Supplementary Information Available: *XYZ* coordinates for some optimized structures are given (in amstrongs).

Coordinates for $\mathbf{[Fe^{III}_4(H_2O)_2(PW_9O_{34})_2]^{6-}}$ structure computed at OPBE unrestricted (S=10) with bonding energy E= -810.50 eV.

Fe	0.000000	0.000000	1.807325
Fe	-2.405749	1.344198	0.000000
Fe	0.000000	0.000000	-1.807325
Fe	2.405749	-1.344198	0.000000
W	0.011654	6.496924	0.000000
W	2.888057	4.980762	1.856337
W	2.888057	4.980762	-1.856337
W	-2.231663	4.435804	-1.707923
W	-2.231663	4.435804	1.707923
W	0.630632	2.938530	3.612108
W	3.258375	1.526505	1.889104
W	3.258375	1.526505	-1.889104
W	0.630632	2.938530	-3.612108
P	0.497284	2.843033	0.000000
P	-0.497284	-2.843033	0.000000
W	-3.258375	-1.526505	1.889104
W	-2.888057	-4.980762	1.856337
W	-2.888057	-4.980762	-1.856337
W	-0.011654	-6.496924	0.000000
W	-0.630632	-2.938530	3.612108
W	-3.258375	-1.526505	-1.889104
W	-0.630632	-2.938530	-3.612108
W	2.231663	-4.435804	-1.707923
W	2.231663	-4.435804	1.707923
O	0.124885	8.221144	0.000000
O	1.384737	5.993415	1.291673
O	3.954116	6.167937	2.515729
O	3.389394	4.943017	0.000000
O	3.954116	6.167937	-2.515729
O	1.384737	5.993415	-1.291673
O	-1.273939	6.155483	-1.347848
O	-1.273939	6.155483	1.347848
O	1.892888	4.421355	3.397626
O	3.907033	3.344631	2.051040
O	3.907033	3.344631	-2.051040
O	1.892888	4.421355	-3.397626
O	-3.490409	4.933184	-2.787366
O	-3.063897	4.828009	0.000000
O	-3.490409	4.933184	2.787366
O	-0.779641	4.050222	2.948101
O	2.281256	1.840160	3.495629
O	0.350882	2.973856	5.320076
O	4.607811	0.603301	2.467594

O	3.649657	1.629301	0.000000
O	4.607811	0.603301	-2.467594
O	2.281256	1.840160	-3.495629
O	0.350882	2.973856	-5.320076
O	-0.779641	4.050222	-2.948101
O	-0.526689	4.001871	0.000000
O	1.380465	2.954648	1.262565
O	1.380465	2.954648	-1.262565
O	-2.544751	2.639168	-1.421915
O	-2.544751	2.639168	1.421915
O	-0.241358	1.403421	3.044525
O	1.988310	0.135749	1.406382
O	1.988310	0.135749	-1.406382
O	-0.241358	1.403421	-3.044525
O	-0.259166	1.454679	0.000000
O	-4.602638	1.329633	0.000000
O	-1.988310	-0.135749	1.406382
O	-3.907033	-3.344631	2.051040
O	-3.389394	-4.943017	0.000000
O	-1.384737	-5.993415	-1.291673
O	-0.124885	-8.221144	0.000000
O	-1.384737	-5.993415	1.291673
O	-3.954116	-6.167937	2.515729
O	-1.892888	-4.421355	3.397626
O	-2.281256	-1.840160	3.495629
O	-3.649657	-1.629301	0.000000
O	-3.907033	-3.344631	-2.051040
O	-3.954116	-6.167937	-2.515729
O	-1.892888	-4.421355	-3.397626
O	0.779641	-4.050222	-2.948101
O	3.490409	-4.933184	2.787366
O	1.273939	-6.155483	-1.347848
O	1.273939	-6.155483	1.347848
O	3.063897	-4.828009	0.000000
O	3.490409	-4.933184	-2.787366
O	0.526689	-4.001871	0.000000
O	0.779641	-4.050222	2.948101
O	-0.350882	-2.973856	5.320076
O	-1.380465	-2.954648	1.262565
O	-4.607811	-0.603301	2.467594
O	-1.380465	-2.954648	-1.262565
O	-2.281256	-1.840160	-3.495629
O	-4.607811	-0.603301	-2.467594
O	-1.988310	-0.135749	-1.406382
O	0.241358	-1.403421	-3.044525
O	-0.350882	-2.973856	-5.320076
O	0.241358	-1.403421	3.044525
O	0.259166	-1.454679	0.000000
O	2.544751	-2.639168	1.421915
O	2.544751	-2.639168	-1.421915

O	4.602638	-1.329633	0.000000
H	4.972716	-0.854884	0.759358
H	-4.972716	0.854884	-0.759358
H	-4.972716	0.854884	0.759358
H	4.972716	-0.854884	-0.759358

Coordinates for **$[Fe^{II}_2(H_2O)_2Fe^{III}_2H_2(PW_9O_{34})_2]^{6-}$** structure computed at OPBE unrestricted (S = 9) with bonding energy E= -818.65 eV.

Fe	0.186626	-0.146928	1.774597
Fe	-2.341116	1.458587	-0.153031
Fe	-0.186626	0.146928	-1.774597
Fe	2.341116	-1.458587	0.153031
W	0.029150	6.586344	0.031122
W	2.916388	5.023293	1.839104
W	2.900103	5.136965	-1.886305
W	-2.195963	4.554724	-1.775746
W	-2.232673	4.450988	1.664822
W	0.633514	2.913109	3.538080
W	3.327458	1.574286	1.857910
W	3.402325	1.725139	-1.951499
W	0.654474	3.017830	-3.644975
P	0.546677	2.870895	-0.057359
P	-0.546677	-2.870895	0.057359
W	-3.402325	-1.725139	1.951499
W	-2.900103	-5.136965	1.886305
W	-2.916388	-5.023293	-1.839104
W	-0.029150	-6.586344	-0.031122
W	-0.654474	-3.017830	3.644975
W	-3.327458	-1.574286	-1.857910
W	-0.633514	-2.913109	-3.538080
W	2.232673	-4.450988	-1.664822
W	2.195963	-4.554724	1.775746
O	0.122454	8.312135	0.063648
O	1.409108	6.050644	1.277672
O	3.979671	6.200167	2.525137
O	3.405340	5.030461	-0.040934
O	3.939324	6.348589	-2.546339
O	1.417325	6.132942	-1.308973
O	-1.213198	6.232757	-1.347994
O	-1.255085	6.199870	1.344536
O	1.923488	4.438192	3.347018
O	3.950491	3.403837	1.965161
O	4.006092	3.492897	-2.105404
O	1.926029	4.514500	-3.395055
O	-3.430336	5.142269	-2.841308
O	-3.026281	4.889855	-0.052261
O	-3.492789	4.947623	2.744614
O	-0.775601	4.020298	2.905555

O	2.369031	1.875276	3.445974
O	0.380085	2.925844	5.252602
O	4.722648	0.699461	2.414474
O	3.669725	1.680594	-0.078230
O	4.747037	0.812984	-2.535773
O	2.339330	1.929700	-3.513266
O	0.451570	3.051809	-5.366433
O	-0.742047	4.164196	-3.026047
O	-0.494440	4.013711	-0.046671
O	1.412274	2.953508	1.219802
O	1.444862	3.000263	-1.310872
O	-2.555097	2.759175	-1.567177
O	-2.598237	2.687925	1.390983
O	-0.148098	1.347786	2.995553
O	2.113685	0.158949	1.370942
O	2.082581	0.077002	-1.532774
O	-0.243821	1.506255	-3.118943
O	-0.201245	1.470961	-0.095635
O	-4.643316	1.362323	-0.168432
O	-2.082581	-0.077002	1.532774
O	-4.006092	-3.492897	2.105404
O	-3.405340	-5.030461	0.040934
O	-1.409108	-6.050644	-1.277672
O	-0.122454	-8.312135	-0.063648
O	-1.417325	-6.132942	1.308973
O	-3.939324	-6.348589	2.546339
O	-1.926029	-4.514500	3.395055
O	-2.339330	-1.929700	3.513266
O	-3.669725	-1.680594	0.078230
O	-3.950491	-3.403837	-1.965161
O	-3.979671	-6.200167	-2.525137
O	-1.923488	-4.438192	-3.347018
O	0.775601	-4.020298	-2.905555
O	3.430336	-5.142269	2.841308
O	1.255085	-6.199870	-1.344536
O	1.213198	-6.232757	1.347994
O	3.026281	-4.889855	0.052261
O	3.492789	-4.947623	-2.744614
O	0.494440	-4.013711	0.046671
O	0.742047	-4.164196	3.026047
O	-0.451570	-3.051809	5.366433
O	-1.444862	-3.000263	1.310872
O	-4.747037	-0.812984	2.535773
O	-1.412274	-2.953508	-1.219802
O	-2.369031	-1.875276	-3.445974
O	-4.722648	-0.699461	-2.414474
O	-2.113685	-0.158949	-1.370942
O	0.148098	-1.347786	-2.995553
O	-0.380085	-2.925844	-5.252602
O	0.243821	-1.506255	3.118943

O	0.201245	-1.470961	0.095635
O	2.555097	-2.759175	1.567177
O	2.598237	-2.687925	-1.390983
O	4.643316	-1.362323	0.168432
H	4.962847	-0.764099	0.863044
H	-4.962847	0.764099	-0.863044
H	-5.006008	0.978554	0.642427
H	5.006008	-0.978554	-0.642427
H	-2.192772	0.533224	2.283483
H	2.192772	-0.533224	-2.283483

Coordinates for **$[Fe^{II}_4(H_2O)_2H_4(PW_9O_{34})_2]^{6-}$** structure computed at OPBE unrestricted (S = 8) with bonding energy E = -825.25 eV.

Fe	0.000000	0.000000	1.730910
Fe	-2.482273	1.553545	0.000000
Fe	0.000000	0.000000	-1.730910
Fe	2.482273	-1.553545	0.000000
W	0.029745	6.635801	0.000000
W	2.923616	5.141107	1.858645
W	2.923616	5.141107	-1.858645
W	-2.207273	4.527421	-1.729837
W	-2.207273	4.527421	1.729837
W	0.663757	2.977694	3.563319
W	3.464584	1.739120	1.921106
W	3.464584	1.739120	-1.921106
W	0.663757	2.977694	-3.563319
P	0.559432	2.839135	0.000000
P	-0.559432	-2.839135	0.000000
W	-3.464584	-1.739120	1.921106
W	-2.923616	-5.141107	1.858645
W	-2.923616	-5.141107	-1.858645
W	-0.029745	-6.635801	0.000000
W	-0.663757	-2.977694	3.563319
W	-3.464584	-1.739120	-1.921106
W	-0.663757	-2.977694	-3.563319
W	2.207273	-4.527421	-1.729837
W	2.207273	-4.527421	1.729837
O	0.140218	8.359540	0.000000
O	1.437436	6.141474	1.292157
O	3.953868	6.357417	2.521220
O	3.425966	5.081595	0.000000
O	3.953868	6.357417	-2.521220
O	1.437436	6.141474	-1.292157
O	-1.213464	6.262191	-1.345924
O	-1.213464	6.262191	1.345924
O	1.985586	4.482407	3.352749
O	4.066338	3.515812	2.010455
O	4.066338	3.515812	-2.010455

O	1.985586	4.482407	-3.352749
O	-3.419149	5.124862	-2.820202
O	-2.991821	4.914782	0.000000
O	-3.419149	5.124862	2.820202
O	-0.731327	4.114262	2.958125
O	2.424093	1.914889	3.457519
O	0.458064	3.006607	5.288476
O	4.863612	0.880324	2.472401
O	3.632162	1.690172	0.000000
O	4.863612	0.880324	-2.472401
O	2.424093	1.914889	-3.457519
O	0.458064	3.006607	-5.288476
O	-0.731327	4.114262	-2.958125
O	-0.491011	3.976397	0.000000
O	1.457762	2.972221	1.260795
O	1.457762	2.972221	-1.260795
O	-2.617278	2.751401	-1.534334
O	-2.617278	2.751401	1.534334
O	-0.138781	1.427375	3.048764
O	2.253353	0.023304	1.504831
O	2.253353	0.023304	-1.504831
O	-0.138781	1.427375	-3.048764
O	-0.163106	1.434717	0.000000
O	-4.745023	1.447847	0.000000
O	-2.253353	-0.023304	1.504831
O	-4.066338	-3.515812	2.010455
O	-3.425966	-5.081595	0.000000
O	-1.437436	-6.141474	-1.292157
O	-0.140218	-8.359540	0.000000
O	-1.437436	-6.141474	1.292157
O	-3.953868	-6.357417	2.521220
O	-1.985586	-4.482407	3.352749
O	-2.424093	-1.914889	3.457519
O	-3.632162	-1.690172	0.000000
O	-4.066338	-3.515812	-2.010455
O	-3.953868	-6.357417	-2.521220
O	-1.985586	-4.482407	-3.352749
O	0.731327	-4.114262	-2.958125
O	3.419149	-5.124862	2.820202
O	1.213464	-6.262191	-1.345924
O	1.213464	-6.262191	1.345924
O	2.991821	-4.914782	0.000000
O	3.419149	-5.124862	-2.820202
O	0.491011	-3.976397	0.000000
O	0.731327	-4.114262	2.958125
O	-0.458064	-3.006607	5.288476
O	-1.457762	-2.972221	1.260795
O	-4.863612	-0.880324	2.472401
O	-1.457762	-2.972221	-1.260795
O	-2.424093	-1.914889	-3.457519

O	-4.863612	-0.880324	-2.472401
O	-2.253353	-0.023304	-1.504831
O	0.138781	-1.427375	-3.048764
O	-0.458064	-3.006607	-5.288476
O	0.138781	-1.427375	3.048764
O	0.163106	-1.434717	0.000000
O	2.617278	-2.751401	1.534334
O	2.617278	-2.751401	-1.534334
O	4.745023	-1.447847	0.000000
H	5.110420	-0.970233	0.757745
H	-5.110420	0.970233	-0.757745
H	-5.110420	0.970233	0.757745
H	5.110420	-0.970233	-0.757745
H	-2.405044	0.562772	2.266925
H	2.405044	-0.562772	-2.266925
H	2.405044	-0.562772	2.266925
H	-2.405044	0.562772	-2.266925

Table S1. Spin densities and energy differences computed with OPBE and BP functionals

Method	Species	Fe^e	Fe^i	ΔEnergy [a]
OPBE	20 e	4.18	4.18	
BP	20 e	4.11	4.08	
OPBE	21 e (Fe^e)	4.06	4.13	0.0
	21 e (Fe^i)	4.17	4.05	+0.217
BP	21 e (Fe^e)	4.01	4.04	
	21 e (Fe^i)	4.10	3.94	+0.311

a) Energy difference between Fe^e reduced and Fe^i reduced species in eV.

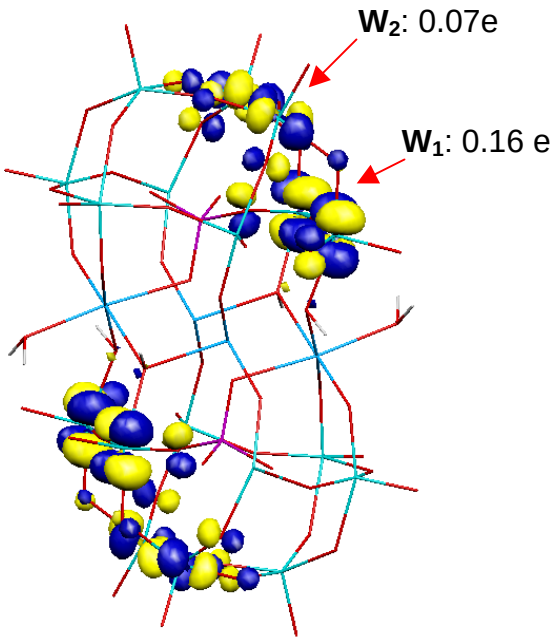

Figure S1. LUMO computed for $H_4[Fe(II)_4\text{-}POM]^{6-}$ and spin densities determined for selected tungstens for $H_4[Fe(II)_4\text{-}POM]^{7-}$.