Solar Light Harvesting by Energy Transfer: Learning from Nature

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Introduction
- Solar light harvesting is key to solving tomorrow's energy problems
- Excitation energy transfer underlies most light harvesting applications

Project goal: Understand how nature optimizes excitation energy transfer rate

Light-harvesting antenna complex LHZ²: Too complicated!

Xanthorhodopsin in bacterium S. ruber:

UC Irvine is the world's leading university in xanthorhodopsin research
- Spectroscopically well-characterized²,⁴
- X-ray structure has been determined²
- Single antenna (salinixinanthin(SXN)) and single reaction center (retin(LYR))
- Amenable to electronic structure methods and x-ray diffraction

Methods
- Multi-pronged approach:
  1. State-of-the-art quantum mechanical computations of the chromophores using TURBOMOLE
  2. Molecular dynamics simulations of 20ns of movement of the entire protein
  3. Comparison to and validation of x-ray structures
  4. Absorption, fluorescence steady state, and femtosecond spectroscopy

Results

Salinixinanthin:
Relevant excitation: First $\pi \rightarrow \pi^*$ transition

- Validation on beta-carotene: Must blue shift computed salinixinanthin spectra 50nm.
- Oscillator strengths: 2-3 times larger than experiment (within experimental uncertainty).

Retinal:
Relevant excitation: First $\pi \rightarrow \pi^*$ transition

Vertical excitation wavelengths of salinixinanthin (shifted as indicated by beta-carotene computations) and retinal (nm)

<table>
<thead>
<tr>
<th></th>
<th>SXN</th>
<th>LYR</th>
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<tbody>
<tr>
<td>Best TDDFT</td>
<td>494</td>
<td>490</td>
</tr>
<tr>
<td>Best RI-CC2</td>
<td>565*</td>
<td>526</td>
</tr>
<tr>
<td>Exp.</td>
<td>565</td>
<td>521</td>
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*Gas phase

Effect of the environment on energy (shift in nm relative to gas phase):

<table>
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<tr>
<th></th>
<th>P</th>
<th>PC</th>
<th>PCL</th>
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<tbody>
<tr>
<td>SXN</td>
<td>+4</td>
<td>+4</td>
<td>+4</td>
</tr>
<tr>
<td>LYR</td>
<td>-62</td>
<td>-62</td>
<td>-89</td>
</tr>
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Interactions included: P=protein, C=other chromophore, L=lipid

Conclusions and Outlook
- Nature uses protein environment to fine-tune chromophore properties
- Importance of interactions: Steric(chromophore structure) > electrostatics with protein > other
- Protonation state: His¹H Asp
- After calibration of energy levels, our method will allow us to model the rate of excitation energy transfer
- Future work: Excited state deactivation vs. energy transfer

References
4 T. Polivka et al., Biophys. J. 96, 2268-77 (2009)