Long Distance proton transfer and multimeric interfaces in photosystem II

K.L.Buzar[1], A-N.Bondar

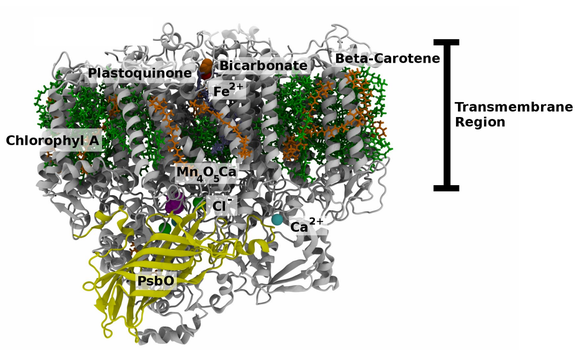
kbuzar@zedat.fu-berlin.de

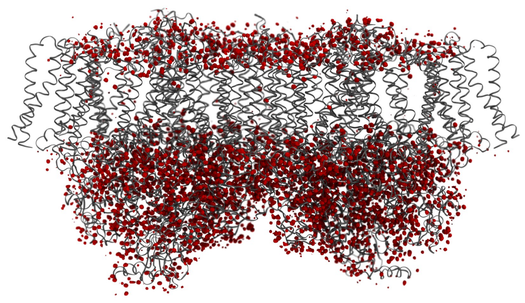
Abstract

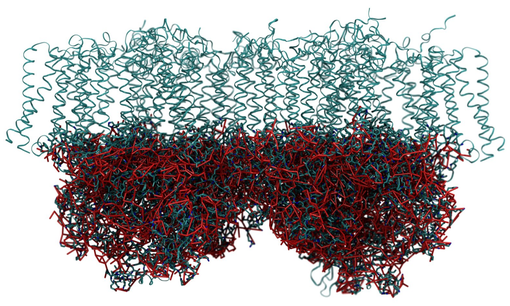
Photosystem II generates molecular oxygen, protons and electrons, by splitting two water molecules at its manganese reaction center. To characterize the mechanism by which protons are transferred from the vicinity of the manganese cluster to the bulk, we are setting up all-atom simulations of a photosystem II dimer in a hydrated lipid membrane environment. Additionally we analyze multiple crystallographic structures at once with water shared and averaged between all the structures. Implementation of the Bridge algorithm and machine learning methods to study the water positions and water mediated hydrogen bonds that would possibly transfer a proton from the manganese cluster to the luminal side of the thylakoid membrane.

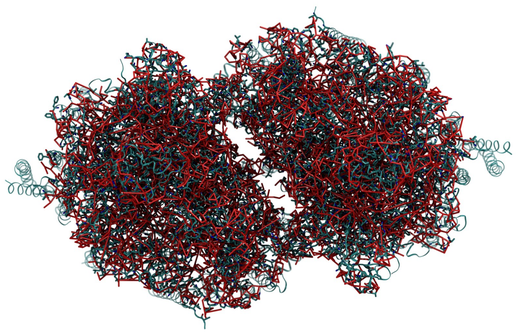
Models

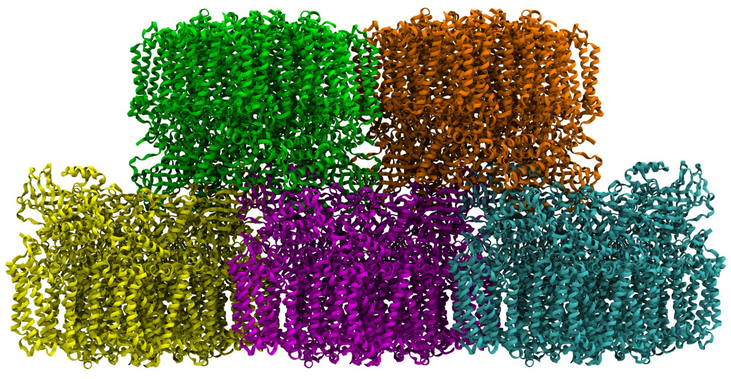
Photosystem II (PSII) structure. Water clustering on the top right, all proton conducting connections in the middle and multiple dimer stacking on the bottom panel.











Methodology

Selection of crystal structures for analyses of H-bond networks

We chose a set of PSII structures with resolution of 2.5Å or better from RCS PDB with the highest amount of crystallographic waters. The amount of waters found in the chosen structures was between 891 to 1901, with the exception of PDBID: 4PJ0 with 152 waters per monomer. The structure was resolved with a different detergent enabling proper stacking of PSII dimers along the lipid bilayer which was useful for this study. Resulting set of files was edited to uniform naming scheme for the manganese cluster for the Bridge algorithm to produce consistent results and visualisation for all crystallographic data

Criteria for H bonding

The analysis of the chosen structures was performed with Bridge algorithm using direct amino-acid to amino-acid hydrogen bonds and water mediated hydrogen-bonds. For initial analysis with bridge, we processed the structures as-is, without adding or optimizing of the hydrogen atoms. The analysis of crystal structures in Bridge requires the non-hydrogenated donor and acceptor being included by the program. With this setting the angle parameter for hydrogen bonding is not taken into account and the distance parameter kept at default 3.5Å.

Computing H-bond networks with Bridge

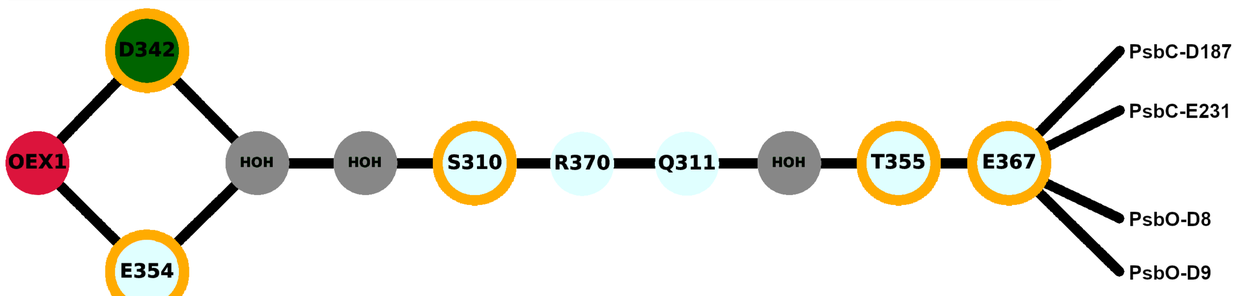
Application of the Bridge algorithm for sidechain-sidechain H-bonds can be performed with 2 restraining functions backbone-backbone interactions and atomistic node creation in different combinations. For water-mediated H-bonds there is a 3rd criterion that enabled us to include direct H-bonds that allow sidechain-sidechain H-bonds without any waters in between which in total results in 8 types of separate analyses.

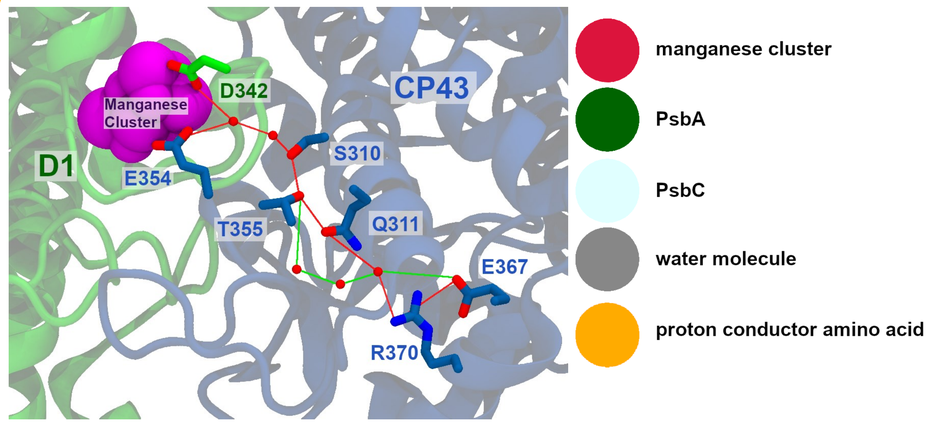
Creation of multiple dimer system

To analyse multiple PSII dimer interactions across two lipid bilayer membranes We created a system using replicated PDBID: 4PJ0 structures along its crystal lattice vectors creating 5 dimers interacting with each other. Initially two created layers along the membrane were facing each other with the grana sides, but after application of a translation vector, the two layers were found to match perfectly simulating the aggregation of PSII dimers in light-rich conditions in bacterial membranes.

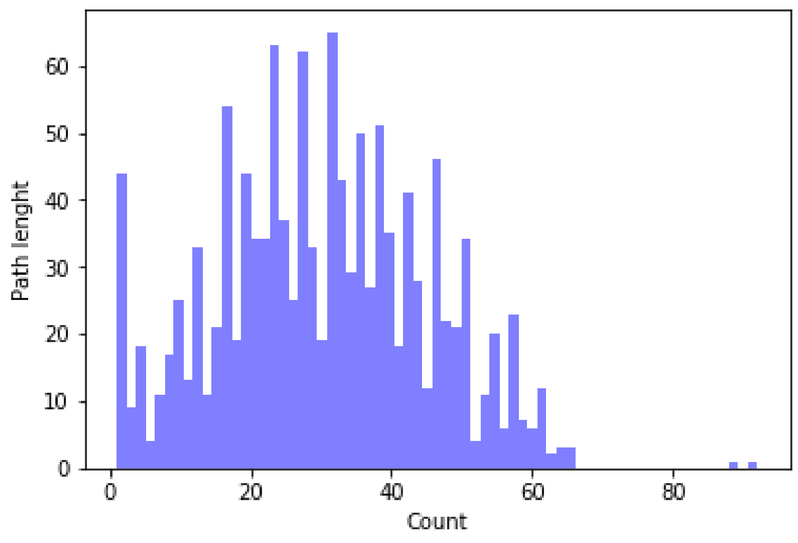
Results and Discussion

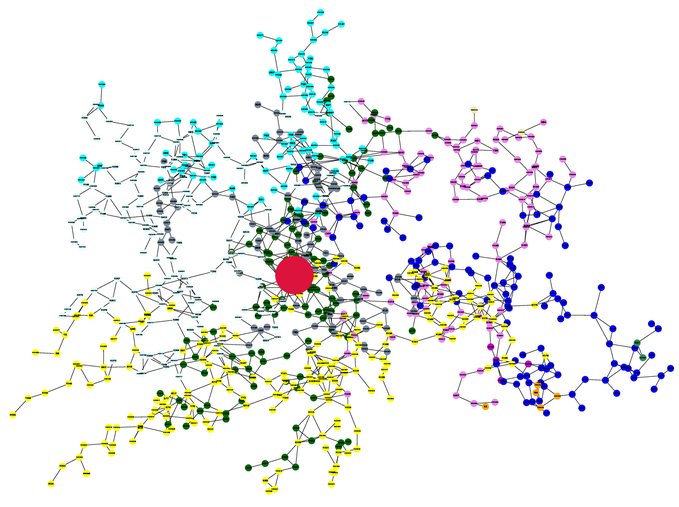
1. CP43-E367 junction connecting 4 equal proton release residues





2. Distribution of connection lengths in the PSII monomer hydrogen-bonding network that originates from the





Conclusions

- **We have studied multiple redundant proton release pathways in the vast network of the hydrogen bonding connections found with the Bridge algorithm**
- **Highly occupied water mediated hydrogen bonds starting from the manganese cluster have a high chance of conducting protons to the luminal side of the thylakoid membrane**
- **It is required to develop additional methods to obtain reliable average water positions shared between different PSII crystal structures**

References

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Acknowledgements

The study is founded from the IGK SFB 1078 Protonation Dynamics in Protein Function. The computing time provided by HLRN Supercomputing centre as a part of grant bec00172.