The Dioxygen Adducts of Iron and Manganese Porphyrins: Electronic Structure and Binding Energy

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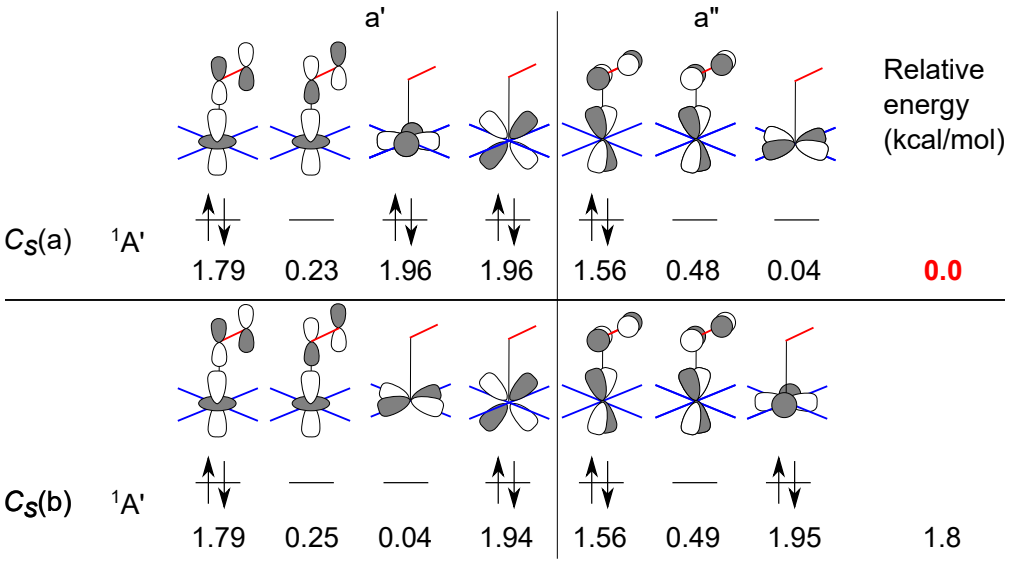


Figure S1: Electron configurations and NOONs of investigated states of FeP$-O_2$. The relative energies without 3s3p correlation (in kcal mol^{-1}) were calculated with DMRG-CASPT2/BS1

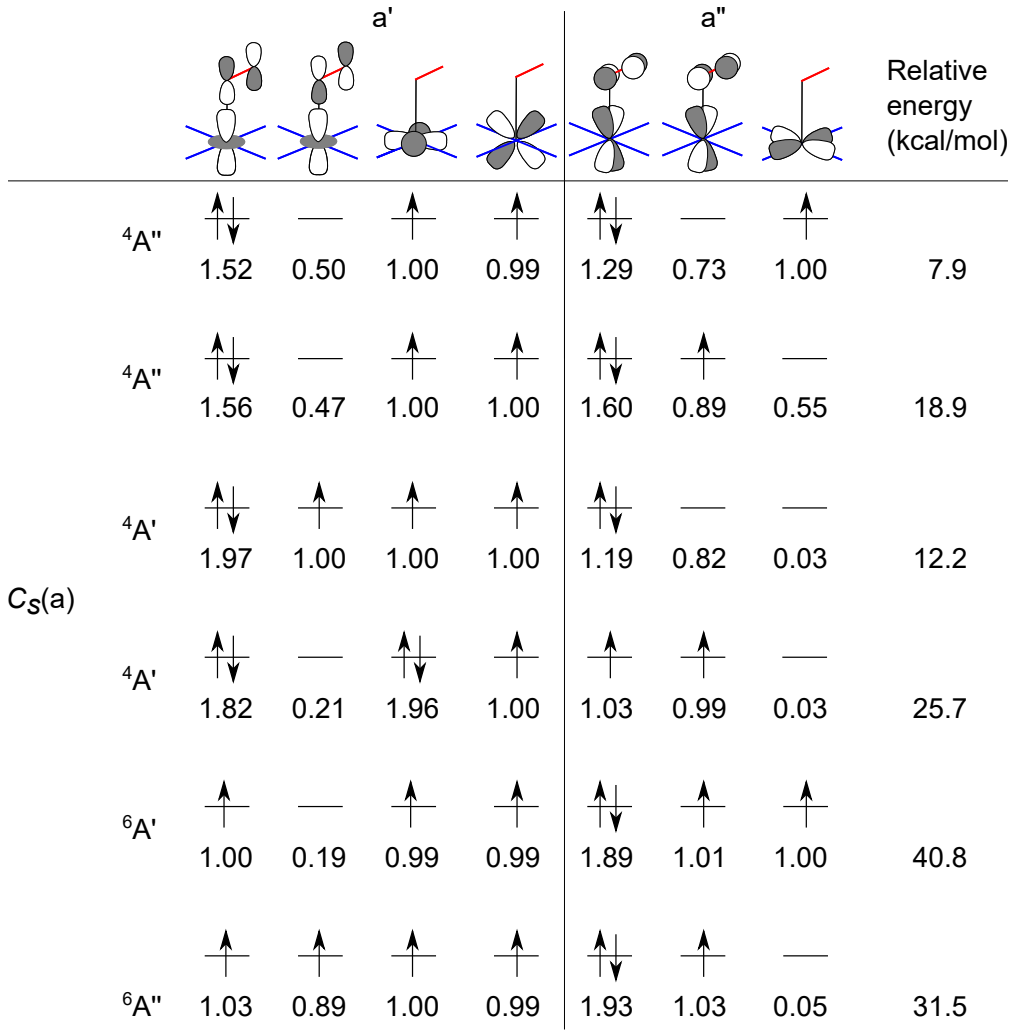


Figure S2: Electron configurations and NOONs of investigated states of C_s(a) MnP$-$O$_2$. The relative energies without 3s3p correlation (in kcal mol^{-1}) were calculated with DMRG-CASPT2/BS1

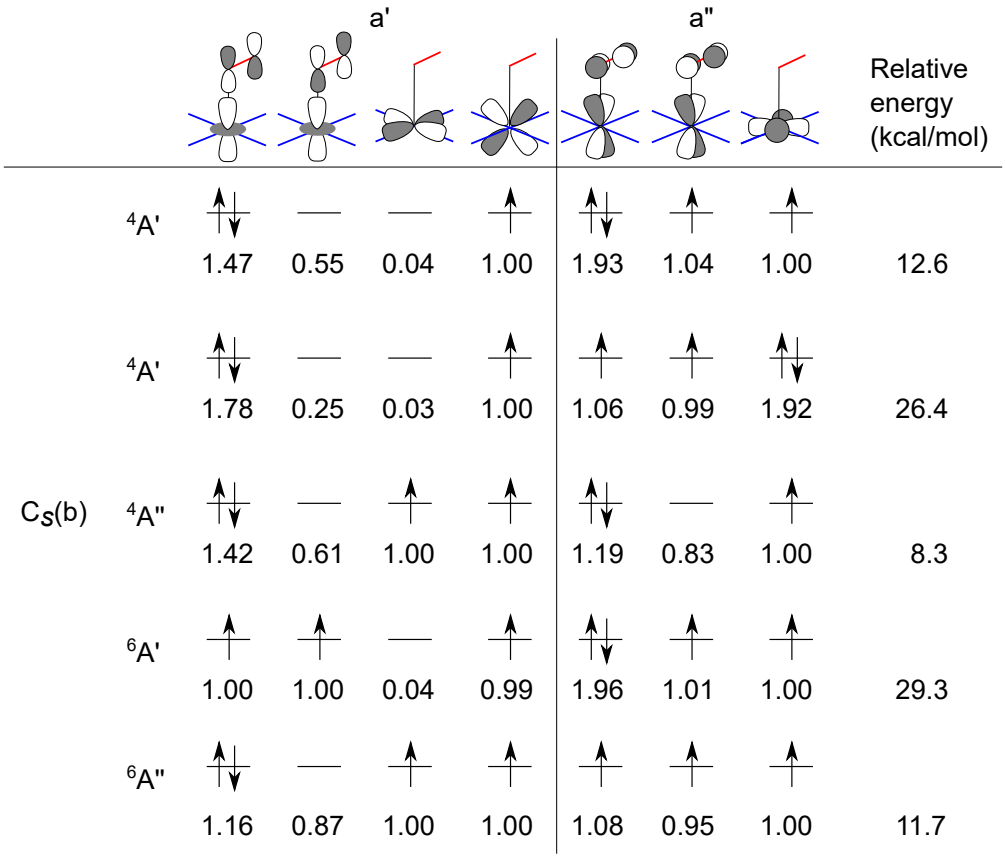
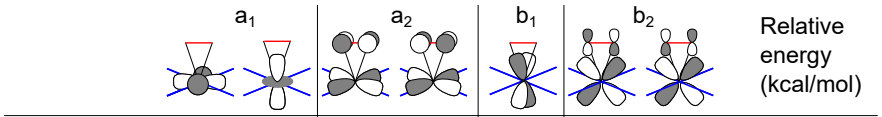


Figure S3: Electron configurations and NOONs of investigated states of C_s(b) MnP$-$O$_2$. The relative energies without 3s3p correlation (in kcal mol^{-1}) were calculated with DMRG-CASPT2/BS1



		a1		a2		b1	b2		Relative energy (kcal/mol)
	$^4B_1$	0.99	1.00	1.31	0.71	1.00	1.79	0.22	13.3
	$^4B_1$	1.00	0.07	1.04	0.04	1.93	1.94	1.01	49.9
	$^4B_1$	1.94	0.98	1.02	0.04	0.08	1.94	1.02	64.1
	$^4A_2$	0.99	1.00	1.94	1.00	0.11	1.78	0.27	52.0
	$^4A_2$	0.98	1.00	1.03	0.06	1.93	1.64	0.39	37.9
	$^4A_2$	1.97	0.99	0.69	0.02	0.99	1.44	0.98	55.2
C_{2v}(a)	$^4A_1$	1.90	0.11	1.02	0.03	1.00	1.94	1.02	48.9
	$^4B_2$	1.00	0.08	1.97	1.00	1.00	1.72	0.30	40.7
	$^4B_2$	1.01	0.98	0.67	0.05	1.94	1.46	0.98	62.1
	$^4B_2$	0.99	1.96	1.02	0.03	0.99	1.83	0.20	26.3
	$^6A_1$	1.00	1.00	1.02	0.04	1.00	1.96	1.01	8.9
	$^6A_2$	0.05	1.00	1.03	1.00	1.00	1.95	1.01	52.3
	$^6B_1$	1.00	0.99	1.03	1.00	1.00	1.73	0.29	15.9
	$^6B_2$	1.00	1.00	1.02	1.00	0.03	1.96	1.01	67.4

Figure S4: Electron configurations and NOONs of investigated states of C_{2v}(a) MnP−O_2. The relative energies without 3s3p correlation (in kcal mol^{-1}) were calculated with DMRG-CASPT2/BS1

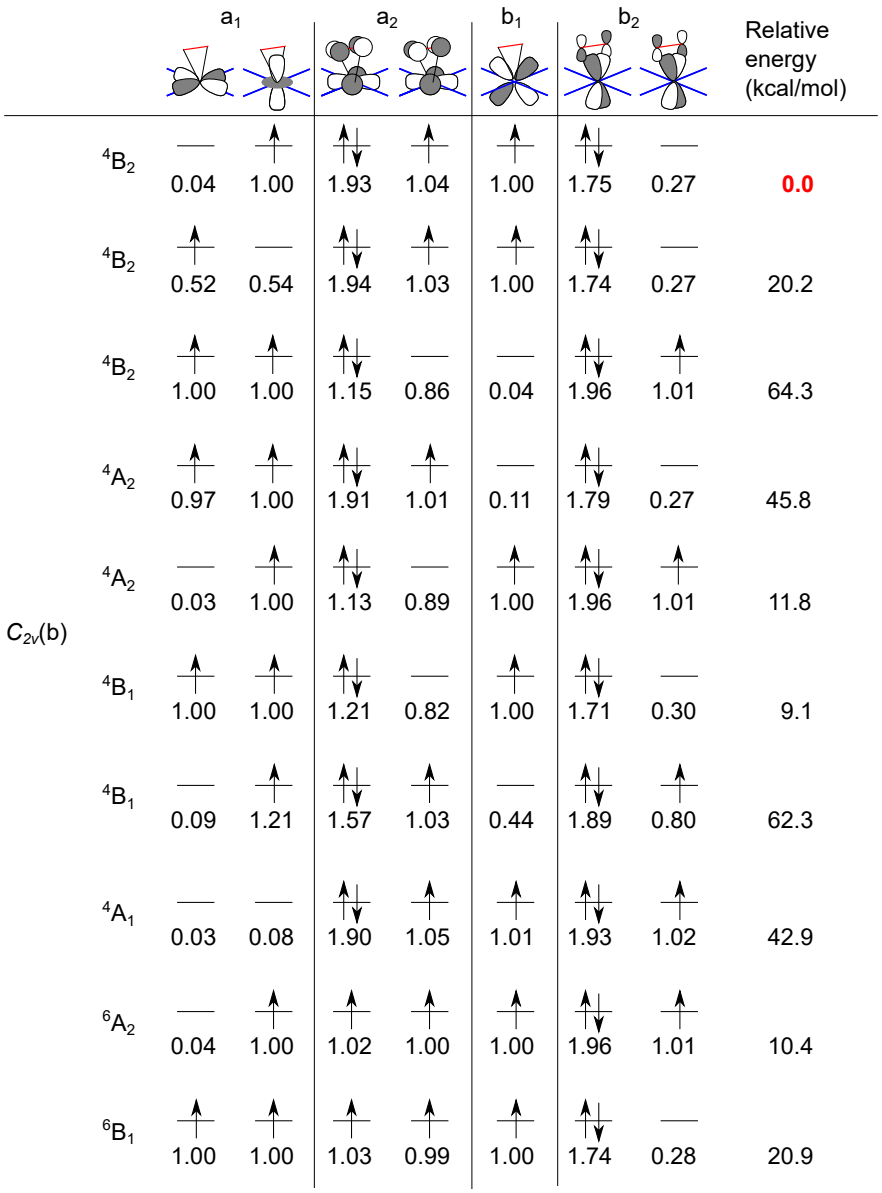


Figure S5: Electron configurations and NOONs of investigated states of C_{2v}(b) MnP$-$O$_2$. The relative energies without 3s3p correlation (in kcal mol^{-1}) were calculated with DMRG-CASPT2/BS1

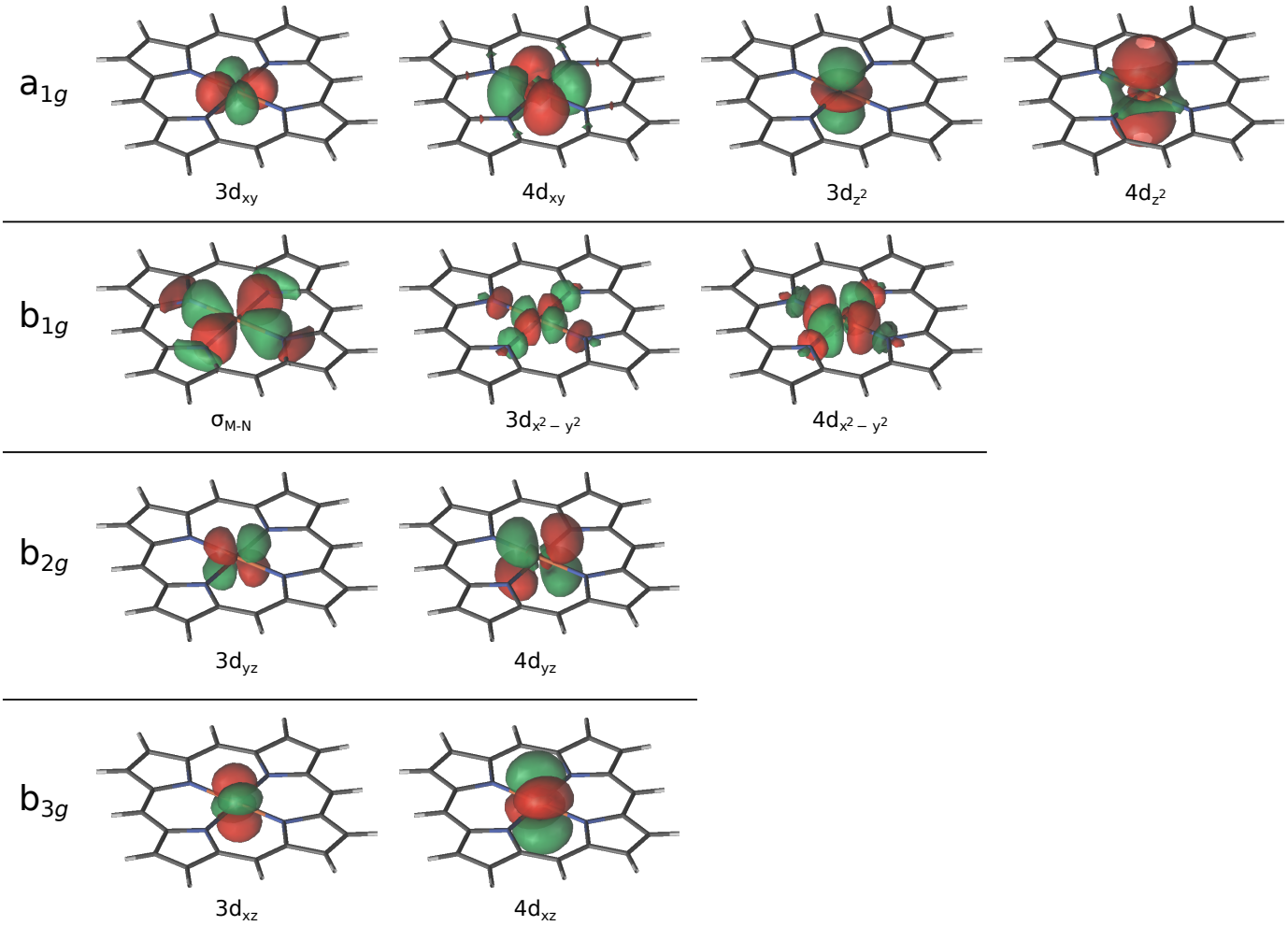


Figure S6: Active orbitals of MP

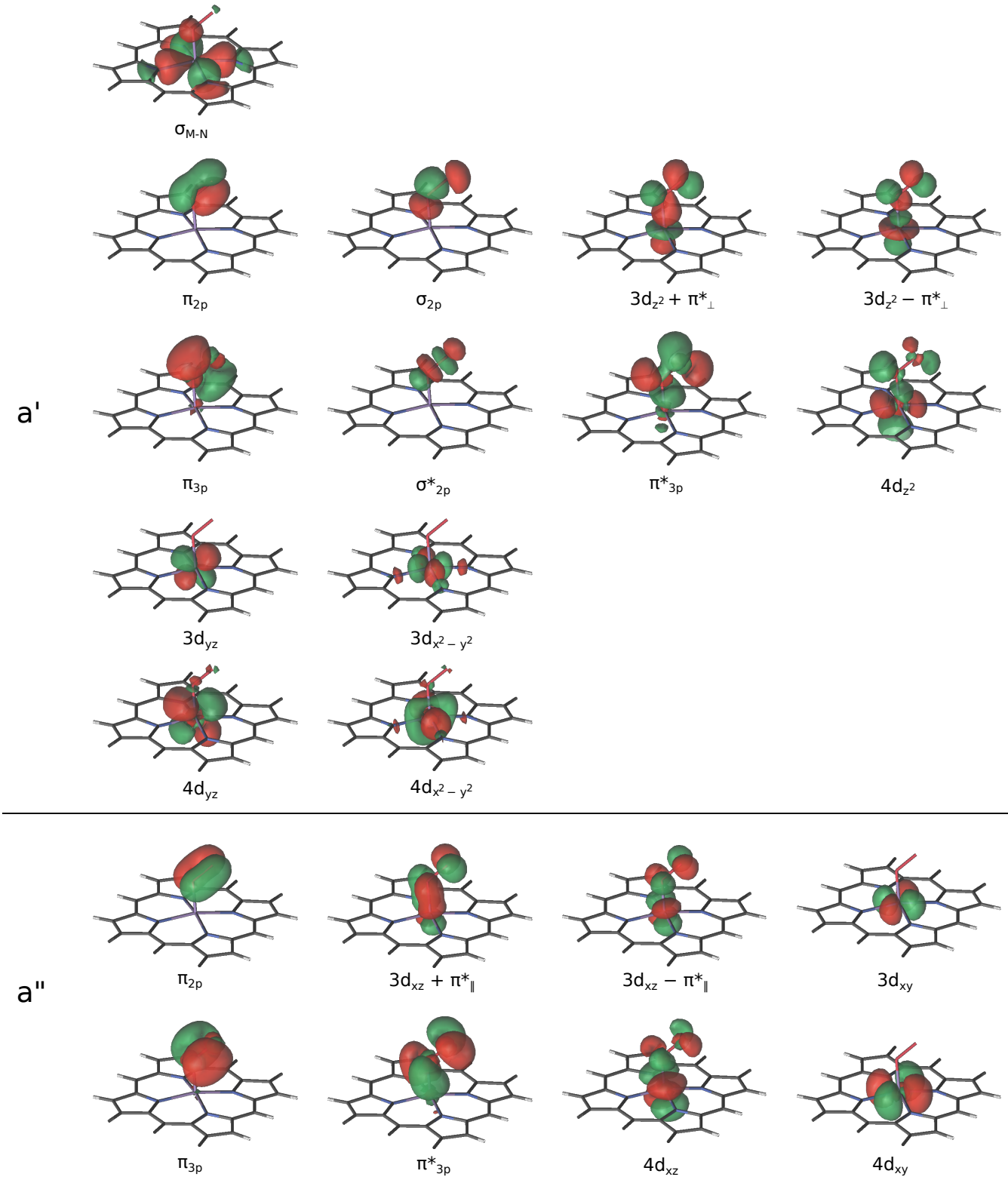


Figure S7: Active orbitals of end-on MP$-O_2$

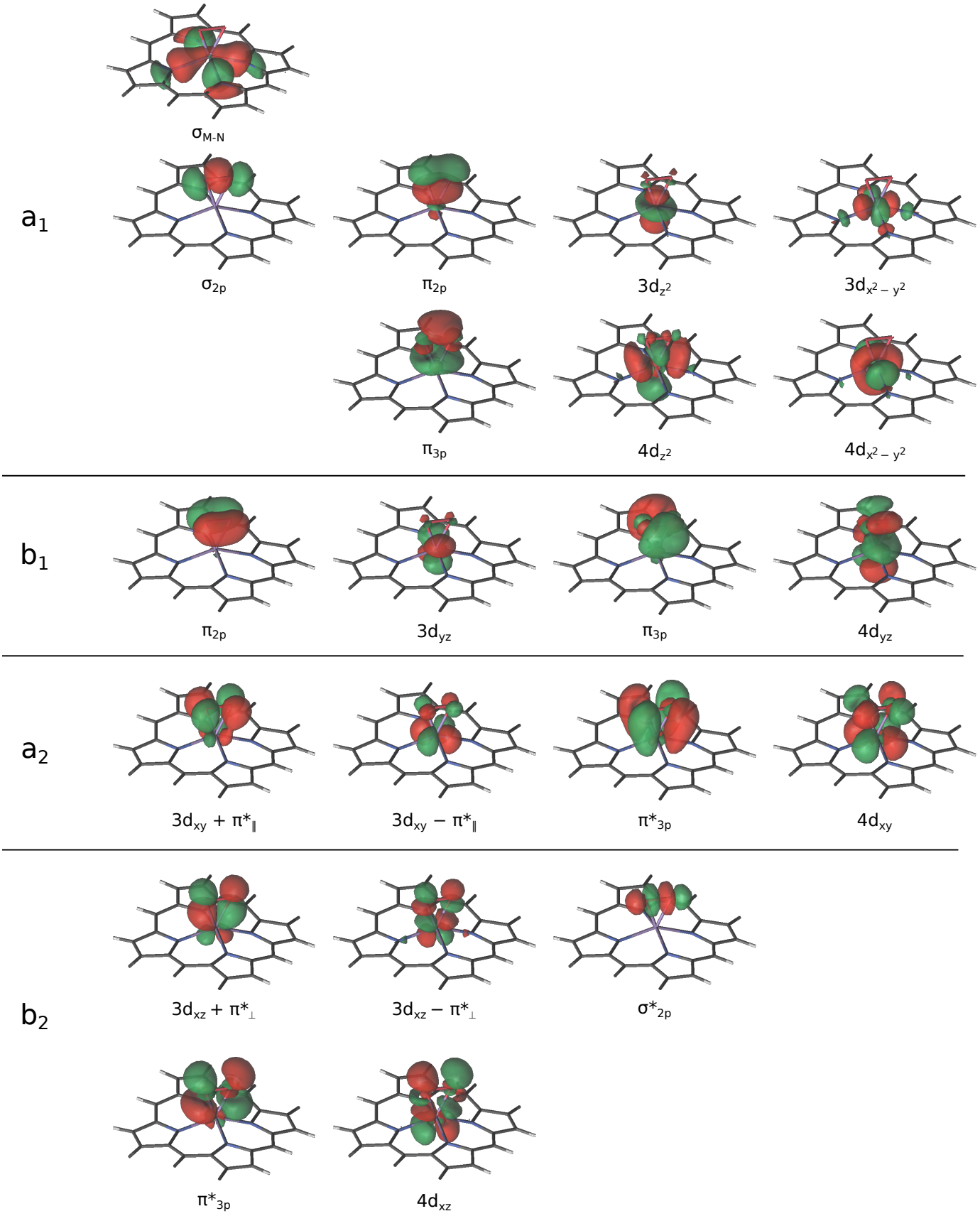


Figure S8: Active orbitals of side-on MP$-O_2$

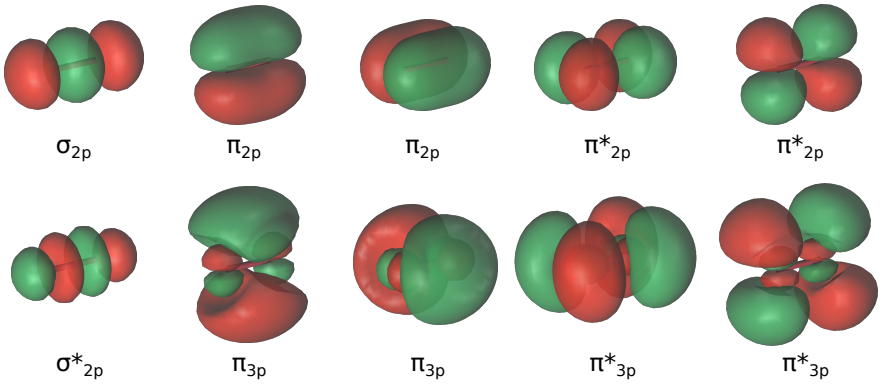


Figure S9: Active orbitals of O_2

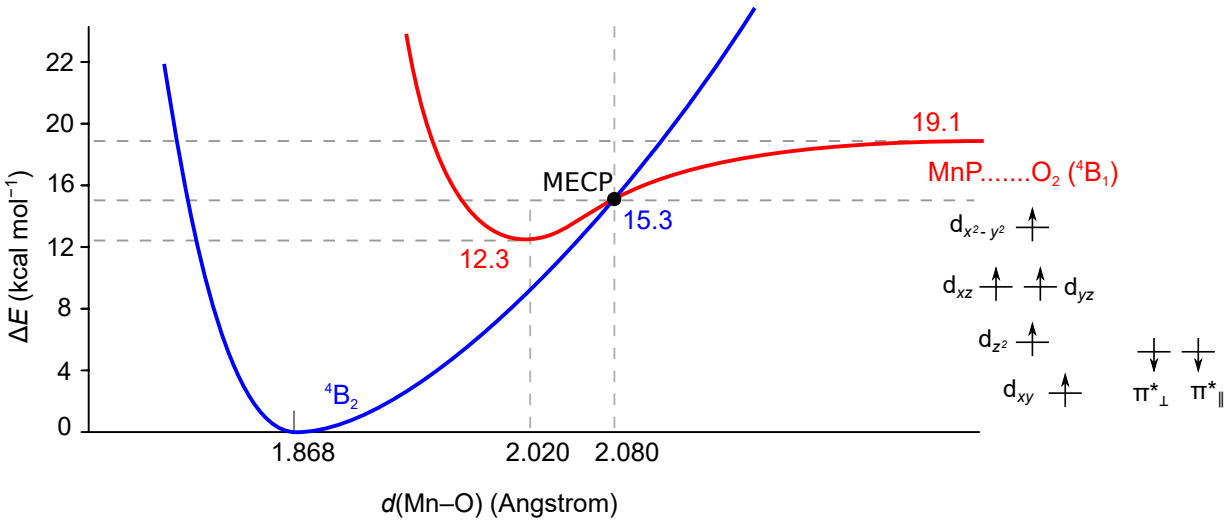


Figure S10: Schematic representation for the dissociation curves of the ground state $^4B_2$ and excited state $^4B_1$ of MnP−O_2. The calculations were done with B97-D/def2-TZVP.

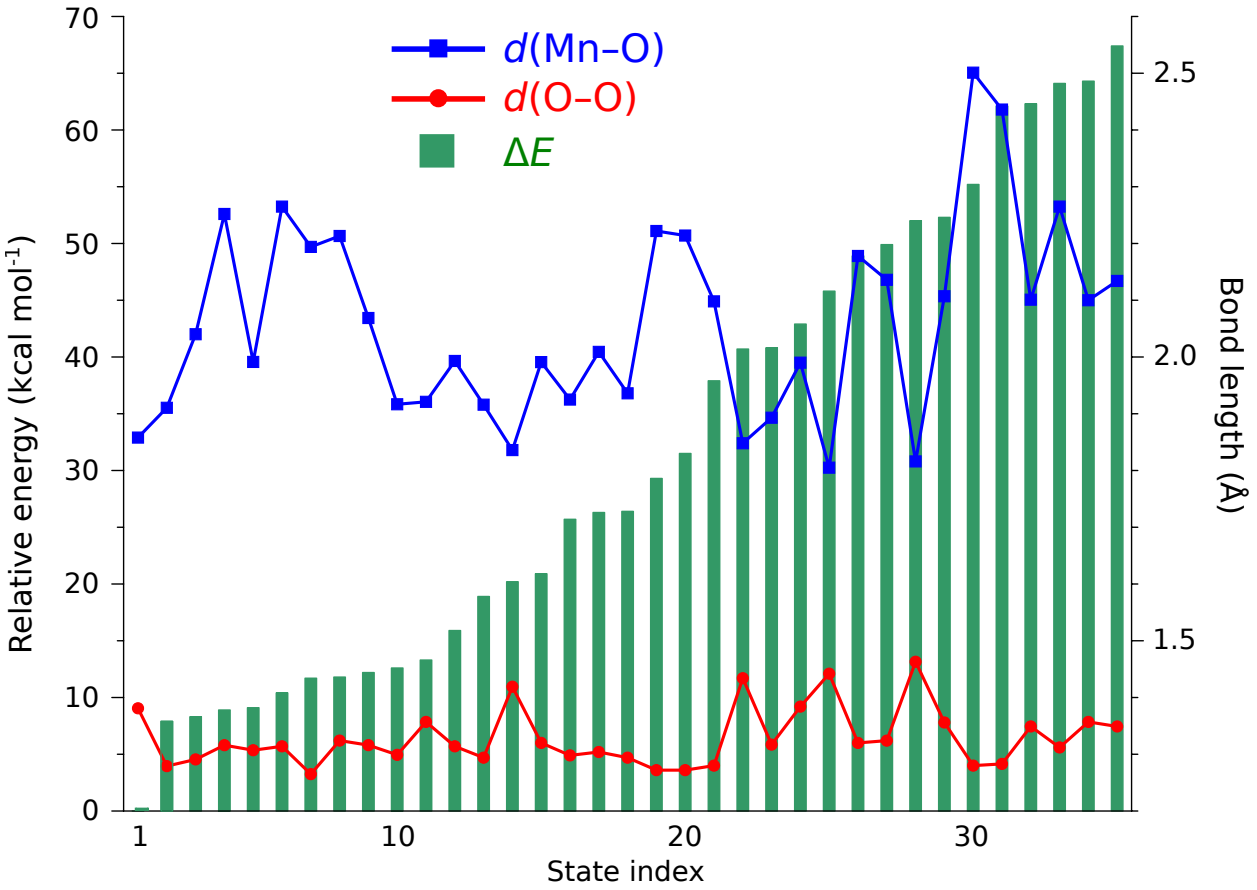


Figure S11: Structural parameters d(O–O) (red line) and d(Mn–O) (blue line) (in Angstrom) of investigated states of MnP$-$O$_2$

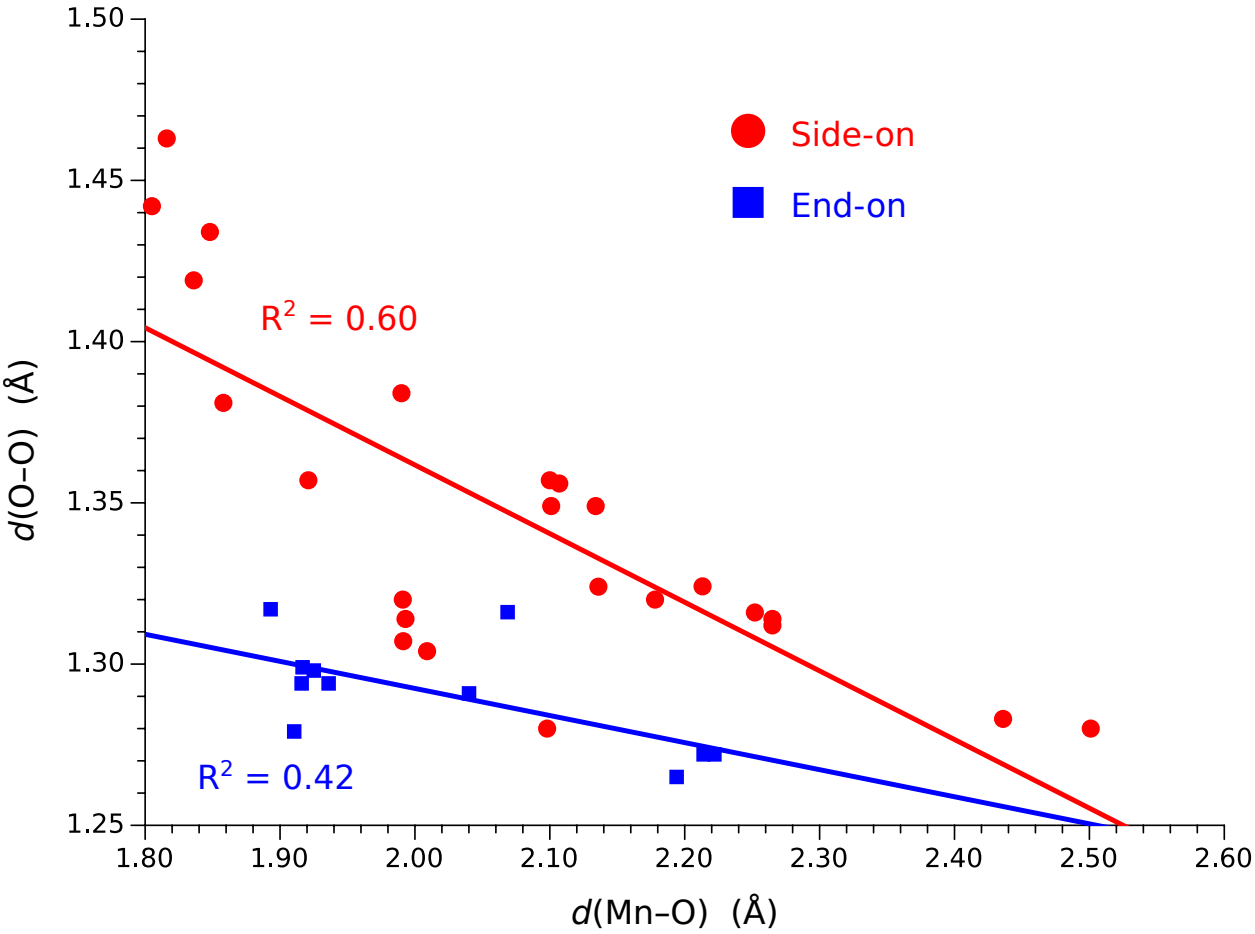


Figure S12: Correlation between d(O–O) and d(Mn–O) (in Angstrom) in end-on (blue line) and side-on (red line) configurations

Table S1: Binding energies of O_2 to MP (in kcal mol^{-1}), calculated with BP86-D3BJ/def2-QZVPP/def2-TZVP

	ΔE	Model correction[a]
FeP–O_2	19.57	
$[Fe(tpps)]^{4-}$–O_2	21.27	1.70
$[FehemeH]^{+}$–O_2	15.29	−4.28
MnP–O_2	35.53	
$[Mn(tpps)]^{4-}$–O_2	38.05	2.52

[a]Model correction going from MP to the large complexes.

Table S2: Binding energies of O_2 to MP (in kcal mol^{-1}) and counterpoise corrections, calculated with CASPT2 and different basis sets[c]

	FeP–O_2		MnP–O_2	
	*no*sp[a]	+sp[b]	*no*sp[a]	+sp[b]
Binding energy				
ANO-RCC	13.60	15.62	9.80	13.36
awCQZ/aTZ	14.32	15.17	11.45	13.88
awCQZ/aQZ	13.13	14.03	10.18	12.71
awC5Z/aQZ	13.28	14.11	10.67	12.93
CBS[Q:5]/Q	13.44	14.20	11.17	13.15
Counterpoise correction				
ANO-RCC	4.67	6.08	5.53	6.81
awCQZ/aTZ	3.21	3.29	4.24	4.34
awCQZ/aQZ	1.29	1.39	1.51	1.65
awC5Z/aQZ	1.31	1.40	1.66	1.81

[a]Only valence correlation. [b]Including 3s3p correlation. [c]Basis set notation: awCnZ/a($n-1$)Z = aug-cc-pwCnZ-DK for the metal atom; aug-cc-pV($n-1$)Z-DK for C, N, O; cc-pV($n-1$)Z-DK for H. CBS[Q:5]/Q = complete basis set extrapolation from awCQZ/aQZ and awC5Z/aQZ results.

Table S3: 3s3p correlation contributions to the binding of O_2 to MP (in kcal mol^{-1}), calculated with RCCSD, RCCSD(T), and CC-CR(2,3)

	FeP–O_2	MnP–O_2
RCCSD	−4.13	−0.94
RCCSD(T)	−5.27	1.56
CC-CR(2,3)	−4.72	2.47

Table S4: 3s3p correlation contributions to the ionization of Fe and Mn (in kcal mol^{-1}), calculated with RCCSD(T) and CASPT2, aug-cc-pwCVTZ-DK basis set

	CCSD(T)			CASPT2		
	*no*sp[a]	+sp[b]	Δ_{sp}[c]	*no*sp[a]	+sp[b]	Δ_{sp}[c]
Fe						
$3d^4\ ^5D$	0.00	0.00	0.00	0.00	0.00	0.00
$3d^4\ ^3H$				73.65	70.80	−2.85
$3d^4\ ^3I$				110.94	106.91	−4.02
$3d^5\ ^6S$	−1258.07	−1261.95	−3.89	−1259.77	−1266.23	−6.46
$3d^5\ ^4G$				−1159.75	−1171.27	−11.51
$3d^5\ ^2I$				−1114.43	−1127.34	−12.91
$3d^6\ ^5D$	−1949.56	−1961.81	−12.25	−1949.23	−1963.76	−14.53
$3d^6\ ^3H$				−1887.40	−1905.90	−18.50
$3d^6\ ^1I$				−1856.55	−1876.45	−19.90
Mn						
$3d^3\ ^4F$	0.00	0.00	0.00	0.00	0.00	0.00
$3d^3\ ^2G$				54.10	49.12	−4.97
$3d^4\ ^5D$	−1174.23	−1182.23	−8.00	−1174.35	−1184.55	−10.20
$3d^4\ ^3H$				−1110.59	−1124.01	−13.41
$3d^5\ ^6S$	−1943.65	−1956.69	−13.04	−1945.02	−1962.95	−17.93
$3d^5\ ^4G$				−1861.12	−1883.91	−22.78
$3d^5\ ^2I$				−1822.74	−1847.20	−24.47

[a]Only valence correlation. [b]Including 3s3p correlation. [c]3s3p correlation contribution

Table S5: NPA charge of the metal atom in FeP, MnP, $[Fe(tpps)]^{4-}$, $[Mn(tpps)]^{4-}$, and $[FehemeH]^{+}$, calculated with BP86-D3BJ/def2-QZVPP/def2-TZVP

	NPA charge
FeP	0.879
$[Fe(tpps)]^{4-}$	0.865
$[FehemeH]^{+}$	1.079
MnP	1.434
$[Mn(tpps)]^{4-}$	1.428

Table S6: Approximated computational cost of the most expensive calculations: computational time, memory, disk space

	$FePO_2$ ($^1A'$ C_s)	$MnPO_2$ ($^4B_1$ C_{2v})
Computational time		
DMRG sweep (m=2000)	∼3 h/iteration	∼1 h/iteration
4RDM calculation (m=2000)	∼8 h	∼2.5 h
CASPT2	∼2.5 d	∼1 d
CR-CC(2,3)[b]	∼2.5 d	∼ 10 d
CASPT2 memory	<30 GB/proc	<15 GB/proc
CASPT2 disk space	∼200 GB/proc	∼100 GB/proc

[a]Calculations done in parallel with 4 processors 256 GB memory, 911 GB disk space, Intel(R) Xeon(R) CPU E5-2680 v3 @ 2.50GHz, 12 cores, 24 threads. [b]Serial calculations

Table S7: BP86 structure of MnP $^6A_{1g}$

37

MN	-0.000000	0.000000	0.000000
N	-1.477351	-1.477351	0.000000
C	3.461810	0.000000	0.000000
C	0.000000	-3.461810	0.000000
C	2.549709	-3.522800	0.000000
C	3.522800	-2.549709	0.000000
C	1.266796	-2.842791	0.000000
C	2.842791	-1.266796	0.000000
H	4.557133	0.000000	0.000000
H	0.000000	-4.557133	0.000000
H	4.605370	-2.687615	0.000000
H	2.687615	-4.605370	0.000000
N	-1.477351	1.477351	0.000000
N	1.477351	-1.477351	0.000000
N	1.477351	1.477351	0.000000
C	-3.461810	-0.000000	0.000000
C	0.000000	3.461810	0.000000
C	2.549709	3.522800	0.000000
C	-2.549709	-3.522800	0.000000
C	-2.549709	3.522800	0.000000
C	3.522800	2.549709	0.000000
C	-3.522800	-2.549709	0.000000
C	-3.522800	2.549709	0.000000
C	1.266796	2.842791	0.000000
C	-1.266796	-2.842791	0.000000
C	-1.266796	2.842791	0.000000
C	2.842791	1.266796	0.000000
C	-2.842791	-1.266796	0.000000
C	-2.842791	1.266796	0.000000
H	-4.557133	0.000000	0.000000
H	0.000000	4.557133	0.000000
H	4.605370	2.687615	0.000000
H	-4.605370	-2.687615	0.000000
H	-4.605370	2.687615	0.000000
H	2.687615	4.605370	0.000000
H	-2.687615	-4.605370	0.000000
H	-2.687615	4.605370	0.000000

Table S8: BP86 structure of MnP$-O_2$ $^4B_2$

39

MN	0.000000	0.000000	-0.419971
O	0.000000	-0.690632	-2.145037
O	0.000000	0.690632	-2.145037
N	0.000000	1.994564	0.201396
N	2.012664	0.000000	-0.088239
N	-2.012664	0.000000	-0.088239
N	0.000000	-1.994564	0.201396
C	-1.101867	2.829377	0.250721
C	2.847991	-1.104753	-0.068042
C	1.101867	2.829377	0.250721
C	2.847991	1.104753	-0.068042
C	0.685172	4.204719	0.417416
C	4.229977	0.686012	-0.103032
C	-0.685172	4.204719	0.417416
C	4.229977	-0.686012	-0.103032
C	-2.847991	-1.104753	-0.068042
C	-1.101867	-2.829377	0.250721
C	-4.229977	-0.686012	-0.103032
C	-0.685172	-4.204719	0.417416
C	-4.229977	0.686012	-0.103032
C	0.685172	-4.204719	0.417416
C	-2.847991	1.104753	-0.068042
C	1.101867	-2.829377	0.250721
C	-2.427695	-2.425180	0.090438
C	-2.427695	2.425180	0.090438
C	2.427695	-2.425180	0.090438
C	2.427695	2.425180	0.090438
H	-3.198772	3.200491	0.117483
H	3.198772	-3.200491	0.117483
H	-5.083078	1.365445	-0.092074
H	1.366215	-5.051821	0.508024
H	-5.083078	-1.365445	-0.092074
H	-1.366215	-5.051821	0.508024
H	-3.198772	-3.200491	0.117483
H	3.198772	3.200491	0.117483
H	1.366215	5.051821	0.508024
H	5.083078	1.365445	-0.092074
H	-1.366215	5.051821	0.508024
H	5.083078	-1.365445	-0.092074

Table S9: BP86 structure of FeP $^3A_{2g}$

37

FE	-0.000000	0.000000	0.000000
N	-1.412573	-1.412573	0.000000
C	3.437277	-0.000000	0.000000
C	-0.000000	-3.437277	0.000000
C	2.504407	-3.473828	0.000000
C	3.473828	-2.504407	0.000000
C	1.233048	-2.789799	0.000000
C	2.789799	-1.233048	0.000000
H	4.531268	0.000000	0.000000
H	0.000000	-4.531268	0.000000
H	4.557963	-2.625070	0.000000
H	2.625070	-4.557963	0.000000
N	-1.412573	1.412573	0.000000
N	1.412573	-1.412573	0.000000
N	1.412573	1.412573	0.000000
C	-3.437277	0.000000	0.000000
C	0.000000	3.437277	0.000000
C	2.504407	3.473828	0.000000
C	-2.504407	-3.473828	0.000000
C	-2.504407	3.473828	0.000000
C	3.473828	2.504407	0.000000
C	-3.473828	-2.504407	0.000000
C	-3.473828	2.504407	0.000000
C	1.233048	2.789799	0.000000
C	-1.233048	-2.789799	0.000000
C	-1.233048	2.789799	0.000000
C	2.789799	1.233048	0.000000
C	-2.789799	-1.233048	0.000000
C	-2.789799	1.233048	0.000000
H	-4.531268	0.000000	0.000000
H	0.000000	4.531268	0.000000
H	4.557963	2.625070	0.000000
H	-4.557963	-2.625070	0.000000
H	-4.557963	2.625070	0.000000
H	2.625070	4.557963	0.000000
H	-2.625070	-4.557963	0.000000
H	-2.625070	4.557963	0.000000

Table S10: BP86 structure of FeP$-$O$_2$ ^{1}A$'$

39

FE	-0.035477	0.001436	0.000000
O	-0.005914	-1.808768	0.000000
O	1.107650	-2.438912	0.000000
N	1.362796	0.250373	1.409282
N	1.362796	0.250373	-1.409282
N	-1.463257	0.160510	1.408574
N	-1.463257	0.160510	-1.408574
C	1.181755	0.225776	2.784175
C	1.181755	0.225776	-2.784175
C	2.739197	0.307341	1.231533
C	2.739197	0.307341	-1.231533
C	3.421596	0.333840	2.503499
C	3.421596	0.333840	-2.503499
C	2.452072	0.282953	3.469865
C	2.452072	0.282953	-3.469865
C	-2.841076	0.165785	1.231129
C	-2.841076	0.165785	-1.231129
C	-3.523986	0.171659	2.503559
C	-3.523986	0.171659	-2.503559
C	-2.553811	0.162097	3.470407
C	-2.553811	0.162097	-3.470407
C	-1.282189	0.154233	2.785129
C	-1.282189	0.154233	-2.785129
C	-3.489024	0.165274	0.000000
C	-0.049760	0.168345	3.430778
C	-0.049760	0.168345	-3.430778
C	3.385639	0.330261	0.000000
H	-0.048987	0.157159	4.524646
H	-0.048987	0.157159	-4.524646
H	-2.671491	0.167468	4.554832
H	-2.671491	0.167468	-4.554832
H	-4.607891	0.187748	2.623715
H	-4.607891	0.187748	-2.623715
H	-4.582888	0.166326	0.000000
H	4.478863	0.368105	0.000000
H	4.504139	0.388212	2.624084
H	4.504139	0.388212	-2.624084
H	2.569176	0.284253	4.554361
H	2.569176	0.284253	-4.554361