1.5264035
C	-6.0137648	1.3276009	-0.6378599
H	-5.7245748	0.9657680	0.3448815
C	6.7626130	-2.2389295	-3.1668544
H	7.0493991	-2.5924085	-4.1581288
C	-7.6659111	2.3180234	-2.1039179
H	-8.6623255	2.7324413	-2.2617659

C	-5.4889913	1.7055250	-2.9630364
H	-4.7814491	1.6398845	-3.7910993
C	7.2835101	-1.8667740	-0.8382346
H	7.9749930	-1.9312739	0.0025075
C	6.0137648	-1.3276009	-0.6378599
H	5.7245748	-0.9657680	0.3448815
C	7.1580181	2.1949492	-2.2291441
H	7.8237675	2.2924677	-3.0874331
C	5.9090344	1.5950987	-2.3883093
H	5.6035088	1.2192383	-3.3647547
C	-5.9090344	-1.5950987	-2.3883093
H	-5.6035088	-1.2192383	-3.3647547
C	-7.1580181	-2.1949492	-2.2291441
H	-7.8237675	-2.2924677	-3.0874331
C	5.4889913	-1.7055250	-2.9630364
H	4.7814491	-1.6398845	-3.7910993
C	-6.7626130	2.2389295	-3.1668544
H	-7.0493991	2.5924085	-4.1581288
C	-7.2835101	1.8667740	-0.8382346
H	-7.9749930	1.9312739	0.0025075
N	0.0000000	-0.0000000	0.3329789
O	0.0000000	-0.0000000	3.7938862

O=Fe(Pc)-N-Fe(Ppc) $Fe^{IV}Fe^{IV}(P^{\bullet+})$

Fe	0.0000000	-0.0000000	2.1036149
N	-0.5902054	-1.8623134	2.0241648
N	0.5902054	1.8623134	2.0241648
N	-1.5443561	2.9956105	1.8241999
N	-2.9838383	-1.5366408	2.2225675
N	2.9838383	1.5366408	2.2225675
N	-1.8619838	0.6049038	2.0741044
N	1.8619838	-0.6049038	2.0741044
N	1.5443561	-2.9956105	1.8241999

C	-1.9528163	-3.7107756	1.7439139
C	-2.2844267	1.9078750	2.0089033
C	0.2204737	-2.9489797	1.7981836
C	-0.2204737	2.9489797	1.7981836
C	1.9004613	2.2727729	2.0198345
C	2.9493348	0.2099203	2.2610764
C	0.3119322	5.4527215	1.2731180
H	-0.7243012	5.7686474	1.1541020
C	-3.7346883	1.9509815	2.2157133
C	0.6186482	4.1326069	1.5827352
C	-1.9004613	-2.2727729	2.0198345
C	-5.9734502	2.6961601	2.5944125
H	-6.7081624	3.4988544	2.6610622
C	3.7346883	-1.9509815	2.2157133
C	2.2844267	-1.9078750	2.0089033
C	1.9528163	3.7107756	1.7439139
C	-2.9493348	-0.2099203	2.2610764
C	-0.3119322	-5.4527215	1.2731180
H	0.7243012	-5.7686474	1.1541020
C	-0.6186482	-4.1326069	1.5827352
C	-4.1469418	0.6167330	2.4195962
C	4.1469418	-0.6167330	2.4195962
C	4.6419910	-3.0026890	2.2824008
H	4.3172191	-4.0279520	2.1075603
C	3.0127208	4.5989186	1.6019507
H	4.0424174	4.2635966	1.7210965
C	-4.6419910	3.0026890	2.2824008
H	-4.3172191	4.0279520	2.1075603
C	-6.3780217	1.3729218	2.8271093
H	-7.4190413	1.1673817	3.0777505
C	1.3790026	6.3482449	1.1173041
H	1.1754905	7.3903416	0.8681538
C	-5.4685113	0.3106923	2.7313841

H	-5.7787148	-0.7194656	2.9016137
C	5.9734502	-2.6961601	2.5944125
H	6.7081624	-3.4988544	2.6610622
C	5.4685113	-0.3106923	2.7313841
H	5.7787148	0.7194656	2.9016137
C	-1.3790026	-6.3482449	1.1173041
H	-1.1754905	-7.3903416	0.8681538
C	6.3780217	-1.3729218	2.8271093
H	7.4190413	-1.1673817	3.0777505
C	-3.0127208	-4.5989186	1.6019507
H	-4.0424174	-4.2635966	1.7210965
C	-2.7081157	-5.9278980	1.2806452
H	-3.5159945	-6.6490363	1.1528969
C	2.7081157	5.9278980	1.2806452
H	3.5159945	6.6490363	1.1528969
Fe	0.0000000	0.0000000	-1.2629762
N	1.2819620	1.4683204	-1.5180698
N	1.3191192	-1.4217170	-1.5465123
N	-1.2819620	-1.4683204	-1.5180698
N	-1.3191192	1.4217170	-1.5465123
C	-1.7431179	3.6862229	-1.5641070
H	-1.5682752	4.7570860	-1.5673321
C	2.6893543	-1.5976710	-1.5244579
C	-2.9483829	3.0271978	-1.5286776
H	-3.9354518	3.4723216	-1.4909460
C	-0.7402287	2.6757405	-1.5779993
C	-2.6427168	-1.6910966	-1.4581149
C	-0.6623674	-2.7007106	-1.5833335
C	-2.6893543	1.5976710	-1.5244579
C	-2.8576086	-3.1252559	-1.5262185
H	-3.8294197	-3.6037483	-1.5277415
C	2.6427168	1.6910966	-1.4581149
C	-5.0952157	1.2602849	-1.6831892

C	1.7431179	-3.6862229	-1.5641070
H	1.5682752	-4.7570860	-1.5673321
C	5.0952157	-1.2602849	-1.6831892
C	0.7402287	-2.6757405	-1.5779993
C	-1.6317715	-3.7423683	-1.6074786
H	-1.4263614	-4.8064996	-1.6573636
C	2.9483829	-3.0271978	-1.5286776
H	3.9354518	-3.4723216	-1.4909460
C	0.6623674	2.7007106	-1.5833335
C	5.0594285	1.4327739	-1.2891163
C	5.4546816	1.9515234	-0.0491148
H	4.7704293	1.8822598	0.7984010
C	-6.7105571	-2.5429258	0.1002246
H	-7.0114622	-2.9323426	1.0743772
C	2.8576086	3.1252559	-1.5262185
H	3.8294197	3.6037483	-1.5277415
C	7.5795631	2.6343813	-0.9890927
H	8.5628625	3.0913885	-0.8714445
C	-5.0594285	-1.4327739	-1.2891163
C	7.6452095	-2.3648321	-2.0943238
H	8.6380669	-2.7868587	-2.2545221
C	3.7351388	-0.6416665	-1.5097242
C	3.7158041	0.7660526	-1.4140360
C	-5.4546816	-1.9515234	-0.0491148
H	-4.7704293	-1.8822598	0.7984010
C	1.6317715	3.7423683	-1.6074786
H	1.4263614	4.8064996	-1.6573636
C	-3.7158041	-0.7660526	-1.4140360
C	6.7105571	2.5429258	0.1002246
H	7.0114622	2.9323426	1.0743772
C	-7.5795631	-2.6343813	-0.9890927
H	-8.5628625	-3.0913885	-0.8714445
C	-3.7351388	0.6416665	-1.5097242

C	-6.0139690	1.3345907	-0.6328166
H	-5.7385392	0.9463110	0.3434607
C	6.7300545	-2.3035941	-3.1482254
H	7.0041380	-2.6789844	-4.1350701
C	-7.6452095	2.3648321	-2.0943238
H	-8.6380669	2.7868587	-2.2545221
C	-5.4612564	1.7595561	-2.9416935
H	-4.7448759	1.7077761	-3.7630004
C	7.2789945	-1.8842109	-0.8345414
H	7.9807061	-1.9323135	-0.0010708
C	6.0139690	-1.3345907	-0.6328166
H	5.7385392	-0.9463110	0.3434607
C	7.1787361	2.1423184	-2.2345176
H	7.8460382	2.2188072	-3.0937840
C	5.9260877	1.5474058	-2.3835779
H	5.6194446	1.1544910	-3.3528615
C	-5.9260877	-1.5474058	-2.3835779
H	-5.6194446	-1.1544910	-3.3528615
C	-7.1787361	-2.1423184	-2.2345176
H	-7.8460382	-2.2188072	-3.0937840
C	5.4612564	-1.7595561	-2.9416935
H	4.7448759	-1.7077761	-3.7630004
C	-6.7300545	2.3035941	-3.1482254
H	-7.0041380	2.6789844	-4.1350701
C	-7.2789945	1.8842109	-0.8345414
H	-7.9807061	1.9323135	-0.0010708
N	0.0000000	-0.0000000	0.3342910
O	0.0000000	-0.0000000	3.8051867

O=Fe(Ppc)-N-Fe(Pc) $Fe^{IV}Fe^{V}$

Fe	-0.0000000	0.0000000	1.8390862
N	-0.5983308	-1.8398171	2.0619177
N	0.5983308	1.8398171	2.0619177

N	-1.5244341	3.0087386	1.9134128
N	-2.9969475	-1.5186877	2.2378293
N	2.9969475	1.5186877	2.2378293
N	-1.8300443	0.6068458	2.1013686
N	1.8300443	-0.6068458	2.1013686
N	1.5244341	-3.0087386	1.9134128
C	-1.9655705	-3.7071304	1.9313467
C	-2.2625728	1.9227790	2.0523184
C	0.2046696	-2.9599017	1.9136802
C	-0.2046696	2.9599017	1.9136802
C	1.9163535	2.2645531	2.0881408
C	2.9448931	0.1994879	2.2668854
C	0.3262301	5.4860416	1.5834933
H	-0.7090338	5.8108508	1.4830739
C	-3.7046162	1.9656791	2.2358847
C	0.6311995	4.1428089	1.8054377
C	-1.9163535	-2.2645531	2.0881408
C	-5.9450870	2.7204744	2.5661346
H	-6.6814297	3.5230106	2.6128928
C	3.7046162	-1.9656791	2.2358847
C	2.2625728	-1.9227790	2.0523184
C	1.9655705	3.7071304	1.9313467
C	-2.9448931	-0.1994879	2.2668854
C	-0.3262301	-5.4860416	1.5834933
H	0.7090338	-5.8108508	1.4830739
C	-0.6311995	-4.1428089	1.8054377
C	-4.1269120	0.6330449	2.4186749
C	4.1269120	-0.6330449	2.4186749
C	4.6103794	-3.0251822	2.2934271
H	4.2765095	-4.0495187	2.1323866
C	3.0312815	4.6024657	1.8382463
H	4.0604869	4.2551079	1.9201408
C	-4.6103794	3.0251822	2.2934271

H	-4.2765095	4.0495187	2.1323866
C	-6.3614753	1.3928663	2.7827858
H	-7.4106732	1.1921581	3.0011034
C	1.3930022	6.3799663	1.4782667
H	1.1948841	7.4360588	1.2919620
C	-5.4594236	0.3299390	2.7047695
H	-5.7775932	-0.7002088	2.8586269
C	5.9450870	-2.7204744	2.5661346
H	6.6814297	-3.5230106	2.6128928
C	5.4594236	-0.3299390	2.7047695
H	5.7775932	0.7002088	2.8586269
C	-1.3930022	-6.3799663	1.4782667
H	-1.1948841	-7.4360588	1.2919620
C	6.3614753	-1.3928663	2.7827858
H	7.4106732	-1.1921581	3.0011034
C	-3.0312815	-4.6024657	1.8382463
H	-4.0604869	-4.2551079	1.9201408
C	-2.7271776	-5.9437320	1.6046347
H	-3.5348329	-6.6702849	1.5106117
C	2.7271776	5.9437320	1.6046347
H	3.5348329	6.6702849	1.5106117
Fe	0.0000000	-0.0000000	-1.4851678
N	1.2833334	1.4857354	-1.4154064
N	1.3494464	-1.4325907	-1.4704883
N	-1.2833334	-1.4857354	-1.4154064
N	-1.3494464	1.4325907	-1.4704883
C	-1.7668746	3.6864968	-1.3777197
H	-1.5909816	4.7551868	-1.3096357
C	2.7050969	-1.5962513	-1.4814080
C	-2.9713125	3.0302855	-1.4150152
H	-3.9604441	3.4715622	-1.3773610
C	-0.7603124	2.6700540	-1.4216647
C	-2.6343965	-1.7037778	-1.3831177

C	-0.6400564	-2.6994244	-1.4085564
C	-2.7050969	1.5962513	-1.4814080
C	-2.8343986	-3.1482002	-1.3723715
H	-3.8016352	-3.6359858	-1.3608806
C	2.6343965	1.7037778	-1.3831177
C	-5.0979018	1.2422779	-1.7195294
C	1.7668746	-3.6864968	-1.3777197
H	1.5909816	-4.7551868	-1.3096357
C	5.0979018	-1.2422779	-1.7195294
C	0.7603124	-2.6700540	-1.4216647
C	-1.6033887	-3.7549329	-1.3881155
H	-1.3860494	-4.8179043	-1.3742814
C	2.9713125	-3.0302855	-1.4150152
H	3.9604441	-3.4715622	-1.3773610
C	0.6400564	2.6994244	-1.4085564
C	5.0567590	1.4510744	-1.3231635
C	5.4897344	1.9623466	-0.0921336
H	4.8298537	1.8871088	0.7737701
C	-6.7481853	-2.5553001	0.0245976
H	-7.0774669	-2.9403861	0.9913803
C	2.8343986	3.1482002	-1.3723715
H	3.8016352	3.6359858	-1.3608806
C	7.5849365	2.6532442	-1.0894002
H	8.5707067	3.1110678	-0.9982159
C	-5.0567590	-1.4510744	-1.3231635
C	7.6283316	-2.3757274	-2.1767521
H	8.6131733	-2.8091912	-2.3552999
C	3.7413149	-0.6257195	-1.5165195
C	3.7124623	0.7801437	-1.4124935
C	-5.4897344	-1.9623466	-0.0921336
H	-4.8298537	-1.8871088	0.7737701
C	1.6033887	3.7549329	-1.3881155
H	1.3860494	4.8179043	-1.3742814

C	-3.7124623	-0.7801437	-1.4124935
C	6.7481853	2.5553001	0.0245976
H	7.0774669	2.9403861	0.9913803
C	-7.5849365	-2.6532442	-1.0894002
H	-8.5707067	-3.1110678	-0.9982159
C	-3.7413149	0.6257195	-1.5165195
C	-6.0426888	1.3103813	-0.6910912
H	-5.7933538	0.9083356	0.2869956
C	6.6871249	-2.3222221	-3.2079141
H	6.9327999	-2.7157968	-4.1951930
C	-7.6283316	2.3757274	-2.1767521
H	-8.6131733	2.8091912	-2.3552999
C	-5.4281179	1.7643486	-2.9784595
H	-4.6899749	1.7208921	-3.7806063
C	7.2979286	-1.8733480	-0.9153654
H	8.0208180	-1.9160233	-0.0995346
C	6.0426888	-1.3103813	-0.6910912
H	5.7933538	-0.9083356	0.2869956
C	7.1483276	2.1667146	-2.3248231
H	7.7904452	2.2480328	-3.2026696
C	5.8917721	1.5723635	-2.4409079
H	5.5559409	1.1850512	-3.4027265
C	-5.8917721	-1.5723635	-2.4409079
H	-5.5559409	-1.1850512	-3.4027265
C	-7.1483276	-2.1667146	-2.3248231
H	-7.7904452	-2.2480328	-3.2026696
C	5.4281179	-1.7643486	-2.9784595
H	4.6899749	-1.7208921	-3.7806063
C	-6.6871249	2.3222221	-3.2079141
H	-6.9327999	2.7157968	-4.1951930
C	-7.2979286	1.8733480	-0.9153654
H	-8.0208180	1.9160233	-0.0995346
N	0.0000000	0.0000000	0.2407475

O	0.0000000	-0.0000000	-3.1694173

O=Fe(Ppc)-N-Fe(Pc) $Fe^{IV}Fe^{IV}(P^{\bullet+})$

Fe	-0.0000000	0.0000000	1.8611318
N	-0.5699410	-1.8480918	2.0153303
N	0.5699410	1.8480918	2.0153303
N	-1.5760073	2.9780863	1.8724855
N	-2.9746285	-1.5728529	2.1881937
N	2.9746285	1.5728529	2.1881937
N	-1.8377767	0.5705355	2.0738006
N	1.8377767	-0.5705355	2.0738006
N	1.5760073	-2.9780863	1.8724855
C	-1.9029124	-3.7422479	1.8562644
C	-2.2933508	1.8805787	2.0333981
C	0.2538069	-2.9521721	1.8535452
C	-0.2538069	2.9521721	1.8535452
C	1.8778695	2.2981473	2.0300768
C	2.9401837	0.2524616	2.2389007
C	0.2324836	5.4889030	1.5049952
H	-0.8088384	5.7956224	1.4085978
C	-3.7353298	1.9018732	2.2453315
C	0.5609962	4.1526233	1.7282078
C	-1.8778695	-2.2981473	2.0300768
C	-5.9821980	2.6196483	2.6246747
H	-6.7271820	3.4122712	2.6978984
C	3.7353298	-1.9018732	2.2453315
C	2.2933508	-1.8805787	2.0333981
C	1.9029124	3.7422479	1.8562644
C	-2.9401837	-0.2524616	2.2389007
C	-0.2324836	-5.4889030	1.5049952
H	0.8088384	-5.7956224	1.4085978
C	-0.5609962	-4.1526233	1.7282078
C	-4.1358768	0.5613823	2.4171585

C	4.1358768	-0.5613823	2.4171585
C	4.6543962	-2.9459875	2.3335662
H	4.3376292	-3.9775522	2.1831720
C	2.9504508	4.6570388	1.7643311
H	3.9857860	4.3296790	1.8534447
C	-4.6543962	2.9459875	2.3335662
H	-4.3376292	3.9775522	2.1831720
C	-6.3766827	1.2848810	2.8263264
H	-7.4188895	1.0650094	3.0593945
C	1.2829103	6.4045051	1.3980901
H	1.0640159	7.4565738	1.2118979
C	-5.4583203	0.2358163	2.7184927
H	-5.7589891	-0.8008440	2.8643801
C	5.9821980	-2.6196483	2.6246747
H	6.7271820	-3.4122712	2.6978984
C	5.4583203	-0.2358163	2.7184927
H	5.7589891	0.8008440	2.8643801
C	-1.2829103	-6.4045051	1.3980901
H	-1.0640159	-7.4565738	1.2118979
C	6.3766827	-1.2848810	2.8263264
H	7.4188895	-1.0650094	3.0593945
C	-2.9504508	-4.6570388	1.7643311
H	-3.9857860	-4.3296790	1.8534447
C	-2.6234652	-5.9939795	1.5265854
H	-3.4182937	-6.7348581	1.4346153
C	2.6234652	5.9939795	1.5265854
H	3.4182937	6.7348581	1.4346153
Fe	0.0000000	-0.0000000	-1.4728764
N	1.2986904	1.4824066	-1.4567822
N	1.3264897	-1.4485555	-1.4557174
N	-1.2986904	-1.4824066	-1.4567822
N	-1.3264897	1.4485555	-1.4557174
C	-1.7316324	3.7070152	-1.3547984

H	-1.5400946	4.7727975	-1.2860574
C	2.6860934	-1.6225952	-1.4340666
C	-2.9394380	3.0656746	-1.3538008
H	-3.9224717	3.5154340	-1.2794131
C	-0.7343955	2.6735646	-1.4270950
C	-2.6539370	-1.6928007	-1.4220317
C	-0.6762075	-2.6938280	-1.4546235
C	-2.6860934	1.6225952	-1.4340666
C	-2.8707072	-3.1393408	-1.4315387
H	-3.8407913	-3.6212942	-1.4226181
C	2.6539370	1.6928007	-1.4220317
C	-5.0763079	1.2961494	-1.6660638
C	1.7316324	-3.7070152	-1.3547984
H	1.5400946	-4.7727975	-1.2860574
C	5.0763079	-1.2961494	-1.6660638
C	0.7343955	-2.6735646	-1.4270950
C	-1.6453858	-3.7515235	-1.4479990
H	-1.4332149	-4.8156233	-1.4391321
C	2.9394380	-3.0656746	-1.3538008
H	3.9224717	-3.5154340	-1.2794131
C	0.6762075	2.6938280	-1.4546235
C	5.0645663	1.4044557	-1.3195390
C	5.4777051	1.9615436	-0.1013297
H	4.7974623	1.9340148	0.7518398
C	-6.7451947	-2.5344653	0.0177866
H	-7.0604814	-2.9541731	0.9745896
C	2.8707072	3.1393408	-1.4315387
H	3.8407913	3.6212942	-1.4226181
C	7.6068492	2.5703904	-1.0804833
H	8.5987505	3.0141415	-0.9867225
C	-5.0645663	-1.4044557	-1.3195390
C	7.5959052	-2.4574900	-2.1023889
H	8.5772823	-2.9019514	-2.2725791

C	3.7241701	-0.6674831	-1.4794958
C	3.7114317	0.7558582	-1.4103140
C	-5.4777051	-1.9615436	-0.1013297
H	-4.7974623	-1.9340148	0.7518398
C	1.6453858	3.7515235	-1.4479990
H	1.4332149	4.8156233	-1.4391321
C	-3.7114317	-0.7558582	-1.4103140
C	6.7451947	2.5344653	0.0177866
H	7.0604814	2.9541731	0.9745896
C	-7.6068492	-2.5703904	-1.0804833
H	-8.5987505	-3.0141415	-0.9867225
C	-3.7241701	0.6674831	-1.4794958
C	-6.0310484	1.3245998	-0.6445150
H	-5.7944573	0.8823516	0.3192844
C	6.6458151	-2.4412332	-3.1261716
H	6.8803141	-2.8747072	-4.0992355
C	-7.5959052	2.4574900	-2.1023889
H	-8.5772823	2.9019514	-2.2725791
C	-5.3908083	1.8701411	-2.9068982
H	-4.6451617	1.8538049	-3.7029929
C	7.2799147	-1.9039204	-0.8582498
H	8.0093911	-1.9191376	-0.0475704
C	6.0310484	-1.3245998	-0.6445150
H	5.7944573	-0.8823516	0.3192844
C	7.1877137	2.0415193	-2.3049435
H	7.8487290	2.0772011	-3.1716145
C	5.9251283	1.4623868	-2.4237743
H	5.6033741	1.0412448	-3.3759386
C	-5.9251283	-1.4623868	-2.4237743
H	-5.6033741	-1.0412448	-3.3759386
C	-7.1877137	-2.0415193	-2.3049435
H	-7.8487290	-2.0772011	-3.1716145
C	5.3908083	-1.8701411	-2.9068982

H	4.6451617	-1.8538049	-3.7029929
C	-6.6458151	2.4412332	-3.1261716
H	-6.8803141	2.8747072	-4.0992355
C	-7.2799147	1.9039204	-0.8582498
H	-8.0093911	1.9191376	-0.0475704
N	0.0000000	0.0000000	0.2159732
O	-0.0000000	-0.0000000	-3.1645514

HOO-Fe(Pc)-N-Fe(Ppc)

Fe	-0.0064290	0.0046730	1.9794549
N	-0.6014661	-1.8606534	2.0167313
N	0.5954821	1.8693596	2.0200964
N	-1.5397338	3.0023889	1.8179934
N	-2.9921084	-1.5250227	2.2168702
N	2.9871351	1.5304355	2.2245815
N	-1.8591563	0.6109158	2.0655092
N	1.8509006	-0.6073608	2.0888866
N	1.5323025	-2.9967150	1.8285685
C	-1.9653441	-3.7074890	1.7858924
C	-2.2783047	1.9194485	2.0101474
C	0.2086194	-2.9547965	1.8143101
C	-0.2152011	2.9635190	1.8081216
C	1.9088719	2.2781101	2.0304576
C	2.9430287	0.2068891	2.2766522
C	0.3243018	5.4673743	1.3124689
H	-0.7109215	5.7870980	1.1932474
C	-3.7214840	1.9635375	2.2270628
C	0.6241580	4.1409380	1.6218129
C	-1.9121787	-2.2703357	2.0307300
C	-5.9580012	2.7133598	2.6094224
H	-6.6926220	3.5163084	2.6772268
C	3.7159907	-1.9578985	2.2363285
C	2.2721391	-1.9141901	2.0246514

C	1.9610884	3.7126064	1.7793864
C	-2.9483149	-0.2012389	2.2613881
C	-0.3284553	-5.4616648	1.3254257
H	0.7069212	-5.7817757	1.2086647
C	-0.6296306	-4.1355959	1.6307617
C	-4.1365469	0.6292393	2.4293695
C	4.1319214	-0.6231350	2.4374931
C	4.6244421	-3.0129385	2.3054106
H	4.2960271	-4.0383897	2.1383201
C	3.0249699	4.6019386	1.6308698
H	4.0543328	4.2624464	1.7423304
C	-4.6291471	3.0184918	2.3013620
H	-4.3017466	4.0441500	2.1334392
C	-6.3663428	1.3871202	2.8388121
H	-7.4084414	1.1842049	3.0878210
C	1.3916016	6.3546987	1.1529541
H	1.1931812	7.3978495	0.9034283
C	-5.4609495	0.3259950	2.7439684
H	-5.7714816	-0.7039149	2.9155885
C	5.9545932	-2.7080828	2.6069011
H	6.6895026	-3.5110695	2.6706957
C	5.4588833	-0.3205141	2.7440237
H	5.7713928	0.7093936	2.9123604
C	-1.3960452	-6.3501813	1.1670234
H	-1.1969811	-7.3939711	0.9206562
C	6.3643915	-1.3815933	2.8339408
H	7.4080499	-1.1787332	3.0764092
C	-3.0289726	-4.5960004	1.6399707
H	-4.0582425	-4.2565289	1.7520507
C	-2.7278835	-5.9230259	1.3231067
H	-3.5370425	-6.6424206	1.1921695
C	2.7241067	5.9273589	1.3106674
H	3.5333081	6.6462448	1.1772653

Fe	0.0001746	0.0007482	-1.2748200
N	1.2783161	1.4734629	-1.5611504
N	1.3182800	-1.4198983	-1.6110849
N	-1.2789504	-1.4714227	-1.5600342
N	-1.3180980	1.4211277	-1.6014992
C	-1.7499040	3.6835671	-1.6274374
H	-1.5796820	4.7551756	-1.6317853
C	2.6896000	-1.5914116	-1.5837096
C	-2.9519757	3.0203453	-1.5865438
H	-3.9408091	3.4614805	-1.5539175
C	-0.7415846	2.6800535	-1.6363154
C	-2.6394999	-1.6944076	-1.4760822
C	-0.6576473	-2.7054225	-1.6288511
C	-2.6897020	1.5920959	-1.5733993
C	-2.8515838	-3.1309850	-1.5275260
H	-3.8228771	-3.6098099	-1.5049378
C	2.6390819	1.6956398	-1.4810011
C	-5.0964970	1.2508904	-1.6966677
C	1.7489293	-3.6824541	-1.6375162
H	1.5781350	-4.7539785	-1.6413606
C	5.0968307	-1.2495876	-1.6999528
C	0.7410000	-2.6783348	-1.6441015
C	-1.6288088	-3.7474786	-1.6244435
H	-1.4235499	-4.8119847	-1.6651985
C	2.9513883	-3.0198802	-1.5981917
H	3.9400341	-3.4615839	-1.5671542
C	0.6571138	2.7074681	-1.6271231
C	5.0532552	1.4385674	-1.2916237
C	5.4359798	1.9439670	-0.0424447
H	4.7461558	1.8635878	0.7999360
C	-6.6969681	-2.5342203	0.1175698
H	-6.9924278	-2.9144390	1.0968489
C	2.8516077	3.1321639	-1.5331222

H	3.8231338	3.6106942	-1.5139640
C	7.5656742	2.6442358	-0.9594495
H	8.5462183	3.1037349	-0.8293027
C	-5.0546293	-1.4375420	-1.2900637
C	7.6540536	-2.3487212	-2.0655737
H	8.6501666	-2.7695140	-2.2077382
C	3.7327197	-0.6347786	-1.5468610
C	3.7110438	0.7732782	-1.4377304
C	-5.4420598	-1.9433503	-0.0425356
H	-4.7543759	-1.8657742	0.8018930
C	1.6286946	3.7491250	-1.6263581
H	1.4236782	4.8136780	-1.6672443
C	-3.7117530	-0.7726159	-1.4320673
C	6.6887491	2.5381134	0.1219359
H	6.9805298	2.9180836	1.1024404
C	-7.5712312	-2.6365248	-0.9663097
H	-8.5535697	-3.0930622	-0.8392837
C	-3.7329880	0.6356180	-1.5395031
C	-5.9915846	1.3441133	-0.6273331
H	-5.6954705	0.9759728	0.3510770
C	6.7668722	-2.2670362	-3.1418070
H	7.0660803	-2.6247422	-4.1278914
C	-7.6525219	2.3491863	-2.0734119
H	-8.6482364	2.7694402	-2.2199190
C	-5.4874920	1.7282501	-2.9560510
H	-4.7884828	1.6617209	-3.7912692
C	7.2559531	-1.8917566	-0.8067767
H	7.9346920	-1.9578416	0.0441180
C	5.9866725	-1.3445780	-0.6264202
H	5.6856851	-0.9775109	0.3509236
C	7.1772230	2.1631536	-2.2131479
H	7.8511650	2.2505234	-3.0661264
C	5.9280533	1.5655994	-2.3782292

H	5.6304416	1.1818864	-3.3539942
C	-5.9264487	-1.5615722	-2.3794564
H	-5.6250403	-1.1776791	-3.3539952
C	-7.1777650	-2.1556746	-2.2185397
H	-7.8494954	-2.2403183	-3.0735403
C	5.4936165	-1.7255415	-2.9579885
H	4.7986270	-1.6578685	-3.7964597
C	-6.7601144	2.2692591	-3.1454490
H	-7.0547437	2.6278261	-4.1326029
C	-7.2602160	1.8909575	-0.8132491
H	-7.9431062	1.9555750	0.0344352
N	0.0061098	-0.0044467	0.3088407
O	0.0425479	-0.0683920	3.9040077
O	-0.6189794	1.0156429	4.5656503
H	0.0916392	1.6896987	4.5974641

HOO-Fe(Ppc)-N-Fe(Pc)

Fe	0.0002494	0.0065396	1.8609892
N	-0.5723282	-1.8457796	2.0386838
N	0.5746171	1.8609191	2.0500305
N	-1.5688441	2.9892823	1.9174649
N	-2.9723883	-1.5595282	2.2259150
N	2.9744367	1.5725076	2.2239547
N	-1.8375035	0.5847870	2.1331282
N	1.8381386	-0.5716502	2.1158389
N	1.5693968	-2.9764918	1.9039881
C	-1.9123111	-3.7247738	1.8324178
C	-2.2881664	1.8948731	2.0939931
C	0.2489268	-2.9487107	1.8687657
C	-0.2480441	2.9628513	1.8829676
C	1.8847784	2.3024627	2.0520908
C	2.9390318	0.2528248	2.2844673
C	0.2450580	5.4853711	1.4634094

H	-0.7955975	5.7930730	1.3646275
C	-3.7269625	1.9154284	2.3082710
C	0.5703190	4.1541262	1.7232711
C	-1.8832019	-2.2873018	2.0433568
C	-5.9735503	2.6337101	2.6799134
H	-6.7195626	3.4256214	2.7499232
C	3.7269208	-1.9035841	2.2953974
C	2.2888180	-1.8819726	2.0780289
C	1.9127729	3.7408687	1.8474862
C	-2.9377943	-0.2403030	2.2967704
C	-0.2460646	-5.4698722	1.4454479
H	0.7943730	-5.7782304	1.3466116
C	-0.5704388	-4.1390244	1.7077386
C	-4.1289302	0.5739752	2.4781604
C	4.1293594	-0.5626045	2.4663611
C	4.6447442	-2.9502832	2.3864791
H	4.3268006	-3.9812328	2.2353890
C	2.9641753	4.6478190	1.7173718
H	3.9990142	4.3175879	1.8001990
C	-4.6469015	2.9607787	2.3936883
H	-4.3300345	3.9920810	2.2427080
C	-6.3700098	1.2972134	2.8777893
H	-7.4138259	1.0784207	3.1043883
C	1.2982774	6.3908769	1.3203496
H	1.0829989	7.4380806	1.1048371
C	-5.4543546	0.2483198	2.7718202
H	-5.7569498	-0.7886005	2.9110164
C	5.9703444	-2.6249420	2.6794778
H	6.7148286	-3.4178237	2.7544736
C	5.4537424	-0.2386840	2.7667826
H	5.7569936	0.7977116	2.9082649
C	-1.3001361	-6.3739021	1.2989429
H	-1.0857107	-7.4207339	1.0808307

C	6.3674876	-1.2887521	2.8780972
H	7.4104081	-1.0711234	3.1098996
C	-2.9645872	-4.6300921	1.6984981
H	-3.9991812	-4.2990121	1.7803880
C	-2.6407030	-5.9595479	1.4245187
H	-3.4378964	-6.6926868	1.2978350
C	2.6392686	5.9777263	1.4469704
H	3.4357612	6.7123547	1.3243972
Fe	0.0071216	-0.0080126	-1.3771855
N	1.3077970	1.4605329	-1.4794293
N	1.3264830	-1.4404607	-1.4521392
N	-1.2952797	-1.4666094	-1.4622386
N	-1.3233732	1.4301122	-1.5052445
C	-1.7142733	3.6933185	-1.4886175
H	-1.5235931	4.7614306	-1.4681600
C	2.6825947	-1.6186298	-1.4554162
C	-2.9264326	3.0512888	-1.4755468
H	-3.9090743	3.5064180	-1.4407412
C	-0.7224680	2.6644015	-1.5115896
C	-2.6482164	-1.6757311	-1.4367450
C	-0.6708103	-2.6885955	-1.4961661
C	-2.6803128	1.6135378	-1.4965460
C	-2.8663230	-3.1183992	-1.4861885
H	-3.8397232	-3.5937401	-1.4980443
C	2.6630585	1.6760013	-1.4212805
C	-5.0884319	1.2920489	-1.6572602
C	1.7211895	-3.7019248	-1.4621138
H	1.5330060	-4.7705357	-1.4543794
C	5.0886431	-1.3010431	-1.6465302
C	0.7270019	-2.6751242	-1.4757433
C	-1.6435301	-3.7363782	-1.5236357
H	-1.4351688	-4.8008516	-1.5505984
C	2.9311623	-3.0568636	-1.4444175

H	3.9148050	-3.5099809	-1.4138750
C	0.6774637	2.6830431	-1.5108861
C	5.0801341	1.3987147	-1.2975844
C	5.4932537	1.9416632	-0.0734847
H	4.8159680	1.8974723	0.7809843
C	-6.7345107	-2.5301187	0.0492120
H	-7.0441511	-2.9344642	1.0145942
C	2.8743257	3.1160860	-1.4531466
H	3.8450156	3.5970382	-1.4402031
C	7.6136169	2.5868621	-1.0485207
H	8.6016068	3.0384609	-0.9507324
C	-5.0667503	-1.4070746	-1.3120376
C	7.6206158	-2.4450314	-2.0617661
H	8.6064089	-2.8827308	-2.2239883
C	3.7362413	-0.6668945	-1.4702605
C	3.7303580	0.7403977	-1.3958605
C	-5.4746024	-1.9434964	-0.0832797
H	-4.7949958	-1.8923635	0.7689841
C	1.6470375	3.7308934	-1.5064602
H	1.4375393	4.7954957	-1.5226381
C	-3.7188211	-0.7458959	-1.4172513
C	6.7543357	2.5275933	0.0508327
H	7.0677581	2.9376702	1.0125470
C	-7.5970285	-2.5981249	-1.0470826
H	-8.5835991	-3.0515607	-0.9434758
C	-3.7324656	0.6615593	-1.4978415
C	-6.0030810	1.3543456	-0.6017515
H	-5.7275763	0.9435080	0.3656260
C	6.6954596	-2.3912499	-3.1075861
H	6.9547649	-2.7887082	-4.0898179
C	-7.6299873	2.4289562	-2.0353786
H	-8.6195148	2.8632595	-2.1833022
C	-5.4546085	1.8204710	-2.9036570

H	-4.7411049	1.7782975	-3.7278845
C	7.2734692	-1.9368105	-0.8074120
H	7.9840552	-1.9781969	0.0191314
C	6.0169891	-1.3682758	-0.6036798
H	5.7560820	-0.9581500	0.3680118
C	7.1968076	2.0694344	-2.2782434
H	7.8566035	2.1199970	-3.1452061
C	5.9375706	1.4826098	-2.4019611
H	5.6188340	1.0693928	-3.3588214
C	-5.9278264	-1.4981977	-2.4129409
H	-5.6113048	-1.0925590	-3.3736885
C	-7.1851129	-2.0875652	-2.2813831
H	-7.8472532	-2.1459913	-3.1460745
C	5.4356176	-1.8274000	-2.8993619
H	4.7091949	-1.7826943	-3.7121822
C	-6.7188863	2.3808624	-3.0935667
H	-6.9929584	2.7790438	-4.0714787
C	-7.2640203	1.9189198	-0.7871169
H	-7.9632964	1.9558490	0.0491665
N	-0.0151485	0.0218229	0.2526008
O	-0.0514193	-0.0179802	-3.3015307
O	1.2155550	-0.0655075	-3.9531341
H	1.5760935	0.8255425	-3.7509070

OH

O	0.9241189	-0.6375602	4.3258109
H	0.5130230	-1.5307084	4.3990134

Table S7. Amounts of the oxidized products observed in the reactions under CH_4 (1.0 MPa) atmosphere using $\mathbf{4}^+ \cdot I_3^-$ or $\mathbf{1}^+ \cdot I^-$ on silica support.

Entry	Catalyst	Reaction Time / h	Gas	Additive	[CH_3OH] / mM	[HCHO] / mM	[HCOOH] / mM	TTN_{eff}	MCN_{eff}
1	$\mathbf{4}^+ \cdot I_3^-/SiO_2$	8	CH_4 (1.0 MPa)	•••	0.11	0.21	0.19	3	3
2	$\mathbf{4}^+ \cdot I_3^-/SiO_2$	16	CH_4 (1.0 MPa)	•••	0.15	0.21	0.39	12	6
3	$\mathbf{4}^+ \cdot I_3^-/SiO_2$	24	CH_4 (1.0 MPa)	•••	0.13	0.29	0.61	27	11
4	$\mathbf{4}^+ \cdot I_3^-/SiO_2$	32	CH_4 (1.0 MPa)	•••	0.13	0.44	0.78	35	14
5	$\mathbf{4}^+ \cdot I_3^-/SiO_2$	48	CH_4 (1.0 MPa)	•••	0.14	0.78	1.82	116	44
6	$\mathbf{4}^+ \cdot I_3^-/SiO_2$	24	CH_4 (1.0 MPa)	100 mM Na_2SO_3	0.087	0.50	0.30	17	6
7	$\mathbf{4}^+ \cdot I_3^-/SiO_2$	48	CH_4 (1.0 MPa)	100 mM Na_2SO_3	0.11	0.69	0.81	58	23
8	$\mathbf{1}^+ \cdot I^-/SiO_2$	24	CH_4 (1.0 MPa)	•••	0.06	0.65	1.16	56	22

All reactions were performed in the presence of CH_4 (1.0 MPa), H_2O_2 (189 mM), and TFA (51 mM) in H_2O (3.0 mL) containing a silica-supported catalyst (55 μM as $\mathbf{4}^+$ or $\mathbf{1}^+$). Concentrations of the oxidized products observed in the presence of CH_4 are the mean values of three different reactions. The TTN_{eff} and MCN_{eff} values were calculated using equations (i) - (iv) in the main text.

Table S8. Amounts of the oxidized products observed in the reactions under N_2 (1.0 MPa) atmosphere using $\mathbf{4}^{+}\cdot I_3^-$ or $\mathbf{1}^{+}\cdot I^-$ on silica support.

Entry	Catalyst	Reaction Time / h	Gas	Additive	[CH_3OH] / mM	[HCHO] / mM	[HCOOH] / mM	TTN(N_2)	MCN(N_2)
1	$\mathbf{4}^{+}\cdot I_3^-/SiO_2$	8	N_2 (1.0 MPa)	•••	0.046	0.095	0.23	17	7
2	$\mathbf{4}^{+}\cdot I_3^-/SiO_2$	16	N_2 (1.0 MPa)	•••	0.039	0.10	0.28	19	7
3	$\mathbf{4}^{+}\cdot I_3^-/SiO_2$	24	N_2 (1.0 MPa)	•••	0.039	0.15	0.23	18	8
4	$\mathbf{4}^{+}\cdot I_3^-/SiO_2$	32	N_2 (1.0 MPa)	•••	0.026	0.19	0.33	25	10
5	$\mathbf{4}^{+}\cdot I_3^-/SiO_2$	48	N_2 (1.0 MPa)	•••	0.018	0.17	0.10	12	5
6	$\mathbf{1}^{+}\cdot I^-/SiO_2$	24	N_2 (1.0 MPa)	•••	0	0.25	0.40	30	12

All reactions were performed in the absence of CH_4 (under N_2 (1.0 MPa)), H_2O_2 (189 mM), and TFA (51 mM) in H_2O (3.0 mL) containing a silica-supported catalyst (55 μM as $\mathbf{4}^{+}$ or $\mathbf{1}^{+}$). The TTN and MCN values were calculated using equations (ii) and (iv) in the main text.

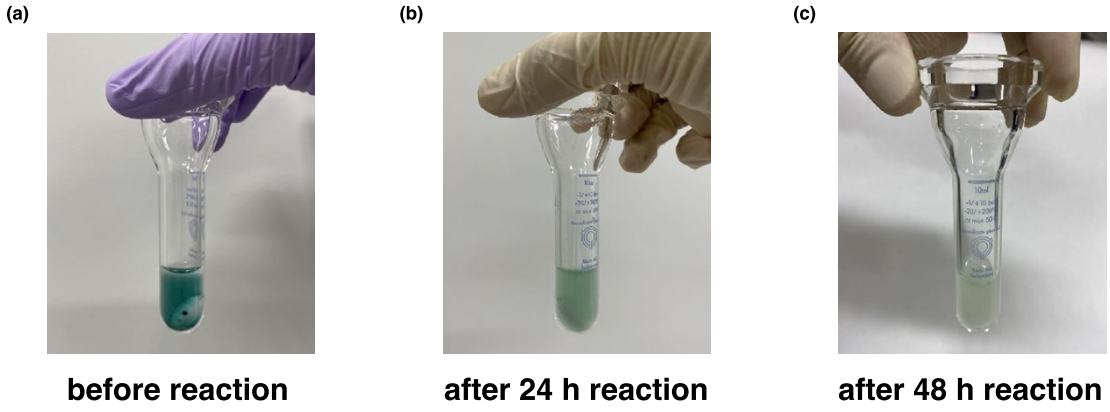

Figure S5. Comparison of the pictures of the reaction mixtures (a) before and after (b) 24 hour and (c) 48 hour CH_4 oxidation reaction by using $\mathbf{4}^{+}\cdot I_3^{-}/SiO_2$.