

Supporting Information for:

Thermodynamics of the S₂-to-S₃ State Transition of the Oxygen-Evolving Complex of Photosystem II

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1- Mn spin densities for optimized S₃ state structure.

Table S1. The total energies and atomic spin densities of the Mn centers in the S ₃ state		
	Spin densities	
	Mn1-O7, E189 ⁰	Mn1-E189 ⁻
Mn1	2.942898	3.110379
Mn2	3.027931	3.016139
Mn3	2.939744	2.909465
Mn4	3.037126	2.972186
DFT (B97D) Energies (Hartree)		
	-6372.99867963	-6372.99484693

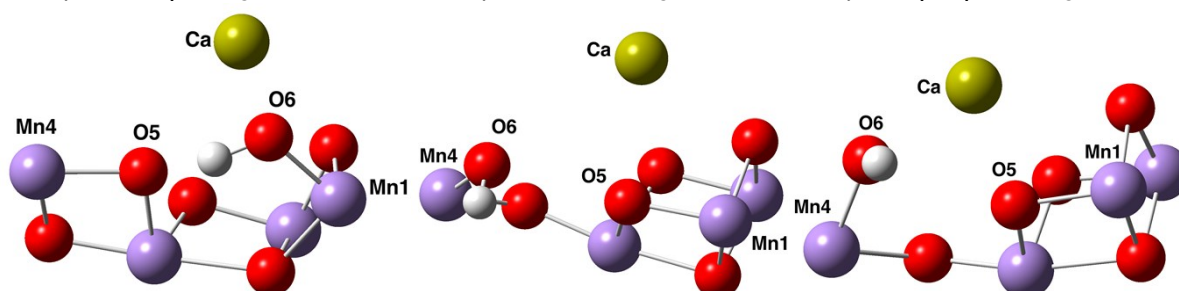
The difference in total energy between the 2 states is 2.4 kcal/mol. Thus, the two states are isoenergetic.

2- Figure S1. The Mn cluster in the S₃ state.

a) The open S₃ model.

b) The closed S₃ model.

c) The proposed S₃ model.



a) The atomic coordinates of the S₃ state model with O7 bound to Mn1 and D1-E189 protonated:

C	8.31218	3.59127	-1.06653
C	7.64049	3.40489	0.30683
C	6.13521	3.65811	0.25782
O	5.43217	2.89152	1.09338
O	5.63343	4.50706	-0.48640
H	8.05668	4.13304	1.02305
H	8.08662	4.59153	-1.45913
H	7.83570	2.40986	0.72654
H	9.40297	3.48723	-0.97559
H	7.95388	2.85144	-1.79861
C	-4.42580	6.89976	0.96293
C	-5.63927	6.02215	0.58770
C	-5.28077	4.83211	-0.28434
C	-5.32517	3.52011	0.22169
C	-4.90442	5.00220	-1.63332
C	-5.03621	2.40811	-0.58269
C	-4.61968	3.90232	-2.45514
C	-4.70803	2.59183	-1.94179
O	-4.49801	1.53268	-2.79209
H	-5.09149	0.73584	-2.49237
H	-3.67717	6.31314	1.51622
H	-6.37617	6.65125	0.06203
H	-5.61456	3.36299	1.26390
H	-4.83895	6.01280	-2.04224
H	-5.09250	1.39938	-0.17561
H	-4.35750	4.03221	-3.50523
H	-6.13190	5.66160	1.50497
C	-0.98004	8.14610	2.49347
C	-0.69713	6.98608	1.53967
O	-0.11515	5.95181	1.93759
C	-1.71244	7.64952	3.75721
H	-0.00636	8.57344	2.78017
H	-1.82600	8.46566	4.48374
H	-1.13864	6.83850	4.22654
N	-1.12686	7.14126	0.27110
C	-1.84611	6.70012	-1.98557
O	-2.50459	7.75002	-1.90379
C	-1.07205	6.11926	-0.77262
C	-1.70257	4.76655	-0.33494
C	-0.77083	3.56580	-0.18377
O	-1.31881	2.46756	0.07499
O	0.48854	3.78844	-0.34596
H	-2.46589	4.43935	-1.05257

H	-2.23245	4.88531	0.61548
N	-1.76997	5.95189	-3.11090
C	-2.53233	6.34275	-4.27637
C	-2.42925	5.39121	-5.44854
O	-1.76393	4.36961	-5.49841
H	-3.04885	5.71409	-6.32009
H	-2.23696	7.34720	-4.63660
H	-3.60637	6.44435	-4.02930
H	-1.18094	5.10206	-3.13476
C	-6.98586	-5.33471	-2.33971
O	-6.70918	-6.08019	-1.39435
C	-6.10070	-5.21774	-3.58392
C	-5.02928	-4.11671	-3.35990
C	-4.24991	-4.37223	-2.06450
C	-3.02784	-3.51553	-1.85473
O	-2.44395	-2.89230	-2.76202
O	-2.62033	-3.52921	-0.59358
H	-3.89078	-5.41285	-2.01951
H	-5.50962	-3.12681	-3.31228
H	-4.89870	-4.26368	-1.18778
H	-4.33611	-4.10185	-4.21251
N	-8.04677	-4.46141	-2.31516
C	-8.73169	-4.09484	-1.07723
C	-8.88033	-2.55556	-0.97083
C	-7.59176	-1.81975	-1.19497
C	-7.22643	-0.85083	-2.11260
N	-6.44612	-2.06844	-0.45972
C	-5.45412	-1.27069	-0.93879
N	-5.89716	-0.51458	-1.94230
H	-8.12918	-4.48952	-0.24750
H	-9.30379	-2.32156	0.01976
H	-7.84246	-0.37289	-2.86771
H	-4.45051	-1.24981	-0.52850
H	-9.60585	-2.19631	-1.71702
C	7.72881	-2.12987	-2.17996
O	7.72126	-3.00585	-1.28588
C	7.37611	-2.49417	-3.62497
C	5.94705	-2.02223	-4.02364
C	4.83549	-2.55622	-3.16650
C	3.74105	-1.93992	-2.59121
N	4.67018	-3.90826	-2.87640
C	3.52240	-4.07376	-2.16540
N	2.94782	-2.89084	-1.97506
H	5.77251	-2.32443	-5.06979
H	3.45416	-0.89652	-2.58688
H	3.13062	-5.01938	-1.81292
H	5.90935	-0.92360	-4.00368
N	8.02274	-0.82762	-1.97230

C	8.11087	-0.23933	-0.63061
C	6.71683	-0.06315	0.01402
C	5.73436	0.55834	-0.98086
C	4.28599	0.62270	-0.55567
O	3.88018	-0.19469	0.33989
O	3.56887	1.44255	-1.21592
H	5.72057	-0.03632	-1.90507
H	8.74424	-0.88313	-0.00604
H	6.79156	0.56712	0.90967
H	6.03117	1.56442	-1.28855
H	8.60386	0.73418	-0.74674
H	6.34446	-1.03613	0.34158
C	8.49663	-3.71102	2.86210
C	7.30848	-4.69998	2.82744
C	6.10886	-4.12886	2.13230
C	4.78153	-4.02480	2.50020
N	6.19292	-3.54297	0.87476
C	4.98162	-3.10229	0.50484
N	4.10795	-3.38952	1.47017
H	8.82134	-3.44933	1.84355
H	7.01118	-4.97921	3.84806
H	4.27685	-4.35157	3.40061
H	4.76776	-2.53600	-0.38711
H	7.61903	-5.62930	2.32101
H	8.21742	-2.78455	3.38419
H	9.35153	-4.16317	3.38277
C	-2.26391	-6.63428	0.74477
O	-2.44321	-6.56495	-0.47004
C	-0.90433	-7.03076	1.34760
C	0.25464	-6.56492	0.44850
C	0.42231	-5.04294	0.38303
O	0.06875	-4.37679	1.42084
O	0.92463	-4.57030	-0.69063
H	0.10384	-6.92957	-0.57440
H	1.20326	-6.98067	0.82628
N	-3.25235	-6.38560	1.67450
C	-4.60429	-5.96636	1.32658
C	-4.92994	-4.49249	1.63203
O	-6.07689	-4.05830	1.40585
H	-4.75997	-6.11855	0.25032
N	-3.93236	-3.74473	2.15345
C	-4.00637	-2.29030	2.32982
C	-2.67565	-1.67241	1.84561
O	-2.66879	-0.63493	1.15219
C	-4.27332	-1.90633	3.80020
O	-1.64599	-2.34471	2.27222
H	-4.32771	-0.81205	3.90336
H	-4.81553	-1.90392	1.70143

H	-3.46618	-2.28724	4.44110
H	-3.00151	-4.15195	2.18393
H	-5.22948	-2.34119	4.12064
C	1.67205	0.39540	7.06346
C	1.42718	0.12351	5.57124
C	2.20657	-1.12714	5.08401
C	1.91660	-1.34523	3.60790
O	1.03003	-2.24375	3.32606
O	2.52073	-0.58280	2.78631
H	1.90049	-2.01283	5.65798
H	2.74125	0.57052	7.25957
H	1.73915	0.98916	4.96830
H	3.28550	-0.95723	5.21516
H	1.34869	-0.45825	7.67936
H	0.35263	-0.02986	5.38398
H	1.11543	1.28498	7.39312
C	-3.81623	3.42480	6.76441
C	-3.25268	3.98612	5.44932
C	-3.44560	3.01802	4.27055
C	-2.84985	3.55277	2.95596
N	-1.39510	3.74578	3.01003
C	-0.50381	2.74944	2.87509
N	-0.89203	1.45494	2.95503
N	0.80936	3.03884	2.75185
H	1.35278	2.34855	2.20788
H	-3.67127	4.13060	7.59521
H	-2.17747	4.19863	5.56091
H	-4.52077	2.83475	4.10581
H	-3.27752	4.54075	2.73916
H	-1.02405	4.67956	2.78885
H	-1.86137	1.25804	2.73685
H	1.02607	3.99327	2.47423
H	-3.31604	2.47990	7.02978
H	-3.74107	4.94600	5.20833
H	-2.98915	2.04625	4.51947
H	-3.10093	2.90824	2.09707
H	-0.25686	0.74100	2.56907
H	-4.89497	3.22112	6.67537
O	3.01985	3.56130	0.54927
H	4.42470	3.09736	0.94337
H	3.29415	4.35582	0.04690
O	2.57346	3.70778	-2.03891
H	1.82012	3.95108	-2.62239
O	-2.35453	-0.07691	-2.33288
H	-3.07714	0.54422	-2.60452
H	-2.52638	-0.95744	-2.71610
O	-0.50313	-2.27570	-0.21727
O	0.24930	-0.55314	1.45987

O	1.85513	-2.39800	0.77569
O	1.63754	1.36844	0.74015
O	1.49278	-0.71718	-0.97948
O	0.02031	3.76108	-3.30752
H	-0.26611	3.57632	-4.21681
H	0.14743	2.88282	-2.84314
O	6.95536	1.26020	-3.70755
H	7.38553	1.67166	-4.46957
H	6.27766	1.93901	-3.41483
O	5.25740	3.24005	-3.02967
H	5.58142	3.83473	-2.32717
H	4.30996	3.14432	-2.78776
Mn	1.10915	-2.51061	-1.08102
Mn	0.14824	-2.33973	1.53412
Mn	1.97361	-0.36378	0.77653
Mn	1.99588	2.58241	-0.69369
Ca	-0.82566	0.25786	-0.55895
O	0.74831	1.65260	-1.90653
H	1.29098	1.03253	-2.42160
H	-6.34688	-2.77281	0.29467
H	7.81815	-0.15306	-2.72167
H	-8.15172	-3.83407	-3.10432
H	-5.61059	-6.18898	-3.73318
H	-6.69409	-4.98231	-4.48164
H	-0.78737	-6.62588	2.36291
H	-0.87691	-8.13003	1.41715
H	-5.35274	-6.58053	1.84785
H	7.47559	-3.58389	-3.72172
H	8.08795	-2.02771	-4.32126
H	5.31892	-4.64367	-3.12709
H	7.01308	-3.38813	0.25751
H	-4.73412	7.74564	1.59673
H	-3.93736	7.29713	0.06323
H	-1.55657	8.93923	1.99401
H	-9.73034	-4.55786	-1.01998
H	-3.03278	-6.52421	2.65358
H	-1.65668	7.97094	0.00579
H	-2.71521	7.27196	3.50578
H	-0.02760	5.93904	-1.06598
O	0.35896	-2.54074	-2.70219
H	-0.62101	-2.69073	-2.68746
H	3.08536	-3.06936	1.36431
H	-1.71266	-3.03912	-0.48479

b) The atomic coordinates of the S₃ state model with D1-E189 ionized and bound to Mn1:

C	-3.61712	-7.98411	-0.49812
C	-3.03985	-7.38027	0.79481
C	-1.74094	-6.60961	0.55605

O	-1.55831	-5.58735	1.37737
O	-0.94095	-6.94433	-0.33235
H	-2.79961	-8.18875	1.50567
H	-2.86499	-8.62343	-0.97886
H	-3.76259	-6.72881	1.30331
H	-4.50571	-8.59272	-0.27527
H	-3.90402	-7.20309	-1.21933
C	8.01049	-1.98665	-1.05358
C	8.24155	-0.88068	-2.10544
C	6.96785	-0.17633	-2.54200
C	6.76459	1.18737	-2.26352
C	5.96558	-0.85402	-3.27062
C	5.62804	1.87160	-2.71888
C	4.81704	-0.19190	-3.72602
C	4.65350	1.18593	-3.47208
O	3.56393	1.82780	-4.00332
H	3.54049	2.81851	-3.72999
H	7.52801	-1.57427	-0.15414
H	8.72994	-1.33291	-2.98488
H	7.52713	1.73541	-1.70468
H	6.09232	-1.91121	-3.51065
H	5.50799	2.93811	-2.52950
H	4.06453	-0.72225	-4.30941
H	8.94554	-0.13402	-1.70544
C	7.58017	-4.20963	2.53845
C	6.18194	-3.98894	1.96469
O	5.21646	-3.64583	2.68689
C	7.54430	-4.87446	3.92542
H	8.19330	-4.79163	1.83327
H	8.55560	-4.92600	4.35137
H	7.14167	-5.89526	3.85903
N	6.05259	-4.15689	0.63052
C	4.86154	-4.50231	-1.45871
O	5.94684	-4.75347	-2.01614
C	4.81247	-3.83380	-0.06950
C	4.62889	-2.29281	-0.17495
C	3.17764	-1.84496	-0.32823
O	2.91136	-0.62662	-0.31207
O	2.35972	-2.84402	-0.41680
H	5.20773	-1.86682	-1.00584
H	5.00136	-1.82813	0.74783
N	3.67314	-4.78738	-2.03736
C	3.66420	-5.45577	-3.33349
C	4.52134	-4.70330	-4.36428
O	4.29340	-3.54694	-4.69952
H	5.35621	-5.27283	-4.82545
H	2.61905	-5.46639	-3.67390
H	4.03539	-6.48787	-3.23963

H	2.77867	-4.48531	-1.64213
C	-1.01506	7.58419	-1.95121
O	-1.29141	8.44567	-1.10585
C	-2.01755	6.49977	-2.38036
C	-1.40054	5.10668	-2.60997
C	-2.47567	4.01653	-2.81066
C	-1.80924	2.69526	-3.16216
O	-1.03843	2.61585	-4.13220
O	-2.06287	1.62285	-2.42712
H	-3.12113	4.29197	-3.66164
H	-0.77950	4.83841	-1.74593
H	-3.09798	3.91020	-1.91606
H	-0.76231	5.10159	-3.50726
N	0.19284	7.54807	-2.59012
C	1.31105	8.40628	-2.19844
C	2.58761	8.00084	-2.97030
C	2.90068	6.53653	-2.84467
C	3.08366	5.54123	-3.78887
N	2.99580	5.89175	-1.62114
C	3.22644	4.57310	-1.85731
N	3.29266	4.32595	-3.16418
H	1.48859	8.31415	-1.11623
H	3.41957	8.61674	-2.59273
H	3.08881	5.63528	-4.87021
H	3.31228	3.83282	-1.06920
H	2.47186	8.23184	-4.03956
C	-7.05607	-3.40564	-1.28931
O	-7.52258	-2.72175	-0.34446
C	-7.20217	-2.93288	-2.73607
C	-5.89040	-2.27583	-3.26041
C	-5.36781	-1.16098	-2.40332
C	-4.10881	-0.90347	-1.90491
N	-6.14347	-0.08181	-1.98494
C	-5.36289	0.77407	-1.27394
N	-4.12665	0.28986	-1.20230
H	-6.07882	-1.90371	-4.28106
H	-3.18684	-1.45533	-2.03671
H	-5.69987	1.69813	-0.82326
H	-5.11039	-3.04599	-3.34101
N	-6.38560	-4.56203	-1.12020
C	-5.93809	-5.02451	0.20025
C	-4.75162	-4.18508	0.72721
C	-3.69810	-4.01319	-0.36803
C	-2.49291	-3.15142	-0.06278
O	-2.57367	-2.28097	0.87628
O	-1.51776	-3.32392	-0.85624
H	-4.15603	-3.54109	-1.24722
H	-6.78573	-4.96977	0.89551

H	-4.30911	-4.66786	1.60885
H	-3.32466	-4.97901	-0.71897
H	-5.64124	-6.07392	0.08145
H	-5.13475	-3.21309	1.04937
C	-9.35234	-0.85467	2.14347
C	-8.62787	0.29688	1.40874
C	-7.13926	0.24958	1.57969
C	-6.22228	1.17436	2.03368
N	-6.40642	-0.88941	1.26111
C	-5.10572	-0.66651	1.49354
N	-4.97589	0.57220	1.98085
H	-9.03986	-1.82639	1.73667
H	-8.98549	1.27323	1.76534
H	-6.36262	2.18411	2.39680
H	-4.27117	-1.33172	1.28735
H	-8.86663	0.23706	0.33311
H	-9.12990	-0.83177	3.21972
H	-10.43853	-0.76086	2.00878
C	-1.70133	6.27740	1.50928
O	-1.23506	5.73863	0.50670
C	-3.13115	6.03050	2.01258
C	-3.88752	5.03792	1.11975
C	-3.23370	3.65736	1.03685
O	-2.40420	3.35035	1.95901
O	-3.59794	2.90773	0.06296
H	-3.96169	5.41827	0.09255
H	-4.91690	4.91040	1.49253
N	-0.94926	7.13000	2.29186
C	0.27202	7.72955	1.74550
C	1.44979	6.76467	1.54905
O	2.39622	7.11600	0.82049
H	0.06749	8.17517	0.76042
N	1.41437	5.59269	2.22986
C	2.32035	4.47727	1.95545
C	1.50592	3.26850	1.43603
O	1.92458	2.58609	0.48240
C	3.10872	4.05962	3.21447
O	0.43735	3.06268	2.15276
H	3.79096	3.22998	2.97075
H	3.01465	4.79881	1.17210
H	2.41625	3.73689	4.00513
H	0.54699	5.35375	2.70160
H	3.70531	4.90592	3.58018
C	0.38681	-1.41159	7.19023
C	0.25316	-1.00270	5.71549
C	-1.12291	-0.34788	5.42949
C	-1.24785	-0.00697	3.95126
O	-1.19479	1.24026	3.63216

O	-1.34904	-0.99530	3.15069
H	-1.24915	0.56374	6.02941
H	-0.39378	-2.13720	7.46698
H	0.36421	-1.88074	5.06289
H	-1.91993	-1.06222	5.68750
H	0.28815	-0.53900	7.85498
H	1.05060	-0.29539	5.43929
H	1.36581	-1.87428	7.38088
C	3.91338	-0.24127	7.69247
C	4.41184	-0.69924	6.31248
C	4.42122	0.45359	5.29519
C	4.95646	0.03961	3.90916
N	4.25605	-1.10305	3.31606
C	2.96278	-1.09549	2.93761
N	2.24578	0.04767	2.96738
N	2.36662	-2.24731	2.59294
H	1.48572	-2.22196	2.04873
H	3.89496	-1.07624	8.40785
H	3.76818	-1.50773	5.93097
H	5.05317	1.27845	5.66362
H	6.00819	-0.26584	3.99118
H	4.73716	-2.00883	3.26690
H	2.76474	0.91470	2.98403
H	2.95123	-3.07333	2.51050
H	2.89314	0.16570	7.62117
H	5.42883	-1.11934	6.39793
H	3.39987	0.85357	5.19774
H	4.92861	0.89476	3.21001
H	1.34864	0.09891	2.44309
H	4.56430	0.54574	8.10399
O	0.55005	-4.57962	0.50720
H	-0.65487	-5.08190	1.08291
H	0.70926	-5.34561	-0.07929
O	0.72585	-4.20909	-2.09679
H	0.95767	-3.66463	-2.89565
O	1.10663	1.23980	-3.14925
H	1.98961	1.39168	-3.57879
H	0.41843	1.73415	-3.65170
O	-0.96795	2.25648	-0.06600
O	0.07720	0.47286	1.42256
O	-2.46417	0.73089	1.29036
O	0.13370	-1.99914	0.92060
O	-1.42066	-0.30148	-0.65456
O	1.57807	-2.82558	-4.35183
H	2.55437	-2.93197	-4.33947
H	1.30837	-3.21250	-5.19707
O	-4.39571	-5.35978	-3.06061
H	-4.52111	-5.96118	-3.80734

H	-3.40634	-5.39521	-2.88695
O	-1.75072	-5.68885	-2.73652
H	-1.53439	-6.34213	-2.04153
H	-1.10271	-4.97691	-2.54529
Mn	-2.39500	1.25605	-0.54371
Mn	-1.01528	1.87246	1.72775
Mn	-1.18024	-0.86960	1.09644
Mn	0.45138	-3.04563	-0.66162
Ca	0.93884	0.61737	-0.86826
O	0.47756	-1.58515	-1.77157
H	-0.25666	-1.53967	-2.44018
H	2.85757	6.32996	-0.69778
H	-5.85114	-4.93909	-1.91689
H	0.41594	6.74667	-3.16952
H	-2.76461	6.45539	-1.57847
H	-2.53218	6.83725	-3.29672
H	-3.08278	5.65786	3.04676
H	-3.66939	6.99166	2.03241
H	0.59877	8.52610	2.42792
H	-8.03952	-2.22220	-2.76481
H	-7.44834	-3.77527	-3.39803
H	-7.13786	0.01947	-2.14140
H	-6.79696	-1.72715	0.76675
H	8.96527	-2.44898	-0.75560
H	7.36227	-2.77361	-1.46286
H	8.04971	-3.21320	2.61284
H	1.06354	9.45827	-2.40424
H	-1.42886	7.64680	3.01967
H	6.84763	-4.41624	0.05297
H	6.89887	-4.29845	4.60161
H	3.97885	-4.24708	0.50983
O	-1.22501	-0.80859	-3.73300
H	-1.53551	0.01640	-3.30095
H	-0.41722	-0.52436	-4.19266
H	-4.01345	0.97248	2.01379