Occupancy Analysis of Water Molecules inside Channels within 25 Å Radius of the Oxygen Evolving Center of Photosystem II in Molecular Dynamics Simulations

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S1. Code to create occupancy maps with CCP4.

```
# Run using: ccp4 ./NuclearDensity.com
#!/bin/bash for ID in S1 S2 ; do sfall xyzin ${ID}_oxygen.pdb mapout
${ID}_oxygen_1A.map.ccp4 hklout
    ${ID}_oxygen_1A.mtz ATOMSF atomsf_neutron.lib << eof
mode SFCALC XYZIN ATMMAP
CELL 80 80 80 90 90 90
GRID 240 240 240
SFSGROUP P1
SYMMETRY P1
RESOLUTION 100 1.0
BRESET 10.0
FORMFACT NEUTRON
end
eof
done
```

S2. Scripts to Generate Probability Density Functions and Decay.

A: Probability densities

A1- SphericalAveraging.com

#Replace columns 3-5 with coordinates of water position

#Replace column 14 with the name of the map to be analyzed

#Replace column 15 with the desired output name

#Run as ./SphericalAveraging.com

```
#!/bin/csh source CalSphereDensity.com 39.410 34.380 46.468 30.00 0 0 0 0 0 0
0.00
    S2_51_100ns_oxygen_1A S2_51_100ns_W1 source CalSphereDensity.com
41.855 35.461 47.281 30.00 0 0 0 0 0 0 0.00
    S2_51_100ns_oxygen_1A S2_51_100ns_W2 source CalSphereDensity.com
41.429 38.653 49.084 30.00 0 0 0 0 0 0 0.00
    S2_51_100ns_oxygen_1A S2_51_100ns_W3 source CalSphereDensity.com
40.959 41.489 48.405 30.00 0 0 0 0 0 0 0.00
    S2_51_100ns_oxygen_1A S2_51_100ns_W4
...
```

A2- CalSphereDensity.com

 # This code is called by SphericalAveraging.com and produces probability density

 # data that is printed to a file named "foo.SphericalAveraged"

```
# !/bin/csh cp awk_ functions
awk.it
# CRYST1 30.000 30.000 30.000 90.00 90.00 90.00 P 1 cat
«eof »awk.it
BEGIN {cx[1]=30.000; cx[2]=30.000; cx[3]=30.000; cx[4]=90.00; cx[5]=90.00; cx[6]=90.00;
ccpvolr(cx,ac,v); ortho(cx,c2f,f2c);
# ortho(ac,RF,RO); x1[1]=$ 1; x1[2]=$ 2; x1[3]=$ 3; b1=$ 4; ab[1]=$ 5; ab[2]=$ 6;

ab[3]=$ 7; ab[4]=$ 8; ab[5]=$ 9; ab[6]=$ 10;bave=$ 11;

ab[1]=ab[1]*ac[1]*ac[1]/10000.0; ab[2]=ab[2]*ac[2]*ac[2]/10000.0;

ab[3]=ab[3]*ac[3]*ac[3]/10000.0; ab[4]=ab[4]*ac[1]*ac[2]/10000.0;

ab[5]=ab[5]*ac[1]*ac[3]/10000.0; ab[6]=ab[6]*ac[2]*ac[3]/10000.0;

C=0.017453; twopi=6.28319; octahedron(x);
```

```
} eof
cat awk_ newmain_ spherical_ average »awk.it awk -f awk.it
$ { 12}.list >! $ {13}.SphericalAverage
```

A3 awk_functions

#This code is called by CalSphereDensity.com

 # Calculates density along 12 vectors centered at the coordinates provided in

#SphericalAveraging.com

```
#!/bin/csh function ccpvolr(cx,ac,v) dtor=0.017453; a1=cx[1]; b1=cx[2]; c1=cx[3];
alph=dtor*cx[4]; beta=dtor*cx[5];gamm=dtor*cx[6];sum=0.5*(alph+beta+gamm); v=sin(sum-
alph)*sin(sum-beta)*sin(sum-gamm); v=2.0*a1*b1*c1*sqrt(sin(sum)*v);
astar=b1*c1*sin(alph)/v; bstar=c1*a1*sin(beta)/v; cstar=a1*b1*sin(gamm)/v;
cosast=(cos(beta)*cos(gamm)-cos(alph))/(sin(beta)*sin(gamm)); cosbst=(cos(gamm)*cos(alph)-
cos(beta))/(sin(gamm)*sin(alph)); cosgst=(cos(alph)*cos(beta)-
cos(gamm))/(sin(alph)*sin(beta)); ac[1]=astar*astar; ac[2]=bstar*bstar; ac[3]=cstar*cstar;
ac[4]=2.0*bstar*cstar*cosast; ac[5]=2.0*cstar*astar*cosbst; ac[6]=2.0*astar*bstar*cosgst; return
function ortho(cx,c2f,f2c) C=0.017453; cabg[1]=cos(cx[4]*C); cabg[2]=cos(cx[5]*C);
cabg[3]=cos(cx[6]*C); sabg[1]=sin(cx[4]*C); sabg[2]=sin(cx[5]*C); sabg[3]=sin(cx[6]*C);
cabgs[1]=(cabg[2]*cabg[3]-cabg[1])/(sabg[2]*sabg[3]); cabgs[2]=(cabg[3]*cabg[1]-
cabg[2])/(sabg[3]*sabg[1]); cabgs[3]=(cabg[1]*cabg[2]-cabg[3])/(sabg[1]*sabg[2]);
v=cx[1]*cx[2]*cx[3]*sqrt(1.0+2.0*cabg[1]*cabg[2]*cabg[3]-cabg[1]**2-cabg[2]**2-
cabg[3]**2); abcs[1]=cx[2]*cx[3]*sabg[1]/v; abcs[2]=cx[3]*cx[1]*sabg[2]/v;
abcs[3]=cx[1]*cx[2]*sabg[3]/v; sabgs1=sqrt(1.0-cabgs[1]**2); # cartesian to fraction
c2f[1,1]=1.0/cx[1]; c2f[1,2]=-cabg[3]/(sabg[3]*cx[1]); c2f[1,3]=-
(cabg[3]*sabg[2]*cabgs[1]+cabg[2]*sabg[3])/(sabg[2]*sabgs1*sabg[3]*cx[1]); c2f[2,1]=0.0;
c2f[2,2]=1.0/(sabg[3]*cx[2]); c2f[2,3]=cabgs[1]/(sabgs1*sabg[3]*cx[2]); c2f[3,1]=0.0;
c2f[3,2]=0.0; c2f[3,3]=1.0/(sabg[2]*sabgs1*cx[3]);
# fraction to cartesian
f2c[1,1]=cx[1];
f2c[1,2]=cabg[3]*cx[2];
f2c[1,3]=cabg[2]*cx[3];
f2c[2,1]=0;
```

```
f2c[2,2]=sabg[3]*cx[2];
f2c[2,3]=-
sabg[2]*cabgs[1]*cx[3];
f2c[3,1]=0.0; f2c[3,2]=0.0;
f2c[3,3]=sabg[2]*sabgs1*cx[3];
return function product(y,r,x)
y[1]=x[1]*r[1,1]+x[2]*r[1,2]+x[
3]*r[1,3];
y[2]=x[1]*r[2,1]+x[2]*r[2,2]+x[
3]*r[2,3];
y[3]=x[1]*r[3,1]+x[2]*r[3,2]+x[
3]*r[3,3]; return function
formfactor(E,ss,B,afc,bfc,afs,bfs)
form=0; if(E=="C") for(kk=1;
kk<=5; kk+=1)
badd=B/4.+bfc[kk]/4.0;
form=form+afc[kk]*exp(-

badd*ss); if(E=="S") for(kk=1; kk<=5; kk+=1) badd=B/4.+bfs[kk]/4.0;
form=form+afs[kk]*exp(-

badd*ss); return form function octahedron(x) pi=3.141593; d2r=pi/180;
alpha=70.5288*d2r; beta=60.0*d2r; x[1,1]=1.0; x[1,2]=0.0; x[1,3]=0.0;
x[2,1]=1.0/2.0; x[2,2]=sin(beta); x[2,3]=0.0; x[3,1]=-1.0/2.0;
x[3,2]=sin(beta); x[3,3]=0.0 x[4,1]=1.0/2.0; x[4,2]=cos(alpha)*sin(beta);
x[4,3]=sin(alpha)*sin(beta); x[5,1]=-1.0/2.0; x[5,2]=cos(alpha)*sin(beta);
x[5,3]=sin(alpha)*sin(beta); x[6,1]=0.0;x[6,2]=-cos(alpha)*sin(beta)*2;
x[6,3]=sin(alpha)*sin(beta); for(i=7; i<=12; i+=1) x[i,1]=-x[i-6,1]; x[i,2]=-
x[i-6,2]; x[i,3]=-x[i-6,3]
```

A4 awk_newmain_spherical_average

```
# This code is called by CalSphereDensity.com

# Averages the 12 vectors

h[NR]=$ 1; k[NR]=$ 2; l[NR]=$ 3; apart0=$ 4*cos($ 5*C); bpart0=$ 4*sin($ 5*C); #

making B-factor corrections and store into apart[NR] and bpart[NR] ss=ac[1]*$ 1*$

1+ac[2]+ac[2]*$ 2*$ 2+ac[3]*$ 3*$ 3+ac[4]*$ 2*$ 3+ac[5]*

    $ 3*$ 1+ac[6]*$ 1*$ 2;

Btensor=ab[1]*$ 1*$ 1+ab[2]*$ 2*$ 2+ab[3]*$ 3*$ 3+2*ab[4]*$ 2*$ 3+2*ab[5]*

    $ 1*$ 3+2*ab[6]*$ 1*$ 2;

Btensor=2*pi*pi*Btensor; scale=exp(Btensor-bave*ss/4.0); apart[NR]=apart0*scale;
bpart[NR]=bpart0*scale;
}

ENDNX=30; dr=0.05; r=0; srho=0; xnew[1]=x1[1]; xnew[2]=x1[2];

xnew[3]=x1[3]; product(yfract,c2f,xnew); rho=0; for(j=1; j<=NR; j+=1)

alpha=h[j]*yfract[1]+k[j]*yfract[2]+l[j]*yfract[3];

rho=rho+apart[j]*cos(twopi*alpha)+bpart[j]*sin(twopi*alpha);;

rho=2*(rho+129124)/v; printf("%8.3f %12.5f %12.5f

%12.5f\n",r,rho,rho-srho,rho+srho);

# averaging for (i1=1; i1<=NX; i1+=1) r=dr*i1; rho0=0; sumxx=0;

for(i2=1; i2<=12; i2+=1) xnew[1]=x1[1]+x[i2,1]*r;

xnew[2]=x1[2]+x[i2,2]*r; xnew[3]=x1[3]+x[i2,3]*r;

product(yfract,c2f,xnew); rho=0; for(j=1; j<=NR; j+=1)

alpha=h[j]*yfract[1]+k[j]*yfract[2]+l[j]*yfract[3];

rho=rho+apart[j]*cos(twopi*alpha)+bpart[j]*sin(twopi*alpha);;

rho=2*(rho+129124)/v; rho0=rho0+rho; sumxx=sumxx+rho*rho;

rho=rho0/12; srho=sqrt(sumxx/12-rho*rho); printf("%8.3f %12.5f %12.5f

%12.5f\n",r,rho,rho-srho, rho+srho)
```

B: To calculate decay

B1 rrlog.com

```
#Calculates y = log(x2^/max2)^ /2 for the probability density calculated by
SphericalAveraging.com
#Run using ./rrlog.com
# !/bin/csh
foreach Mn (W1 W2 W3 W4)
awk -f awk_rrlog S2_51_100ns_$ {Mn}.SphericalAveraged >!
    S2_51_100ns_${Mn}.SphericalAveraged_rrlog

    end
```

B2 awk_rrlog

```
#This code is called by rrlog.com
# !/bin/csh
{if(NR==1) {ymax=$ 2}; rr=$ 1*$ 1; ylog=log($ 2*$ 2/ymax**2)/2.0; print
    rr,ylog}
```

S3. Matlab Code for Generating Plots.

```
%Load data generated by the codes included in S2
S1W1 = dlmread('/Users/foo/bar/S1_51_100ns_W1.SphericalAveraged');
S1W2 = dlmread('/Users/foo/bar/S1_51_100ns_W2.SphericalAveraged');
S1W3 = dlmread('/Users/foo/bar/S1_51_100ns_W3.SphericalAveraged');
S1W4 = dlmread('/Users/foo/bar/S1_51_100ns_W4.SphericalAveraged');
S1W1_log = dlmread('/Users/fo/bar/S1_51_100ns_W1.SphericalAveraged_rrlog');
S1W2_log = dlmread('/Users/foo/bar/S1_51_100ns_W2.SphericalAveraged_rrlog');
S1W3_log = dlmread('/Users/foo/bar/S1_51_100ns_W3.SphericalAveraged_rrlog');
S1W4_log = dlmread('/Users/foo/bar/S1_51_100ns_W4.SphericalAveraged_rrlog');
%Determining the probability of each position by dividing the number of occurances by the total
number of frames
S1W1(:,2:4) = S1W1(:,2:4)/1250;
S1W2(:,2:4) = S1W2(:,2:4)/1250;
S1W3(:,2:4) = S1W3(:,2:4)/1250;
S1W4(:,2:4) = S1W4(:,2:4)/1250;
%Calculating the scaling factor to normalize the CDF of W1
S1W1tot = trapz(S1W1(:,1),S1W1(:,2));
S1W1scale = trapz(S1W1(:,1),S1W1(:,2))/S1W1tot;
S1W2scale = trapz(S1W2(:,1),S1W2(:,2))/S1W1tot;
S1W3scale = trapz(S1W3(:,1),S1W3(:,2))/S1W1tot; S1W4scale =
trapz(S1W4(:,1),S1W4(:,2))/S1W1tot;

%Calculation of CDF
S1W1cdf = ecdf(S1W1(:,2),'Function','survivor');
S1W2cdf = ecdf(S1W2(:,2),'Function','survivor')*S1W2scale;
S1W3cdf = ecdf(S1W3(:,2),'Function','survivor')*S1W3scale; S1W4cdf =
ecdf(S1W4(:,2),'Function','survivor')*S1W4scale;

%Plotting the PDF, CDF, and decay
```

```
figure('rend','painters')
tiledlayout(1,3) nexttile
hold on
plot(S1W1(:,1),S1W1(:,2),'k','Linewidth',2);
plot(S1W2(:,1),S1W2(:,2),'g','Linewidth',2);
plot(S1W3(:,1),S1W3(:,2),'b','Linewidth',2);
plot(S1W4(:,1),S1W4(:,2),'c','Linewidth',2);
set(gca,'FontSize',25,'XMinorTick','on','YMinorTick','on');
legend('W1','W2','W3','W4','Location','eastoutside')
xlabel('Radius (Å)') ylabel('S_1';'Probability') xlim([0 1.5])
xticks([0:0.5:1.5]) ylim([0 0.25])
```

```
yticks([0:0.05:0.25]) ax=gca; hold off nexttile
hold on

plot(S1W1(:,1),S1W1cdf(1:31,1),'k','Linewidth',2);

plot(S1W2(:,1),S1W2cdf(1:31,1),'g','Linewidth',2);

plot(S1W3(:,1),S1W3cdf(1:31,1),'b','Linewidth',2);

plot(S1W4(:,1),S1W4cdf(1:31,1),'c','Linewidth',2);

set(gca,'FontSize',25,'XMinorTick','on','YMinorTick','on');

legend('W1','W2','W3','W4','Location','eastoutside')

xlabel('Radius (Å)') ylabel('Occupancy') xlim([0 1.5]); ylim([0 1]);

xticks([0:0.5:2.25]); yticks([0:0.25:1]); ax=gca; hold off nexttile

hold on

plot(S1W1_log(:,1),S1W1_log(:,2),'k','Linewidth',2);
plot(S1W2_log(:,1),S1W2_log(:,2),'g','Linewidth',2);
plot(S1W3_log(:,1),S1W3_log(:,2),'b','Linewidth',2);
plot(S1W4_log(:,1),S1W4_log(:,2),'c','Linewidth',2);
plot(S1WX_log(:,1),S1WX_log(:,2),'m','Linewidth',2);
plot(S1WY_log(:,1),S1WY_log(:,2),'r','Linewidth',2);
set(gca,'FontSize',25,'XMinorTick','on','YMinorTick','on');
legend('W1','W2','W3','W4','Location','eastoutside') xlabel('Squared Radius (Å2)^ ')
ylabel('log(Prob2^/Max2)^ /2') xlim([0 2.25]) xticks([0:0.75:2.25]) ax=gca; hold off
```

S4. Occupancy Analysis of Water Molecules in the Broad (Cl1) Channel.

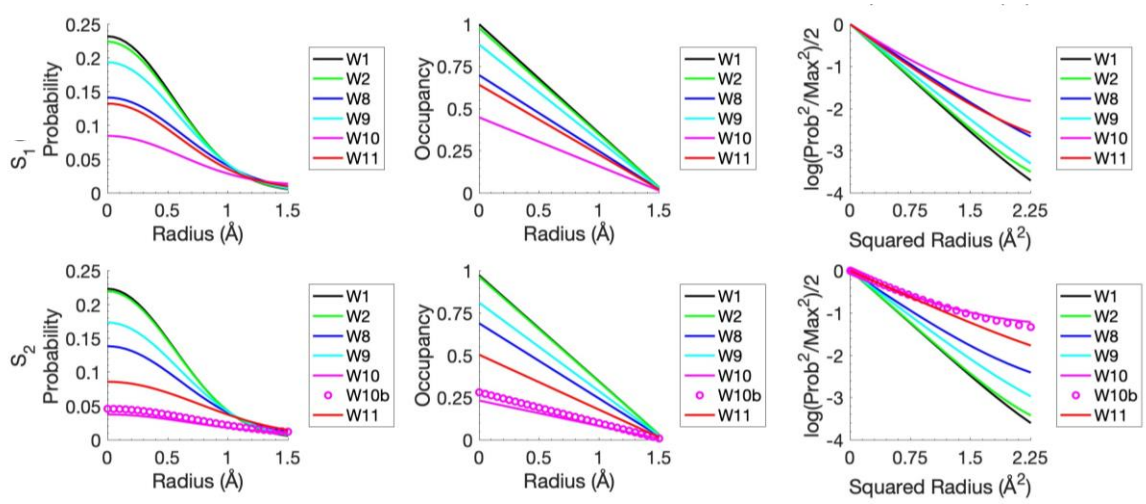

Figure S1. Occupancy analysis of water molecules in the broad channel: PDF (left), occupancy (center), and decay (right) of water molecules in the broad channel. The total occupancy is calculated as a survival function, measuring the probability of finding a water beyond the specified radial distance. The broad channel water molecules behave similarly in the S_1 state compared to those in the S_2 state.

S5. Occupancy Analysis of Water Tetramer next to the Y_Z.

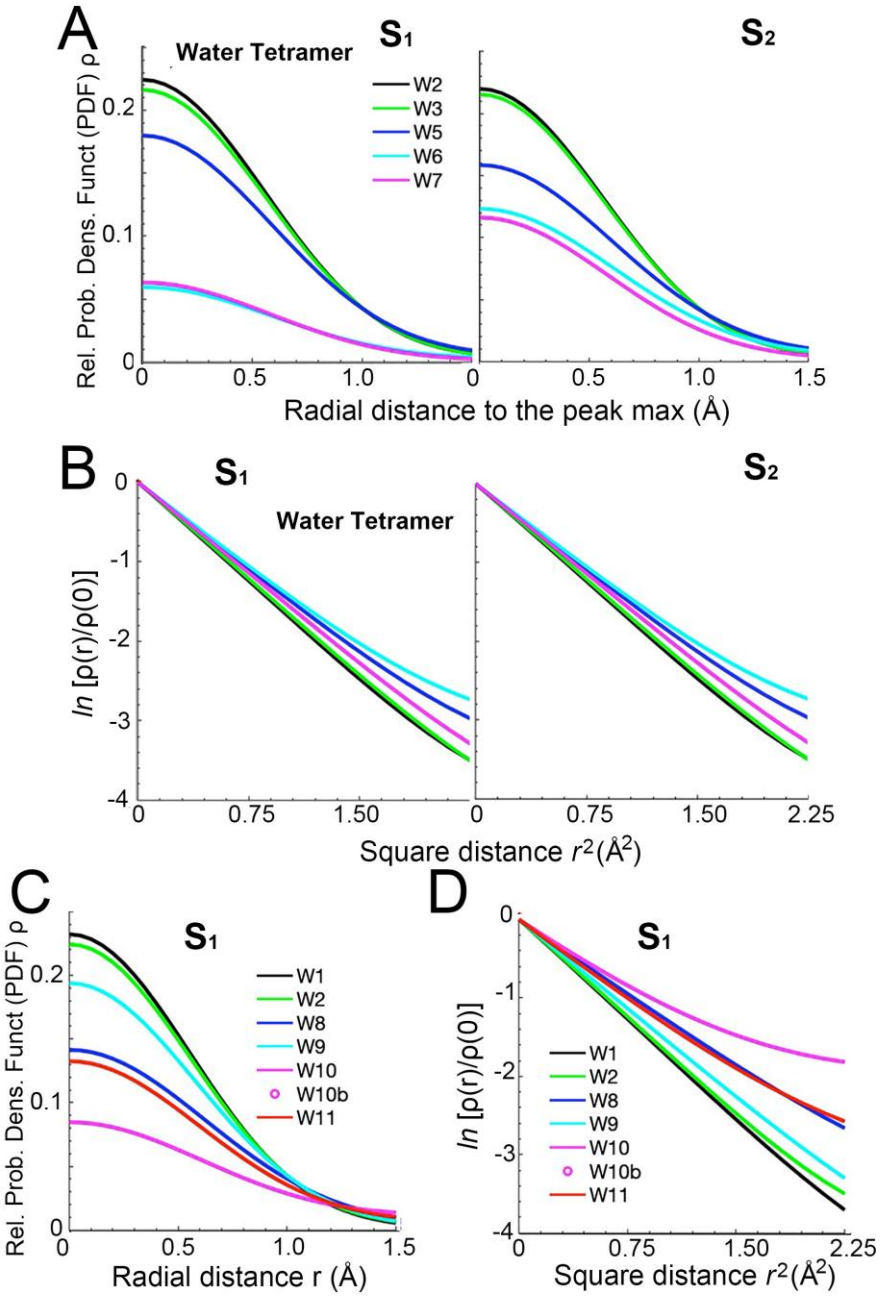

Figure S2. A and B show the occupancy analysis of the water tetramer next to Y_Z in the S_1 and S_2 states. C and D show the probability density and decay for water molecules in the broad channel in the S_1 state. W2, W3, and W5 (black, green, and blue, respectively) are largely unaffected by changing S states or fixing the chloride in the MD simulations. W6 and W7 (cyan and magenta, respectively) have a drastic drop in occupancy exhibiting a close coupling of Cl1 with the water molecules in the broad channel.

S6. Occupancies of Water Tetramer Plus a Reference W2 in the S_1 and S_2 (Table S1) States.

Table S1. Occupancy of water tetramer plus a reference W2 in the S_1 and S_2 states.

Water	**S_1**	**S_2**
(W2)	0.98	0.96
W3	0.95	0.95
W5	0.83	0.76
W6	0.28	0.60
W7	0.29	0.53

S7. Oxygen PDFs of Water Molecules inside the Large (O1) Channel.

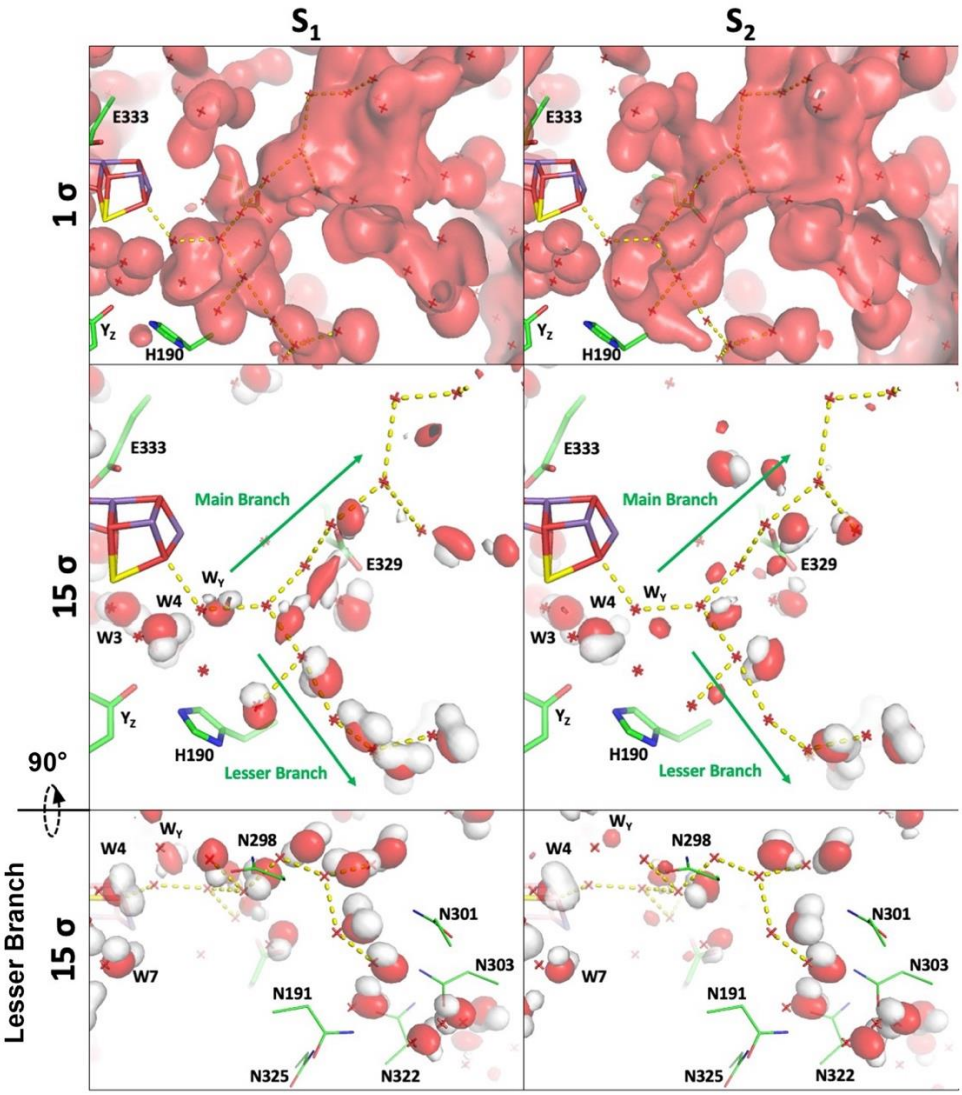

Figure S3. Top: Oxygen PDFs contoured at 1σ for water molecules in the large channel. Unlike the narrow and broad channels, the large channel is characterized by its disorganized globular water arrangement with no defined equilibrium positions. **Middle**: Same as above but contoured at 15σ for both O (red) and H (white) atoms. **Bottom**: A rotated view focusing on the secondary lesser branch to show the network of asparagines that stabilize individual water molecules occupying the lesser branch. Water positions from 3WU2[1] are marked as red crosses.

S8. Topology files for Fe-heme[2]

```
* bis-HIS heme and non-heme iron complexes for CHARMM36
* Compiled by Suliman Adam, Free Universtit Berlin
* Version from June 2017
*

! Parent files that have to be read prior to streaming this file:
! (1)  top_all36_prot.rtf (CHARMM36 protein, doi: 10.1021/ct300400x , 10.1021/ja036959e ,
10.1021/jp973084f )
! (2)  par_all36_prot.prm
! (3a) toppar_all36_prot_heme.str for loading heme B with propionic groups (doi: 10.1016/S0022-
2836(05)80196-2 )
! (3b) toppar_ions_won.str       for loading non-heme iron (doi: 10.1021/jp309150r)

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* Topology for bis-HIS heme and non-heme iron complexes
*
41 1

!reference:
!Adam, S., Knapp-Mohammady, M., Yi, J., Bondar, A.-N. Revised CHARMM force field
!parameters for iron-containing cofactors of photosystem II. (doi: 10.1002/jcc.24918)

MASS   -1 FE2H0  55.84700 ! heme iron, taken from all36_prot_heme: FE
MASS   -1 FE2H   55.84700 ! heme iron, taken from all36_prot_heme: FE
MASS   -1 FE3H   55.84700 ! hematin iron, taken from all36_prot_heme: FE
MASS   -1 FE2NH1 55.84700 ! ferrous non-heme iron in his-bicarbonate system, taken from
all36_prot_heme: FE
MASS   -1 FE3NH1 55.84700 ! ferric  non-heme iron in his-bicarbonate system, taken from
all36_prot_heme: FE
MASS   -1 FE2NH2 55.84700 ! ferrous non-heme iron in his-only system, taken from all36_prot_heme: FE
MASS   -1 FE3NH2 55.84700 ! ferric  non-heme iron in his-only system, taken from all36_prot_heme: FE

RESI HCO3          -1.00 ! Bicarbonate with MK charges
ATOM CT      CC      0.84 !
ATOM OC1     OC     -0.74 ! Use with patch only!
ATOM OC2     OC     -0.74 !
ATOM OC3     OH1    -0.72 !
ATOM HO3     H       0.36 !
BOND CT   OC1    CT   OC3
BOND OC3  HO3
DOUB CT   OC2

!ferrous FeHis
PRES FEBI2          1.00 ! Connect non-heme iron (2+) to four histidines and bicarbonate
                    ! Order: 1-FE2P, 2-HSD, 3-HSD, 4-HSD, 5-HSD, 6-HCO3
GROUP                    ! do NOT use AUTOgenerate ANGLes DIHEdrals after this patch
```

```
ATOM 1FE2P   FE2NH1  0.16 !
GROUP                !
ATOM 2ND1    NR1    -0.40 !
ATOM 2HD1    H       0.34 !                2HD1    2HE1     3HE1    3HD1
ATOM 2CG     CPH1    0.43 !                  |      |        |       |
ATOM 2CB     CT2    -0.24 !            2HB1   2ND1--2CE1      3CE1--3ND1    3HB1
ATOM 2HB1    HA2     0.09 !              |   /      ||        ||      \    |
ATOM 2HB2    HA2     0.09 !        -----2CB--2CG     ||        ||      3CG-3CB-----
GROUP                !             |   \\     ||        ||      //   |
ATOM 2NE2    NR2     0.10 !            2HB2   2CD2--2NE2      3NE2--3CD2    3HB2
ATOM 2CD2    CPH1   -0.48 !                 |       \     /       |
ATOM 2HD2    HR3     0.23 !                2HD2      \   /      3HD2
ATOM 2CE1    CPH2   -0.02 !                        \ /
ATOM 2HE1    HR1     0.19 !                        1FE(2+)
GROUP                !                        /||\
ATOM 3ND1    NR1    -0.40 !                        / || \
ATOM 3HD1    H       0.34 !                       /  ||  \
ATOM 3CG     CPH1    0.43 !                       / /  \ \
ATOM 3CB     CT2    -0.24 !                      /  /(-) \  \
ATOM 3HB1    HA2     0.09 !                      / 6OC1  6OC2 \
ATOM 3HB2    HA2     0.09 !             5HD2      /   \  //   \      4HD2
GROUP                !              |      /     \ //     \      |
ATOM 3NE2    NR2     0.10 !        5HB1   5CD2--5NE2      6CT      4NE2--4CD2    4HB1
ATOM 3CD2    CPH1   -0.48 !         |   //     ||       |        ||      \\   |
ATOM 3HD2    HR3     0.23 !     -----5CB--5CG     ||      6OC3       ||      4CG--4CB-----
ATOM 3CE1    CPH2   -0.02 !         |   \      ||       |        ||      /    |
ATOM 3HE1    HR1     0.19 !        5HB2   5ND1--5CE1     6HO3      4CE1--4ND1    4HB2
GROUP                !              |      \            /       |
ATOM 4ND1    NR1    -0.40 !            5HD1     5HE1          4HE1     4HD1
ATOM 4HD1    H       0.34 !
ATOM 4CG     CPH1    0.43 !
ATOM 4CB     CT2    -0.24 !
ATOM 4HB1    HA2     0.09 !
ATOM 4HB2    HA2     0.09 !
GROUP                !
ATOM 4NE2    NR2     0.10 !
ATOM 4CD2    CPH1   -0.48 !
ATOM 4HD2    HR3     0.23 !
ATOM 4CE1    CPH2   -0.02 !
ATOM 4HE1    HR1     0.19 !
GROUP                !
ATOM 5ND1    NR1    -0.40 !
ATOM 5HD1    H       0.34 !
ATOM 5CG     CPH1    0.43 !
ATOM 5CB     CT2    -0.24 !
ATOM 5HB1    HA2     0.09 !
ATOM 5HB2    HA2     0.09 !
GROUP                !
```

```
ATOM 5NE2    NR2     0.10 !
ATOM 5CD2    CPH1   -0.48 !
ATOM 5HD2    HR3     0.23 !
ATOM 5CE1    CPH2   -0.02 !
ATOM 5HE1    HR1     0.19 !
GROUP                !
ATOM 6CT     CC     0.80 !
ATOM 6OC1    OC    -0.57 !
ATOM 6OC2    OC    -0.57 !
ATOM 6OC3    OH1   -0.54 !
ATOM 6HO3    H      0.40 !
BOND 2NE2    1FE2P    3NE2    1FE2P    4NE2    1FE2P    5NE2    1FE2P
BOND 6OC1    1FE2P    6OC2    1FE2P
ANGL 1FE2P   2NE2    2CD2    1FE2P   2NE2    2CE1    1FE2P   3NE2    3CD2    1FE2P   3NE2    3CE1
ANGL 1FE2P   4NE2    4CD2    1FE2P   4NE2    4CE1    1FE2P   5NE2    5CD2    1FE2P   5NE2    5CE1
ANGL 1FE2P   6OC1    6CT     1FE2P   6OC2    6CT
ANGL 6OC1    1FE2P   6OC2
DIHE 1FE2P   6OC1  6CT   6OC2   1FE2P   6OC1  6CT   6OC3   1FE2P   6OC2  6CT   6OC1   1FE2P   6OC2  6CT
6OC3
DIHE 6CT   6OC1  1FE2P   6OC2   6CT   6OC2  1FE2P   6OC1

!ferric FeHis
PRES FEBI3          2.00 ! Connect non-heme iron (3+) to four histidines and bicarbonate
                    ! Order: 1-FE3P, 2-HSD, 3-HSD, 4-HSD, 5-HSD, 6-HCO3
GROUP                ! do NOT use AUTOgenerate ANGLes DIHEdrals after this patch
ATOM 1FE3P   FE3NH1  0.04 !
GROUP                !
ATOM 2ND1    NR1    -0.36 !
ATOM 2HD1    H       0.38 !                2HD1    2HE1     3HE1    3HD1
ATOM 2CG     CPH1    0.31 !                  |     |        |      |
ATOM 2CB     CT2    -0.09 !            2HB1   2ND1--2CE1      3CE1--3ND1    3HB1
ATOM 2HB1    HA2     0.09 !              |   /     ||        ||      \    |
ATOM 2HB2    HA2     0.09 !        -----2CB--2CG     ||        ||      3CG-3CB-----
GROUP                !             |   \\    ||        ||      //   |
ATOM 2NE2    NR2     0.14 !            2HB2   2CD2--2NE2      3NE2--3CD2    3HB2
ATOM 2CD2    CPH1   -0.45 !                 |      \     /      |
ATOM 2HD2    HR3     0.23 !                2HD2      \   /      3HD2
ATOM 2CE1    CPH2   -0.02 !                          \ /
ATOM 2HE1    HR1     0.22 !                          1FE(3+)
GROUP                !                          /||\
ATOM 3ND1    NR1    -0.36 !                          / || \
ATOM 3HD1    H       0.38 !                        /  ||  \
ATOM 3CG     CPH1    0.31 !                         / /  \ \
ATOM 3CB     CT2    -0.09 !                        /  /(-) \  \
ATOM 3HB1    HA2     0.09 !                        / 6OC1  6OC2 \
ATOM 3HB2    HA2     0.09 !             5HD2      /   \  //   \      4HD2
GROUP                !              |      /     \ //     \      |
ATOM 3NE2    NR2     0.14 !        5HB1   5CD2--5NE2      6CT      4NE2--4CD2    4HB1
```

```
ATOM 3CD2    CPH1   -0.45 !          |   //     ||        |        ||      \\   |
ATOM 3HD2    HR3     0.23 !     -----5CB--5CG      ||      6OC3        ||      4CG--4CB-----
ATOM 3CE1    CPH2   -0.02 !          |   \      ||        |        ||      /    |
ATOM 3HE1    HR1     0.22 !         5HB2   5ND1--5CE1     6HO3       4CE1--4ND1    4HB2
GROUP                 !                |      \             /       |
ATOM 4ND1    NR1    -0.36 !             5HD1     5HE1          4HE1     4HD1
ATOM 4HD1    H       0.38 !
ATOM 4CG     CPH1    0.31 !
ATOM 4CB     CT2    -0.09 !
ATOM 4HB1    HA2     0.09 !
ATOM 4HB2    HA2     0.09 !
GROUP                 !
ATOM 4NE2    NR2     0.14 !
ATOM 4CD2    CPH1   -0.45 !
ATOM 4HD2    HR3     0.23 !
ATOM 4CE1    CPH2   -0.02 !
ATOM 4HE1    HR1     0.22 !
GROUP                 !
ATOM 5ND1    NR1    -0.36 !
ATOM 5HD1    H       0.38 !
ATOM 5CG     CPH1    0.31 !
ATOM 5CB     CT2    -0.09 !
ATOM 5HB1    HA2     0.09 !
ATOM 5HB2    HA2     0.09 !
GROUP                 !
ATOM 5NE2    NR2     0.14 !
ATOM 5CD2    CPH1   -0.45 !
ATOM 5HD2    HR3     0.23 !
ATOM 5CE1    CPH2   -0.02 !
ATOM 5HE1    HR1     0.22 !
GROUP                 !
ATOM 6CT     CC      0.72 !
ATOM 6OC1    OC     -0.47 !
ATOM 6OC2    OC     -0.47 !
ATOM 6OC3    OH1    -0.44 !
ATOM 6HO3    H       0.46 !
BOND 2NE2    1FE3P    3NE2    1FE3P    4NE2    1FE3P    5NE2    1FE3P
BOND 6OC1    1FE3P    6OC2    1FE3P
ANGL 1FE3P   2NE2    2CD2    1FE3P   2NE2    2CE1    1FE3P   3NE2    3CD2    1FE3P   3NE2    3CE1
ANGL 1FE3P   4NE2    4CD2    1FE3P   4NE2    4CE1    1FE3P   5NE2    5CD2    1FE3P   5NE2    5CE1
ANGL 1FE3P   6OC1    6CT     1FE3P   6OC2    6CT
ANGL 6OC1    1FE3P   6OC2
DIHE 1FE3P   6OC1  6CT   6OC2   1FE3P   6OC1  6CT   6OC3   1FE3P   6OC2  6CT   6OC1   1FE3P   6OC2  6CT
6OC3
DIHE 6CT   6OC1  1FE3P   6OC2   6CT   6OC2  1FE3P   6OC1

!ferrous FeHis without bicarbonate
PRES FE4H2          2.00 ! Connect non-heme iron (2+) to four histidines
```

```
                    ! Order: 1-FE2P, 2-HSD, 3-HSD, 4-HSD, 5-HSD
GROUP                   ! do NOT use AUTOgenerate ANGLes DIHEdrals after this patch
ATOM 1FE2P   FE2NH2  0.08 !
GROUP                   !
ATOM 2ND1    NR1    -0.12 !
ATOM 2HD1    H      0.31 !            2HD1     2HE1   3HE1    3HD1
ATOM 2CG     CPH1    0.33 !             |      /      \      |
ATOM 2CB     CT2    -0.11 !        2HB1   2ND1--2CE1       3CE1--3ND1    3HB1
ATOM 2HB1    HA2     0.09 !         |   /      ||        ||      \   |
ATOM 2HB2    HA2     0.09 !    -----2CB--2CG     ||        ||      3CG-3CB-----
GROUP                   !         |   \\     ||        ||      //   |
ATOM 2NE2    NR2    -0.07 !        2HB2   2CD2--2NE2       3NE2--3CD2    3HB2
ATOM 2CD2    CPH1   -0.38 !             |      \     /      |
ATOM 2HD2    HR3     0.24 !            2HD2      \   /      3HD2
ATOM 2CE1    CPH2   -0.13 !                       \ /
ATOM 2HE1    HR1     0.23 !                      1FE(2+)
GROUP                   !                      / \
ATOM 3ND1    NR1    -0.12 !            5HD2      /   \      4HD2
ATOM 3HD1    H      0.31 !             |      /     \      |
ATOM 3CG     CPH1    0.33 !        5HB1   5CD2--5NE2       4NE2--4CD2    4HB1
ATOM 3CB     CT2    -0.11 !         |   //     ||        ||      \\   |
ATOM 3HB1    HA2     0.09 !    -----5CB--5CG     ||        ||      4CG--4CB-----
ATOM 3HB2    HA2     0.09 !         |   \      ||        ||      /    |
GROUP                   !        5HB2   5ND1--5CE1       4CE1--4ND1    4HB2
ATOM 3NE2    NR2    -0.07 !             |      \      /      |
ATOM 3CD2    CPH1   -0.38 !            5HD1     5HE1   4HE1    4HD1
ATOM 3HD2    HR3     0.24 !
ATOM 3CE1    CPH2   -0.13 !
ATOM 3HE1    HR1     0.23 !
GROUP                   !
ATOM 4ND1    NR1    -0.12 !
ATOM 4HD1    H      0.31 !
ATOM 4CG     CPH1    0.33 !
ATOM 4CB     CT2    -0.11 !
ATOM 4HB1    HA2     0.09 !
ATOM 4HB2    HA2     0.09 !
GROUP                   !
ATOM 4NE2    NR2    -0.07 !
ATOM 4CD2    CPH1   -0.38 !
ATOM 4HD2    HR3     0.24 !
ATOM 4CE1    CPH2   -0.13 !
ATOM 4HE1    HR1     0.23 !
GROUP                   !
ATOM 5ND1    NR1    -0.12 !
ATOM 5HD1    H      0.31 !
ATOM 5CG     CPH1    0.33 !
ATOM 5CB     CT2    -0.11 !
ATOM 5HB1    HA2     0.09 !
```

```
ATOM 5HB2    HA2     0.09 !
GROUP                !
ATOM 5NE2    NR2    -0.07 !
ATOM 5CD2    CPH1   -0.38 !
ATOM 5HD2    HR3     0.24 !
ATOM 5CE1    CPH2   -0.13 !
ATOM 5HE1    HR1     0.23 !
BOND 2NE2    1FE2P    3NE2    1FE2P    4NE2    1FE2P    5NE2    1FE2P
ANGL 1FE2P   2NE2    2CD2    1FE2P   2NE2    2CE1    1FE2P   3NE2    3CD2    1FE2P   3NE2    3CE1
ANGL 1FE2P   4NE2    4CD2    1FE2P   4NE2    4CE1    1FE2P   5NE2    5CD2    1FE2P   5NE2    5CE1

!ferric FeHis without bicarbonate
PRES FE4H3          3.00 ! Connect non-heme iron (3+) to four histidines
                    ! Order: 1-FE2P, 2-HSD, 3-HSD, 4-HSD, 5-HSD
GROUP                ! do NOT use AUTOgenerate ANGLes DIHEdrals after this patch
ATOM 1FE3P   FE3NH2  0.12 !
GROUP                !
ATOM 2ND1    NR1    -0.26 !
ATOM 2HD1    H       0.41 !            2HD1     2HE1   3HE1    3HD1
ATOM 2CG     CPH1    0.35 !              |      /      \      |
ATOM 2CB     CT2    -0.09 !        2HB1   2ND1--2CE1       3CE1--3ND1    3HB1
ATOM 2HB1    HA2     0.09 !         |    /      ||         ||      \    |
ATOM 2HB2    HA2     0.09 !    -----2CB--2CG      ||         ||      3CG-3CB-----
GROUP                !         |    \\     ||         ||      //   |
ATOM 2NE2    NR2     0.03 !        2HB2   2CD2--2NE2       3NE2--3CD2    3HB2
ATOM 2CD2    CPH1   -0.40 !              |       \     /       |
ATOM 2HD2    HR3     0.32 !            2HD2      \   /      3HD2
ATOM 2CE1    CPH2   -0.09 !                       \ /
ATOM 2HE1    HR1     0.27 !                      1FE(3+)
GROUP                !                         / \
ATOM 3ND1    NR1    -0.26 !            5HD2      /   \      4HD2
ATOM 3HD1    H       0.41 !              |       /     \      |
ATOM 3CG     CPH1    0.35 !        5HB1   5CD2--5NE2       4NE2--4CD2    4HB1
ATOM 3CB     CT2    -0.09 !         |    //     ||         ||      \\    |
ATOM 3HB1    HA2     0.09 !    -----5CB--5CG      ||         ||      4CG--4CB-----
ATOM 3HB2    HA2     0.09 !         |    \      ||         ||      /     |
GROUP                !        5HB2   5ND1--5CE1       4CE1--4ND1    4HB2
ATOM 3NE2    NR2     0.03 !              |      \       /      |
ATOM 3CD2    CPH1   -0.40 !            5HD1     5HE1   4HE1    4HD1
ATOM 3HD2    HR3     0.32 !
ATOM 3CE1    CPH2   -0.09 !
ATOM 3HE1    HR1     0.27 !
GROUP                !
ATOM 4ND1    NR1    -0.26 !
ATOM 4HD1    H       0.41 !
ATOM 4CG     CPH1    0.35 !
ATOM 4CB     CT2    -0.09 !
ATOM 4HB1    HA2     0.09 !
```

```
ATOM 4HB2    HA2     0.09 !
GROUP                !
ATOM 4NE2    NR2     0.03 !
ATOM 4CD2    CPH1   -0.40 !
ATOM 4HD2    HR3     0.32 !
ATOM 4CE1    CPH2   -0.09 !
ATOM 4HE1    HR1     0.27 !
GROUP                !
ATOM 5ND1    NR1    -0.26 !
ATOM 5HD1    H       0.41 !
ATOM 5CG     CPH1    0.35 !
ATOM 5CB     CT2    -0.09 !
ATOM 5HB1    HA2     0.09 !
ATOM 5HB2    HA2     0.09 !
GROUP                !
ATOM 5NE2    NR2     0.03 !
ATOM 5CD2    CPH1   -0.40 !
ATOM 5HD2    HR3     0.32 !
ATOM 5CE1    CPH2   -0.09 !
ATOM 5HE1    HR1     0.27 !
BOND 2NE2    1FE3P    3NE2    1FE3P    4NE2    1FE3P    5NE2    1FE3P
ANGL 1FE3P   2NE2    2CD2    1FE3P   2NE2    2CE1    1FE3P   3NE2    3CD2    1FE3P   3NE2    3CE1
ANGL 1FE3P   4NE2    4CD2    1FE3P   4NE2    4CE1    1FE3P   5NE2    5CD2    1FE3P   5NE2    5CE1

!ferrous HemeHis, Set 1
PRES HEHI2          0.00 ! bis-HIS heme link
                    ! Order: 1-HEME, 2-HSD, 3-HSD
GROUP                ! do NOT use AUTOgenerate ANGLes DIHEdrals after this patch
ATOM 1FE     FE2H    0.24 !
ATOM 1NA     NPH    -0.18 !
ATOM 1NB     NPH    -0.18 !
ATOM 1NC     NPH    -0.18 !         1O2A  1O1A             1O2D  1O1D
ATOM 1ND     NPH    -0.18 !           \\ //                \\ //
ATOM 1C1A    CPA     0.12 !           1CGA                  1CGD
ATOM 1C2A    CPB    -0.06 !             |                    |
ATOM 1C3A    CPB    -0.06 !       HBA1--1CBA--HBA2    1HA   1HBD1-1CBD-1HBD2
ATOM 1C4A    CPA     0.12 !             |          |          |
ATOM 1C1B    CPA     0.12 !       HAA1--1CAA-HAA2  __1CHA__ 1HAD1-1CAD-1HAD2
ATOM 1C2B    CPB    -0.06 !             |      /      \      /
ATOM 1C3B    CPB    -0.06 !           1C2A---C1A        1C4D--1C3D
ATOM 1C4B    CPA     0.12 !             |     |         |     |
ATOM 1C1C    CPA     0.12 !  1HMA1\       |     |         |     |       /1HMD1
ATOM 1C2C    CPB    -0.06 !  1HMA2-1CMA--1C3A   1NA  (2NE2) 1ND   1C2D--1CMD-1HMD2
ATOM 1C3C    CPB    -0.06 !  1HMA3/       \   / \  2-HSD  / \   /       \1HMD3
ATOM 1C4C    CPA     0.12 !              C4A   \   |   /  1C1D
ATOM 1C1D    CPA     0.12 !             /      \  |  /      \
ATOM 1C2D    CPB    -0.06 !             /       \ | /       \
ATOM 1C3D    CPB    -0.06 !       1HB--1CHB         1FE(2+)     CHD--1HD
```

```
ATOM 1C4D    CPA     0.12 !             \        / | \        /
GROUP                !             \      /  |  \      /
ATOM 1CHA    CPM    -0.10 !             1C1B   /   |   \  1C4C       1HAC
ATOM 1HA     HA      0.10 !  1HMB1\        /   \ /  3-HSD  \ /   \      /
GROUP                !  1HMB2-1CMB--1C2B   1NB  (3NE2) 1NC   1C3C-1CAC   1HBC1
ATOM 1CHB    CPM    -0.10 !  1HMB3/       |     |          |     |    \\  /
ATOM 1HB     HA      0.10 !             |     |          |     |     1CBC
GROUP                !           1C3B--1C4B        1C1C--1C2C      \
ATOM 1CHC    CPM    -0.10 !             |      \__1CHC__/      |        1HBC2
ATOM 1HC     HA      0.10 !           1CAB         |         1CMC--1HMC3
GROUP                !           //  \       1HC        /  |
ATOM 1CHD    CPM    -0.10 !         1CBB  1HAB          1HMC1  1HMC2
ATOM 1HD     HA      0.10 !          /   \
GROUP                !       1HBB1  1HBB2
ATOM 2ND1    NR1    -0.40 !
ATOM 2HD1    H       0.42 !
ATOM 2CG     CPH1   -0.09 !             2HD1      2HE1
ATOM 2CB     CT2    -0.11 !              |       /
ATOM 2HB1    HA2     0.09 !        2HB1   2ND1--2CE1
ATOM 2HB2    HA2     0.09 !         |    /      ||
GROUP                !    -----2CB--2CG      ||
ATOM 2NE2    NR2    -0.70 !         |    \\     ||
ATOM 2CD2    CPH1    0.22 !        2HB2   2CD2--2NE2
ATOM 2HD2    HR3     0.10 !              |       \
ATOM 2CE1    CPH2    0.25 !             2HD2      \
ATOM 2HE1    HR1     0.13 !                  1-HEME(1FE)
GROUP                !                      \       3HD2
ATOM 3ND1    NR1    -0.40 !                      \       |
ATOM 3HD1    H       0.42 !                       3NE2--3CD2    3HB1
ATOM 3CG     CPH1   -0.09 !                        ||      \\    |
ATOM 3CB     CT2    -0.11 !                       ||      3CG--3CB-----
ATOM 3HB1    HA2     0.09 !                        ||      /     |
ATOM 3HB2    HA2     0.09 !                       3CE1--3ND1    3HB2
GROUP                !                      /       |
ATOM 3NE2    NR2    -0.70 !                       3HE1    3HD1
ATOM 3CD2    CPH1    0.22 !
ATOM 3HD2    HR3     0.10 !
ATOM 3CE1    CPH2    0.25 !
ATOM 3HE1    HR1     0.13 !
BOND 1FE   2NE2   1FE   3NE2
ANGL 1FE   2NE2  2CD2   1FE   2NE2  2CE1
ANGL 2NE2  1FE   1NA    2NE2  1FE   1NB    2NE2  1FE   1NC    2NE2  1FE   1ND
ANGL 1FE   3NE2  3CD2   1FE   3NE2  3CE1
ANGL 3NE2  1FE   1NA    3NE2  1FE   1NB    3NE2  1FE   1NC    3NE2  1FE   1ND
DELETE ANGLE 1NA 1FE 1NC  1NB 1FE 1ND
DIHE 2CD2  2NE2  1FE   1NA    3CD2  3NE2  1FE   1NA

!ferric HemeHis
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```
PRES HEHI3          1.00 ! bis-HIS hematin link
                    ! Order: 1-HEME, 2-HSD, 3-HSD
GROUP                   ! do NOT use AUTOgenerate ANGLes DIHEdrals after this patch
ATOM 1FE     FE3H    0.40 !
ATOM 1NA     NPH    -0.17 !
ATOM 1NB     NPH    -0.17 !
ATOM 1NC     NPH    -0.17 !         1O2A  1O1A             1O2D  1O1D
ATOM 1ND     NPH    -0.17 !           \\ //                \\ //
ATOM 1C1A    CPA     0.18 !           1CGA                  1CGD
ATOM 1C2A    CPB    -0.05 !             |                     |
ATOM 1C3A    CPB    -0.05 !       HBA1--1CBA--HBA2    1HA   1HBD1-1CBD-1HBD2
ATOM 1C4A    CPA     0.18 !             |          |          |
ATOM 1C1B    CPA     0.18 !       HAA1--1CAA-HAA2  __1CHA__ 1HAD1-1CAD-1HAD2
ATOM 1C2B    CPB    -0.05 !             |      /      \      /
ATOM 1C3B    CPB    -0.05 !           1C2A---C1A        1C4D--1C3D
ATOM 1C4B    CPA     0.18 !             |     |         |     |
ATOM 1C1C    CPA     0.18 !  1HMA1\       |     |         |     |       /1HMD1
ATOM 1C2C    CPB    -0.05 !  1HMA2-1CMA--1C3A   1NA  (2NE2) 1ND   1C2D--1CMD-1HMD2
ATOM 1C3C    CPB    -0.05 !  1HMA3/       \   / \  2-HSD  / \   /       \1HMD3
ATOM 1C4C    CPA     0.18 !               C4A   \   |   /  1C1D
ATOM 1C1D    CPA     0.18 !             /      \  |  /      \
ATOM 1C2D    CPB    -0.05 !             /       \ | /       \
ATOM 1C3D    CPB    -0.05 !       1HB--1CHB        1FE(3+)     CHD--1HD
ATOM 1C4D    CPA     0.18 !             \       / | \       /
GROUP                   !             \      /  |  \      /
ATOM 1CHA    CPM    -0.10 !             1C1B   /   |   \  1C4C       1HAC
ATOM 1HA     HA      0.10 !  1HMB1\       /   \ /  3-HSD  \ /   \      /
GROUP                   !  1HMB2-1CMB--1C2B   1NB  (3NE2) 1NC   1C3C-1CAC   1HBC1
ATOM 1CHB    CPM    -0.10 !  1HMB3/       |     |         |     |     \\ /
ATOM 1HB     HA      0.10 !             |     |         |     |     1CBC
GROUP                   !           1C3B--1C4B        1C1C--1C2C      \
ATOM 1CHC    CPM    -0.10 !             |      \__1CHC__/      |        1HBC2
ATOM 1HC     HA      0.10 !           1CAB         |         1CMC--1HMC3
GROUP                   !           // \       1HC        /  |
ATOM 1CHD    CPM    -0.10 !         1CBB  1HAB          1HMC1  1HMC2
ATOM 1HD     HA      0.10 !          /   \
GROUP                   !       1HBB1  1HBB2
ATOM 2ND1    NR1    -0.32 !
ATOM 2HD1    H       0.40 !
ATOM 2CG     CPH1   -0.05 !             2HD1      2HE1
ATOM 2CB     CT2    -0.09 !             |       /
ATOM 2HB1    HA2     0.09 !        2HB1   2ND1--2CE1
ATOM 2HB2    HA2     0.09 !         |    /      ||
GROUP                   !    -----2CB--2CG      ||
ATOM 2NE2    NR2    -0.70 !         |    \\     ||
ATOM 2CD2    CPH1    0.22 !        2HB2   2CD2--2NE2
ATOM 2HD2    HR3     0.10 !              |       \
ATOM 2CE1    CPH2    0.25 !             2HD2      \
```

```
ATOM 2HE1    HR1     0.13 !                    1-HEME(1FE)
GROUP                !                      \       3HD2
ATOM 3ND1    NR1    -0.32 !                     \       |
ATOM 3HD1    H       0.40 !                      3NE2--3CD2     3HB1
ATOM 3CG     CPH1   -0.05 !                        ||      \\    |
ATOM 3CB     CT2    -0.09 !                       ||      3CG--3CB-----
ATOM 3HB1    HA2     0.09 !                        ||      /     |
ATOM 3HB2    HA2     0.09 !                        3CE1--3ND1     3HB2
GROUP                !                       /      |
ATOM 3NE2    NR2    -0.70 !                      3HE1     3HD1
ATOM 3CD2    CPH1    0.22 !
ATOM 3HD2    HR3     0.10 !
ATOM 3CE1    CPH2    0.25 !
ATOM 3HE1    HR1     0.13 !
BOND 1FE   2NE2   1FE   3NE2
ANGL 1FE   2NE2  2CD2   1FE   2NE2  2CE1
ANGL 2NE2  1FE   1NA    2NE2  1FE   1NB    2NE2  1FE   1NC    2NE2  1FE   1ND
ANGL 1FE   3NE2  3CD2   1FE   3NE2  3CE1
ANGL 3NE2  1FE   1NA    3NE2  1FE   1NB    3NE2  1FE   1NC    3NE2  1FE   1ND
DELETE ANGLE 1NA 1FE 1NC  1NB 1FE 1ND
DIHE 2CD2  2NE2  1FE   1NA    3CD2  3NE2  1FE   1NA

!ferrous HemeHis, Set 2
PRES HEHI0          0.00 ! bis-HIS heme link using CHARMM HEME and HSD charges
                    ! Order: 1-HEME, 2-HSD, 3-HSD
                    ! do NOT use AUTOgenerate ANGLes DIHEdrals after this patch
ATOM 1FE     FE2H0   0.24 !
BOND 1FE   2NE2   1FE   3NE2
ANGL 1FE   2NE2  2CD2   1FE   2NE2  2CE1
ANGL 2NE2  1FE   1NA    2NE2  1FE   1NB    2NE2  1FE   1NC    2NE2  1FE   1ND
ANGL 1FE   3NE2  3CD2   1FE   3NE2  3CE1
ANGL 3NE2  1FE   1NA    3NE2  1FE   1NB    3NE2  1FE   1NC    3NE2  1FE   1ND
DELETE ANGLE 1NA 1FE 1NC  1NB 1FE 1ND
DIHE 2CD2  2NE2  1FE   1NA    3CD2  3NE2  1FE   1NA

END

read para card flex append
* Parameters for bis-HIS heme and non-heme iron complexes
*

ATOMS
MASS   -1 FE2H0  55.84700 ! heme iron
MASS   -1 FE2H   55.84700 ! heme iron
MASS   -1 FE3H   55.84700 ! hematin iron
MASS   -1 FE2NH1 55.84700 ! ferrous non-heme iron in his-bicarbonate system
MASS   -1 FE3NH1 55.84700 ! ferric  non-heme iron in his-bicarbonate system
MASS   -1 FE2NH2 55.84700 ! ferrous non-heme iron in his-only system
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```
MASS   -1 FE3NH2 55.84700 ! ferric  non-heme iron in his-only system

BONDS
!bis-HIS heme/hematin
NPH    FE2H0  270.200     2.040 ! optimised, from all36_prot_heme: NPH  FE
NR2    FE2H0   80.000     2.110 ! optimised, from all36_prot_heme: NR2  FE
NPH    FE2H   270.200     2.040 ! optimised, from all36_prot_heme: NPH  FE
NR2    FE2H    80.000     2.110 ! optimised, from all36_prot_heme: NR2  FE
NPH    FE3H   270.000     2.030 ! optimised, from all36_prot_heme: NPH  FE
NR2    FE3H    80.000     2.080 ! optimised, from all36_prot_heme: NR2  FE
!non-heme iron with bicarbonate and histidines
NR2    FE2NH1 140.000     1.960 ! optimised, from all36_prot_heme: NR2  FE
OC     FE2NH1 100.000     1.995 ! optimised, from all36_prot_heme: OM   FE
NR2    FE3NH1 140.000     1.960 ! optimised, from all36_prot_heme: NR2  FE
OC     FE3NH1 100.000     1.890 ! optimised, from all36_prot_heme: OM   FE
OH1    CC     230.000     1.380 ! optimised, from all36_prot:      OH1  CD
!non-heme iron with only histidines
NR2    FE2NH2 140.000     1.940 ! optimised, from all36_prot_heme: NR2  FE
NR2    FE3NH2 140.000     1.870 ! optimised, from all36_prot_heme: NR2  FE

ANGLES
!bis-HIS heme/hematin
FE2H0  NR2    CPH1   25.000   135.00 ! optimised, from all36_prot_heme: FE   NR2  CPH1
FE2H0  NR2    CPH2   20.000   138.00 ! optimised, from all36_prot_heme: FE   NR2  CPH2
NPH    FE2H0  NPH    14.390    90.00 ! taken from all36_prot_heme: NPH  FE   NPH
FE2H0  NPH    CPA    96.150   128.05 ! taken from all36_prot_heme: FE   NPH  CPA
NR2    FE2H0  NPH    65.000    90.00 ! taken from all36_prot_heme: NR2  FE   NPH
FE2H   NR2    CPH1   25.000   135.00 ! optimised, from all36_prot_heme: FE   NR2  CPH1
FE2H   NR2    CPH2   25.000   137.00 ! optimised, from all36_prot_heme: FE   NR2  CPH2
NPH    FE2H   NPH    14.390    90.00 ! taken from all36_prot_heme: NPH  FE   NPH
FE2H   NPH    CPA    96.150   128.05 ! taken from all36_prot_heme: FE   NPH  CPA
NR2    FE2H   NPH    65.000    90.00 ! taken from all36_prot_heme: NR2  FE   NPH
FE3H   NR2    CPH1   25.000   135.00 ! optimised, from all36_prot_heme: FE   NR2  CPH1
FE3H   NR2    CPH2   25.000   137.00 ! optimised, from all36_prot_heme: FE   NR2  CPH2
NPH    FE3H   NPH    14.390    90.00 ! taken from all36_prot_heme: NPH  FE   NPH
FE3H   NPH    CPA    96.150   128.05 ! taken from all36_prot_heme: FE   NPH  CPA
NR2    FE3H   NPH    65.000    90.00 ! taken from all36_prot_heme: NR2  FE   NPH
!non-heme iron with bicarbonate and histidines
FE2NH1 NR2    CPH1   25.000   123.70 ! optimised, from all36_prot_heme: FE     NR2    CPH1
FE2NH1 NR2    CPH2   25.000   127.60 ! optimised, from all36_prot_heme: FE     NR2    CPH2
OC     FE2NH1 OC      0.000   101.50 ! optimised, from all36_prot:      OC     CC     OC
FE2NH1 OC     CC     40.000    85.00 ! optimised, from all36_cgenff:    CG2O6  OG302  CG321
FE3NH1 NR2    CPH1   25.000   122.70 ! optimised, from all36_prot_heme: FE     NR2    CPH1
FE3NH1 NR2    CPH2   25.000   125.00 ! optimised, from all36_prot_heme: FE     NR2    CPH2
OC     FE3NH1 OC      0.000   101.50 ! optimised, from all36_prot:      OC     CC     OC
FE3NH1 OC     CC     40.000    98.00 ! optimised, from all36_cgenff:    CG2O6  OG302  CG321
H      OH1    CC     55.000   113.30 ! optimised, from all36_prot:      H      OH1    CD
OH1    CC     OC     50.000   123.00  210.00   2.26200 ! taken from all36_prot:  OH1    CD     OB
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!non-heme iron with only histidines
FE2NH2 NR2    CPH1   25.000   124.00 ! optimised, from all36_prot_heme: FE     NR2    CPH1
FE2NH2 NR2    CPH2   25.000   125.80 ! optimised, from all36_prot_heme: FE     NR2    CPH2
FE3NH2 NR2    CPH1   25.000   127.00 ! optimised, from all36_prot_heme: FE     NR2    CPH1
FE3NH2 NR2    CPH2   25.000   124.00 ! optimised, from all36_prot_heme: FE     NR2    CPH2

DIHEDRALS
!bis-HIS heme/hematin
NPH    FE2H0  NR2    CPH1     0.1900  4    0.00 ! optimised, from all36_prot_heme: X    FE   NR2  X
NPH    FE2H   NR2    CPH1     0.0700  2  180.00 ! optimised, from all36_prot_heme: X    FE   NR2  X
NPH    FE2H   NR2    CPH1     0.0400  3  180.00 ! optimised, from all36_prot_heme: X    FE   NR2  X
NPH    FE2H   NR2    CPH1     0.1400  4    0.00 ! optimised, from all36_prot_heme: X    FE   NR2  X
NPH    FE3H   NR2    CPH1     0.1000  2  180.00 ! optimised, from all36_prot_heme: X    FE   NR2  X
NPH    FE3H   NR2    CPH1     0.0700  3  180.00 ! optimised, from all36_prot_heme: X    FE   NR2  X
NPH    FE3H   NR2    CPH1     0.5500  4    0.00 ! optimised, from all36_prot_heme: X    FE   NR2  X
X     FE2H0  NPH    X       0.0000  2    0.00 ! taken from all36_prot_heme: X    FE   NPH  X
X     FE2H   NPH    X       0.0000  2    0.00 ! taken from all36_prot_heme: X    FE   NPH  X
X     FE3H   NPH    X       0.0000  2    0.00 ! taken from all36_prot_heme: X    FE   NPH  X
!non-heme iron with bicarbonate and histidines
OC     CC     OH1    H       2.2000  2  180.00 ! optimised, from all36_prot:      H    OH1  CA   CA
FE2NH1 OC     CC     OH1     3.0000  2  180.00 ! optimised, from all36_prot:      X    CD   OH1  X
FE2NH1 OC     CC     OC      0.5000  2  180.00 ! optimised, from all36_prot_heme: X    FE   NPH  X
FE3NH1 OC     CC     OH1     3.0000  2  180.00 ! optimised, from all36_prot:      X    CD   OH1  X
FE3NH1 OC     CC     OC      0.0000  2  180.00 ! optimised, from all36_prot_heme: X    FE   NPH  X
CC     OC     FE2NH1 OC      0.0000  2    0.00 ! taken from all36_prot_heme: X    FE   NPH  X
CC     OC     FE3NH1 OC      0.0000  2    0.00 ! taken from all36_prot_heme: X    FE   NPH  X

IMPROPER
!bis-HIS heme/hematin
NPH    CPA    CPA    FE2H0  137.4000  0    0.00 ! taken from all36_prot_heme: NPH  CPA  CPA  FE
NPH    CPA    CPA    FE2H   137.4000  0    0.00 ! taken from all36_prot_heme: NPH  CPA  CPA  FE
NPH    CPA    CPA    FE3H   137.4000  0    0.00 ! taken from all36_prot_heme: NPH  CPA  CPA  FE
CC     OC     OC     OH1    100.0000  0    0.00 !


NONBONDED nbxmod  5 atom cdiel fshift vatom vdistance vfswitch -
cutnb 14.0 ctofnb 12.0 ctonnb 10.0 eps 1.0 e14fac 1.0 wmin 1.5
FE2H0   0.01  0.00  0.65 ! taken from all36_prot_heme: FE
FE2H    0.01  0.00  0.65 ! taken from all36_prot_heme: FE
FE3H    0.01  0.00  0.65 ! taken from all36_prot_heme: FE
FE2NH1  0.01  0.00  0.65 ! taken from all36_prot_heme: FE
FE3NH1  0.01  0.00  0.65 ! taken from all36_prot_heme: FE
FE2NH2  0.01  0.00  0.65 ! taken from all36_prot_heme: FE
FE3NH2  0.01  0.00  0.65 ! taken from all36_prot_heme: FE

END

RETUrn
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S9. Partial charges for S_1 and S_2 states

Table S2. Partial charges for the OEC and all its ligands. The ligand atoms bonded directly to metals are shown in green and their connecting metal is given in the right column.

Residue	Atom Name	S_1	S_2	Bonded Metal
D170	N	-0.412722	-0.353957	
	H	0.287283	0.277665	
	CA	-0.037046	-0.080858	
	HA	0.098351	0.100847	
	CB	-0.153619	-0.122125	
	HB2	0.070464	0.079061	
	HB3	0.070464	0.079061	
	CG	0.710785	0.638044	
	OD1	-0.729252	-0.679346	Ca
	OD2	-0.622624	-0.540711	Mn4
	C	0.634896	0.668528	
	O	-0.571203	-0.571515	
E189	N	-0.421232	-0.380459	
	H	0.258161	0.241925	
	CA	-0.160303	-0.202430	
	HA	0.126136	0.131927	
	CB	-0.050677	-0.016391	
	HB2	0.036657	0.025893	
	HB3	0.036657	0.025893	
	CG	-0.012791	-0.004925	
	HG2	0.048654	0.049166	
	HG3	0.048654	0.049166	
	CD	0.735867	0.735911	
	OE1	-0.686968	-0.670056	Ca
	OE2	-0.766089	-0.762824	Mn1
	C	0.740758	0.770375	
	O	-0.628308	-0.630089	
H332	N	-0.437188	-0.383396	
	H	0.307659	0.292661	
	CA	0.032564	0.012182	
	HA	0.080944	0.092749	
	CB	-0.157182	-0.159734	
	HB2	0.091730	0.099545	
	HB3	0.091730	0.099545	
	CG	0.004364	0.012728	
	ND1	-0.083474	-0.067646	
	HD1	0.270322	0.283781	

	CE1	-0.033089	-0.055960	
	HE1	0.182721	0.192610	
	NE2	-0.098682	-0.061086	Mn1
	CD2	-0.143965	-0.162103	
	HD2	0.167712	0.158607	
	C	0.313613	0.299999	
	O	-0.414947	-0.408191	
E333	N	-0.330458	-0.338321	
	H	0.272439	0.276193	
	CA	-0.019977	-0.035829	
	HA	0.042048	0.056299	
	CB	0.087030	0.070535	
	HB2	0.016571	0.016967	
	HB3	0.016571	0.016967	
	CG	0.006747	-0.024022	
	HG2	0.004191	0.030919	
	HG3	0.004191	0.030919	
	CD	0.693254	0.763389	
	OE1	-0.649638	-0.611164	Mn3
	OE2	-0.714770	-0.645159	Mn4
	C	0.623419	0.677359	
	O	-0.561559	-0.567986	
D342	N	-0.495232	-0.449089	
	H	0.299107	0.292504	
	CA	0.016452	-0.004732	
	HA	0.101167	0.100816	
	CB	-0.053892	-0.047024	
	HB2	0.058547	0.061306	
	HB3	0.058547	0.061306	
	CG	0.651884	0.640522	
	OD1	-0.520575	-0.524538	Mn2
	OD2	-0.680678	-0.658547	Mn1
	C	0.448128	0.529629	
	O	-0.565479	-0.564081	
A344	N	-0.106031	-0.040830	
	H	0.042673	0.032321	
	CA	-0.082924	-0.098928	
	HA	0.135341	0.143041	
	CB	-0.056605	-0.059893	
	HB1	0.039255	0.046474	
	HB2	0.039255	0.046474	
	HB3	0.039255	0.046474	

	C	0.555560	0.502720	
	O	-0.547306	-0.491117	Ca
	OXT	-0.402547	-0.401111	Mn2
E354	N	-0.477690	-0.415963	
	H	0.307245	0.292691	
	CA	-0.122279	-0.163075	
	HA	0.136732	0.140240	
	CB	0.006709	0.038969	
	HB2	0.009947	0.007447	
	HB3	0.009947	0.007447	
	CG	0.003582	-0.025190	
	HG2	0.021200	0.035502	
	HG3	0.021200	0.035502	
	CD	0.722695	0.664836	
	OE1	-0.605705	-0.568448	Mn2
	OE2	-0.659950	-0.577666	Mn3
	C	0.711064	0.752817	
	O	-0.611401	-0.593413	
OEC	Ca	1.518360	1.395880	
	Mn1	1.204720	1.193870	
	Mn2	1.194920	1.244060	
	Mn3	1.664330	1.520380	
	Mn4	1.518050	1.397600	
	O1	-0.705061	-0.675102	Ca, Mn1, & Mn2
	O2	-0.655159	-0.613125	Ca, Mn2, & Mn3
	O3	-0.759029	-0.752491	Mn1, Mn2, & Mn3
	O4	-0.763103	-0.639714	Mn3 & Mn4
	O5	-1.007389	-0.903511	Ca, Mn3, & Mn4
W1	O	-0.947418	-0.791523	Mn4
	H1	0.475156	0.420592	
	H2	0.447678	0.417292	
W2	O	-0.800687	-0.748772	Mn4
	H1	0.401290	0.413316	
	H2	0.454604	0.446788	
W3	O	-0.883468	-0.819177	Ca
	H1	0.465729	0.452215	
	H2	0.404244	0.394640	
W4	O	-0.780993	-0.766078	Ca
	H1	0.374077	0.377802	
	H2	0.416107	0.418535	

S10. Bond Parameters for S_1 and S_2 states

Table S3. Bond parameters connecting the OEC and its ligands. Bonds are based on optimized QM/MM structures and held rigidly with a universal force constant of 1000 kcal/(mol*Å^2).

Metal	Residue-Atom	S_1 (Å)	S_2 (Å)
Mn4	D170-OD2	2.1717	2.4105
Mn4	E333-OE2	2.1180	1.8488
Ca	OEC-O1	2.4456	2.4205
Ca	OEC-O2	2.6725	2.7167
Ca	OEC-O5	2.5174	2.5805
Ca	WAT4-O	2.4438	2.4631
Ca	WAT3-O	2.4811	2.4561
Mn1	OEC-O1	1.8467	1.8500
Mn1	OEC-O3	1.8795	1.8916
Mn2	OEC-O1	1.8403	1.8340
Mn2	OEC-O2	1.7661	1.7896
Mn2	OEC-O3	1.8697	1.8767
Mn3	OEC-O2	1.8418	1.7992
Mn3	OEC-O5	1.7987	1.8048
Mn3	OEC-O3	2.0290	1.9853
Mn3	OEC-O4	1.7903	1.8108
Mn4	WAT2-O	2.0283	2.0825
Mn4	WAT1-O	2.1008	1.9542
Mn4	OEC-O5	1.9067	1.9147
Mn4	OEC-O4	1.8351	1.7851
Ca	D170-OD1	2.4773	2.5980
Ca	E189-OE1	2.8023	2.6871
Ca	A344-O	2.5091	2.5999
Mn1	E189-OE2	1.9218	1.8756
Mn1	H332-NE2	2.0146	1.9524
Mn1	D342-OD2	2.1645	2.1517
Mn2	D342-OD1	2.0533	2.0264
Mn2	A344-OXT	1.9067	1.9712
Mn2	E354-OE1	1.9966	2.0097
Mn3	E333-OE1	1.9587	1.9006
Mn3	E354-OE2	2.0647	2.0518

S11. Angle Parameters for S_1 and S_2 states

Table S4. Angle parameters connecting the OEC and its ligands. Angles are based on optimized QM/MM structures and held rigidly with a universal force constant of 200 kcal/(Rad*Å^2).

Atom 1	Atom 2	Atom 3	S_1 (°)	S_2 (°)
D170-OD2	Mn4	E333-OE2	158.59	163.32
D170-OD2	Mn4	WAT2-O	88.59	81.21
D170-OD2	Mn4	WAT1-O	84.10	81.22
D170-OD2	Mn4	OEC-O5	104.54	94.42
D170-OD2	Mn4	OEC-O4	98.34	100.01
E333-OE2	Mn4	WAT2-O	82.53	87.98
E333-OE2	Mn4	WAT1-O	76.72	86.97
E333-OE2	Mn4	OEC-O5	95.31	97.63
E333-OE2	Mn4	OEC-O4	92.90	93.52
WAT2-O	Mn4	OEC-O5	92.47	86.80
WAT2-O	Mn4	OEC-O4	170.78	166.22
WAT1-O	Mn4	WAT2-O	91.43	94.12
WAT1-O	Mn4	OEC-O5	170.59	175.34
WAT1-O	Mn4	OEC-O4	95.32	99.64
A344-C	A344-O	Ca	133.25	131.57
A344-C	A344-OXT	Mn2	125.19	125.51
D170-CG	D170-OD2	Mn4	141.57	143.74
E333-CD	E333-OE2	Mn4	120.78	121.84
D170-CG	D170-OD1	Ca	110.91	109.44
E189-CD	E189-OE1	Ca	129.63	128.54
E189-CD	E189-OE2	Mn1	128.39	130.25
D342-CG	D342-OD2	Mn1	121.40	123.42
D342-CG	D342-OD1	Mn2	126.14	124.48
E354-CD	E354-OE1	Mn2	121.06	120.54
E333-CD	E333-OE1	Mn3	126.62	127.75
E354-CD	E354-OE2	Mn3	127.94	128.10
H332-CE1	H332-NE2	Mn1	121.73	121.09
Ca	OEC-O1	Mn1	111.80	110.23
Ca	OEC-O1	Mn2	104.84	106.17
Ca	OEC-O2	Mn2	98.60	96.57
Ca	OEC-O2	Mn3	99.36	100.07
Ca	OEC-O5	Mn3	106.45	105.00
Ca	OEC-O5	Mn4	109.57	118.93
Ca	WAT4-O	HW	119.15	120.19
Ca	WAT3-O	HW	123.16	122.36
Mn1	OEC-O1	Mn2	96.03	96.54
Mn1	H332-NE2	H332-CD2	127.50	127.61

Mn1	OEC-O3	Mn2	93.94	93.70
Mn1	OEC-O3	Mn3	113.48	115.97
Mn2	OEC-O2	Mn3	100.31	100.27
Mn2	OEC-O3	Mn3	90.48	90.96
Mn3	OEC-O5	Mn4	93.49	94.83
Mn3	OEC-O4	Mn4	96.25	99.26
Mn4	WAT2-O	WAT2-HW	114.62	114.09
Mn4	WAT1-O	WAT1-HW	120.00	120.24
D170-OD1	Ca	E189-OE1	148.64	148.27
D170-OD1	Ca	A344-O	79.01	75.22
D170-OD1	Ca	OEC-O1	142.20	139.58
D170-OD1	Ca	OEC-O2	83.93	82.03
D170-OD1	Ca	OEC-O5	99.29	96.02
D170-OD1	Ca	WAT4-O	97.11	93.54
D170-OD1	Ca	WAT3-O	79.96	78.09
E189-OE1	Ca	A344-O	112.56	113.47
E189-OE1	Ca	OEC-O1	68.22	70.30
E189-OE1	Ca	OEC-O2	127.29	129.70
E189-OE1	Ca	OEC-O5	94.86	100.24
E189-OE1	Ca	WAT4-O	64.30	65.92
E189-OE1	Ca	WAT3-O	71.64	74.07
A344-O	Ca	OEC-O1	74.77	75.44
A344-O	Ca	OEC-O2	68.60	68.70
A344-O	Ca	OEC-O5	129.52	128.62
A344-O	Ca	WAT4-O	67.21	65.52
A344-O	Ca	WAT3-O	135.69	132.14
OEC-O2	Ca	OEC-O1	61.40	61.64
OEC-O2	Mn2	OEC-O1	93.18	93.72
OEC-O5	Ca	OEC-O1	77.82	81.34
OEC-O5	Ca	OEC-O2	61.12	59.93
OEC-O5	Mn3	OEC-O2	93.06	94.60
OEC-O5	Mn3	OEC-O3	93.92	97.21
OEC-O5	Mn3	OEC-O4	84.11	81.75
OEC-O5	Mn4	OEC-O4	79.93	79.43
WAT4-O	Ca	OEC-O1	97.28	98.94
WAT4-O	Ca	OEC-O2	134.68	133.55
WAT4-O	Ca	OEC-O5	158.64	164.72
WAT3-O	Ca	OEC-O1	137.41	142.14
WAT3-O	Ca	OEC-O2	145.97	144.27
WAT3-O	Ca	OEC-O5	92.14	92.90
WAT3-O	Ca	WAT4-O	77.33	77.43
E189-OE2	Mn1	OEC-O1	95.96	94.98

E189-OE2	Mn1	H332-NE2	84.62	87.62
E189-OE2	Mn1	D342-OD2	91.80	93.50
E189-OE2	Mn1	OEC-O3	173.63	171.71
H332-NE2	Mn1	OEC-O1	179.26	177.30
H332-NE2	Mn1	D342-OD2	90.82	92.91
H332-NE2	Mn1	OEC-O3	96.39	94.88
D342-OD2	Mn1	OEC-O1	89.63	87.65
D342-OD2	Mn1	OEC-O3	94.47	94.27
OEC-O3	Mn1	OEC-O1	82.98	82.44
OEC-O3	Mn2	OEC-O1	83.43	83.28
OEC-O3	Mn2	OEC-O2	87.59	85.65
OEC-O3	Mn3	OEC-O2	80.98	82.24
D342-OD1	Mn2	OEC-O1	89.95	90.41
D342-OD1	Mn2	OEC-O2	175.86	174.52
D342-OD1	Mn2	OEC-O3	95.47	98.43
D342-OD1	Mn2	A344-OXT	83.18	82.30
D342-OD1	Mn2	E354-OE1	84.68	85.05
A344-OXT	Mn2	OEC-O1	96.02	96.13
A344-OXT	Mn2	OEC-O2	93.79	93.66
A344-OXT	Mn2	OEC-O3	178.55	179.05
A344-OXT	Mn2	E354-OE1	91.19	88.95
E354-OE1	Mn2	OEC-O1	170.45	172.69
E354-OE1	Mn2	OEC-O2	92.59	91.20
E354-OE1	Mn2	OEC-O3	89.22	91.71
E333-OE1	Mn3	OEC-O2	167.59	169.77
E333-OE1	Mn3	OEC-O5	96.07	94.16
E333-OE1	Mn3	OEC-O3	90.00	91.43
E333-OE1	Mn3	E354-OE2	84.15	85.98
E333-OE1	Mn3	OEC-O4	94.99	85.85
E354-OE2	Mn3	OEC-O2	86.25	85.53
E354-OE2	Mn3	OEC-O5	176.59	177.25
E354-OE2	Mn3	OEC-O3	82.68	85.53
E354-OE2	Mn3	OEC-O4	99.27	95.52
OEC-O4	Mn3	OEC-O2	94.30	100.63
OEC-O4	Mn3	OEC-O3	174.80	176.99

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