LMU LUDWIG-MAXIMILIANS-UNIVERSITÄT MÜNCHEN

Atomistic characterization of the tuning mechanisms for chlorophyll excitation energies in photosystem 1

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Abstract

Our research interest

- Photosystem 1 (PS1) is one of the most efficient light-harvesting systems found in nature.
- The local environment can affect the absorption energy of the individual chlorophylls (site energy).[1,2]
- Identifying these chlorophylls can help elucidate the energy transfer mechanisms occuring in PS1 at a microscopic level.

The challenge

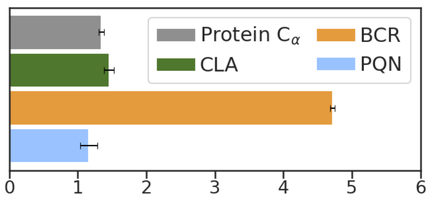
- Inhomogenous environment requires explicit modelling.
- Accurate site energies are difficult to obtain and there is lack of consensus among studies due to different approximations.

What we present

- Site energies in PS1 including dynamics.
- A method to elucidate environmental effects on site energies.

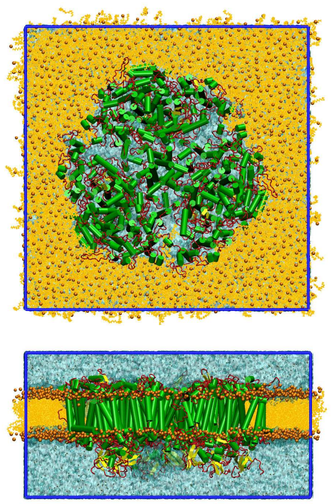
Modelling the Photosystem

- Trimeric complex embedded in POPC double-layer and water
- Model contains all cofactors, protein residues and crystal water
- Only approximation: incomplete phytyl chains replaced by CH_3
- Molecular Dynamics:
  - consistent use of Amber FF
  - 15ns NPT @ 300K, 1bar



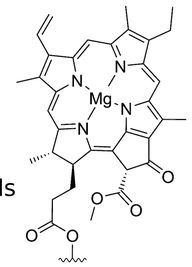
Crystal structure: 1JB0[3]

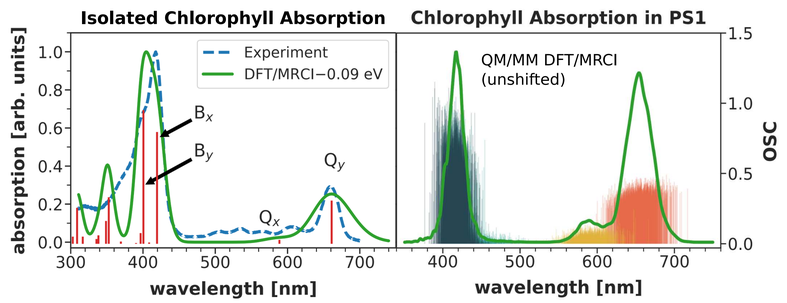
Click for 3D view



Absorption Spectra

- DFT/MRCI[4] gives highly accurate spectra for chlorophyll (BHLYP/def2-SVP, E_{sel}=0.8)
- QM/MM scheme (electrostatic embedding):
  - QM: chlorophyll without phytyl chain
  - MM: rest of of PS1 as point charges
- 20 MD snapshots for each of the 96 chlorophylls
  → 1920 single point calculations

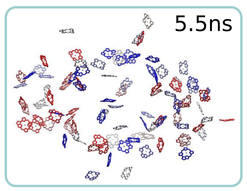


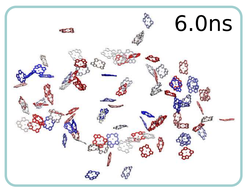


Site Energies in PSI

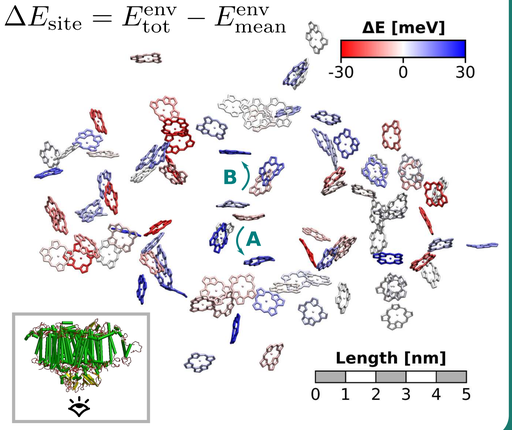
Where are the energy sinks?

- Average over 20 MD snapshots for each chlorophyll (Q_y)
- Strong fluctuations suggest multiple energy transfer channels
- Asymmetry in special pair is consistent with preferred electron transfer along A-branch (see also poster 171)





$$\Delta E_{site} = E^{env}_{tot} - E^{env}_{mean}$$



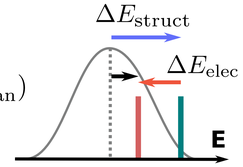
Electrostatics vs. Conformation

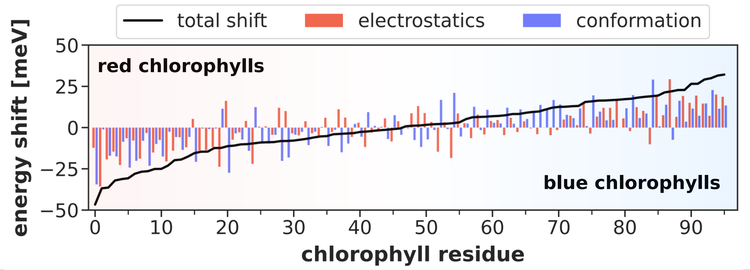
- electrostatics red-shift the whole spectrum by ~17 meV

$$\Delta E^{env}_{tot} = E^{env}_{mean} + \Delta E_{elec} + \Delta E_{conf}$$

$$\Delta E_{elec} = (E^{env}_{tot} - E^{env}_{mean}) - (E^{vac}_{tot} - E^{vac}_{mean})$$

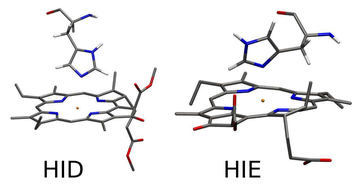
$$\Delta E_{conf} = E^{vac}_{tot} - E^{vac}_{mean}$$

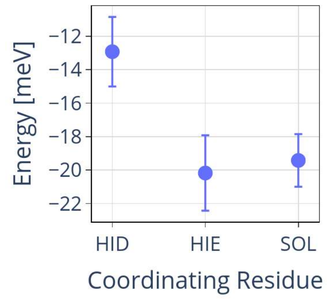




Coordination Effects

- Protonation of axial ligand can tune electrostatic shift (see also poster 194)





Outlook

- Determine structural motives that tune site energies
- Charge transfer and excitonic coupling (see also poster 171)
- Excited state dynamics of energy transfer pathways

References

[1] J. Adolphs et al., J. Am. Chem. Soc. **2010**, 132, 3331–3343.
[2] A. Sirohiwal et. al, J. Am. Chem. Soc. **2020**, 142, 18174–18190.
[3] P. Jordan et al., Nature **2001**, 411, 909–917.
[4] C. M. Marian et al., WIREs Comput. Mol. Sci. **2019**, 9, e1394.

IMPRS APS e-conversion Leibniz Supercomputing Centre of the Bavarian Academy of Sciences and Humanities