Supporting Online Material for

Theoretical EXAFS studies of a model of the oxygen-evolving complex of photosystem II obtained with the quantum cluster approach.

Xichen Li[1,2,], Eduardo M Sproviero[4], Ulf Ryde[3], Victor S Batista[4], Guangju Chen[1].*

1. College of Chemistry, Beijing Normal University, 100875, Beijing, China. 2. Department of Physics, ALBA NOVA, and Department of Biochemistry and Biophysics, Arrhenius Laboratory, Stockholm University, SE-106 91 Stockholm, Sweden. 3. Department of Theoretical Chemistry, Lund University, Chemical Center, P.O. Box 124, S-221 00 Lund, Sweden. 4. Department of Chemistry, Yale University, PO Box 208107, New Haven, CT 06520-8107, USA.

RECEIVED DATE (to be automatically inserted after your manuscript is accepted if required according to the journal that you are submitting your paper to)

Corresponding author:

*To whom correspondence should be addressed. E-mail: xli@fysik.su.se.

This file includes the following parts:

Cartesian coordinates of the refined cluster model

Figures S1-S8.

- Calculated polarized EXAFS spectra in *k*-space.

- Comparison of the experimental and the calculated polarized EXAFS spectra with certain atoms removed.

- Comparison of calculated isotropic EXAFS spectrum.

- Individual atomic contributions to whole isotropic spectrum.

- Scatter contributions to the isotropic EXAFS spectrum of Mn1 based on path analysis.

- Scatter contributions to the isotropic EXAFS spectrum of Mn2 based on path analysis.

- Scatter contributions to the isotropic EXAFS spectrum of Mn3 based on path analysis.

- Scatter contributions to the isotropic EXAFS spectrum of Mn4 based on path analysis.

References

Cartesian coordinates of the refined cluster model

Mn	29.6201456	38.2278094	66.4149376
Mn	26.5717874	40.1116494	69.3324181
Mn	28.8366467	38.0116989	68.9520148
Mn	28.5872679	39.7084067	71.0818856
O	28.5516491	39.2752043	67.7191088
O	29.8323303	39.1703234	69.9200289
O	28.0225735	41.0745615	69.9802001
O	27.4367903	38.6398682	70.1038117
Ca	29.9276503	41.2324733	68.4401020
C	33.3151681	40.0124718	64.0344725
H	34.0154229	39.2058538	64.1938794
H	33.5463982	40.6512998	63.1949290
H	32.3692763	39.5250805	63.7724428
C	33.0943499	40.8240235	65.3252551
H	32.5659837	41.7796784	65.0988486
H	34.0687456	41.1313814	65.8013652
C	32.2261139	40.1046266	66.3767952
O	31.9666979	40.7423817	67.4565768
O	31.7718300	38.9586604	66.0889967
C	24.3931826	46.2892876	68.4847244
H	23.6554789	46.0724808	67.7263122
H	24.7089561	47.3202042	68.5471610
H	23.9123224	46.0597218	69.4465201
C	25.5612800	45.2974688	68.2882020
H	26.3188760	45.4206408	69.0938854
H	26.0927351	45.4585226	67.3284237
C	25.0213282	43.8407831	68.2919385
H	24.2576649	43.7262022	67.4947327
H	24.5172698	43.6025579	69.2457375
C	26.1039315	42.7609662	68.0386336
O	27.1580886	43.0415275	67.4550921
O	25.7665603	41.5635088	68.4496889
C	21.8812679	36.4390735	66.3011212
H	20.8572268	36.1455858	66.0349134
H	22.4224421	36.5932889	65.3635157
C	22.5206516	35.2815780	67.0778314
O	22.1952067	35.0346075	68.2648142
C	21.7620443	37.7353123	67.1505187
H	20.9731701	37.6001924	67.9141414
H	21.4577860	38.5754060	66.4948738
C	23.0503171	38.1114461	67.8501516
N	23.6120570	37.2337475	68.7655719
H	23.1624631	36.3273557	68.9834998
C	23.9450124	39.1673755	67.7681376
H	23.8981414	40.1014561	67.1814487
C	24.7816908	37.6918072	69.1613036
H	25.5057977	37.1820212	69.8055211
N	25.0269552	38.8950926	68.5933119

N	23.5080093	34.5926781	66.4252174
H	23.6277688	34.8403663	65.3983448
C	24.4187735	33.7086757	67.0891161
H	24.7464842	32.9816221	66.3359148
H	23.8955380	33.1669524	67.8820200
C	25.6381012	34.4376590	67.7004080
H	26.2789201	33.7010611	68.2404710
H	25.2745917	35.1540617	68.4681305
C	26.4530789	35.1648744	66.6252054
H	25.7700779	35.6418024	65.8830650
H	27.0433788	34.4330675	66.0320024
C	27.4207527	36.2724565	67.0138291
O	28.0375179	36.7996320	66.0398946
O	27.5655028	36.6450432	68.2398002
C	26.0923255	41.0622870	74.8555534
H	26.5886664	40.1056425	75.0461360
H	25.4262936	41.2628038	75.7063588
C	25.2553518	40.9676037	73.5733911
H	24.8148671	41.9616622	73.3313779
H	24.4248042	40.2556960	73.7100879
C	26.0304138	40.5276519	72.3274427
O	27.2758737	40.1787460	72.4966760
O	25.4169450	40.5020506	71.2329277
C	27.1338200	42.1203149	74.7847152
O	27.0276262	43.1565656	74.0164145
N	28.1430400	42.0831810	75.6901340
H	28.2813060	41.2032848	76.1916891
C	29.1931998	43.0890631	75.8013125
H	29.5009403	43.1718207	76.8467589
H	28.7580066	44.0353158	75.4724771
C	30.4490040	42.7458957	74.9759873
O	31.4575136	42.2740800	75.5021990
N	30.3069085	42.9806893	73.6408070
H	29.4109791	43.2880288	73.2472122
C	31.2989135	42.5465511	72.6883091
H	31.7617097	43.3943647	72.1379632
H	32.0937745	42.0171943	73.2524134
C	30.6831943	41.6057650	71.6484458
O	31.1082232	41.6608993	70.4664416
O	29.7699113	40.8040234	72.0848211
C	31.6073128	34.8395030	73.9938031
H	31.1227211	34.2178310	74.7321087
H	32.5557924	35.2392131	74.3209398
H	31.8223576	34.1919768	73.1325066
C	30.8273883	36.0704069	73.4996661
H	31.5293749	36.6605756	72.8604863
H	30.5670282	36.7494821	74.3496643
C	29.5553145	35.7676309	72.6824810
H	28.7025652	35.6034304	73.3740105
H	29.6815388	34.8339830	72.0896201
C	29.2169554	36.9057889	71.7133013

O	29.2079561	36.6237902	70.4685945
O	28.9750943	38.0405402	72.2334025
C	37.9196244	35.9678988	72.8110976
H	37.2804789	35.3360318	73.4099607
H	38.5611340	36.5836131	73.4240927
H	38.5906915	35.2706860	72.2897911
C	37.1828978	36.7817400	71.7350010
H	36.4497263	36.1199072	71.2105705
H	37.9288977	37.0822292	70.9551404
C	36.4717557	38.0729031	72.2302917
H	37.2237247	38.6836100	72.7991205
H	35.6487738	37.8276793	72.9336783
C	35.9432877	38.9398969	71.0862159
H	36.7641086	39.1173035	70.3418813
H	35.6443760	39.9420453	71.4986617
N	34.7813988	38.3878567	70.4275824
H	34.7681739	37.3871957	70.2726666
C	33.5692985	39.0422912	70.3341380
N	33.6041508	40.3920093	70.4311600
H	32.6932263	40.9162417	70.3049999
H	34.4072957	40.8574593	70.0114833
N	32.4330442	38.3835777	70.2196733
H	32.3890410	37.3275345	70.0387346
H	31.5159169	38.8578177	70.0381491
C	25.6607639	33.6509143	74.5456565
H	25.6914074	33.0766281	73.6315154
H	25.3094543	33.0696166	75.3853448
H	26.6541080	34.0537042	74.7687899
C	24.5785481	34.7557591	74.4656408
H	24.4485342	35.1970589	75.4829299
H	23.5975678	34.2820748	74.2287575
C	24.8139572	35.8965204	73.5103877
N	23.8718359	36.8706452	73.3193366
C	25.9452827	36.1529791	72.7507319
H	26.8742902	35.5926933	72.5894259
C	24.4210151	37.7291924	72.4699891
H	23.9549425	38.6305830	72.0568047
N	25.6882609	37.3503907	72.1063996
H	26.3530328	37.8529045	71.4782486
C	31.8431326	31.7674711	66.5253976
H	32.0576466	31.3899462	65.5365306
H	32.3011560	31.2118453	67.3303163
H	32.3349262	32.7485763	66.5653029
C	30.3418871	32.0628389	66.6393269
H	29.7051082	31.2184589	66.3337827
H	30.0831795	32.3283915	67.6943567
C	29.9791157	33.3173555	65.7849385
O	30.7012156	34.3397213	65.9157730
O	28.9510489	33.2582007	65.0083994
C	21.6408069	32.8538287	59.6262598
H	21.5012043	32.2100472	58.7704234

H	21.0470910	33.7534480	59.5585403
H	21.2688134	32.3162585	60.5086620
C	23.1380821	33.1994170	59.8727360
H	23.6559371	33.4255519	58.9008203
H	23.1953764	34.1356864	60.4806612
C	23.8941960	32.0875616	60.6183686
H	23.5518364	32.0712666	61.6775480
H	23.5993482	31.1012092	60.1904648
C	25.4349096	32.1477413	60.5743473
H	25.8416934	31.2184021	61.0562964
H	25.7617467	32.0989684	59.5043167
C	26.1712970	33.3544763	61.1742535
H	27.2579722	33.2552033	60.9711623
H	25.8681487	34.3252786	60.7501115
N	26.0050728	33.4709142	62.6540436
H	26.6745017	34.2847849	63.0099264
H	25.0515595	33.8622137	62.9080838
H	26.2929388	32.6375499	63.2261720
Cl	23.5850868	35.2174329	63.3347755
O	29.1301964	39.3923223	65.0295008
H	29.6657364	39.1749026	64.2314144
O	30.2067964	37.3000103	67.9379074
O	31.8006579	35.8523081	69.4327024
H	30.9971772	35.6858898	69.9816944
H	31.3502125	36.2726203	68.6263163
O	29.2617436	41.7446815	66.2076638
H	29.1894594	40.8777610	65.6575448
H	28.3394395	42.0948040	66.3492063
O	29.4044611	43.6215004	68.8275273
H	29.0732873	43.7910290	69.7539083
H	28.5679184	43.6745785	68.2523838
O	28.2180841	43.4065384	71.3904562
H	28.0273901	42.4892574	70.9950089
H	27.5577409	43.5137909	72.1215992
O	30.6272340	36.8291240	65.0697297
H	31.5597936	37.1296141	65.2328301
H	30.5802450	35.8318505	65.3652692
O	27.8964579	35.2765989	63.6288034
H	28.4800428	34.5611420	64.0569834
H	27.8221664	35.9592501	64.3642730
O	26.0939728	36.4898483	61.6120870
H	26.8724014	36.2741118	62.1835720
H	25.3044930	36.3135783	62.2037757
O	27.0353273	31.5682686	64.3805175
H	27.8656199	32.1088888	64.6675105
H	26.5081852	31.4394246	65.1981159

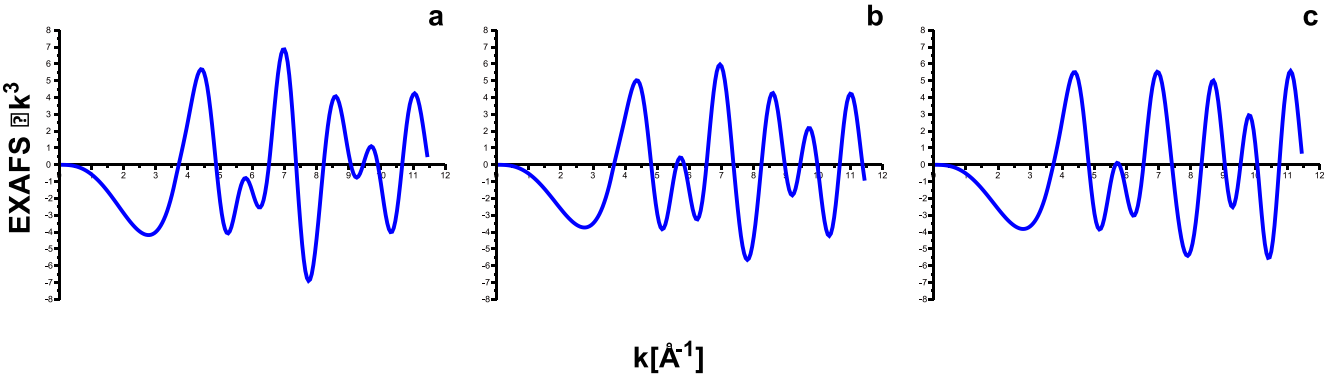

Figure S1. Calculated polarized EXAFS spectra in *k*-space for the refined cluster model structure. Unfortunately, we cannot compare to the experimental spectrum in *k* space, because it has not been published.

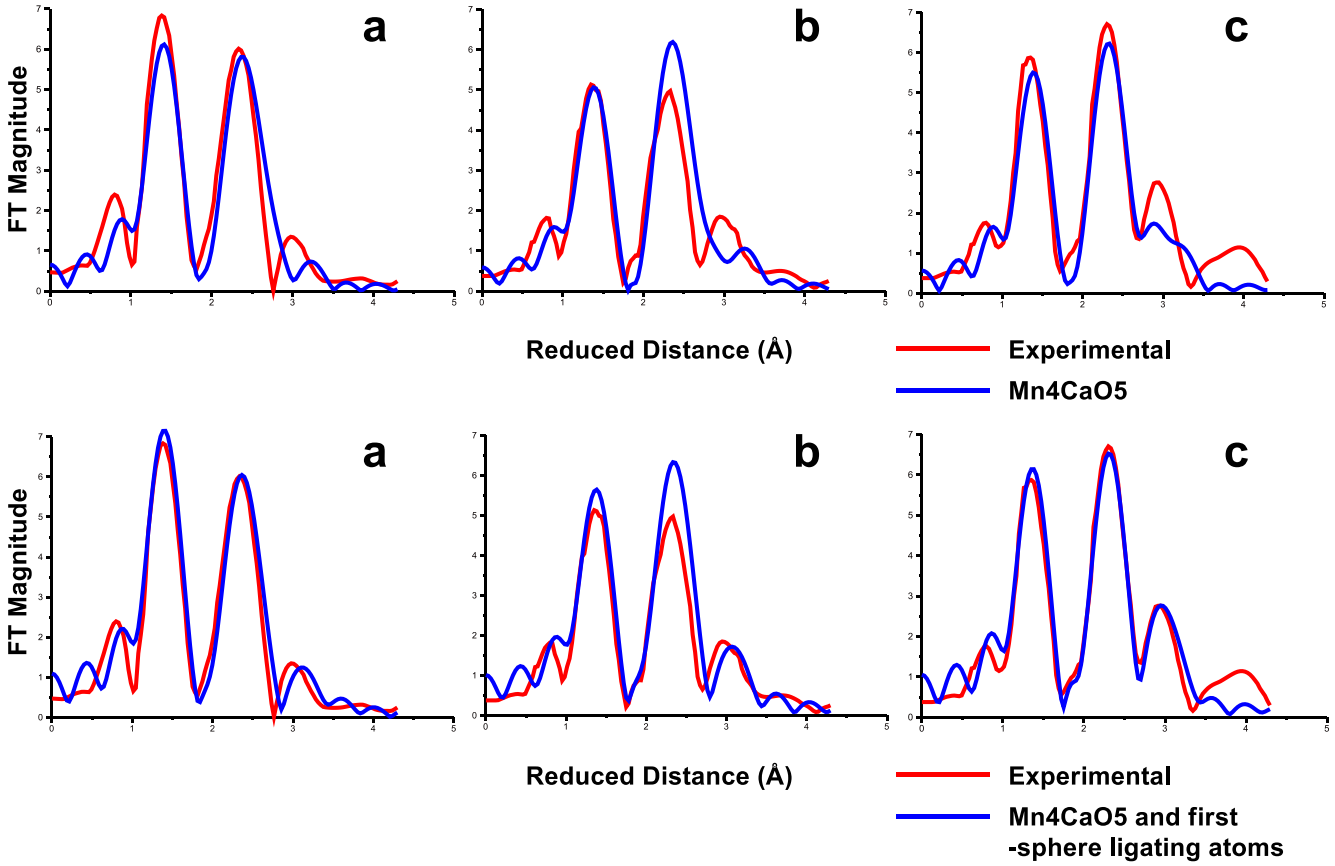

Figure S2. Comparison of the experimental (red) and the calculated polarized EXAFS spectra of the refined cluster model (blue) with certain atoms removed. Upper panel: only Mn_4CaO_5 was retained. Bottom panel: Mn_4CaO_5 and the first-sphere ligating atoms were retained. It can be noted that the general features of the spectra are reproduced already with Mn_4CaO_5, but the finer details require inclusion also of the first-sphere ligating atoms.

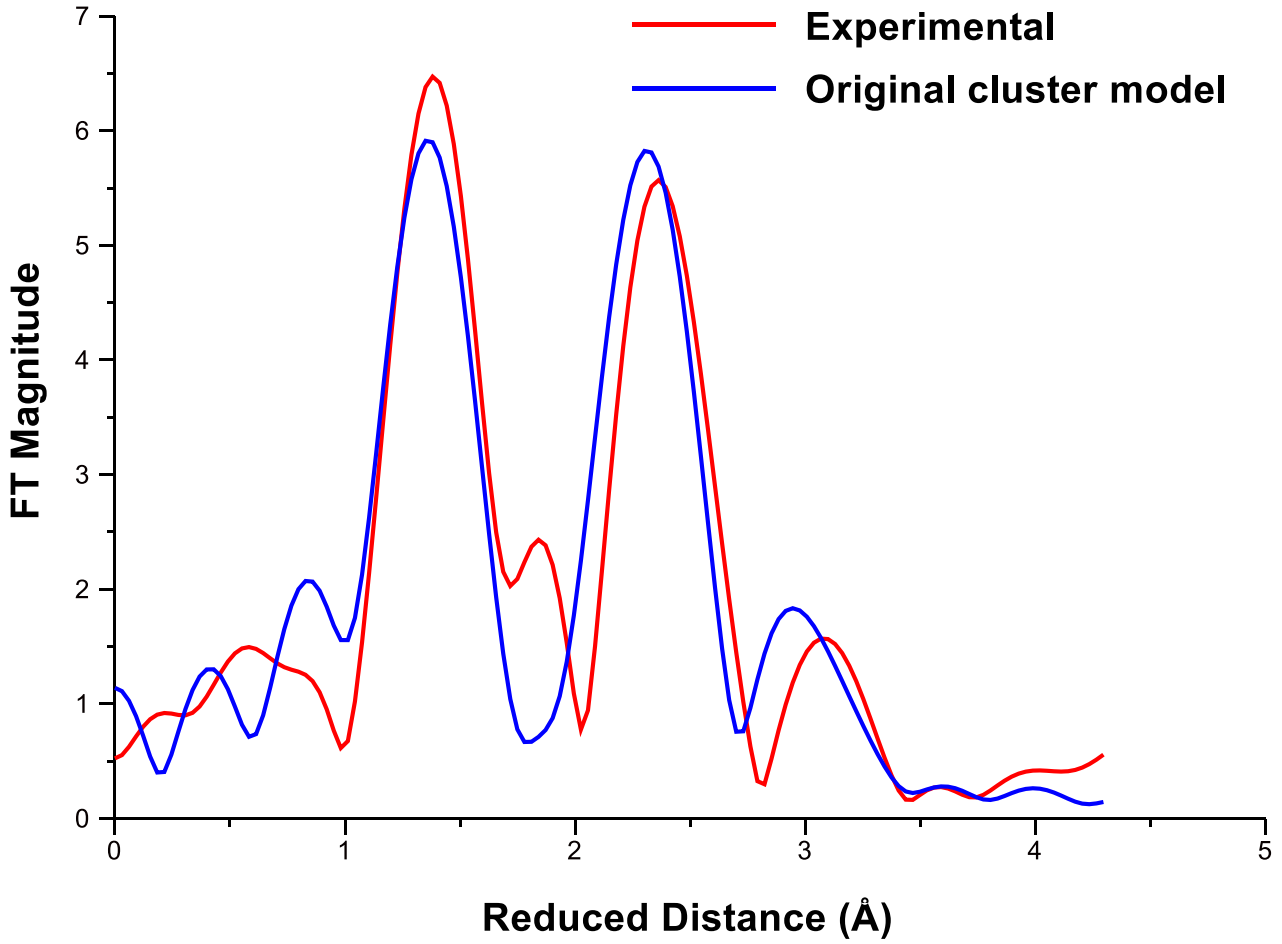

Figure S3. Comparison of calculated isotropic EXAFS spectrum for the refined cluster model (blue) and one set of experimental data[1] (red) (first converted from *k*-space into *R*-space).

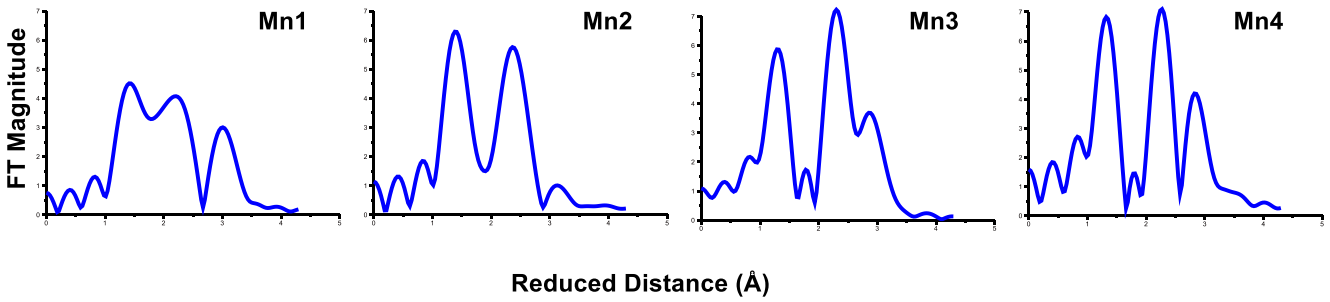

Figure S4. Individual contributions from the four Mn ions to the calculated isotropic EXAFS spectrum.

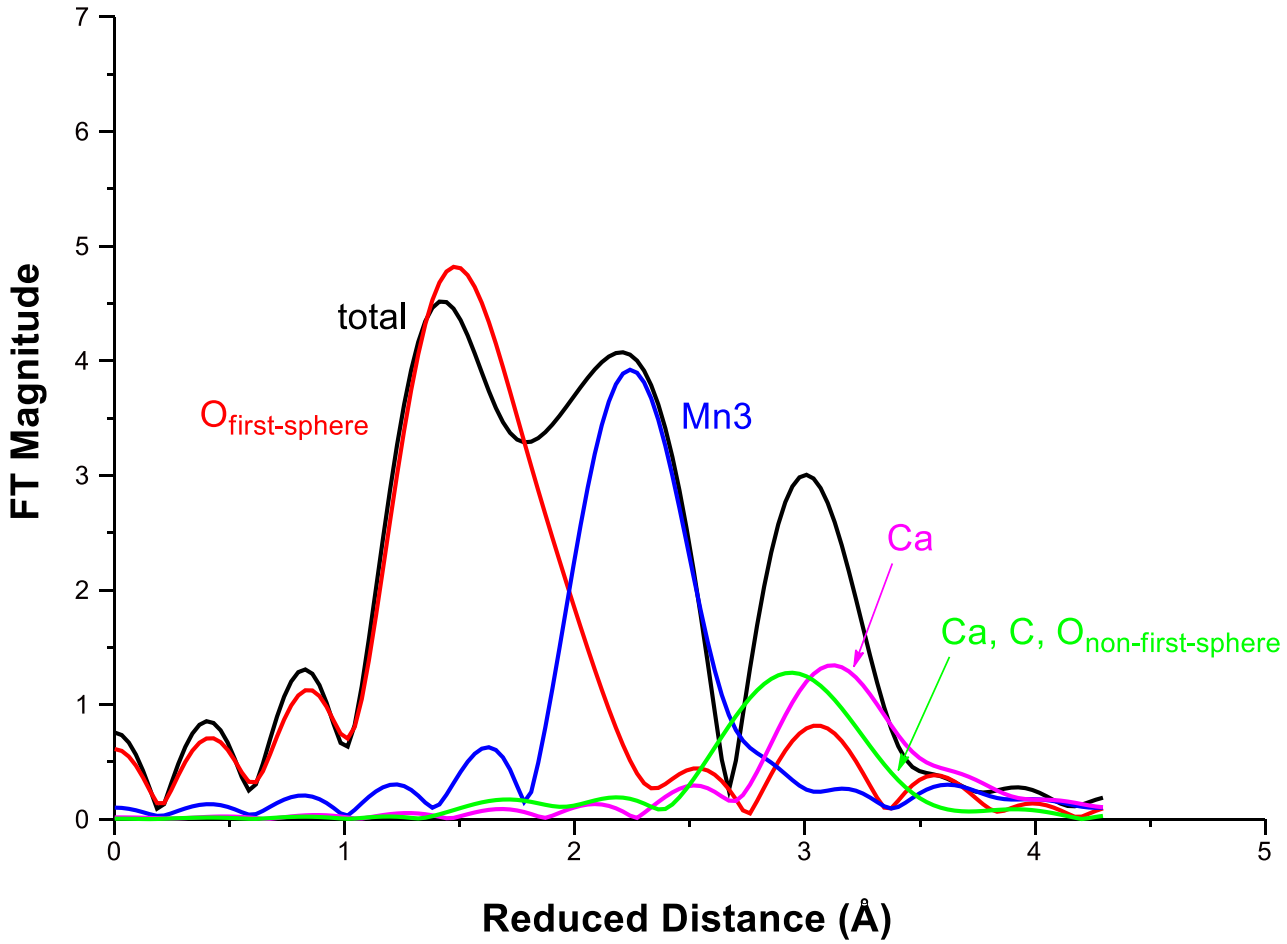

Figure S5. Path analysis of the Mn1 contribution to the isotropic EXAFS spectrum of the cluster model. The black curve is the total contribution, shown in Figure S4a, whereas the colored curves show the contributions from paths involving certain atoms. The first peak (around R = 1.4 Å) is caused by paths involving Mn1 and its first-sphere ligating oxygen atoms (red). The second peak (around R = 2.3 Å) is mainly due to paths involving Mn1 and the other Mn ions (blue). The third peak (around R = 3.1 Å) is mainly due to paths involving Mn1 and Ca, whereas the contribution from C and other O atoms is minor.

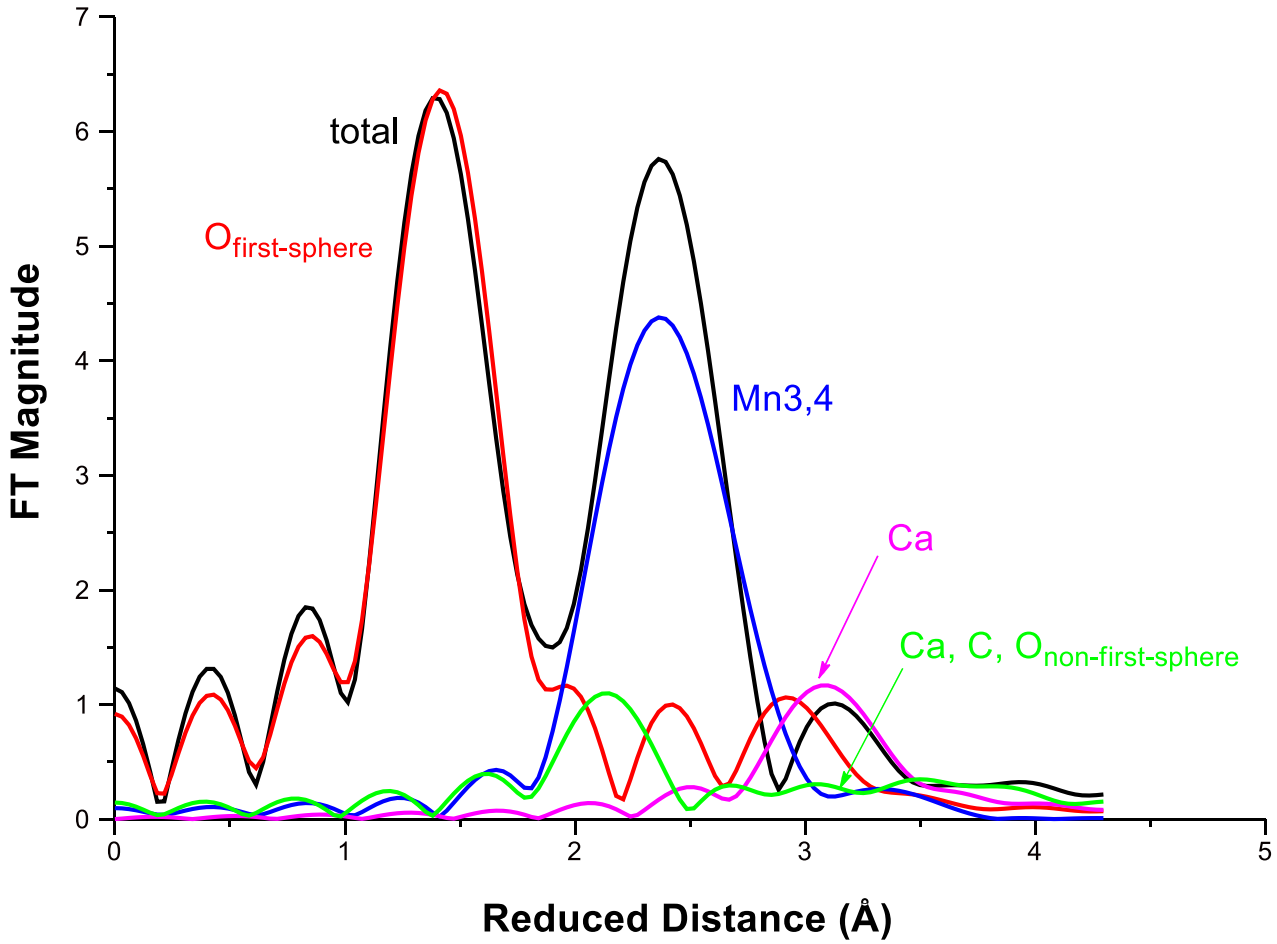

Figure S6. Path analysis of the Mn2 contribution to the isotropic EXAFS spectrum of the cluster model. The first peak is caused by paths involving Mn2 and its first-sphere ligating oxygen and nitrogen atoms (red). The second peak is mainly due to paths involving Mn2 and the Mn3 or Mn4 ions (blue). The third peak is mainly due to paths involving Mn2 and Ca, C, and the other oxygen atoms.

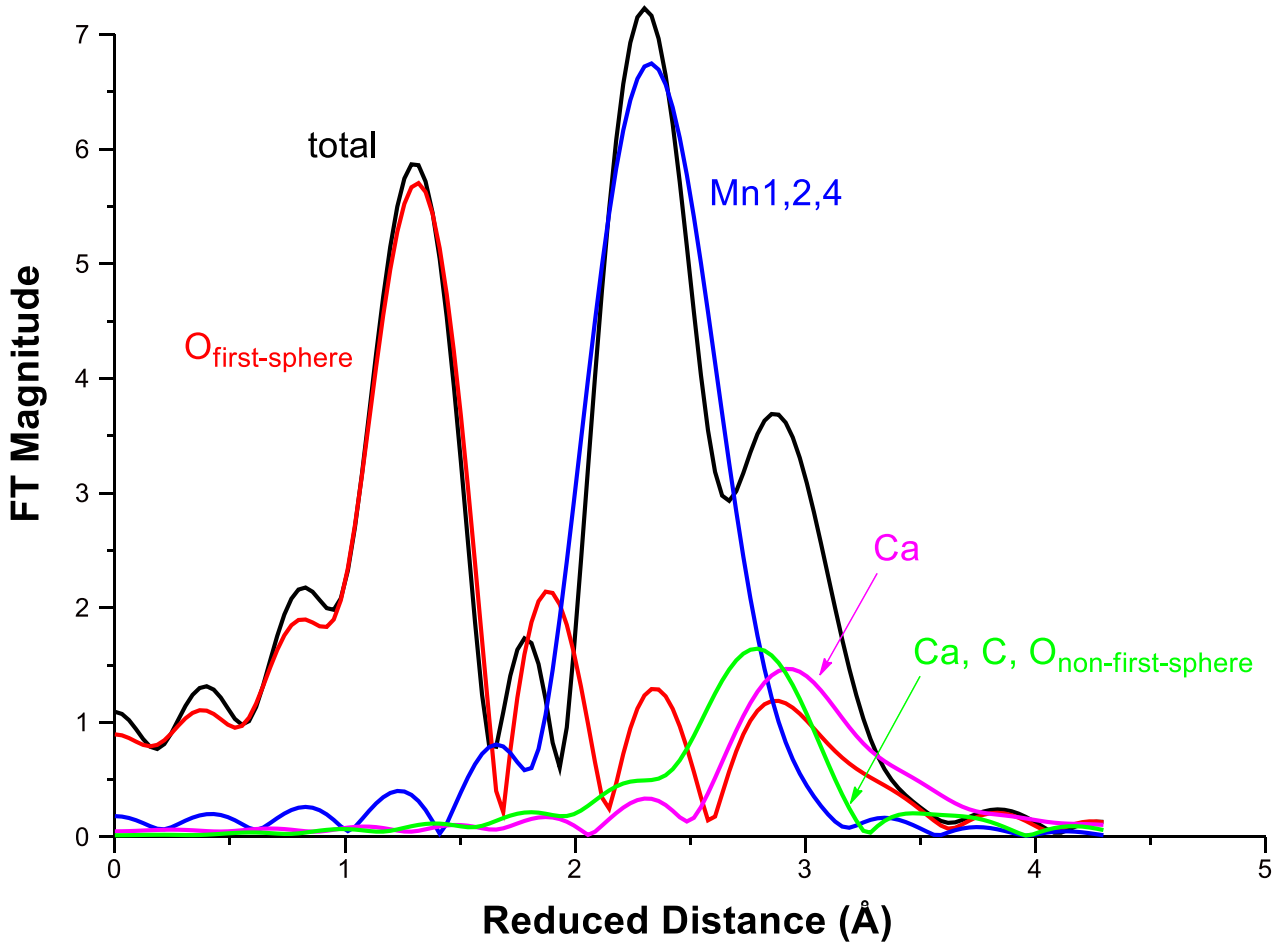

Figure S7. Path analysis of the Mn3 contribution to the isotropic EXAFS spectrum of the cluster model. The first peaks (R < 1.5 Å) are caused mainly by paths involving Mn3 and its first-sphere ligating oxygen atoms (red). The second peak is mainly due to paths involving Mn3 and the other Mn ions (blue). The third peak is mainly due to paths involving Mn3 and Ca, C, and the other oxygen atoms.

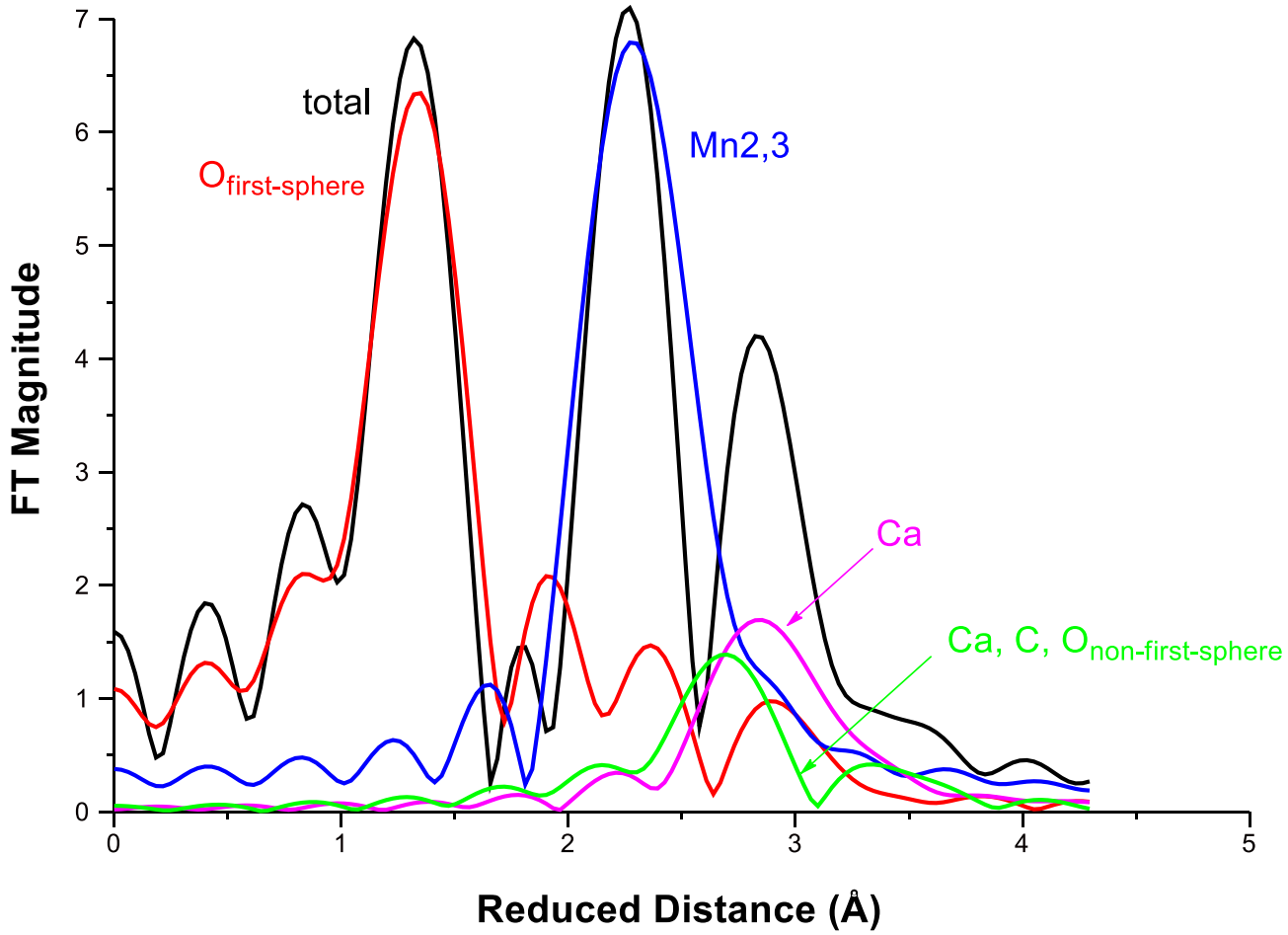

Figure S8. Path analysis of the Mn4 contribution to the isotropic EXAFS spectrum of the cluster model. The first peak is caused by paths involving Mn4 and its first-sphere ligating oxygen atoms (red). The second peak is mainly due to paths involving Mn4 and the Mn2 or Mn3 ions (blue). The third peak is mainly due to the paths involving Mn4 and Ca,C, and the other oxygen atoms.

References

1. Haumann, M.; Müller, C.; Liebisch, P.; Iuzzolino, L.; Dittmer, J.; Grabolle, M.; Neisius, T.; Meyer-Klaucke, W.; Dau, H., Structural and Oxidation State Changes of the Photosystem II Manganese Complex in Four Transitions of the Water Oxidation Cycle (S0 → S1, S1 → S2, S2 → S3, and S3,4 → S0) Characterized by X-ray Absorption Spectroscopy at 20 K and Room Temperature† . *Biochemistry* **2005,** *44* (6), 1894-1908.