Electronic Supplementary Information:

A Force Field for a Manganese-Vanadium Water Oxidation Catalyst: Redox Potentials in Solution as Showcase

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S1 Force field parameters

S1.1 Bond parameters

The energy is given according to this equation:

$$E_{\text{bonds}} = \sum_{i}^{n_{\text{bonds}}} K_{r,i}(r_i - r_{i,\text{eq}})^2 \tag{1}$$

with $K_{r,i}$ in kcal mol^{-1}Å^{-2} and $r_{i,\text{eq}}$ in Å. Table S1 lists all of these parameters, based on the definition of the atom types in Figure 1 in the main text.

The parameters in Table S1 were obtained by iterative and manual adjustment as described in the main manuscript in Section 3.4.

Table S1: List of all obtained parameters for bonds. Parameters $K_{r,i}$ are in kcal mol^{-1}Å^{-2} and $r_{i,\text{eq}}$ in Å.

		$-[Mn_4^{IV}]-$		$-[Mn^{III}Mn_3^{IV}]-$	
Atom 1	Atom 2	$K_{r,i}$	$r_{i,\text{eq}}$	$K_{r,i}$	$r_{i,\text{eq}}$
MA	o	390.89	1.974	272.15	2.025
MA	OE	484.89	1.834	402.50	1.846
MA	OF	476.81	1.830	326.25	1.857
MA	OJ	214.17	1.997	342.36	1.918
MA	OK	354.70	1.949	338.57	1.948
MA	OL	309.29	1.944	300.53	1.963
MB	OK	430.13	1.859	476.11	1.873
MB	OL	529.00	1.866	501.68	1.852
MB	OM	422.90	1.866	465.13	1.854
MB	ON	359.13	1.961	307.96	2.003
MB	OO	288.80	1.978	414.55	1.943
MB	OP	336.68	1.978	320.98	2.013
MC	o	309.73	1.972	180.98	2.211
MC	OD	501.96	1.826	365.23	1.874
MC	OI	501.09	1.826	491.52	1.871
MC	OJ	262.29	1.986	105.87	2.295
MC	OL	410.56	1.944	290.72	2.002
MC	OM	366.18	1.963	263.25	1.990
MD	o	305.92	1.971	244.44	2.026
MD	OG	509.52	1.833	401.89	1.845
MD	OH	437.51	1.823	514.28	1.847
MD	OJ	333.46	1.982	111.49	1.943
MD	OK	466.53	1.945	300.05	1.950
MD	OM	441.96	1.945	273.58	1.982
VA	OA	3154.63	1.605	1465.76	1.616
VA	OB	731.22	1.787	706.66	1.781
VA	OR	731.22	1.787	649.53	1.779
VB	OB	727.53	1.812	698.35	1.822
VB	OC	3845.17	1.611	852.44	1.622
VB	OD	609.25	1.769	595.83	1.754
VB	OE	810.59	1.767	553.47	1.766
VB	OH	703.17	1.769	750.34	1.764
VB	OI	656.22	1.772	665.24	1.753
VC	OF	703.69	1.771	442.89	1.771
VC	OG	827.46	1.762	607.14	1.770
VC	OQ	3845.17	1.611	1158.56	1.618
VC	OR	727.53	1.812	563.63	1.832
c	o	895.67	1.288	1070.23	1.275
c	ON	781.31	1.293	724.79	1.290
c	OO	771.11	1.290	703.55	1.304
c	OP	956.53	1.286	871.97	1.288

S1.2 Angle parameters

The energy is given according to this equation:

$$E_{\text{angles}} = \sum_{i}^{n_{\text{angles}}} K_{\alpha,i}(\alpha_i - \alpha_{i,\text{eq}})^2 \tag{2}$$

with $K_{\alpha,i}$ in kcal mol^{-1}rad^{-2} and $\alpha_{i,\text{eq}}$ in degree. Table S2 lists all of these parameters, based on the definition of the atom types in Figure 1 in the main text.

The parameters in Table S2 were obtained by iterative and manual adjustment as described in the main manuscript in Section 3.4.

Table S2: List of all obtained parameters for angles. Parameters $K_{\alpha,i}$ are in kcal mol^{-1}rad^{-2} and $r_{i,\mathrm{eq}}$ in degree.

			$-[Mn_4^{IV}]-$		$-[Mn^{III}Mn_3^{IV}]-$					$-[Mn_4^{IV}]-$		$-[Mn^{III}Mn_3^{IV}]-$	
Atom 1	Atom 2	Atom 3	$K_{\alpha,i}$	$\alpha_{i,\mathrm{eq}}$	$K_{\alpha,i}$	$\alpha_{i,\mathrm{eq}}$	Atom 1	Atom 2	Atom 3	$K_{\alpha,i}$	$\alpha_{i,\mathrm{eq}}$	$K_{\alpha,i}$	$\alpha_{i,\mathrm{eq}}$
MA	OJ	MC	600	96.43	600	94.024	OG	MD	o	200	97.17	200	97.014
MA	OJ	MD	600	96.95	600	99.215	OH	MD	o	200	97.80	200	96.936
MC	OJ	MD	600	96.47	600	93.590	OG	MD	OH	200	95.71	200	96.166
MA	OK	MB	600	96.34	600	95.312	OJ	MD	o	200	164.20	200	164.407
MA	OK	MD	600	99.82	600	97.940	OJ	MD	OG	200	92.35	200	90.116
MB	OK	MD	600	95.33	600	95.711	OJ	MD	OH	200	92.55	200	94.665
MA	OL	MB	600	96.24	600	95.494	OK	MD	o	200	87.16	200	86.348
MA	OL	MC	600	99.69	600	102.534	OK	MD	OG	150	90.37	150	91.781
MB	OL	MC	600	96.31	600	96.661	OK	MD	OH	150	170.12	150	169.483
MB	OM	MC	600	95.71	600	96.968	OK	MD	OJ	150	81.32	150	80.804
MB	OM	MD	600	95.11	600	95.252	OK	MD	OM	200	82.02	200	81.289
MC	OM	MD	600	98.46	600	102.656	OM	MD	o	200	86.81	200	85.926
OE	MA	o	200	97.78	200	96.185	OM	MD	OG	150	169.81	150	170.637
OF	MA	o	200	97.80	200	96.316	OM	MD	OH	150	91.32	150	90.281
OE	MA	OF	200	95.36	200	95.998	OM	MD	OJ	150	82.25	150	85.427
OJ	MA	o	200	163.36	200	165.622	MC	OD	VB	200	120.41	200	120.013
OJ	MA	OE	200	93.25	200	94.241	MA	OE	VB	200	119.83	200	119.946
OJ	MA	OF	200	92.49	200	90.247	MA	OF	VC	200	120.31	200	115.819
OK	MA	o	200	86.75	200	87.049	MD	OG	VC	200	120.84	200	116.271
OK	MA	OE	150	169.44	150	169.752	MD	OH	VB	200	120.44	200	120.093
OK	MA	OF	150	91.28	150	91.590	MC	OI	VB	200	120.06	200	119.743
OK	MA	OJ	150	80.85	150	81.503	VA	OB	VB	50	140.35	50	140.396
OK	MA	OL	200	80.91	200	81.657	VA	OR	VC	50	140.35	50	136.211
OL	MA	o	200	87.07	200	86.089	OA	VA	OB	100	106.56	100	105.619
OL	MA	OE	150	91.65	150	90.387	OB	VA	OB	90	111.83	90	111.697
OL	MA	OF	150	169.32	150	170.907	OA	VA	OR	100	106.56	100	106.089
OL	MA	OJ	150	81.09	150	86.081	OB	VA	OR	90	111.83	90	113.054
OK	MB	OL	600	85.43	600	86.718	OB	VB	OC	100	109.82	100	108.818
OK	MB	OM	600	86.51	600	86.858	OB	VB	OD	90	111.21	90	110.370
OK	MB	ON	200	88.28	200	87.183	OB	VB	OE	90	109.75	90	109.033
OK	MB	OO	200	169.43	200	173.967	OR	VC	OF	90	110.35	90	113.060
OK	MB	OP	200	88.38	200	87.174	OR	VC	OG	90	111.03	90	112.120
OL	MB	OM	600	85.89	600	85.911	OB	VB	OH	90	111.16	90	108.791
OL	MB	ON	200	170.27	200	170.477	OB	VB	OI	90	110.30	90	110.946
OL	MB	OO	200	87.47	200	92.218	OC	VB	OD	100	109.28	100	109.052
OL	MB	OP	200	87.70	200	88.419	OC	VB	OE	100	109.31	100	109.020
OM	MB	ON	200	88.50	200	89.328	OQ	VC	OF	100	109.07	100	107.082
OM	MB	OO	200	87.66	200	92.683	OQ	VC	OG	100	109.50	100	107.537
OM	MB	OP	200	170.35	200	170.127	OC	VB	OH	100	109.50	100	108.489
ON	MB	OO	150	98.25	150	93.75	OC	VB	OI	100	109.24	100	108.884
ON	MB	OP	150	97.31	150	95.617	OD	VB	OE	90	106.75	90	109.702
OO	MB	OP	150	96.58	150	93.129	OF	VC	OG	90	106.30	90	108.898
OD	MC	o	200	97.85	200	103.646	OH	VB	OI	90	105.50	90	109.820
OI	MC	o	200	97.47	200	105.641	OQ	VC	OR	100	109.82	100	106.999
OD	MC	OI	200	95.26	200	95.922	MA	o	c	250	125.28	250	124.000
OJ	MC	o	200	163.39	200	153.838	MC	o	c	250	125.24	250	124.487
OJ	MC	OD	200	92.89	200	91.403	MD	o	c	250	124.73	250	125.231
OJ	MC	OI	200	92.80	200	92.362	MB	ON	c	250	123.47	250	123.352
OL	MC	o	200	86.76	200	83.547	MB	OO	c	250	123.74	250	124.725
OL	MC	OD	150	92.05	150	91.693	MB	OP	c	250	123.93	250	123.152
OL	MC	OI	150	169.26	150	164.914	c3	c	o	84	116.82	84	117.676
OL	MC	OJ	150	81.37	150	75.711	c3	c	ON	84	117.10	84	116.891
OL	MC	OM	200	81.17	200	78.462	c3	c	OO	84	117.38	84	115.301
OM	MC	o	200	86.28	200	85.324	c3	c	OP	84	117.13	84	116.724
OM	MC	OD	150	170.61	150	164.813	OP	c	o	118	125.64	118	126.108
OM	MC	OI	150	90.94	150	91.545	ON	c	o	118	125.28	118	125.941
OM	MC	OJ	150	81.66	150	76.501	OO	c	o	118	125.50	118	125.008

S1.3 Dihedral parameters

The energy is given according to this equation:

$$E_{\text{dihedrals}} = \sum_{i}^{n_{\text{dihedrals}}} V_i \left(1 + \cos(n_i \phi_i - \gamma_i)\right) \tag{3}$$

with V_i (half the torsion barrier) in kcal mol^{-1}, n_i the periodicity, and γ_i the phase in degrees. Tables S3, S4, S5, S6, and S7 lists all of these parameters, based on the definition of the atom types in Figure 1 in the main text.

The parameters in these tables were adapted from References [1] and [2].

Table S3: List of all obtained parameters for dihedrals. Parameters V_i are in kcal mol^{-1}, γ_i is in degrees, and n_i is unitless.

				— $[Mn_4^{IV}]$ —			— $[Mn^{III}Mn_3^{IV}]$ —		
Atom 1	Atom 2	Atom 3	Atom 4	V_i	γ_i	n_i	V_i	γ_i	n_i
MA	OJ	MC	OL	0.00	93.24	1	3.00	8.03	1
MA	OJ	MC	OM	0.00	93.24	1	3.00	8.03	1
MA	OJ	MD	OK	0.00	93.24	1	3.00	93.24	1
MA	OJ	MD	OM	0.00	93.24	1	3.00	8.03	1
MA	OK	MB	OL	0.00	93.05	1	3.00	8.03	1
MA	OK	MB	OM	0.00	93.05	1	3.00	8.03	1
MA	OK	MD	OJ	0.00	8.03	1	3.00	8.03	1
MA	OK	MD	OM	0.00	90.72	1	3.00	8.03	1
MA	OL	MB	OK	0.00	93.05	1	3.00	8.03	1
MA	OL	MB	OM	0.00	93.05	1	3.00	8.03	1
MA	OL	MC	OJ	0.00	8.03	1	3.00	8.03	1
MA	OL	MC	OM	0.00	90.72	1	3.00	8.03	1
MB	OK	MA	OJ	0.00	94.40	1	3.00	94.40	1
MB	OK	MA	OL	0.00	5.51	1	3.00	8.03	1
MB	OK	MD	OJ	0.00	94.40	1	3.00	94.40	1
MB	OK	MD	OM	0.00	5.51	1	3.00	8.03	1
MB	OL	MA	OJ	0.00	94.40	1	3.00	8.03	1
MB	OL	MA	OK	0.00	5.51	1	3.00	8.03	1
MB	OL	MC	OJ	0.00	94.40	1	3.00	8.03	1
MB	OL	MC	OM	0.00	5.51	1	3.00	8.03	1
MB	OM	MC	OJ	0.00	94.40	1	3.00	8.03	1
MB	OM	MC	OL	0.00	5.51	1	3.00	8.03	1
MB	OM	MD	OJ	0.00	94.40	1	3.00	8.03	1
MB	OM	MD	OK	0.00	5.51	1	3.00	8.03	1
MC	OJ	MA	OK	0.00	93.24	1	3.00	93.24	1
MC	OJ	MA	OL	0.00	93.24	1	3.00	8.03	1
MC	OJ	MD	OK	0.00	93.24	1	3.00	93.24	1
MC	OJ	MD	OM	0.00	93.24	1	3.00	8.03	1
MC	OL	MA	OJ	0.00	8.03	1	3.00	8.03	1
MC	OL	MA	OK	0.00	90.72	1	3.00	8.03	1
MC	OL	MB	OK	0.00	93.05	1	3.00	8.03	1
MC	OL	MB	OM	0.00	93.05	1	3.00	8.03	1
MC	OM	MB	OK	0.00	93.05	1	3.00	8.03	1
MC	OM	MB	OL	0.00	93.05	1	3.00	8.03	1
MC	OM	MD	OJ	0.00	8.03	1	3.00	8.03	1
MC	OM	MD	OK	0.00	90.72	1	3.00	8.03	1

Table S4: Continuation of Table S3.

				$-$ [Mn_4^{IV}] $-$			$-$ [$Mn^{III}Mn_3^{IV}$] $-$		
Atom 1	Atom 2	Atom 3	Atom 4	V_i	γ_i	n_i	V_i	γ_i	n_i
MD	OJ	MA	OK	0.00	93.24	1	3.00	93.24	1
MD	OJ	MA	OL	0.00	93.24	1	3.00	8.03	1
MD	OJ	MC	OL	0.00	93.24	1	3.00	8.03	1
MD	OJ	MC	OM	0.00	93.24	1	3.00	8.03	1
MD	OK	MA	OJ	0.00	8.03	1	3.00	8.03	1
MD	OK	MA	OL	0.00	90.72	1	3.00	8.03	1
MD	OK	MB	OL	0.00	93.05	1	3.00	8.03	1
MD	OK	MB	OM	0.00	93.05	1	3.00	8.03	1
MD	OM	MB	OK	0.00	93.05	1	3.00	8.03	1
MD	OM	MB	OL	0.00	93.05	1	3.00	8.03	1
MD	OM	MC	OJ	0.00	8.03	1	3.00	8.03	1
MD	OM	MC	OL	0.00	90.72	1	3.00	8.03	1
MA	OJ	MC	o	0.00	25.90	1	3.00	25.90	1
MA	OJ	MC	OD	0.00	75.20	1	3.00	75.20	1
MA	OJ	MC	OI	0.00	75.20	1	3.00	75.20	1
MA	OJ	MD	o	0.00	25.90	1	3.00	74.40	1
MA	OJ	MD	OG	0.00	75.20	1	3.00	8.03	1
MA	OJ	MD	OH	0.00	75.20	1	3.00	8.03	1
MA	OK	MB	ON	0.00	27.20	1	3.00	72.90	1
MA	OK	MB	OO	0.00	27.20	1	3.00	72.90	1
MA	OK	MB	OP	0.00	27.20	1	3.00	72.90	1
MA	OK	MD	o	0.00	177.23	1	5.00	177.23	1
MA	OK	MD	OG	0.00	75.52	1	3.00	8.03	1
MA	OK	MD	OH	0.00	75.52	1	3.00	8.03	1
MA	OL	MB	ON	0.00	27.20	1	3.00	8.03	1
MA	OL	MB	OO	0.00	27.20	1	3.00	8.03	1
MA	OL	MB	OP	0.00	27.20	1	3.00	8.03	1
MA	OL	MC	o	0.00	177.23	1	3.00	8.03	1
MA	OL	MC	OD	0.00	75.52	1	3.00	8.03	1
MA	OL	MC	OI	0.00	75.52	1	3.00	8.03	1
MB	OK	MA	o	0.00	81.34	1	3.00	81.34	1
MB	OK	MA	OE	0.00	105.34	1	3.00	8.03	1
MB	OK	MA	OF	0.00	105.34	1	3.00	8.03	1
MB	OK	MD	o	0.00	81.34	1	3.00	81.34	1
MB	OK	MD	OG	0.00	105.34	1	3.00	8.03	1
MB	OK	MD	OH	0.00	105.34	1	3.00	8.03	1
MB	OL	MA	o	0.00	81.34	1	3.00	8.03	1
MB	OL	MA	OE	0.00	105.34	1	3.00	8.03	1
MB	OL	MA	OF	0.00	105.34	1	3.00	8.03	1
MB	OL	MC	o	0.00	81.34	1	3.00	8.03	1
MB	OL	MC	OD	0.00	105.34	1	3.00	8.03	1
MB	OL	MC	OI	0.00	105.34	1	3.00	8.03	1
MB	OM	MC	o	0.00	81.34	1	3.00	8.03	1
MB	OM	MC	OD	0.00	105.34	1	3.00	8.03	1
MB	OM	MC	OI	0.00	105.34	1	3.00	8.03	1
MB	OM	MD	o	0.00	81.34	1	3.00	8.03	1
MB	OM	MD	OG	0.00	105.34	1	3.00	8.03	1
MB	OM	MD	OH	0.00	105.34	1	3.00	8.03	1

Table S5: Continuation #2 of Table S3.

				— $[Mn_4^{IV}]$ —			— $[Mn^{III}Mn_3^{IV}]$ —		
Atom 1	Atom 2	Atom 3	Atom 4	V_i	γ_i	n_i	V_i	γ_i	n_i
MC	OJ	MA	o	0.00	25.90	1	3.00	74.40	1
MC	OJ	MA	OE	0.00	75.20	1	3.00	8.03	1
MC	OJ	MA	OF	0.00	75.20	1	3.00	8.03	1
MC	OJ	MD	o	0.00	25.90	1	3.00	74.40	1
MC	OJ	MD	OG	0.00	75.20	1	3.00	8.03	1
MC	OJ	MD	OH	0.00	75.20	1	3.00	8.03	1
MC	OL	MA	o	0.00	177.23	1	3.00	8.03	1
MC	OL	MA	OE	0.00	75.52	1	3.00	8.03	1
MC	OL	MA	OF	0.00	75.52	1	3.00	8.03	1
MC	OL	MB	ON	0.00	27.20	1	3.00	8.03	1
MC	OL	MB	OO	0.00	27.20	1	3.00	8.03	1
MC	OL	MB	OP	0.00	27.20	1	3.00	8.03	1
MC	OM	MB	ON	0.00	27.20	1	3.00	8.03	1
MC	OM	MB	OO	0.00	27.20	1	3.00	8.03	1
MC	OM	MB	OP	0.00	27.20	1	3.00	8.03	1
MC	OM	MD	o	0.00	177.23	1	3.00	8.03	1
MC	OM	MD	OG	0.00	75.52	1	3.00	8.03	1
MC	OM	MD	OH	0.00	75.52	1	3.00	8.03	1
MD	OJ	MA	o	0.00	25.90	1	3.00	74.40	1
MD	OJ	MA	OE	0.00	75.20	1	3.00	8.03	1
MD	OJ	MA	OF	0.00	75.20	1	3.00	8.03	1
MD	OJ	MC	o	0.00	25.90	1	3.00	25.90	1
MD	OJ	MC	OD	0.00	75.20	1	3.00	75.20	1
MD	OJ	MC	OI	0.00	75.20	1	3.00	75.20	1
MD	OK	MA	o	0.00	177.23	1	5.00	177.23	1
MD	OK	MA	OE	0.00	75.52	1	3.00	8.03	1
MD	OK	MA	OF	0.00	75.52	1	3.00	8.03	1
MD	OK	MB	ON	0.00	27.20	1	3.00	72.90	1
MD	OK	MB	OO	0.00	27.20	1	3.00	72.90	1
MD	OK	MB	OP	0.00	27.20	1	3.00	72.90	1
MD	OM	MB	ON	0.00	27.20	1	3.00	8.03	1
MD	OM	MB	OO	0.00	27.20	1	3.00	8.03	1
MD	OM	MB	OP	0.00	27.20	1	3.00	8.03	1
MD	OM	MC	o	0.00	177.23	1	3.00	8.03	1
MD	OM	MC	OD	0.00	75.52	1	3.00	8.03	1
MD	OM	MC	OI	0.00	75.52	1	3.00	8.03	1
MA	OE	VB	OB	0.00	76.60	2	3.00	8.03	1
MA	OE	VB	OC	0.00	163.04	1	3.00	8.03	1
MA	OE	VB	OD	0.00	45.53	1	3.00	8.03	1
MA	OF	VC	OG	0.00	45.53	1	3.00	8.03	1
MA	OF	VC	OQ	0.00	163.04	1	3.00	8.03	1
MA	OF	VC	OR	0.00	76.60	2	3.00	8.03	1
MC	OD	VB	OB	0.00	76.60	2	3.00	76.15	1
MC	OD	VB	OC	0.00	163.04	1	3.00	163.04	1
MC	OD	VB	OE	0.00	45.53	1	3.00	8.03	1
MC	OI	VB	OB	0.00	76.60	2	3.00	76.15	1
MC	OI	VB	OC	0.00	163.04	1	3.00	163.04	1
MC	OI	VB	OH	0.00	45.53	1	3.00	8.03	1
MD	OG	VC	OF	0.00	45.53	1	3.00	8.03	1
MD	OG	VC	OQ	0.00	163.04	1	3.00	8.03	1
MD	OG	VC	OR	0.00	76.60	2	3.00	8.03	1
MD	OH	VB	OB	0.00	76.60	2	3.00	8.03	1
MD	OH	VB	OC	0.00	163.04	1	3.00	8.03	1
MD	OH	VB	OI	0.00	45.53	1	3.00	8.03	1

Table S6: Continuation #3 of Table S3.

				$-$ [Mn_4^{IV}] $-$			$-$ [$Mn^{III}Mn_3^{IV}$] $-$		
Atom 1	Atom 2	Atom 3	Atom 4	V_i	γ_i	n_i	V_i	γ_i	n_i
VB	OE	MA	o	0.00	152.37	1	3.00	8.03	1
VB	OE	MA	OF	0.00	110.21	1	3.00	8.03	1
VB	OE	MA	OJ	0.00	16.09	1	3.00	8.03	1
VB	OE	MA	OK	0.00	54.10	1	3.00	8.03	1
VB	OE	MA	OL	0.00	54.10	1	3.00	8.03	1
VC	OF	MA	o	0.00	152.37	1	3.00	8.03	1
VC	OF	MA	OE	0.00	110.21	1	3.00	8.03	1
VC	OF	MA	OJ	0.00	16.09	1	3.00	8.03	1
VC	OF	MA	OK	0.00	54.10	1	3.00	8.03	1
VC	OF	MA	OL	0.00	54.10	1	3.00	8.03	1
VB	OD	MC	o	0.00	152.37	1	3.00	152.37	1
VB	OD	MC	OI	0.00	110.21	1	3.00	110.50	1
VB	OD	MC	OJ	0.00	16.09	1	3.00	16.09	1
VB	OD	MC	OL	0.00	54.10	1	3.00	8.03	1
VB	OD	MC	OM	0.00	54.10	1	3.00	8.03	1
VB	OI	MC	o	0.00	152.37	1	3.00	152.37	1
VB	OI	MC	OD	0.00	110.21	1	3.00	110.50	1
VB	OI	MC	OJ	0.00	16.09	1	3.00	16.09	1
VB	OI	MC	OL	0.00	54.10	1	3.00	8.03	1
VB	OI	MC	OM	0.00	54.10	1	3.00	8.03	1
VB	OH	MD	o	0.00	152.37	1	3.00	8.03	1
VB	OH	MD	OG	0.00	110.21	1	3.00	8.03	1
VB	OH	MD	OJ	0.00	16.09	1	3.00	8.03	1
VB	OH	MD	OK	0.00	54.10	1	3.00	8.03	1
VB	OH	MD	OM	0.00	54.10	1	3.00	8.03	1
VC	OG	MD	o	0.00	152.37	1	3.00	8.03	1
VC	OG	MD	OH	0.00	110.21	1	3.00	8.03	1
VC	OG	MD	OJ	0.00	16.09	1	3.00	8.03	1
VC	OG	MD	OK	0.00	54.10	1	3.00	8.03	1
VC	OG	MD	OM	0.00	54.10	1	3.00	8.03	1
VA	OB	VB	OC	0.00	180.00	1	1.25	172.80	3
VA	OB	VB	OD	0.00	60.00	2	0.25	59.75	3
VA	OB	VB	OE	0.00	60.00	2	3.00	8.03	1
VA	OB	VB	OH	0.00	60.00	2	3.00	8.03	1
VA	OB	VB	OI	0.00	60.00	2	0.25	59.75	3
VA	OR	VC	OF	0.00	60.00	2	3.00	8.03	1
VA	OR	VC	OG	0.00	60.00	2	3.00	8.03	1
VA	OR	VC	OQ	0.00	180.00	1	3.00	8.03	1
VB	OB	VA	OA	0.00	180.00	1	0.25	172.91	3
VB	OB	VA	OB	0.00	62.60	2	0.25	63.58	3
VB	OB	VA	OR	0.00	62.60	2	3.00	8.03	1
VC	OR	VA	OA	0.00	180.00	1	3.00	8.03	1
VC	OR	VA	OB	0.00	62.60	2	3.00	8.03	1

Table S7: Continuation #4 of Table S3.

				$-$ [Mn_4^{IV}] $-$			$-$ [$Mn^{III}Mn_3^{IV}$] $-$		
Atom 1	Atom 2	Atom 3	Atom 4	V_i	γ_i	n_i	V_i	γ_i	n_i
c	o	MA	OE	0.00	10.95	1	3.00	8.03	1
c	o	MA	OF	0.00	40.90	1	3.00	8.03	1
c	o	MA	OJ	0.00	10.95	1	1.50	10.95	1
c	o	MA	OK	0.00	40.90	1	1.50	40.90	1
c	o	MA	OL	0.00	40.90	1	3.00	8.03	1
c	o	MC	OD	0.00	131.90	1	1.50	131.90	1
c	o	MC	OI	0.00	131.90	1	1.50	131.90	1
c	o	MC	OJ	0.00	10.95	1	1.50	10.95	1
c	o	MC	OL	0.00	40.90	1	3.00	8.03	1
c	o	MC	OM	0.00	40.90	1	3.00	8.03	1
c	o	MD	OG	0.00	131.90	1	3.00	8.03	1
c	o	MD	OH	0.00	131.90	1	3.00	8.03	1
c	o	MD	OJ	0.00	10.95	1	1.50	10.95	1
c	o	MD	OK	0.00	40.90	1	1.50	40.90	1
c	o	MD	OM	0.00	40.90	1	3.00	8.03	1
c	ON	MB	OK	0.00	37.15	1	1.50	37.15	1
c	ON	MB	OL	0.00	37.15	1	3.00	8.03	1
c	ON	MB	OM	0.00	37.15	1	3.00	8.03	1
c	ON	MB	OO	0.00	131.47	1	1.50	131.76	1
c	ON	MB	OP	0.00	131.47	1	1.50	131.76	1
c	OO	MB	OK	0.00	37.15	1	1.50	37.15	1
c	OO	MB	OL	0.00	37.15	1	3.00	8.03	1
c	OO	MB	OM	0.00	37.15	1	3.00	8.03	1
c	OO	MB	ON	0.00	131.47	1	1.50	131.76	1
c	OO	MB	OP	0.00	131.47	1	1.50	131.76	1
c	OP	MB	OK	0.00	37.15	1	1.50	37.15	1
c	OP	MB	OL	0.00	37.15	1	3.00	8.03	1
c	OP	MB	OM	0.00	37.15	1	3.00	8.03	1
c	OP	MB	ON	0.00	131.47	1	1.50	131.76	1
c	OP	MB	OO	0.00	131.47	1	1.50	131.76	1
MA	o	c	c3	0.00	176.11	2	2.80	176.11	2
MB	ON	c	c3	0.00	175.11	2	2.80	175.11	2
MB	OO	c	c3	0.00	175.11	2	2.80	175.11	2
MB	OP	c	c3	0.00	175.11	2	2.80	175.11	2
MC	o	c	c3	0.00	176.11	2	2.80	176.11	2
MD	o	c	c3	0.00	176.11	2	2.80	176.11	2
MB	ON	c	o	0.00	4.89	2	2.80	4.89	2
MB	OO	c	o	0.00	4.89	2	2.80	4.89	2
MB	OP	c	o	0.00	4.89	2	2.80	4.89	2
MD	o	c	ON	0.00	4.09	2	2.80	4.09	2
MC	o	c	OO	0.00	4.09	2	2.80	4.09	2
MA	o	c	OP	0.00	4.09	2	2.80	4.09	2
hc	c3	c	o	0.83	0.00	1	0.83	0.00	1
hc	c3	c	ON	0.83	0.00	1	0.83	0.00	1
hc	c3	c	OO	0.83	0.00	1	0.83	0.00	1
hc	c3	c	OP	0.83	0.00	1	0.83	0.00	1

S1.4 Lennard-Jones parameters

The energy is given according to this equation:

$$E_{\mathrm{LJ}} = \sum_{i<j}^{n_{\mathrm{atoms}}} \sqrt{\varepsilon_i \varepsilon_j} \left[\left(\frac{r_{i,\min} + r_{i,\min}}{2 r_{ij}} \right)^{12} - 2 \left(\frac{r_{i,\min} + r_{i,\min}}{2 r_{ij}} \right)^{6} \right] \tag{4}$$

where ε_i, ε_j are in kcal mol^{-1} and $r_{i,\min}$, $r_{j,\min}$ in Å. Table S8 lists all of these parameters, based on the definition of the atom types in Figure 1 in the main text.

Parameters for Mn, O, C, H, and Na^+ were taken from AMBER [3, 4], whereas the parameters for V were adapted from Reference [1].

Table S8: List of all obtained parameters for the Lennard-Jones interaction. Parameters ε_i are in kcal mol^{-1} and $r_{i,\min}$ in Å.

Atom 1	$-$ [Mn_4^{IV}] / [$Mn^{III}Mn_3^{IV}$] $-$	
	$r_{i,\min}$	ε_i
MA	1.4670	0.0296
MB	1.4670	0.0296
MC	1.4670	0.0296
MD	1.4670	0.0296
OA	1.6562	0.1700
OB	1.6562	0.1700
OC	1.6562	0.1700
OD	1.6562	0.1700
OE	1.6562	0.1700
OF	1.6562	0.1700
OG	1.6562	0.1700
OI	1.6562	0.1700
OJ	1.6562	0.1700
OK	1.6562	0.1700
OL	1.6562	0.1700
OM	1.6562	0.1700
ON	1.6562	0.1700
OO	1.6562	0.1700
OP	1.6562	0.1700
OQ	1.6562	0.1700
OR	1.6562	0.1700
VA	1.5720	0.0160
VB	1.5720	0.0160
VC	1.5720	0.0160
Na+	1.3690	0.0874

S1.5 Coulomb parameters

The energy is given according to this equation:

$$E_{\text{Coulomb}} = \sum_{i<j}^{n_{\text{atoms}}} \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \tag{5}$$

with q_i, q_j are given in multiples of the elementary charge and $\frac{1}{4\pi\varepsilon_0} = 332.05$ Å kcal mol^{-1}. Table S9 lists all of these parameters, based on the definition of the atom types in Figure 1 in the main text.

The parameters were obtained as the Mulliken charges at the optimized geometry. The BP86 level of theory, the ZORA-def2-TZVP basis set for the description of the Mn, V, O atoms and the ZORA-def2-SVP basis set for the C and H atoms, and Grimme's D3 correction were used.

Table S9: List of all obtained parameters for the Coulomb interaction. Parameters q_i are in multiples of the elementary charge.

Atom	Atom type	$-[Mn_4^{IV}]-$ q_i	$-[Mn^{III}Mn_3^{IV}]-$ q_i	Atom	Atom type	$-[Mn_4^{IV}]-$ q_i	$-[Mn^{III}Mn_3^{IV}]-$ q_i
Mn1	MA	+0.4116	+0.3703	C2	c3	-0.2136	-0.2049
O1	OK	-0.2134	-0.2201	H1	hc	+0.1427	+0.0908
Mn2	MB	+0.3238	+0.2972	H2	hc	+0.1471	+0.1030
O2	OL	-0.2125	-0.2778	H3	hc	+0.1651	+0.1075
Mn3	MC	+0.4105	+0.7052	C1	c	+0.2017	+0.1868
O4	OM	-0.2119	-0.2783	O6	ON	-0.2139	-0.2322
Mn4	MD	+0.4113	+0.3710	O5	o	-0.1858	-0.1984
O3	OJ	-0.3745	-0.3687	C3	c3	-0.2137	-0.2047
O20	OQ	-0.4964	-0.5044	H4	hc	+0.1465	+0.0957
V4	VC	+1.1642	+1.1032	H5	hc	+0.1433	+0.0923
O21	OF	-0.4258	-0.4058	H6	hc	+0.1654	+0.0968
O22	OG	-0.4261	-0.4060	C4	c	+0.2011	+0.1823
O23	OR	-0.6460	-0.6329	O8	OO	-0.2135	-0.2434
V3	VA	+1.2883	+1.2263	O7	o	-0.1857	-0.2885
O17	OA	-0.4733	-0.4890	C5	c3	-0.2134	-0.2047
O18	OB	-0.6459	-0.6321	H7	hc	+0.1468	+0.1024
V2	VB	+1.1633	+1.1259	H8	hc	+0.1429	+0.0923
O14	OH	-0.4260	-0.4243	H9	hc	+0.1651	+0.1066
O15	OI	-0.4258	-0.5115	C6	c	+0.2018	+0.1875
O16	OC	-0.4961	-0.5213	O9	o	-0.1856	-0.1976
O12	OC	-0.4965	-0.5213	O10	OP	-0.2140	-0.2337
V1	VB	+1.1645	+1.1263				
O11	OD	-0.4257	-0.5113				
O13	OE	-0.4256	-0.4240				
O19	OB	-0.6464	-0.6324				

S2 Deviations of the MM MD from the reference QM/MM MD

In Figure S1 we present the absolute deviations of the bond lengths and angles between the reference QM/MM MD trajectories and the MM MD trajectories with the final force field parameters. As can be seen, deviations were below 2.5 pm for $[Mn_4^{IV}]$ and below 5.3 pm for the more challenging $[Mn^{III}Mn_3^{IV}]$. For the angles, the deviations were below 5.4 degrees ($[Mn_4^{IV}]$) and 7.7 degrees ($[Mn^{III}Mn_3^{IV}]$).

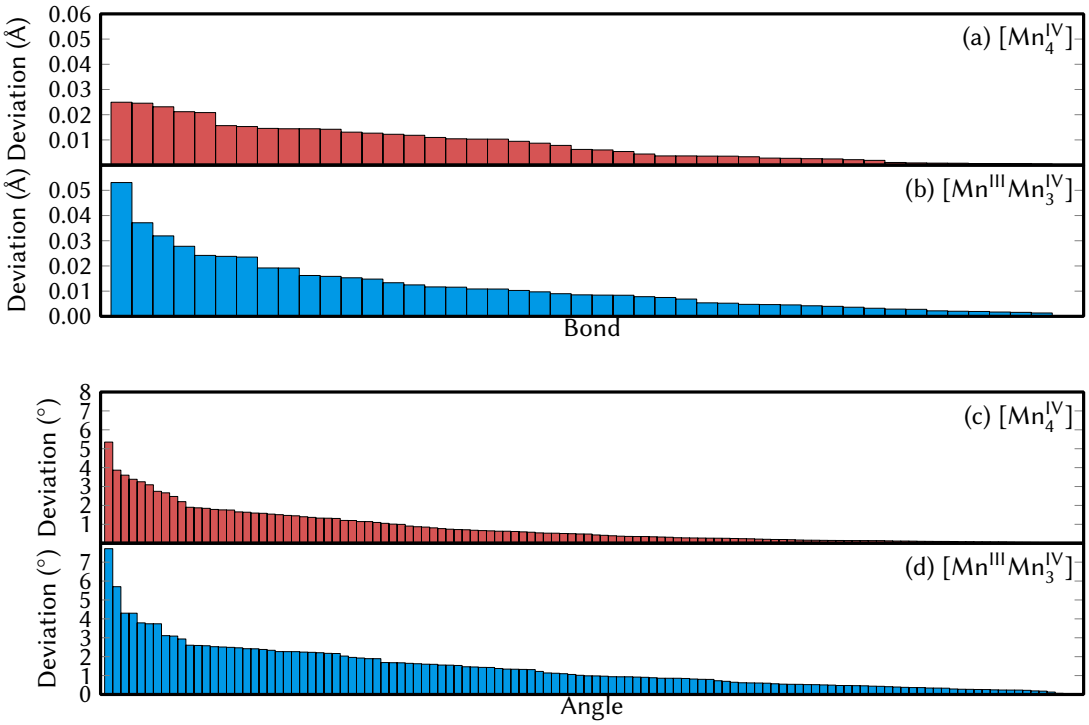

Figure S1: Absolute deviations of the bond lengths and angles between the reference QM/MM MD trajectories and the MM MD trajectories with the final force field parameters, sorted by magnitude. The individual bonds and the MM MD or QM/MM MD distributions are shown in Figure 2 in the main manuscript.

S3 Influence of point charge placement

Here we document the very strong influence of the point charge placement for the single point calculations to obtain the energy gaps. Three different point charge treatment schemes are represented in Figure S2.

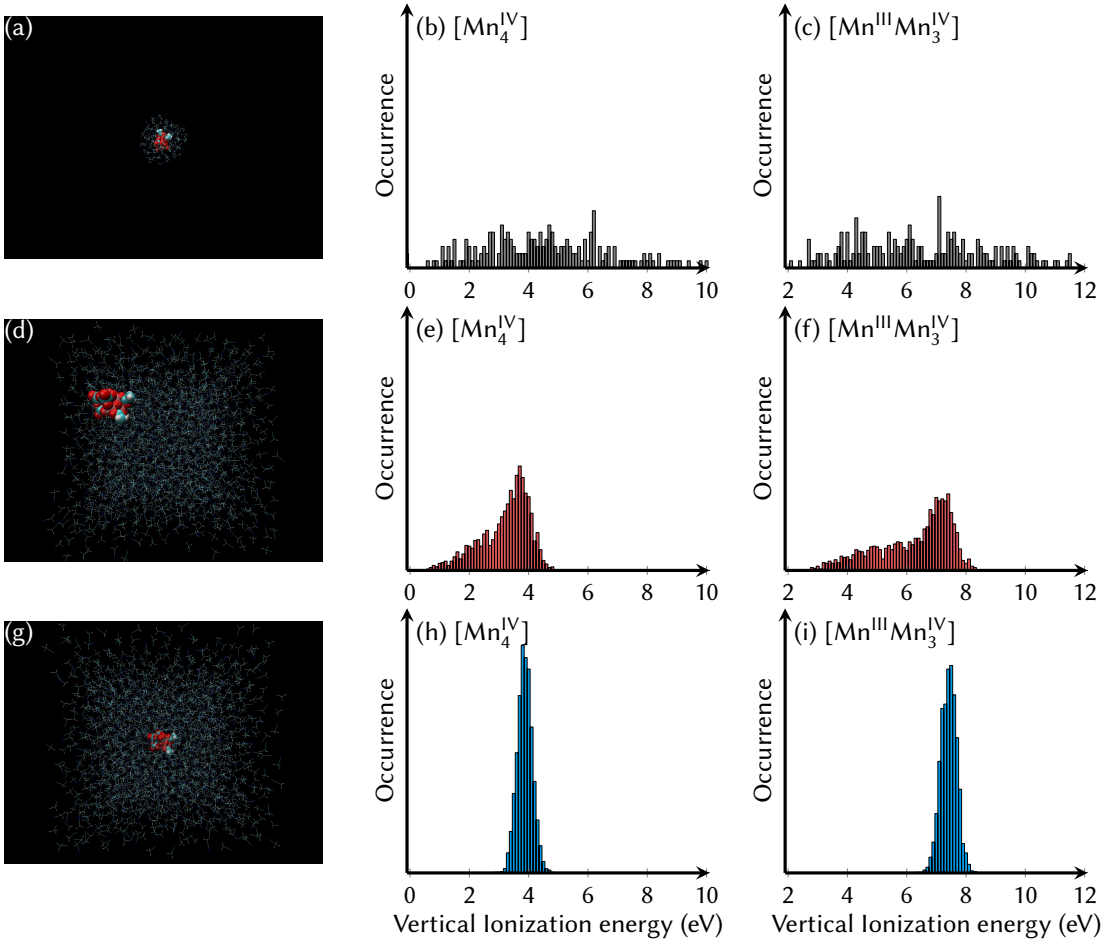

Figure S2: Three different point charge treatments and their influence on the obtained energy gap distributions. (a)–(c) Small cut-off for inclusion of MM point charges. (d)–(f) Large cut-off for inclusion. (g)–(i) Large cut-off and reimaging to place the solute in the center of the cell. These calculations were performed with the BP86 level of theory described in the main manuscript.

In the top row of the figure, we show some preliminary calculations where we included only point charges within 10 Å of the solute, using periodic boundary settings and `qmcut=10` in the AMBER input. With these settings, the single point calculations included between 750 and 850 point charges. Notably, the small number of point charges and the variation in the number of point charges leads to large variations in the energy gaps between reduced and oxidized states. Hence, this point charge treatment is not suitable for the computation of redox potentials.

In the middle row of Figure S2, we turned off periodic boundary conditions for the single point calculation and included every point charge in the primary cell through `qmcut=999`. In this way, the number of point charges is consistent (13801 or 13802 point charges depending on oxidation state of the trajectory). These settings provide a more consistent electrostatic environment for the solute and therefore a tighter distribution of the energy gaps. However, the distributions are non-Gaussian and are also not suitable for computation of redox potentials.

In the bottom row we use the same settings as in the middle row (no periodic boundary conditions, `qmcut=999`). However, prior to the single point calculations we also reimaged the primary cell such that the solute is centered and fully surrounded by point charges in a consistent way. These settings produce the desired narrow, nearly Gaussian distribution of energy gaps that can be used to estimate the redox potentials through Marcus theory.

S4 Solvent shell sampling

As discussed in the main text, there are strong differences between the solvent sampling in the MM MD and QM/MM MD trajectories. In Figures S3 and S4, we compare the solvent distribution.

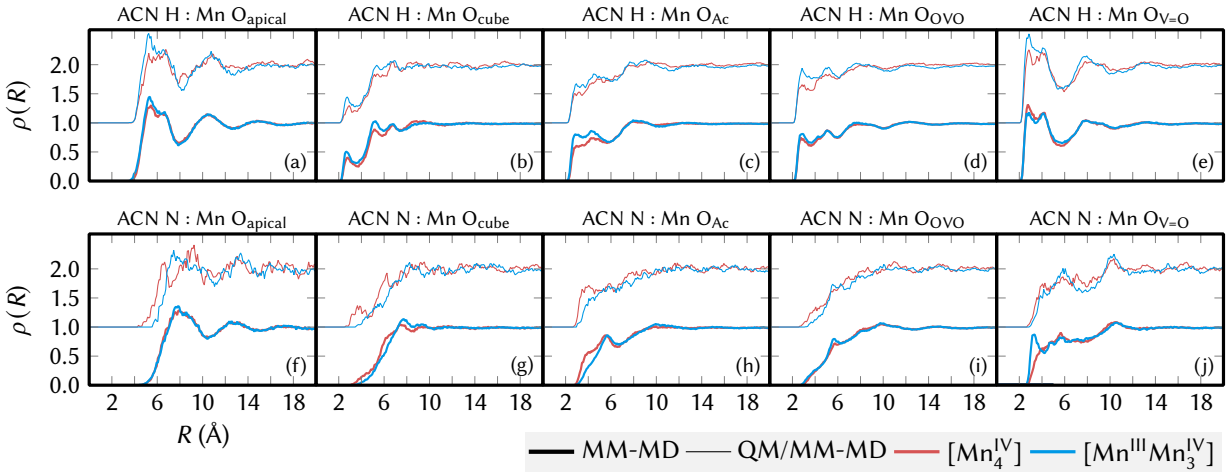

Figure S3: Radial distribution functions between the indicated solvent atoms (either H or N) and solute oxygen atoms. The QM/MM curves (thin lines) are shifted by +1 for clarity.

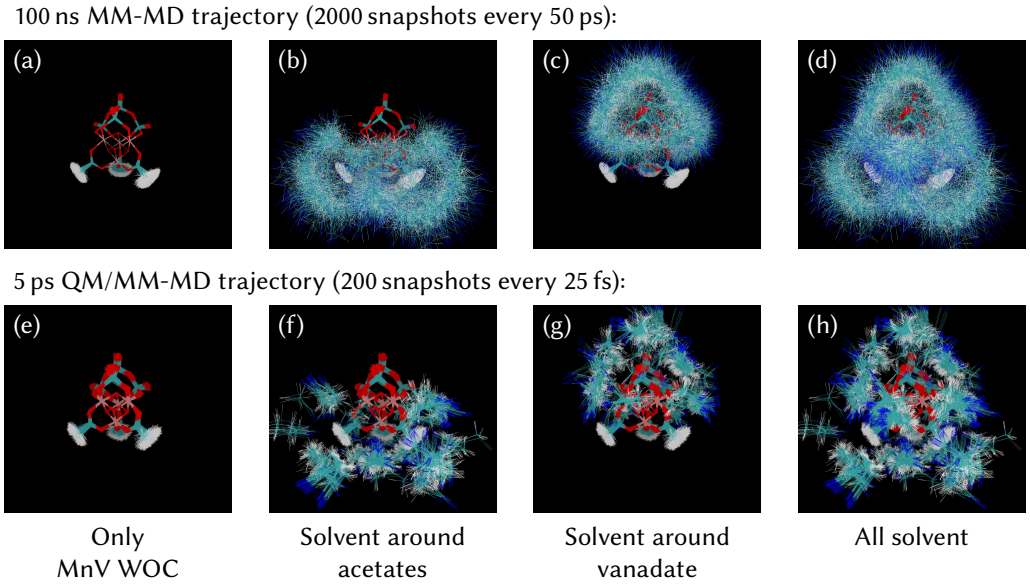

Figure S4: Depiction of the sampled solvent shell (all solvent molecules within 3 Å of the solute) around the $[Mn_4^{IV}]$ complex. Panels (a) to (d) show the sampling for the MM MD trajectory, whereas panels (e) to (h) are for the QM/MM MD trajectory. From left to right, we show the overlay of (a/e) only the solute, (b/f) the solvent close to the acetate ligands, (c/g) the solvent close to the vanadate ligand, and (d/h) the solvent close to any solute atom.

In Figure S3, we show the radial distribution functions between the acetonitrile H and N atoms and groups of solute oxygen atoms. Here, it is observable that the QM/MM MD data are much more noisy than the MM MD data. However, QM/MM and MM agree qualitatively to a large extent. Hence, we estimate that the general description of electrostatic interactions by the FFs through the Mulliken charges is appropriate.

In Figure S4 we show the three-dimensional distribution of solvent molecules. Significant differences between MM MD and QM/MM MD are visible. The QM/MM solvent distribution does not provide a uniform sampling of the first solvation shell. Instead, all solvent coordinates are very similar to the initial coordinates from the equilibration run.

S5 Effect of different MM and QM/MM potential energy surfaces on the vertical energy gaps

In principle, the potential energy surfaces in the MM MD trajectories used for sampling the phase space are not perfectly parallel to the more accurate QM/MM potential energy surfaces, which could introduce a bias in the sampled vertical energy gaps. In Figure S5, we present scatter plots of the vertical energy gaps over the difference in potential energy between an MM treatment and a QM/MM treatment. Here, for consistency the MM potential energies were recomputed with the same non-periodic settings as the QM/MM energies.

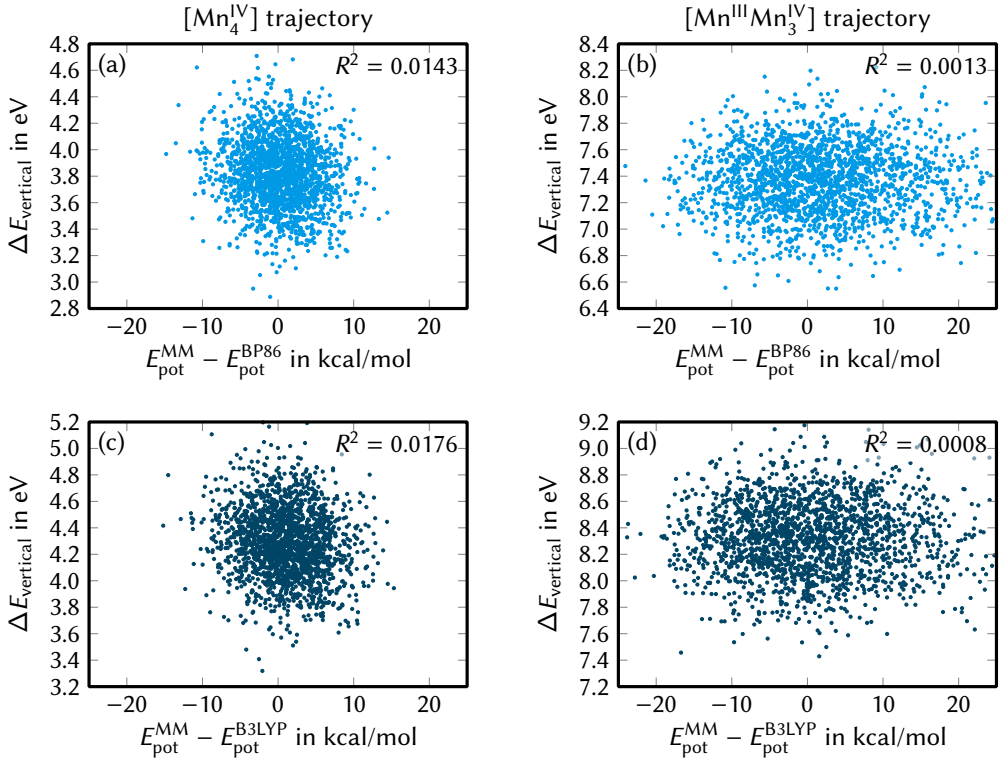

Figure S5: Scatter plots showing the dependence of the vertical energy gaps ΔE on the difference between MM potential energy and QM/MM potential energy. The top row shows the results at the BP86 level of theory, the bottom row shows the analogous results with B3LYP. The left panels correspond to the [Mn_4^{IV}] trajectory (i.e., the oxidized species) and the right panels to the [$Mn^{III}Mn_3^{IV}$] trajectory (the reduced species), and the potential energy differences always refer to the state used to sample the respective trajectory. The potential energy differences were shifted towards zero, as the absolute MM and QM/MM potential energies are very different (on the order of -70,000 kcal/mol for MM and -6,600,000 kcal/mol for QM/MM). The shown R^2 are squared Pearson correlation coefficients of a linear fit to the data.

The standard deviation of the potential energy differences can be used as a measure for the accuracy of the optimized FFs, see, e.g., Ref. [5, 6]. Here, the [Mn_4^{IV}] FF shows a standard deviation of 4.1 kcal/mol to BP86 and 4.4 kcal/mol to B3LYP. For the more challenging [$Mn^{III}Mn_3^{IV}$] system, these values are 10.1 kcal/mol and 9.9 kcal/mol. Although these standard deviations are non-negligible, they are on the same order of magnitude as the intrinsic errors of the electronic structure methods. This can be seen in the fact that the standard deviation of the BP86–B3LYP energy differences are also about 6 kcal/mol.

Most importantly, the figure shows that there is no dependence of the energy gaps on the potential energy differences. Hence, no bias in the redox potential is introduced by including in the histograms those snapshots that have relatively low MM potential energy but relatively high QM/MM potential energy, and that therefore would not have been sampled by a QM/MM trajectory.

Supplementary References

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