Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Oxidation of Methane by an N-bridged High-Valent Diiron-Oxo Species: Electronic Structure Implications to the Reactivity

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Table S1:B3LYP-D2 computed optimized energy of possible spin states of complexes.

Spin states	Energy(kJ/mol)
1	
^{10}**1**$_{(hs, hs)}$	64.7
^{2}**1**$_{(hs, hs)}$	0.0
^{6}**1**$_{(hs, hs)}$	25.7
2	
^{10}**2**$_{(hs, hs)}$	402.1
^{8}**2**$_{(hs, hs)}$	266.2
^{2}**2**$_{(hs, hs)}$	0.0
^{6}**2**$_{(is, is)}$	37.7
^{2}**2**$_{(is, is)}$	46.2
ts1	
^{10}*ts1*$_{(hs, hs)}$	198.0
^{2}*ts1*$_{(hs, hs)}$	26.1
^{2}*ts1*$_{(is, is)}$	0.0
int1	
^{12}*int1*$_{(hs,hs)}$	155.0
^{4}*int1*$_{(hs,hs)}$	100.0
^{2}*int1*$_{(is, is)}$	0.0
^{8}*int1*$_{(is, is)}$	138.9
^{4}*int1*$_{(is, is)}$	126.8
ts2	
^{4}*ts2*$_{(hs, hs)}$	0.0
^{8}*ts2*$_{(is, is)}$	112.6
^{4}*ts2*$_{(is, is)}$	2.3
P	
^{10}*P*$_{(hs,hs)}$	99.4
^{2}*P*$_{(hs,hs)}$	0.0
^{6}*P*$_{(is,is)}$	93.7

Table S2: B3LYP-D2 computed structural parameters (Å) of the complexes

Spin states	Fe(III)-N1	Fe(III)-$N_{(porp)}$	Fe(IV)-N1	Fe(IV)-$N_{(porp)}$	Fe(III)-O1	O1-H1	H1-C	O1-C	∠Fe(III)-O1-C1	∠Fe(III)-O1-H1	∠O1-H1-C1	∠Fe(III)-N1-Fe(IV)
1												
^{10}**1**$_{(hs, hs)}$	1.828	2.081	1.772	2.079	-	-	-	-	-	-	-	151.69
^{2}**1**$_{(hs, hs)}$	1.790	2.096	1.647	2.074	-	-	-	-	-	-	-	158.48
^{6}**1**$_{(is, is)}$	1.917	2.077	1.625	2.004	-	-	-	-	-	-	-	173.86
Exp[48]	1.679	2.010	1.679	2.010								177
2												
^{10}**2**$_{(hs, hs)}$	2.040[a]	2.081[a]	1.920	2.088	1.694[a]	-	-	-	-	-	-	179.89
^{8}**2**$_{(hs, hs)}$	2.008[a]	2.084[a]	1.825	2.005	1.665[a]	-	-	-	-	-	-	179.41
^{2}**2**$_{(hs, hs)}$	1.974[a]	2.082[a]	1.686	2.077	1.661[a]	-	-	-	-	-	-	177.57
^{6}**2**$_{(is, is)}$	2.002[a]	2.022[a]	1.876	2.013	1.673[a]	-	-	-	-	-	-	176.98
^{2}**2**$_{(is, is)}$	2.002[a]	2.022[a]	1.876	2.013	1.673[a]	-	-	-	-	-	-	176.98
ts1												
^{10}*ts1*$_{(hs, hs)}$	1.761[a]	2.082[a]	2.030	2.079	1.857[a]	1.125	1.420	-	-	115.18	176.33	179.06
^{2}*ts1*$_{(hs, hs)}$	1.749[a]	2.078[a]	1.677	2.076	1.827[a]	1.129	1.410	-	-	113.88	178.38	178.95
^{2}*ts1*$_{(is, is)}$	1.718[a]	2.019[a]	1.649	2.017	1.844[a]	1.123	1.418	-	-	113.86	179.07	179.36
int1												
^{12}*int1*$_{(hs,hs)}$	2.180	2.095	1.884	2.077	1.871	0.976	-	-	-	123.40	-	178.58
^{4}*int1*$_{(hs,hs)}$	2.061	2.098	1.795	2.004	1.889	0.977	-	-	-	119.28	-	177.69
^{2}*int1*$_{(is, is)}$	1.697	2.021	1.651	2.017	1.865	0.981	-	-	-	108.73	-	179.63
^{8}*int1*$_{(is, is)}$	2.193	2.036	1.865	2.015	1.908	0.979	-	-	-	117.54	-	179.04
^{4}*int1*$_{(is, is)}$	1.838	1.975	1.717	2.017	1.838	0.982	-	-	-	108.30	-	179.34
ts2												
^{4}*ts2*$_{(hs, hs)}$	1.719	2.082	1.649	2.017	1.901	0.982	2.701	2.488	128.32	108.00	91.63	179.54
^{8}*ts2*$_{(is, is)}$	1.952	2.080	1.880	2.013	1.856	0.983	2.967	2.441	135.43	108.00	112.98	174.86
^{4}*ts2*$_{(is, is)}$	1.886	2.082	1.742	2.040	1.861	0.983	2.934	2.415	135.81	111.40	112.43	178.18
P												
^{10}*P*$_{(hs,hs)}$	1.951	2.085	1.855	2.082	2.285	0.979	2.047	1.462	116.25	96.92	112.44	179.37
^{2}*P*$_{(hs,hs)}$	1.773	2.092	1.652	2.084	2.468	0.981	2.044	1.457	116.39	85.58	112.45	178.66
^{6}*P*$_{(is,is)}$	2.089	2.023	1.743	2.019	2.183	0.979	2.042	1.462	116.73	98.05	112.02	179.73

a) for this species the oxidation state of Fe is IV.

Table S3:B3LYP-D2 computed spin densities of the complexes.

Spin states	Fe(III)	Fe(IV)	N1	O1	C1
		1			
^{10}**1**$_{(hs, hs)}$	3.83	3.62	0.75	--	
^{2}**1**$_{(hs, hs)}$	3.78	-2.92	-0.21	--	
^{6}**1**$_{(is, is)}$	2.63	1.12	1.29	--	
		2			
^{10}**2**$_{(hs, hs)}$	4.07[a]	2.93	0.07	0.97[a]	
^{8}**2**$_{(hs, hs)}$	1.21[a]	2.93	1.82	0.74[a]	
^{2}**2**$_{(hs, hs)}$	2.93[a]	-2.94	0.15	0.79[a]	
^{6}**2**$_{(is, is)}$	0.95[a]	0.99	1.93	1.01[a]	
^{2}**2**$_{(is, is)}$	1.02[a]	1.12	1.93	0.98[a]	
		ts1			
^{10}*ts1*$_{(hs, hs)}$	3.03[a]	4.09	-0.17	0.61[a]	0.70
^{2}*ts1*$_{(hs, hs)}$	2.83[a]	-2.82	-0.04	0.48[a]	0.70
^{2}*ts1*$_{(is, is)}$	0.89[a]	-0.78	-0.18	0.56[a]	0.71
		int1			
^{12}*int1*$_{(hs,hs)}$	4.01	3.02	1.73	0.36	
^{4}*int1*$_{(hs,hs)}$	4.10	-1.17	-1.71	0.36	
^{2}*int1*$_{(is, is)}$	0.93	-0.79	-0.19	0.11	
^{8}*int1*$_{(is, is)}$	2.57	1.06	1.92	0.34	
^{4}*int1*$_{(is, is)}$	0.92	0.95	0.09	0.15	
		ts2			
^{4}*ts2*$_{(hs, hs)}$	3.03	-0.89	-0.19	-0.08	1.01
^{8}*ts2*$_{(is, is)}$	2.97	0.99	1.84	-0.04	1.02
^{4}*ts2*$_{(is, is)}$	2.97	0.80	-1.67	-0.04	1.01
		P			
^{10}*P*$_{(hs,hs)}$	3.71	3.27	1.40	0.02	0.00
^{2}*P*$_{(hs,hs)}$	3.77	-2.73	-0.18	0.01	-0.00
^{6}*P*$_{(is,is)}$	0.56	2.68	1.70	0.10	-0.00

a) for this species the oxidation state of Fe is IV.

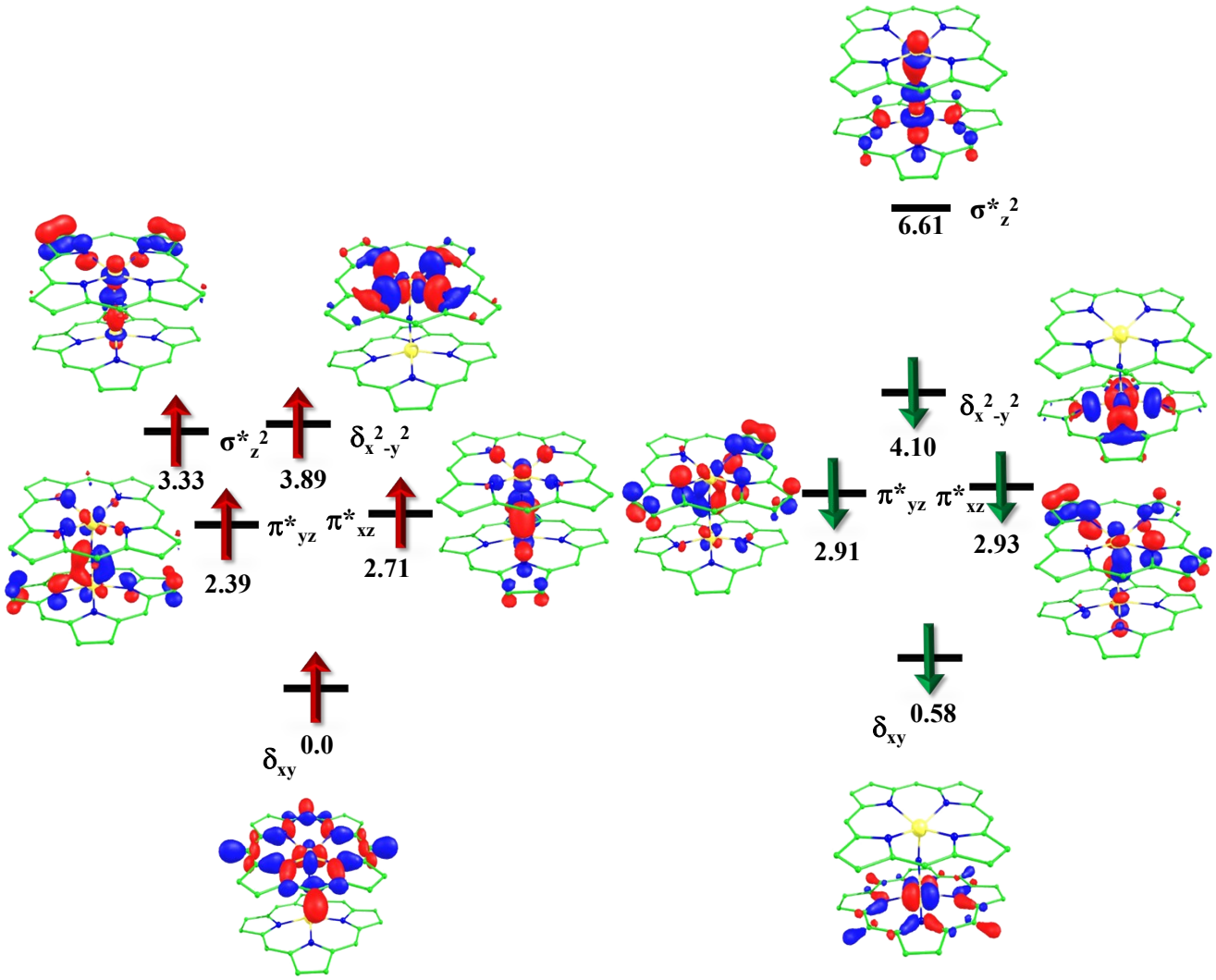
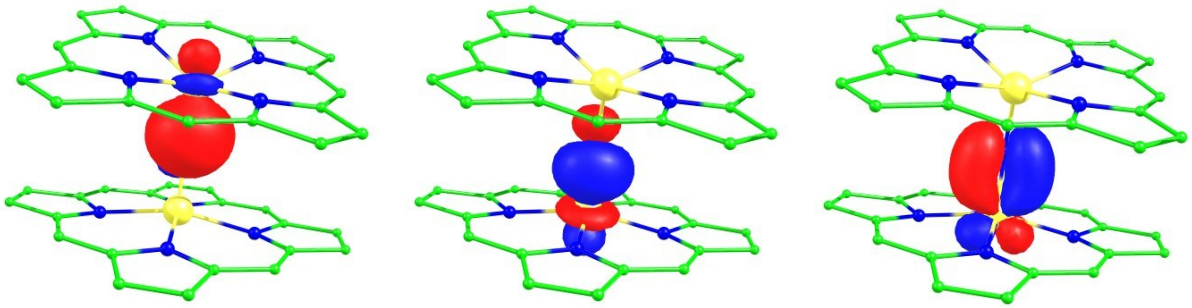


Figure S1: B3LYP-D2 computed Eigen-value plot incorporating energies computed for d-based orbitals for alpha and beta spin of $^{2}\mathbf{1}_{(hs,\ hs)}$ species (energies are given in eV).



Fe(III) (30.60%)
N1 (69.40%)

Fe(IV) (48.45%)
N1(51.55%)

Fe(IV) (67.09%)
N 1(32.91%)

FigureS2. Natural Bond Orbital of ground state of $^{2}\mathbf{1}_{(hs,\ hs)}$ species.

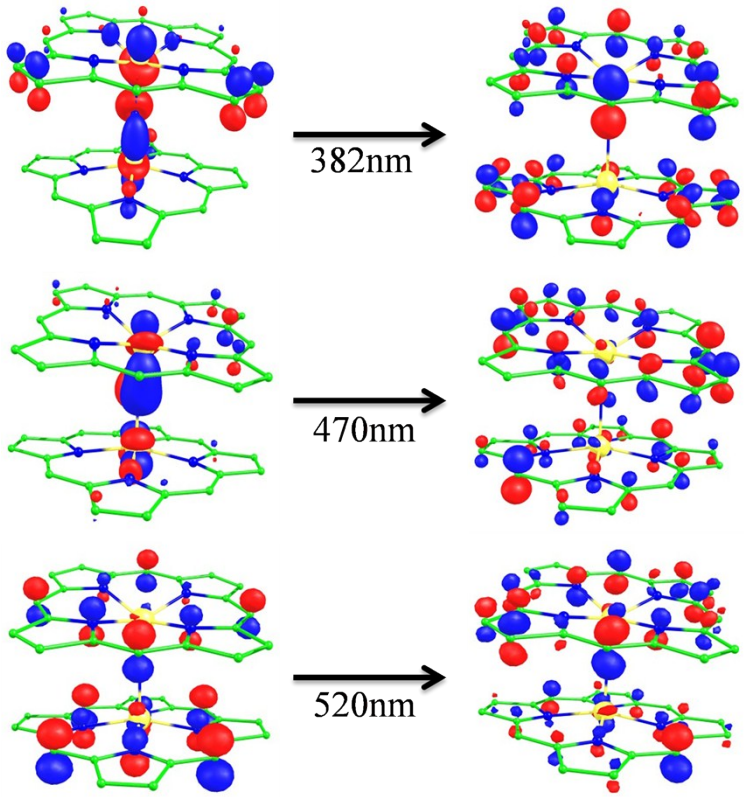
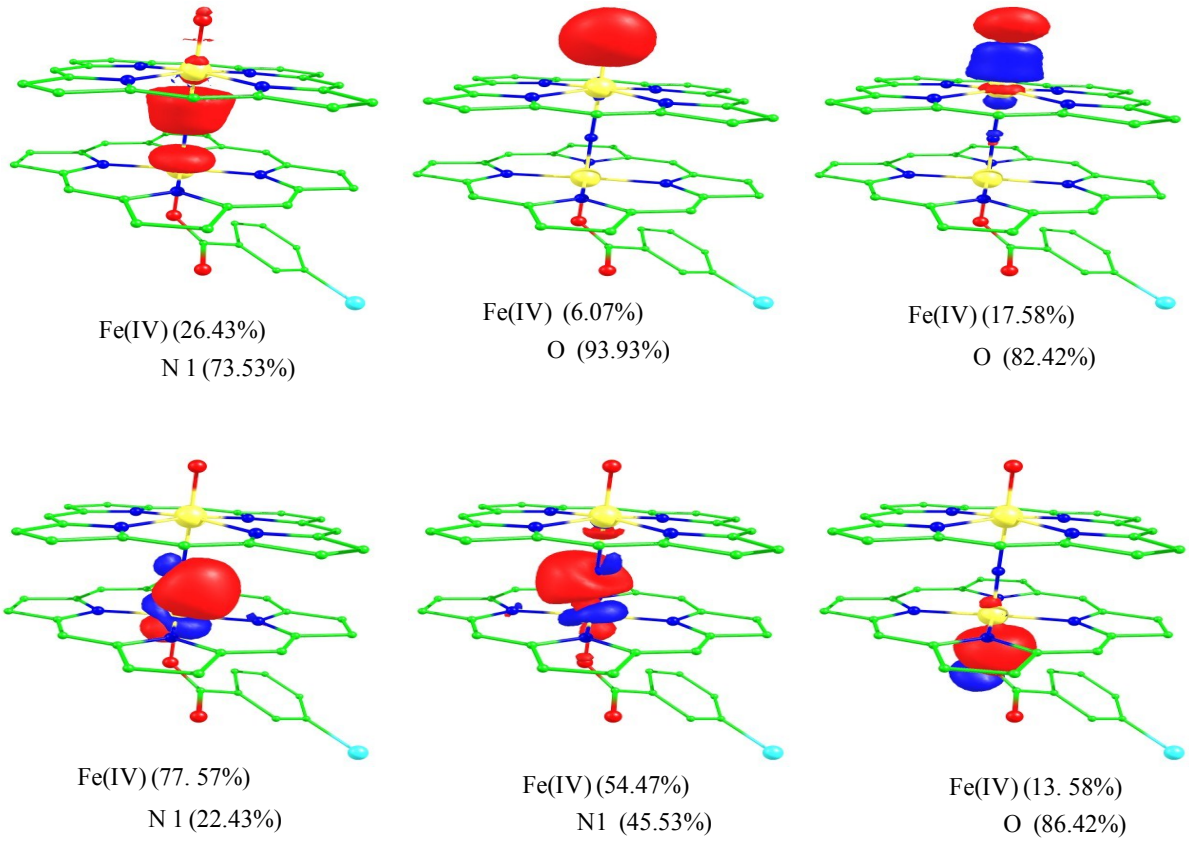
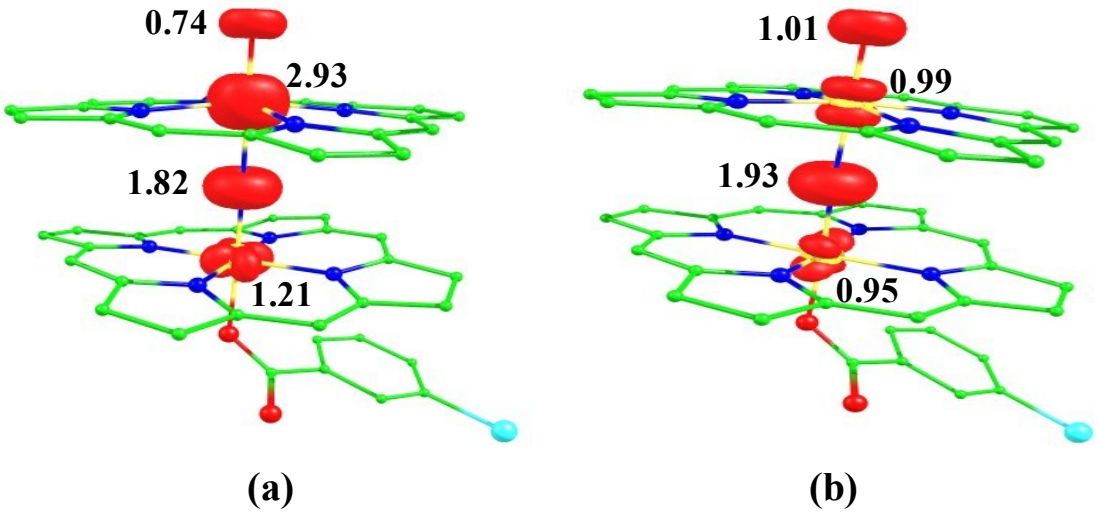


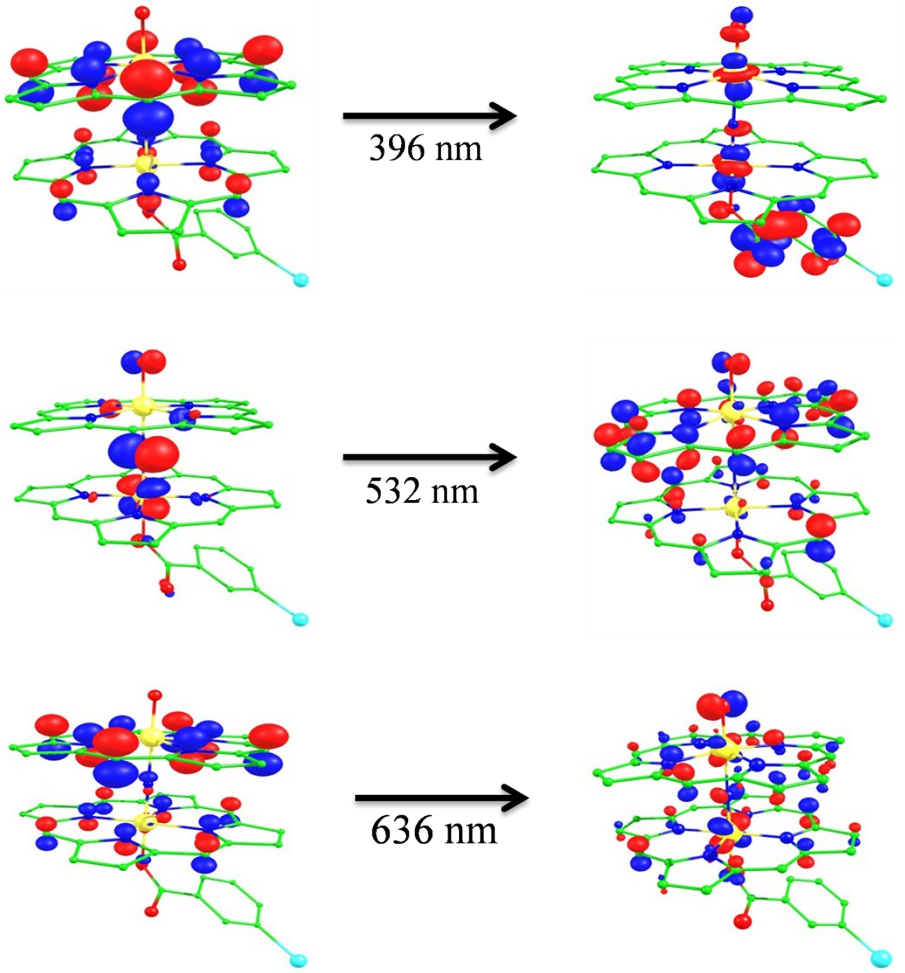
Figure S3: The orbital diagram of the peaks corresponds to TD-DFTsimulated electronic absorption spectra of $^{2}\mathbf{1}_{(hs,\,hs)}$ species.



FigureS4. Natural Bond Orbital of ground state of $^{2}\mathbf{2}_{(hs,\ hs)}$ species.



FigureS5. Computedspin density plots of $^{8}\mathbf{2}_{(hs,\ hs)}$) and $^{6}\mathbf{2}_{(is,is)}$ species.



FigureS6. TD-DFT computed orbitals corresponds to U.V. peaks of species $^{2}\mathbf{2}_{(hs,\ hs)}$.