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Quantum coherent properties of natural and biomimetic light harvesting antennas

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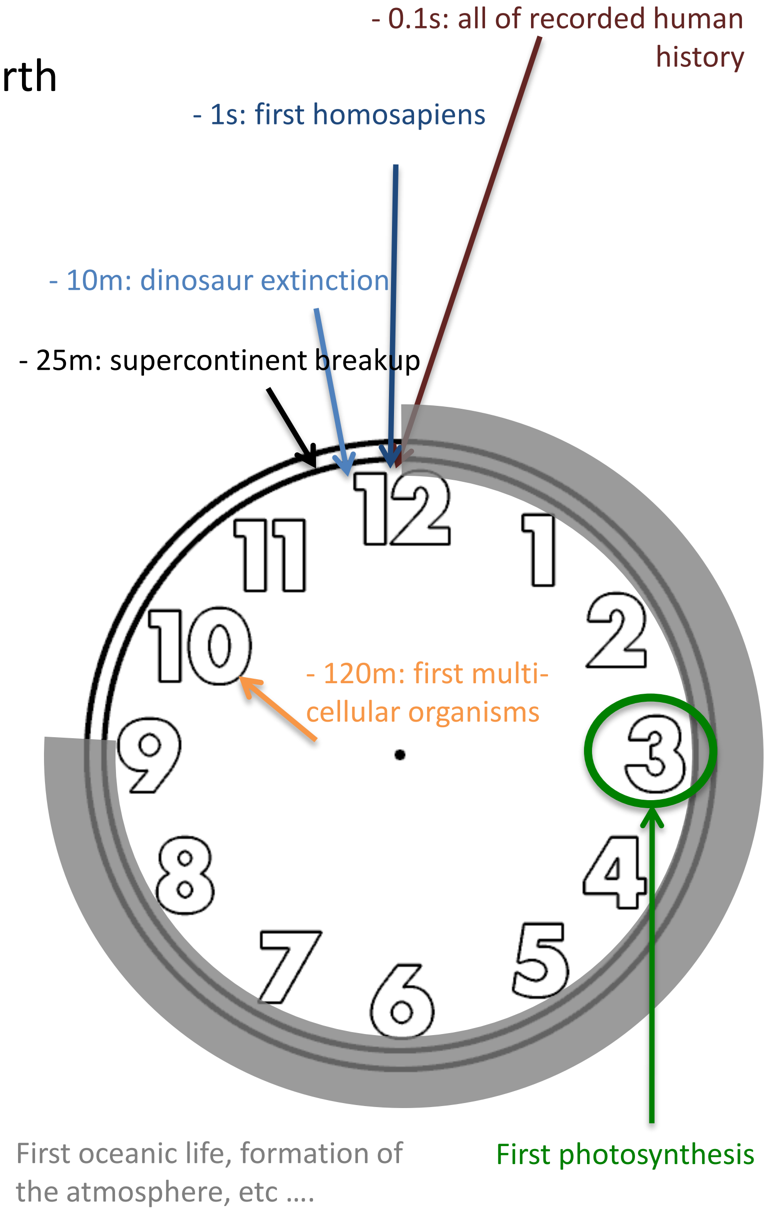
Santa Clara University, November 2011

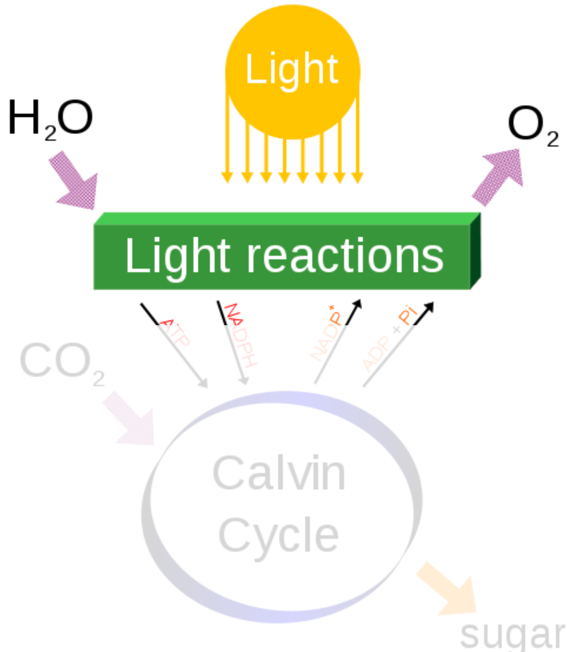
Photosynthesis

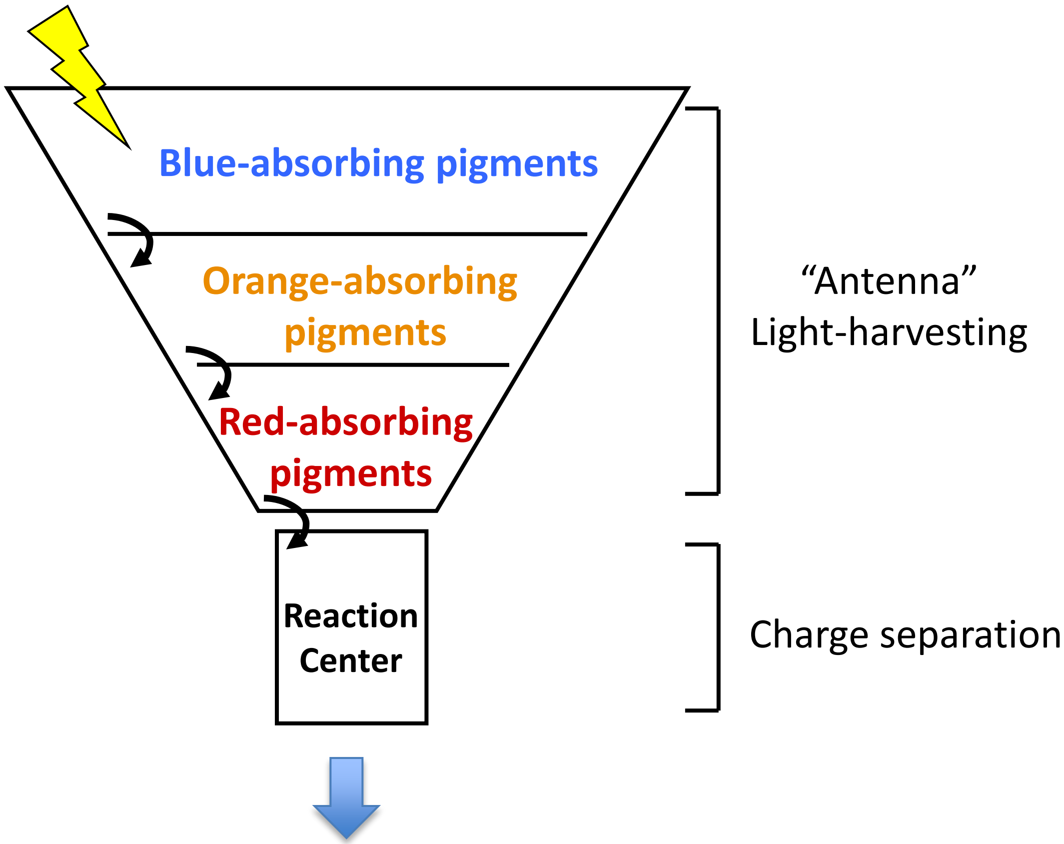
- Arguably the **most important** biological process on Earth
  - converts CO_2 to oxygen
  - ultimately responsible for all food, most fuel
  - performed by plants, algae, bacteria

- One of the **oldest** biological processes on Earth
  - at least 3.25 to 2.7 billion years old,
    (c.f. Earth 4.5 billion years old
    first multi-cellular organisms appear
    0.65 billion years ago)
  - has had a long time to evolve and has been under extreme evolutionary pressure



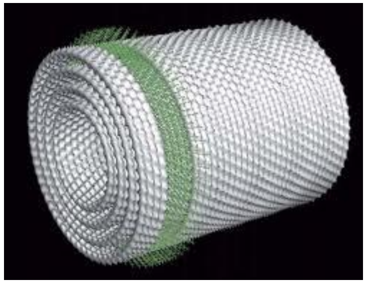
Structure of photosynthesis



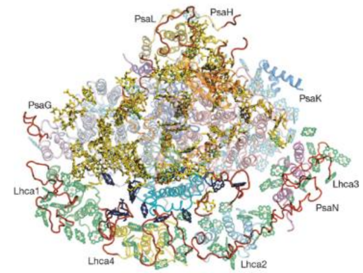


…Secondary electron transfer reactions, Water splitting, Proton transport across thylakoid membrane, Reduction of $NADP^+$, ATP synthesis…

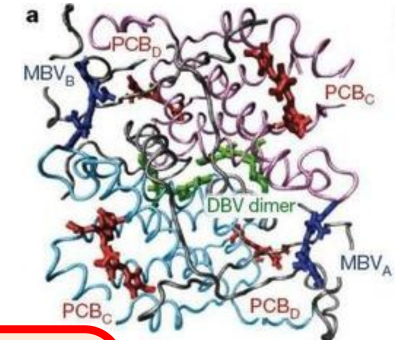
Light harvesting complexes



Hypothesized structure for chlorosome [Bryant]

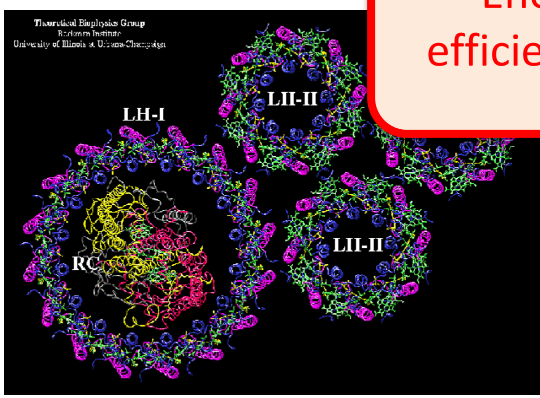


Photosystem I [Nelson *et*

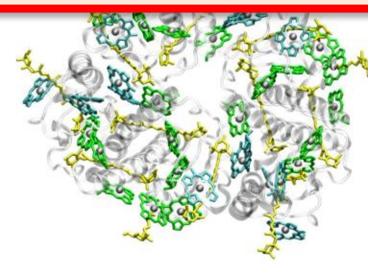


arine algae) [Scholes]

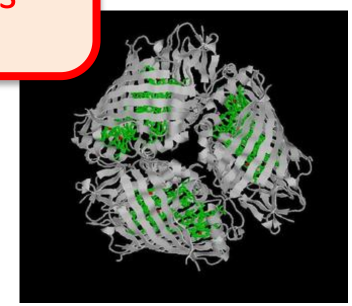
Energy transfer is >95% quantum efficient, and at picosecond timescales



LH-I and LH-II complex (purple bacteria) [Schulten]



LHC-II (photosystem II)



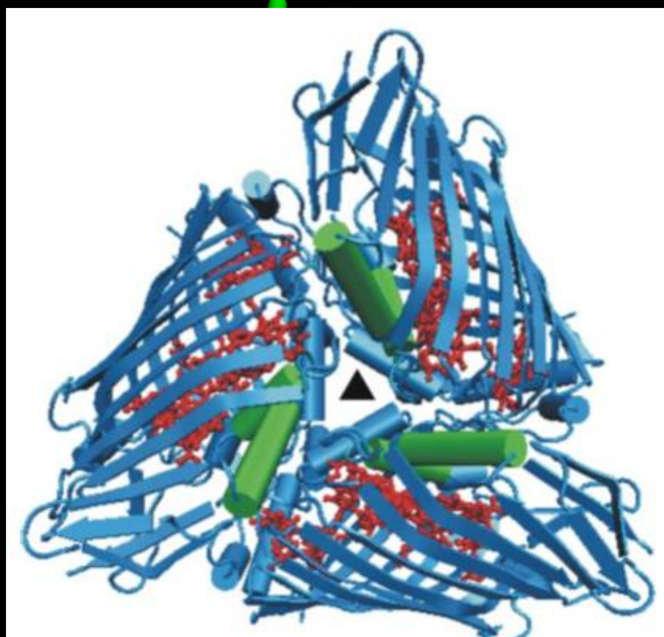
Fenna-Matthews-Olson complex (Green sulfur bacteria)

- A large variety of light harvesting antennae
- All composed of densely packed pigment molecules
- The molecular aggregates are often embedded in protein scaffolds, and always within membranes

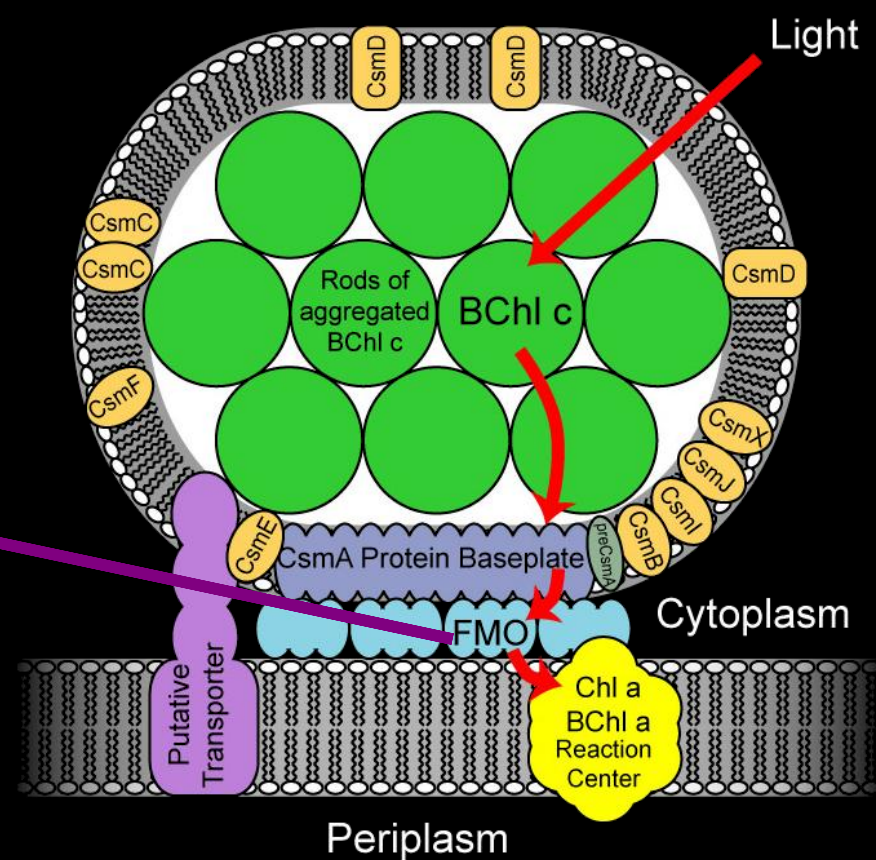
Light harvesting apparatus of green sulfur bacteria

FMO: energy 'wire' connecting chlorosome to reaction center

well characterized system



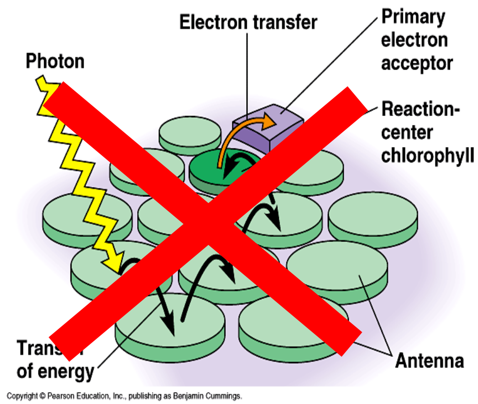
Muh et al. PNAS, **104, 16862 (2007)**

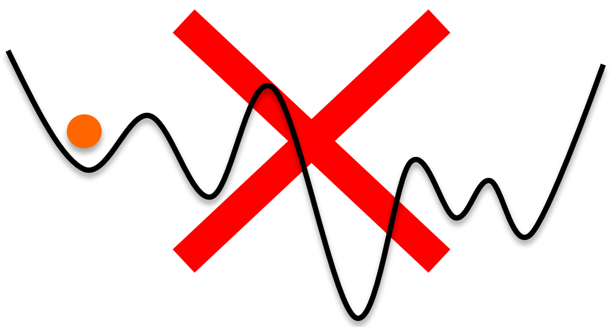


James Allen *et al.*, Photosynth. Res., **75**, 49 (2003)

Dynamics of light harvesting

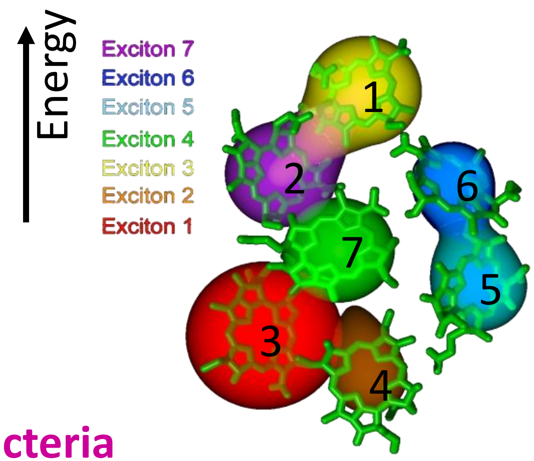
The conventional model



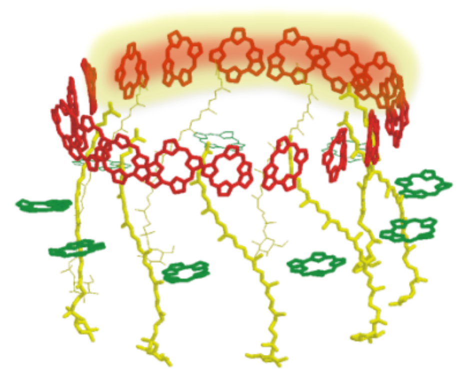


Delocalization of energy – excitons created by strong coupling of chromophores
Confirmed by modeling and spectroscopy

Green sulfur bacteria



Purple bacteria



van Amerongen, Valkunas, van Grondelle, World Scientific (2000)

Dynamic coherence in light harvesting

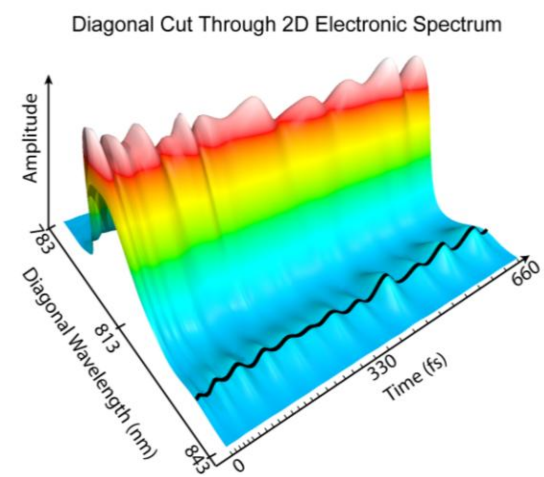
Photon echo experiments

Green sulfur bacteria (7 pigments)

Fenna Matthews Olson (FMO) complex:

Engel et al., Nature, **446**, 782 (2007) (T=77K)

Panitchayangkoon et al., PNAS 107, 12766 (2010) (T=277K)



Marine algae – phycobiliproteins (8 pigments)

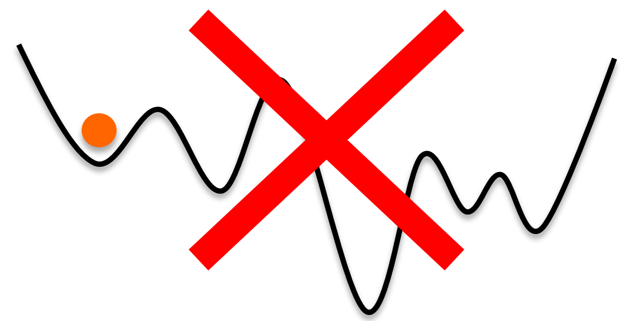
Collini et al., Nature, **463**, 644 (2010) (T=294K)

Womick et al., JCP **133**, 024507 (2010)

Purple bacteria (2-3 pigments)

Reaction center:

Lee et al., Science, **316,** 1462 (2007)



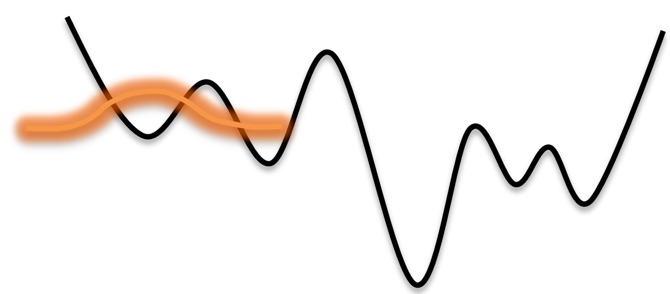
Higher plants (14 pigments)

LHC-II:

Calhoun et al., J. Phys. Chem. B, **113**, 16291 (2009)

ALSO: conjugated polymers

Collini et al., Science **323,** 369 (2009)



- How?

- Why? Functional role?

- Other quantum effects?

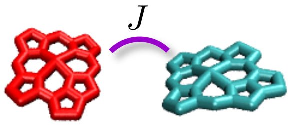
Theoretical modeling of energy transfer dynamics

The Hamiltonian

Electronic degrees of freedom:

Frenkel Hamiltonian (tight-binding, single particle model)

$$H_{\mathrm{el}} = \sum_n E_n \left|n\right\rangle \left\langle n\right| + \sum_{n \neq m} J_{nm} \left|n\right\rangle \left\langle m\right|$$



pigment electronic transition energies

transition dipole couplings

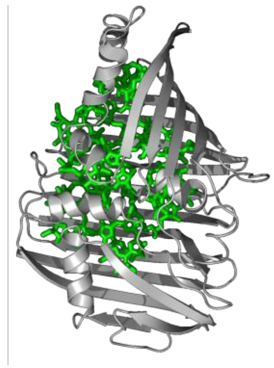
Pigment-protein interactions: open system dynamics

$$H = H_{\mathrm{el}} + H_{\mathrm{el\text{-}ph}} + H_{\mathrm{ph}}$$

reduced dynamics

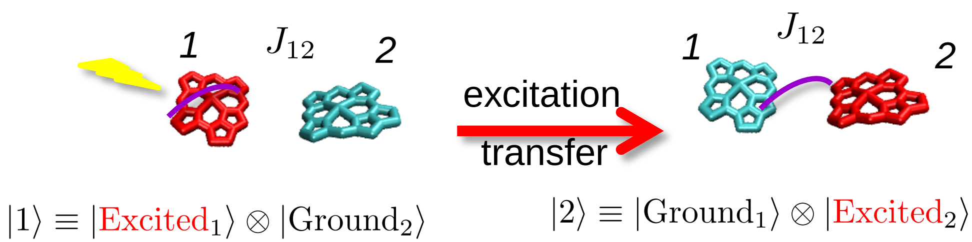
$$\frac{\mathrm{d}\rho_{\mathrm{el}}}{\mathrm{d}t} = \ldots$$

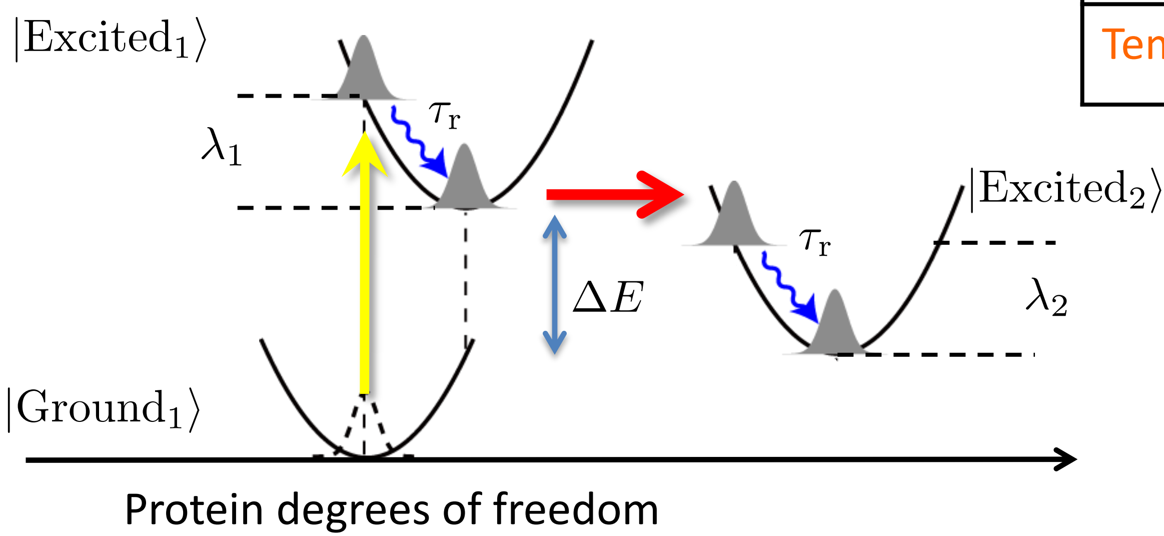
master equation



Theoretical modeling of energy transfer dynamics

Pigment-protein dynamics





Several energy scales

Pigment coupling	J_{12}
Reorganization energy of protein bath	λ
Protein relaxation timescale	$\frac{\hbar}{\tau_r}$
Pigment energy difference	ΔE
Temperature	$k_B T$

Theoretical modeling of energy transfer dynamics

Pigment-protein dynamics: reduced models and approximations

Several energy scales

Pigment coupling	J_{12}
Reorganization energy of protein bath	λ
Protein relaxation timescale	$\frac{\hbar}{\tau_\mathrm{r}}$
Pigment energy difference	ΔE
Temperature	$k_B T$

Typical photosynthetic Systems

$$J_{12} \sim \lambda \sim \frac{\hbar}{\tau_\mathrm{r}} \sim \Delta E \sim k_B T$$

$H = H_\mathrm{el} + H_\text{el-ph} + H_\mathrm{ph}$ → $\frac{\mathrm{d}\rho_\mathrm{el}}{\mathrm{d}t} = \ldots$

Reduced models

Forster theory:

$$J_{12} \ll \lambda, \quad \tau_\mathrm{r} \approx 0$$

Redfield theory:

$$J_{12} \gg \lambda, \quad \tau_\mathrm{r} \approx 0$$

Haken-Strobl:

$$T \gg \Delta E$$

Temperature independent Lindblad:

$$J_{12} \gg \lambda, \quad T \gg \Delta E$$

Generalized Bloch-Redfield:

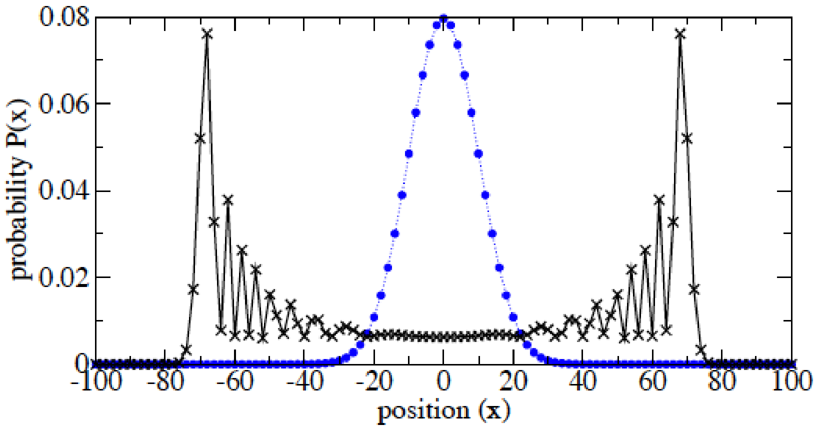
$$\lambda \not\gg J_{12}, \quad \frac{\hbar}{\tau_\mathrm{r}} \not\gg J_{12}$$

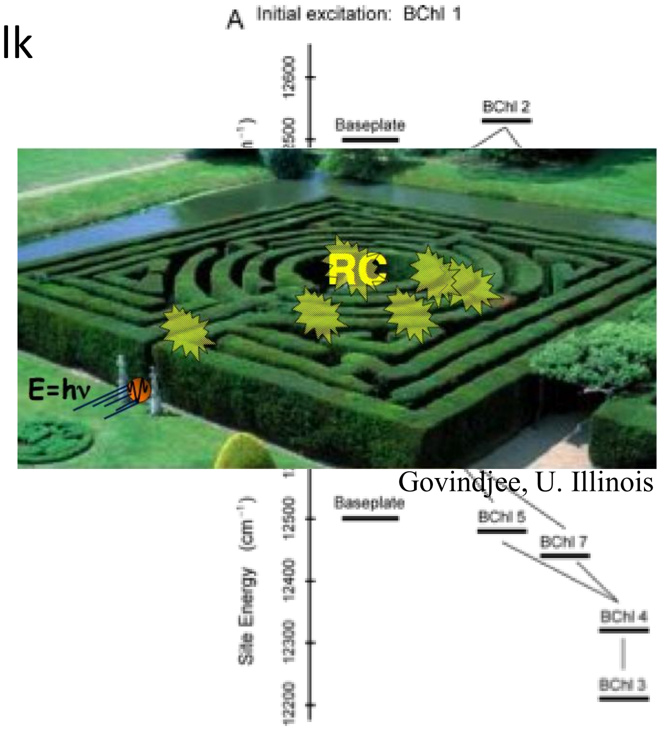
Reduced hierarchy equations approach:

none

Light harvesting complexes as quantum walks

- Single exciton, tight-binding approach = quantum walk
- Quantum walks show quantum speedup





Govindjee, U. Illinois

BUT:

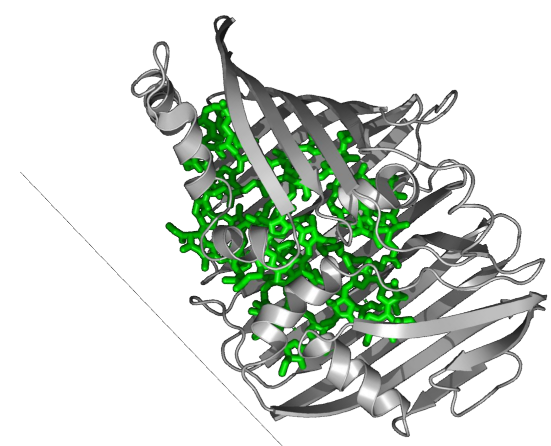
Energy landscapes

Disordered – random environment

Ordered – energy funnels

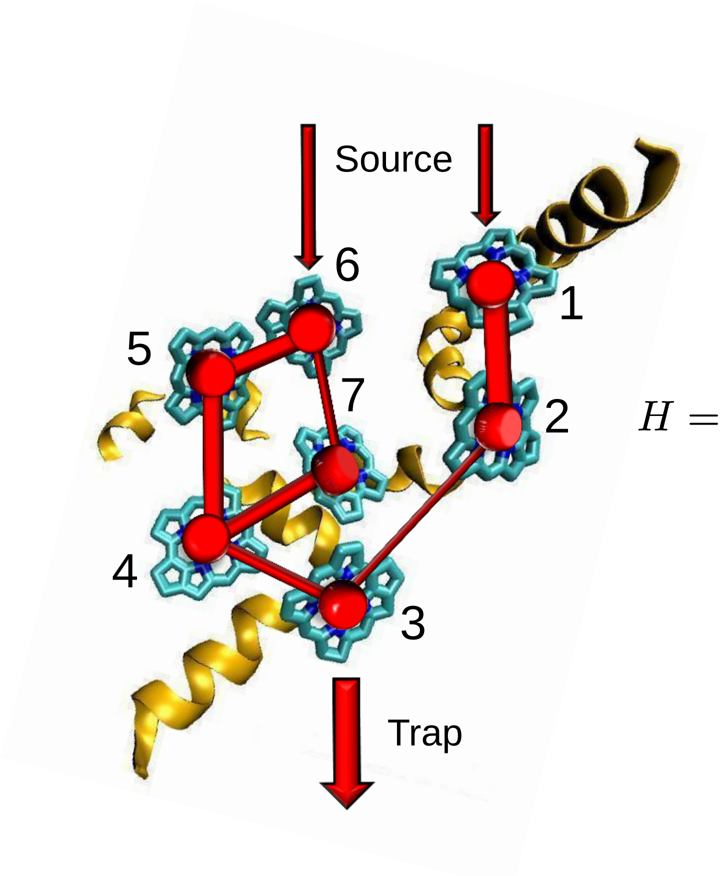
Decoherence

Room temperature in a protein cage



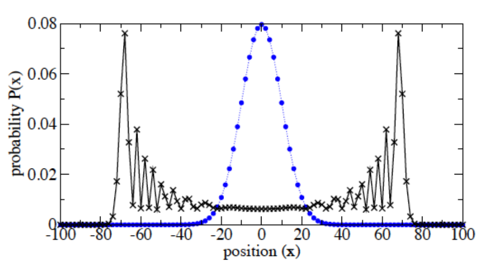
Speedup in this environment?

FMO as a 1-D quantum walk



$$H = \begin{pmatrix} 200 & -96 & \text{[illegible]} & -4.4 & 4.7 & -12.6 & -6.2 \\ -96 & 320 & 33.1 & 6.8 & 4.5 & 7.4 & -0.3 \\ 5 & 33.1 & 0 & -51.1 & 0.8 & -8.4 & 7.6 \\ -4.4 & 6.8 & -51.1 & 110 & -76.6 & -14.2 & -67 \\ 4.7 & 4.5 & 0.8 & -76.6 & 270 & 78.3 & -0.1 \\ -12.6 & 7.4 & -8.4 & -14.2 & 78.3 & 420 & 38.3 \\ -6.2 & -0.3 & 7.6 & -67 & -0.1 & 38.3 & 230 \end{pmatrix}$$

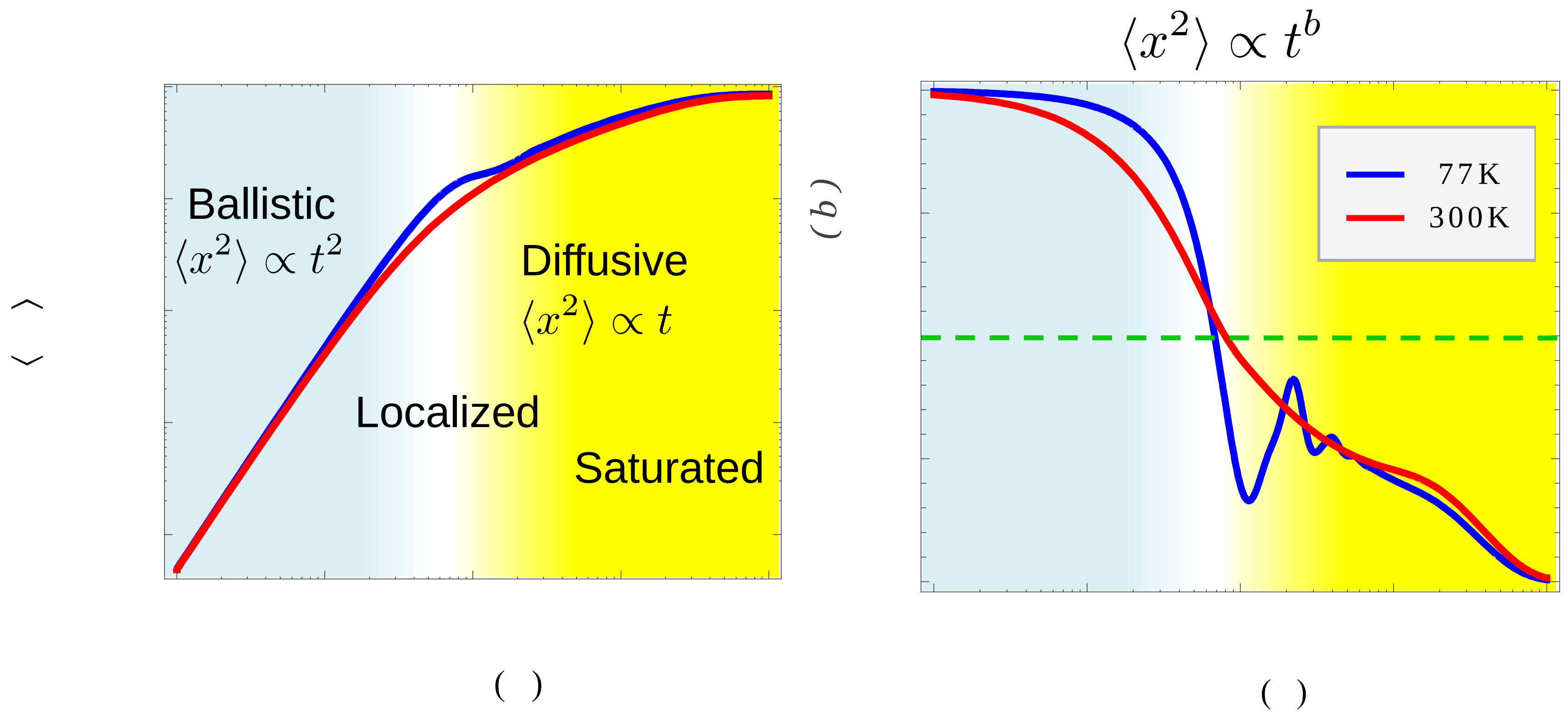
Energies in cm^{-1}



$\langle x^2 \rangle(t)$ — classical → $\propto t$

$\langle x^2 \rangle(t)$ — quantum → $\propto t^2$

(Lack of) quantum speedup in FMO



Initial excitation at site 6

- No quantum speedup in FMO after ~70 fs

  Coherence present for ~700 fs

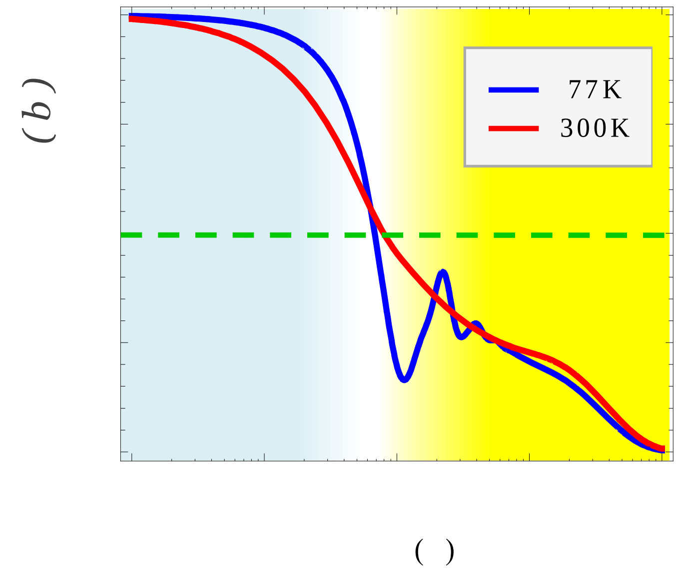
Why? Decoherence effects? Energy landscape?

S. Hoyer, M. S., K. B. Whaley. New J. Phys., 12 065041 (2010).

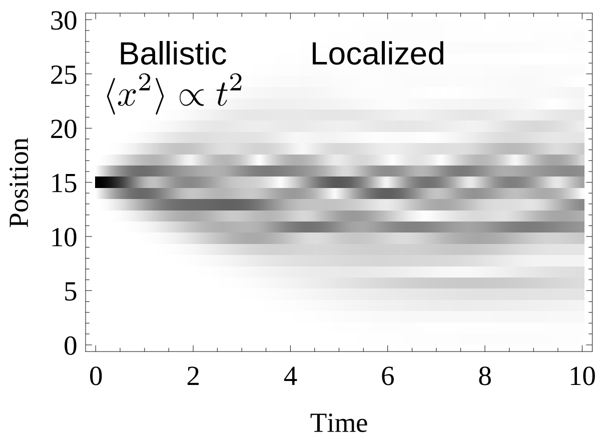
(Lack of) quantum speedup in FMO

Limit of quantum speedup due to a combination of:

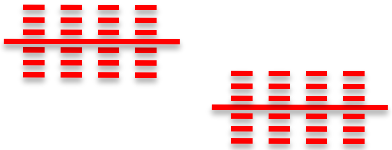
(1) Localization due to energy disorder
(2) Dephasing



Anderson localization



Any variation in site energies lead to localization



Dephasing allows escape of Anderson localization but makes overall transport sub-ballistic

S. Hoyer, M. S., K. B. Whaley. New J. Phys., 12 065041 (2010).

Theoretical studies of energy transfer

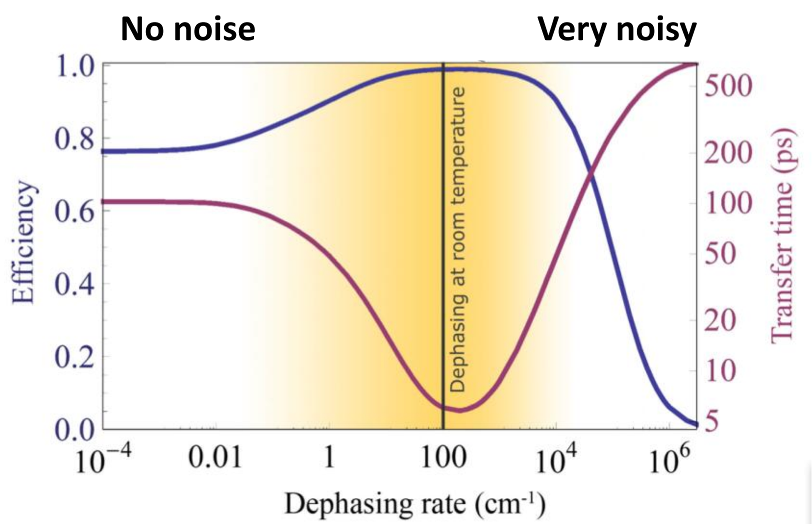
Energy transfer efficiency, speed, timescales…

Green sulfur bacteria (FMO)

e.g. Renger et al, JPCA, 102, 4381 (1998); Mohseni *et al.*, JCP **129**, 174106 2008); Rebentrost *et al.*, New J. Phys. **11**, 033003 (2009); Plenio and Huelga, New J. Phys. **10**, 113019 (2009); Caruso *et al.,* JCP 131, 105106 (2009); shizaki et al., PNAS, **106,** 17255 (2009); Sarovar et al. Phys. Rev. E **83** 011906 2011)

Purple bacteria (LH1/LH2)

e.g. Mukai et al, JPCB 103, 6096 (1999); Scholes et al., JPCB 104, 1854 (2000); Jang et al., PRL 92, 218301 (2004); Cheng et al. PRL 96, 02810 (2006); Olaya-Castro et al., PRB, **78**, 085115 (2008)



[From Rebentrost et al., 2009]

Interplay between **coherent dynamics** and **environmental fluctuations** essential for super-efficient transport.

Only coherent -> wave-like transport, but no appreciable trapping

Only classical -> slow, diffusive transport

Theoretical studies of energy transfer

Delocalization and entanglement

Green sulfur bacteria (FMO)

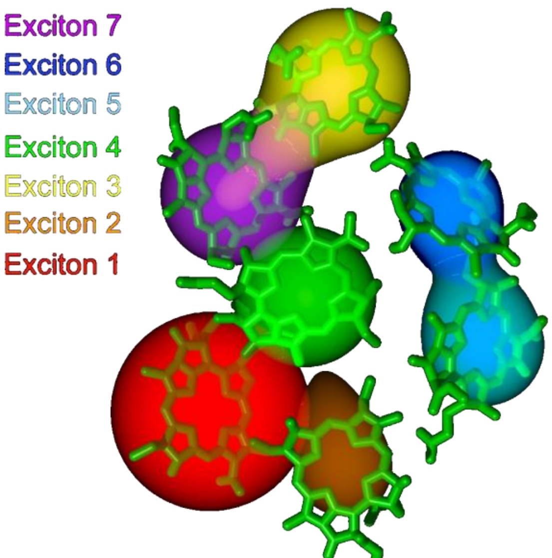
Sarovar et al. Nat. Phys., **6**, 462 (2010); Caruso et al. PRA, **81**, 062346 (2010); Fassiolo, et al., New J. Phys. 12, 085006 (2010); Bradler et al. arXiv:0912.5112

Purple bacteria (LH1/LH2)

Monshouwer et al., JPCB, **101** 7241 (1997); Meier et al., JCP, **107**, 3876 (1997); Dahlbom et al., JPCB, **105**, 5515 (2001)

Higher plants (LHC-II)

Ishizaki et al., New J. Phys. **12**, 055004 (2010)



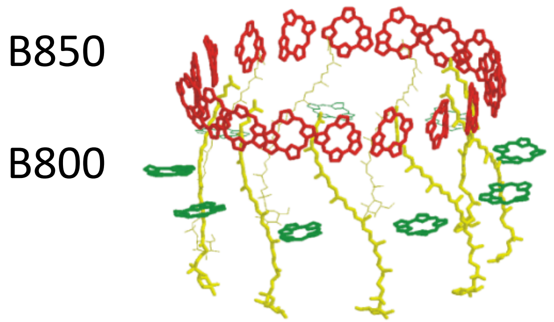
[From Brixner et al., 2005]

Electronic entanglement **inherent** in the delocalized excitonic states of a LHC

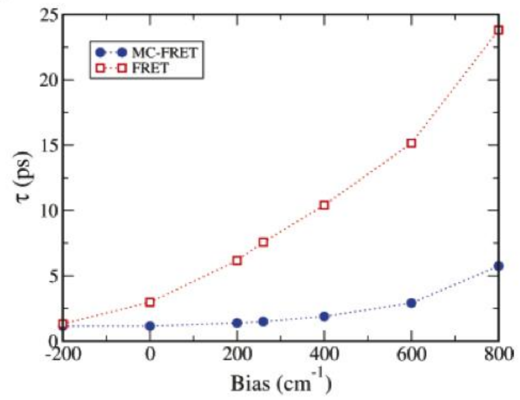
Functional significance of quantum coherence

A quantum advantage?

Speed of transfer and robustness of transfer to disorder

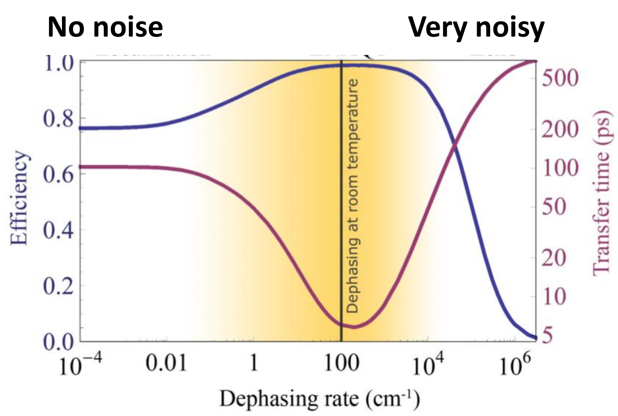


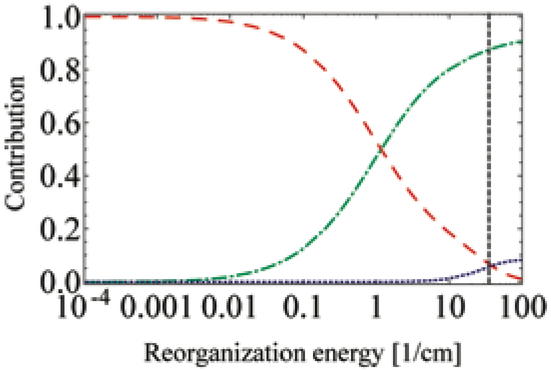
LH2 (purple bacteria)



S. Jang, M. Newton, R. Silbey, J. Phys. Chem. B **111**, 6807 (2007)
Y.-C. Cheng, R. J. Silbey, Phys. Rev. Lett. **96** 028103 (2006)

Greater efficiency of energy transfer





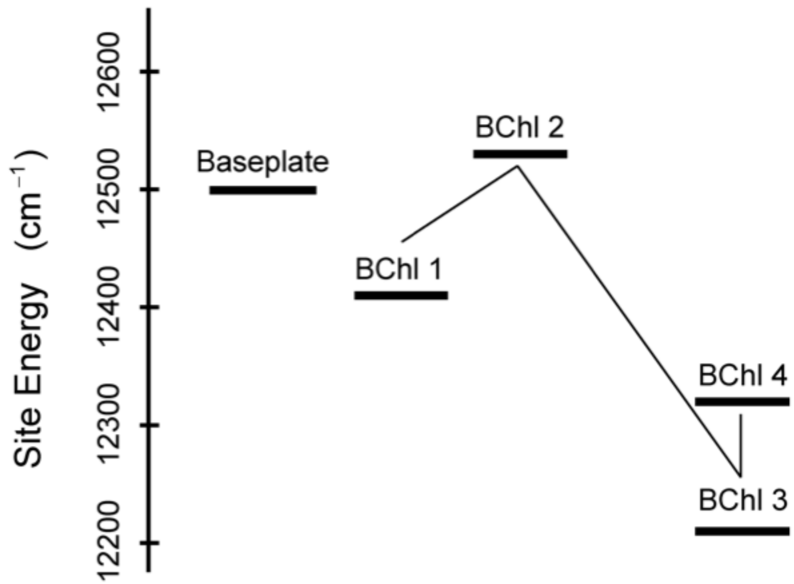
[*e.g.* P. Rebentrost, M. Mohseni, A. Aspuru-Guzik, J. Phys. Chem. B **113** 9942 (2009)]

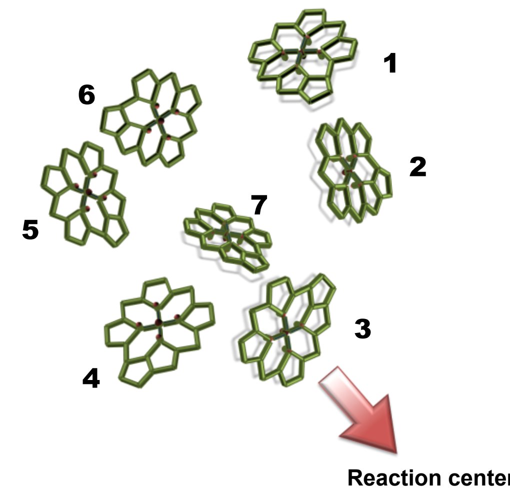
Functional significance of quantum coherence

A quantum advantage?

Unidirectionality of energy transfer

The energy landscape of the FMO pigments:





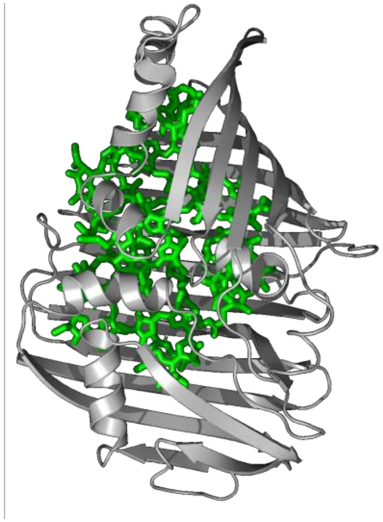
A. Ishizaki, G. R. Fleming, PNAS **106** 17255 (2009)
S. Hoyer, A. Ishizaki, K. B. Whaley (to appear)

Theoretical studies of energy transfer

Optimality

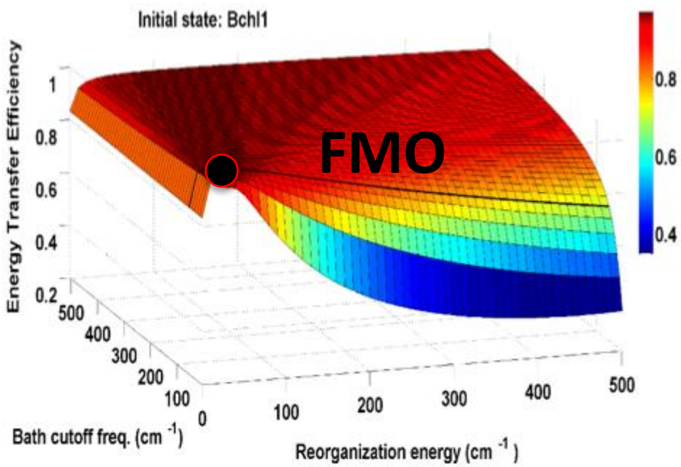
Green sulfur bacteria (FMO)

Wu et al. New J. Phys. **12** 105012 (2010) arXiv: 1008.2236.
Shabani, Mohseni et al. (2011), arXiv: 1104.4812.



Structural and energetic parameters, e.g.:

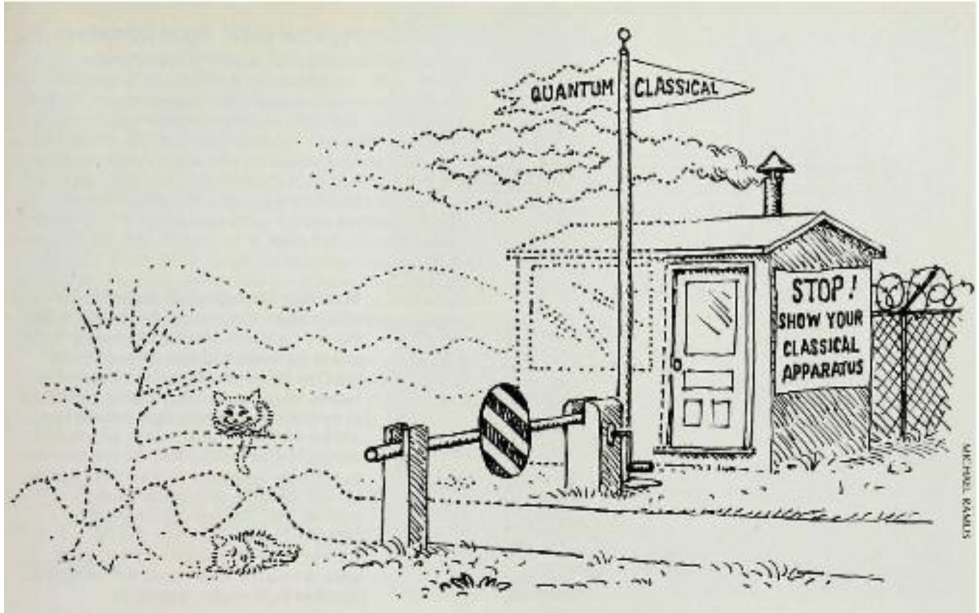
(1) density of pigments
(2) orientation of pigments
(3) strength of pigment-protein coupling
(4) time scale of protein vibrations
(5) length scale of protein vibrations



Natural system resides in small region of optimality

Summary of quantum transport in LHCs

- Efficient transport a result of a delicate interplay of coherent and decoherent dynamics.



Delineating the border between the quantum realm ruled by the Schrödinger equation and the classical realm ruled by Newton's laws is one of the unresolved problems of physics. **Figure 1**

W. H. Zurek, Physics Today, October, 36 (1991)

- A quantum advantage seems to exist
  - Overcome local energy minima
  - Efficiency [1]
  - Robustness[2]
  - Unidirectionality [3]

What’s so special about light harvesting complexes?

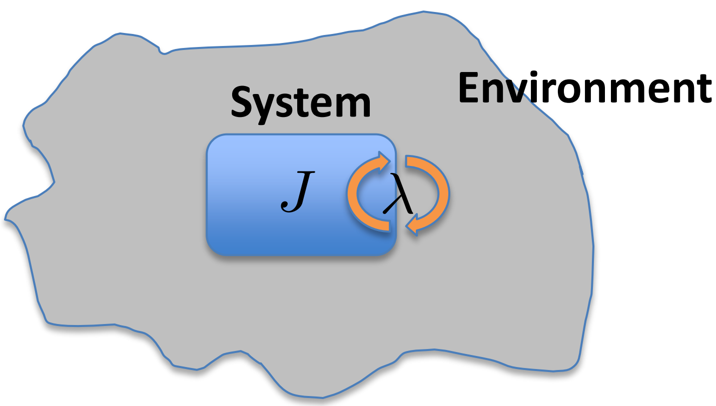
Why the surprise? The arguments against quantum coherent behavior

1. $\hbar\omega < k_B T$ — Thermal energy overwhelms signatures of energy quantization

2. Decoherence theory: W. Zurek et al.

Coherent evolution timescale: $\tau_c \propto \frac{1}{J}$

Decoherence timescale: $\tau_D \propto \frac{1}{\lambda}$



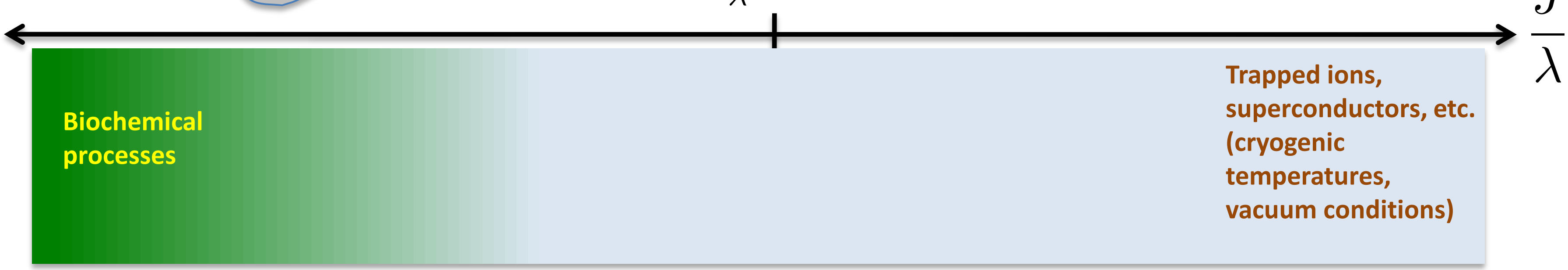
$$\frac{J}{\lambda}$$

$$|\psi\rangle \xrightarrow{J} |\psi\rangle + e^{i\theta}|\phi\rangle$$

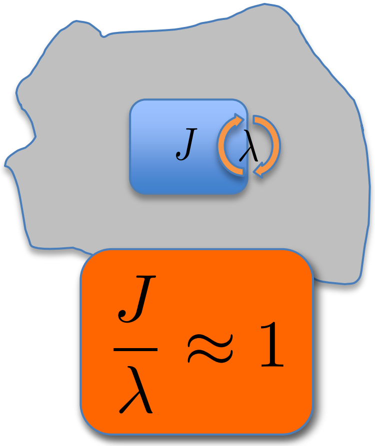
$$\downarrow \lambda$$

$$\frac{1}{2}|\psi\rangle\langle\psi| + \frac{1}{2}|\phi\rangle\langle\phi|$$

$$\frac{J}{\lambda} = 1$$



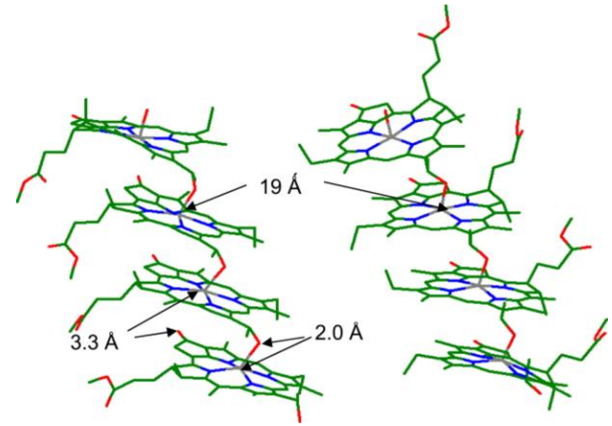
What’s so special about light harvesting complexes?



$$\frac{J}{\lambda} \approx 1$$

J : inter-chromophoric coupling

↑ Densely packed molecular aggregates



λ : chromophore-p ... y)

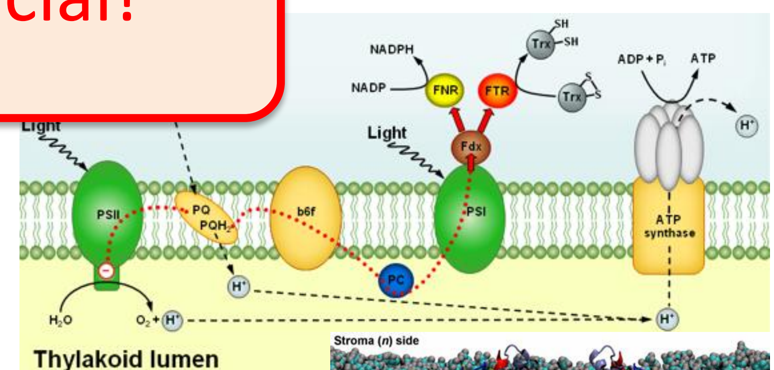
Structure is crucial!

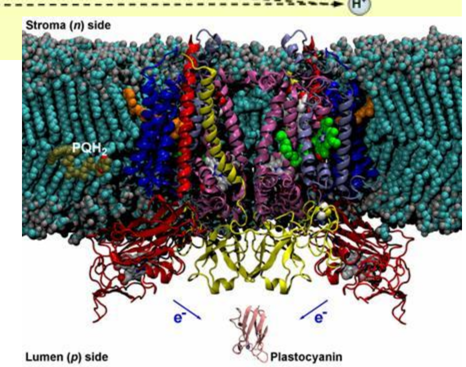
↓ Controlled envi ... embedded):

(1) weaker electron-phonon coupling

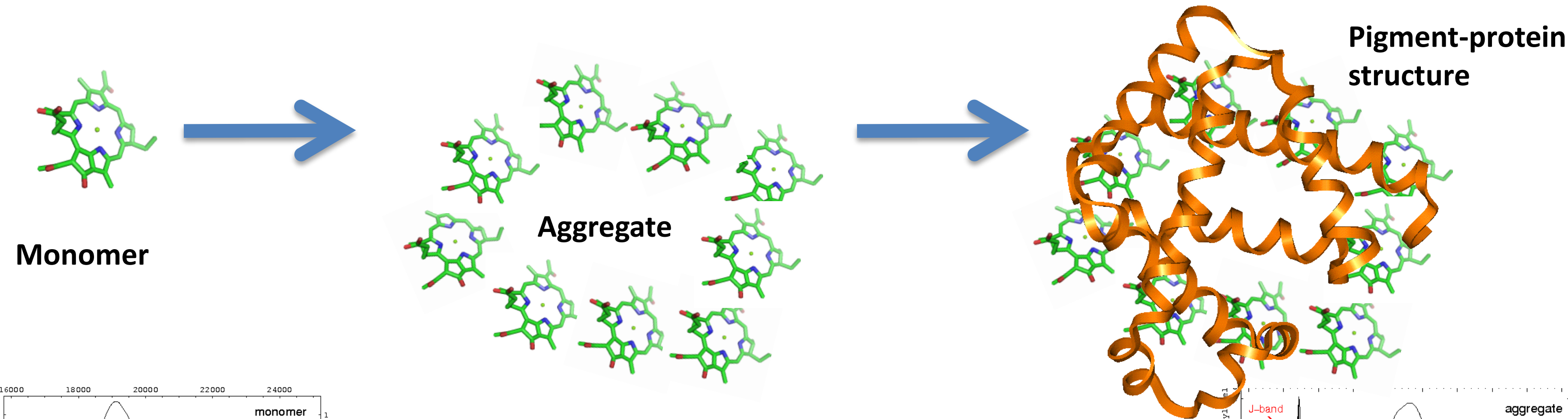
Typical reorganization energies of pigments in solution: 200 – 2000 cm^{-1}
[Gilmore & McKenzie J. Phys. Chem. A, **112**, 2162 (2008)]
c.f. Reorganization energy of FMO: 35cm^{-1}

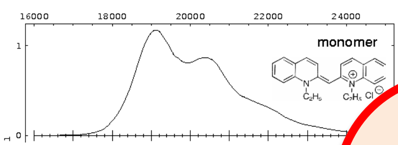
(2) spatially and temporally correlated fluctuations

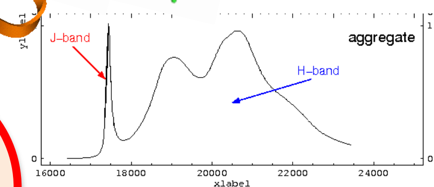




Bottom-up approach: structure-function questions







- Which struc … ce of:
  - Pigmen …
- Can the qua …
- How does n … al properties?

Can we construct an artificial light harvesting complex with quantum coherent properties and enhanced light harvesting function?

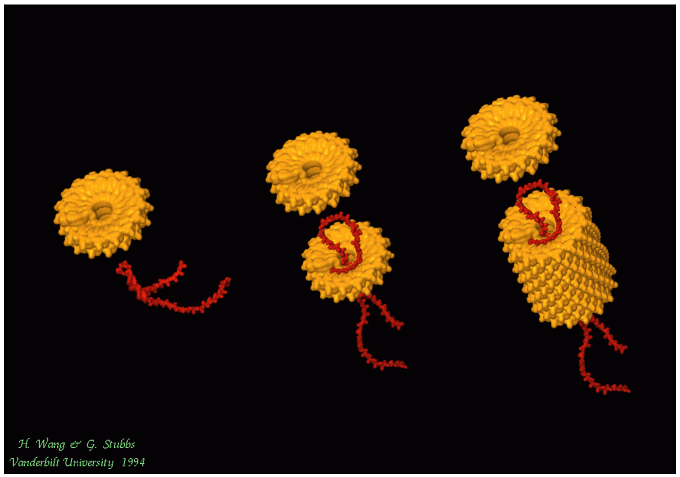
Can we mimic the performance of natural LHCs and build a better solar cell?

How does the nanoscale structure dictate functional performance?

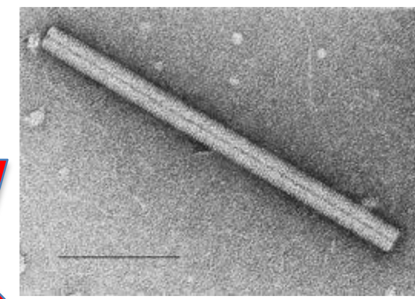
<u>Need to control assembly of pigments at the nanoscale</u>

The tobacco mosaic virus

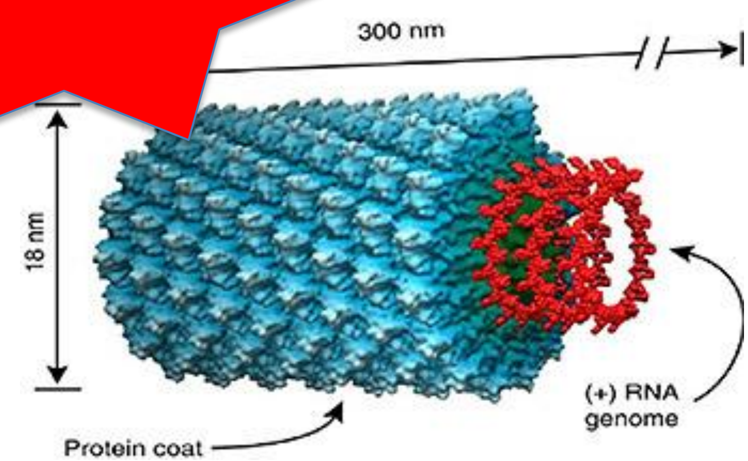
- Extensively studied virus – structure and properties well known
- Robust and well-known self-assembly process



H. Wang, G. Stubbs (1994)

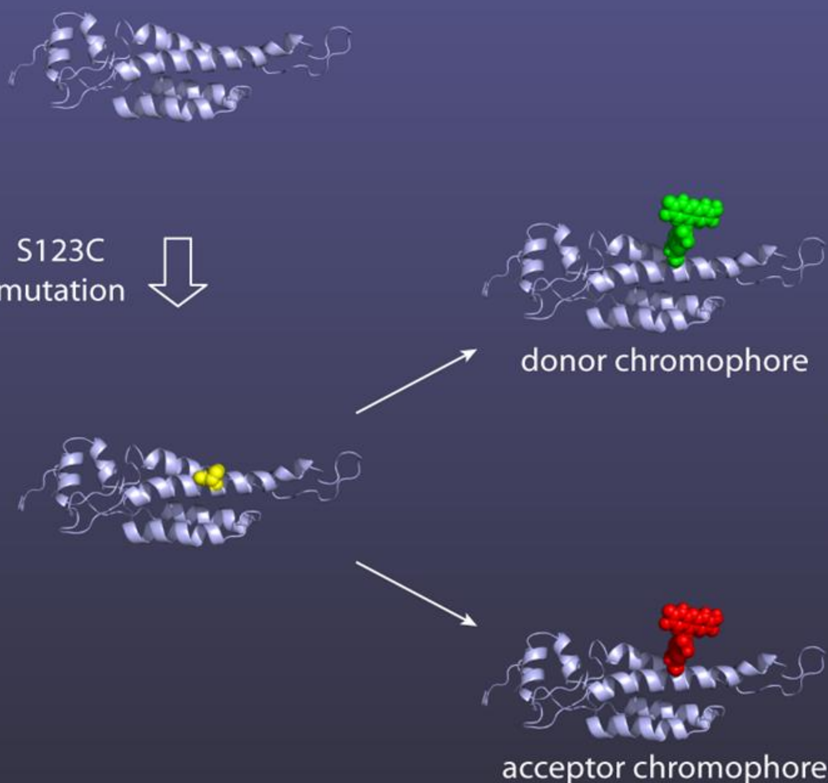


More work



We can leverage the precise self-assembly of this virus to make chromophore assemblies with well defined nanoscale structure

Self-Assembling Chromophore Assemblies

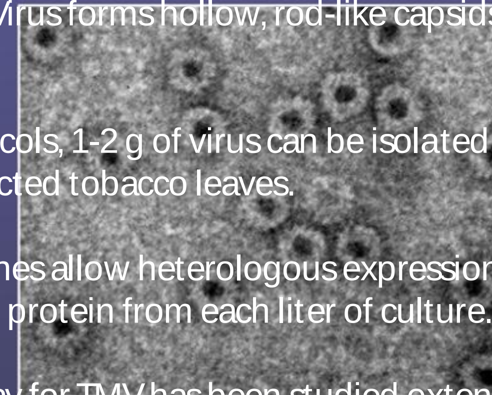


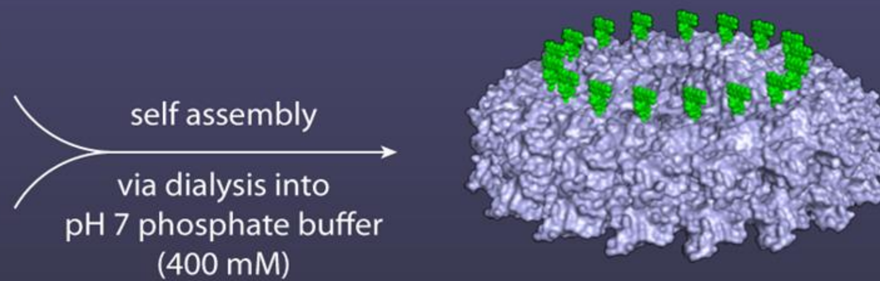
The Tobacco Mosaic Virus forms hollow, rod-like capsids that are 300 nm in length.

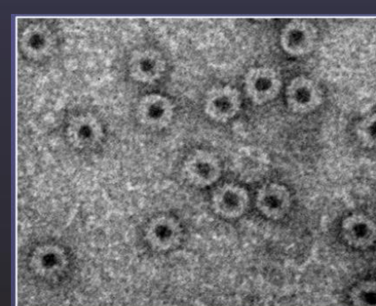
Using standard protocols, 1-2 g of virus can be isolated from each kilogram of infected tobacco leaves.

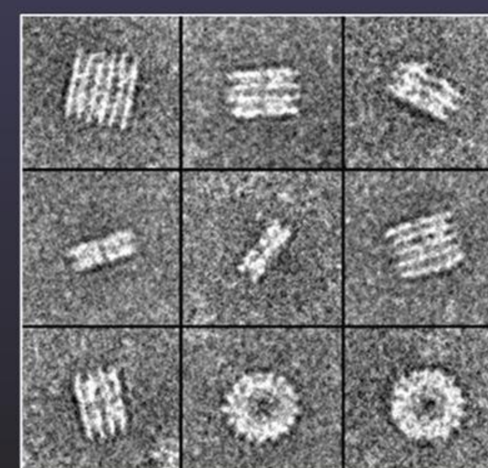
Codon-optimized genes allow heterologous expression of >100 mg of TMV coat protein from each liter of culture.

The assembly pathway for TMV has been studied extensively.







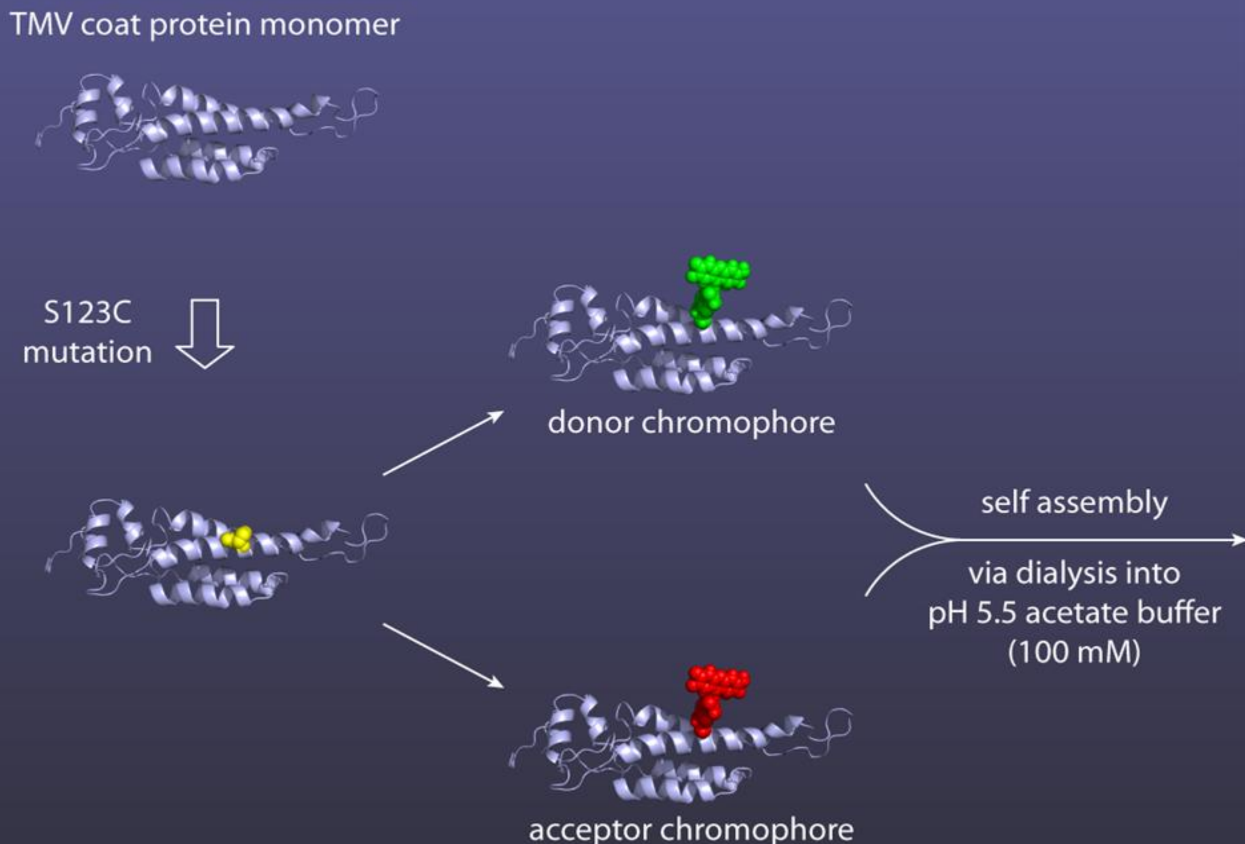


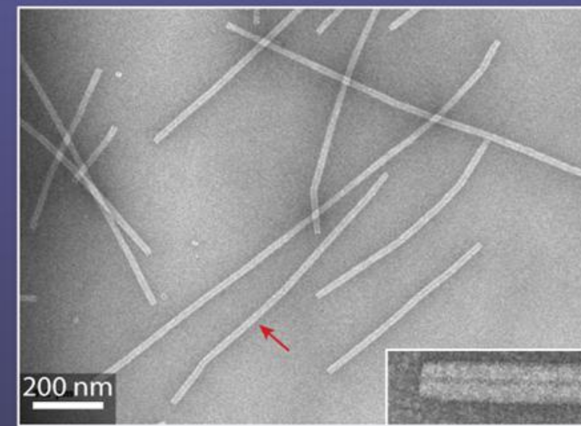
Matthew Francis, UC Berkeley

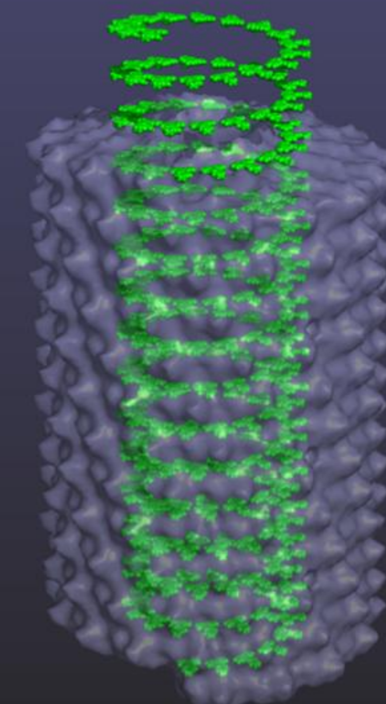
Self assembly based on: Klug, A.
Phil Trans Royal Soc London B **1999**, *354*, 531.

Andrew Presley and Rebekah Miller

Self-Assembling Chromophore Assemblies







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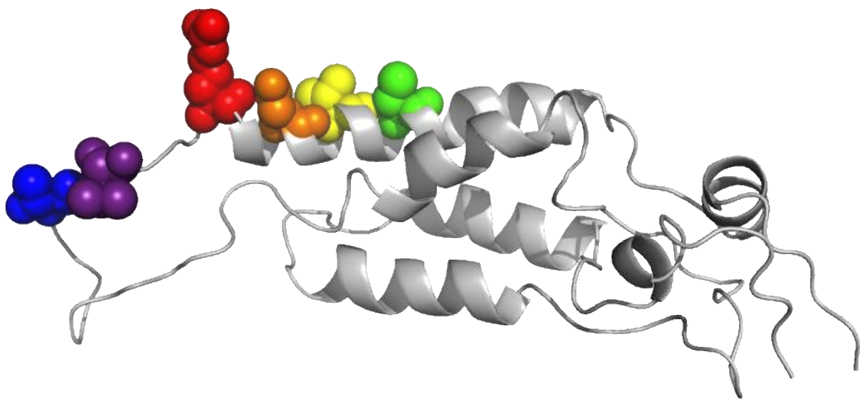
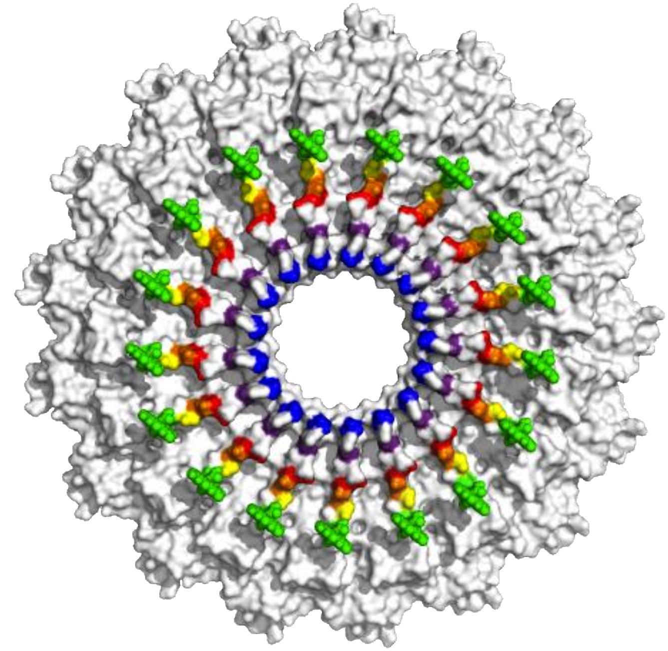
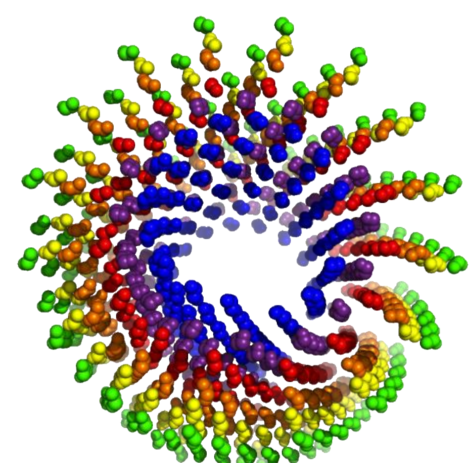
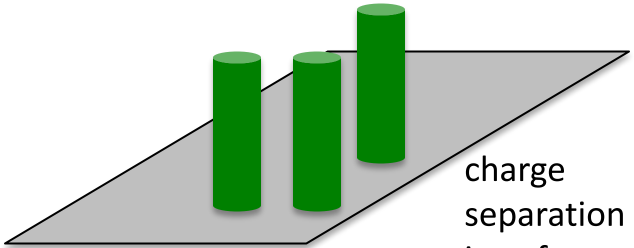


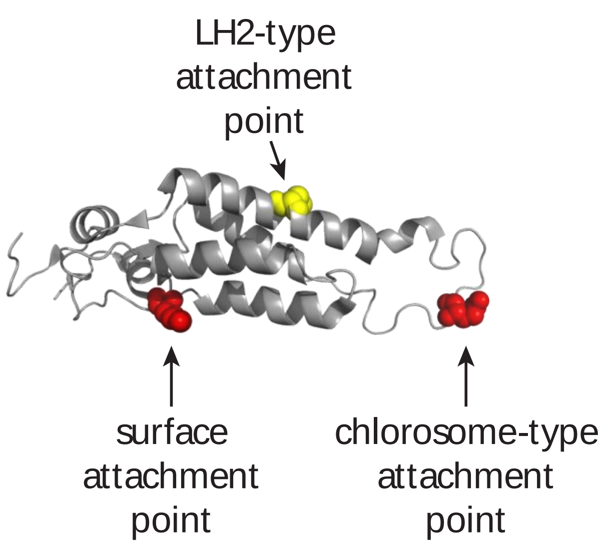


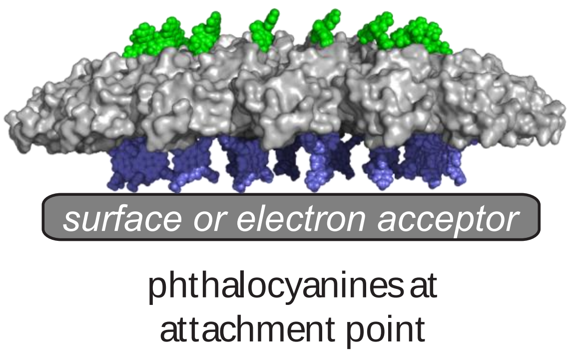


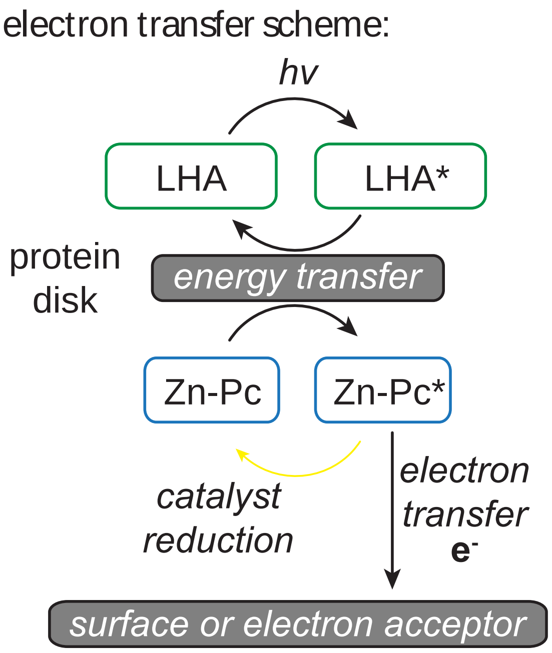
An organic photovoltaic/sensing device



[Michel Dedeo and Dan Finley, UC Berkeley]

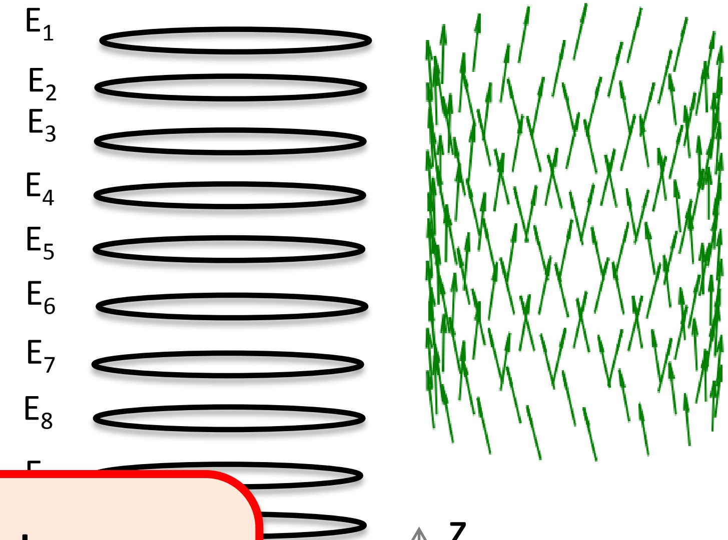






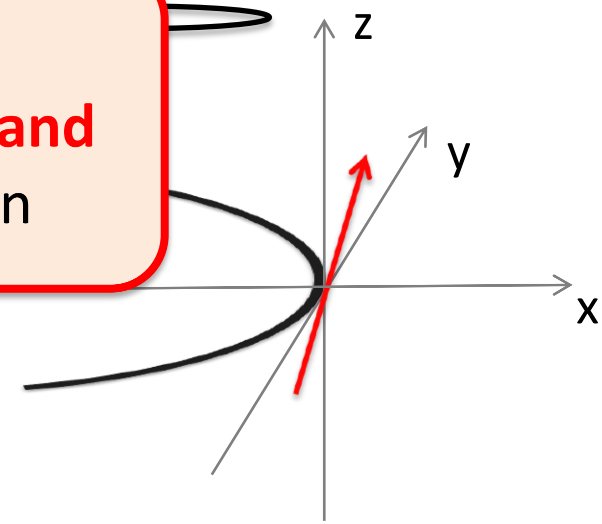
Rational design of a light harvesting architecture

Optimization over 13 parameters:

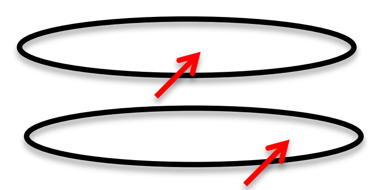


Energies of all chromophores on each disk (10 parameters). Chosen in the range: 400nm – 450nm

Would ideally like: highly efficiency energy transfer **and** broad spectrum absorption



Two dipole angles. range: 0 - 2π. All c the structure form with the disk.



One slip angle. The amount of vertical alignment between subsequent disks. In the range 0 – 2π

Multi-objective optimization

Optimization with multiple objectives:

$$\max_{\mathbf{x}} \mathbf{F}(\mathbf{x}) = [F_1(\mathbf{x}), F_2(\mathbf{x}), ...F_k(\mathbf{x})]^T$$

$$\text{with constraints on } \mathbf{x}$$

Ubiquitous in complex systems and nature. Almost every natural system has to optimize multiple objectives. Trade-offs/compromises between objectives necessary.

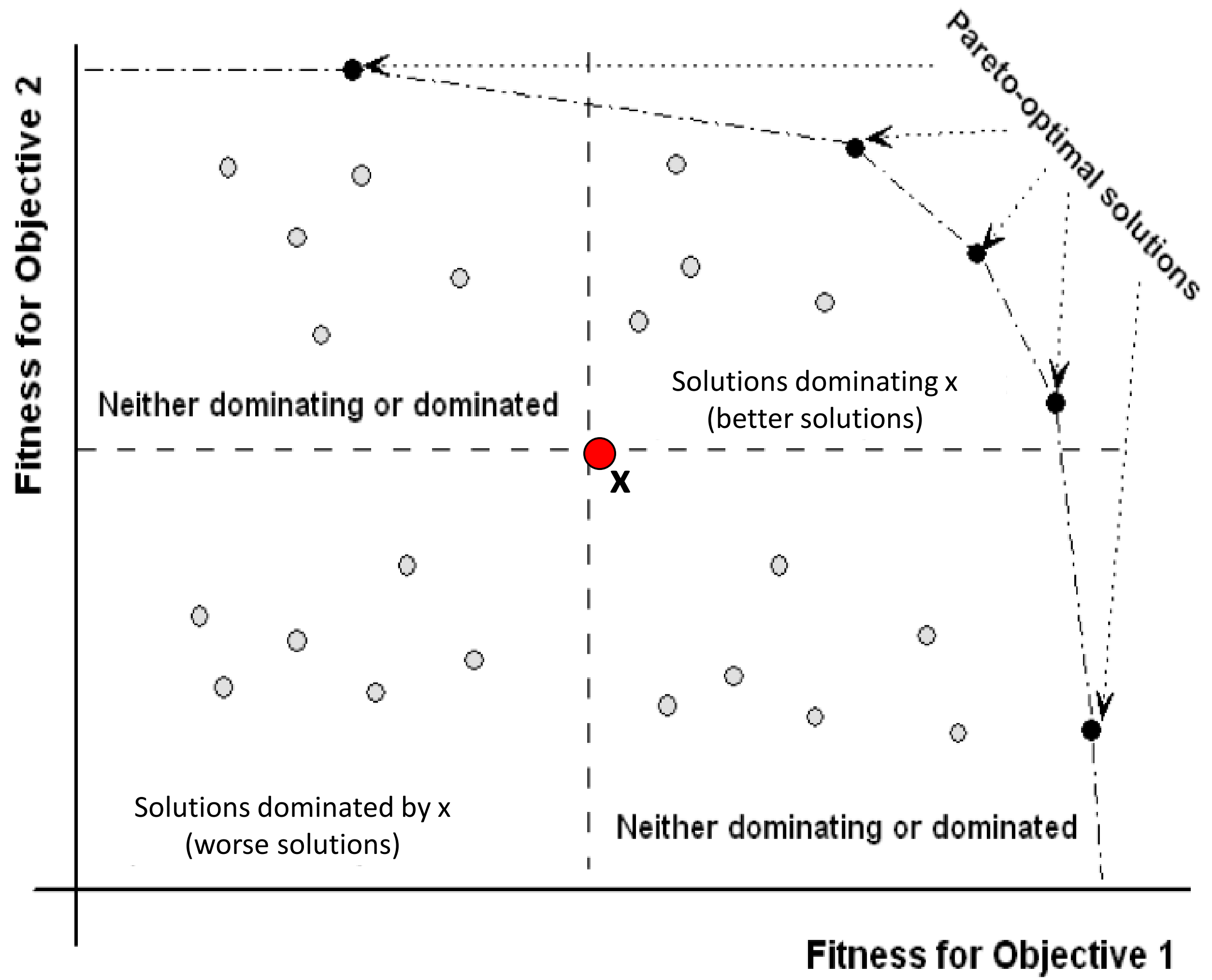
Common heuristic: can combine into one objective:

$$J(\mathbf{x}) = \alpha_1 F_1(\mathbf{x}) + \alpha_2 F_2(\mathbf{x}) + ... + \alpha_k F_k(\mathbf{x})$$

But this presumes we know the relative importance of the objectives and thus assumes one particular trade-off.

Often in design problems we want to know exactly how this trade-off works. How do the objectives compete? This is characterized by the Pareto frontier of solutions.

Multi-objective optimization: trade-offs and the Pareto frontier



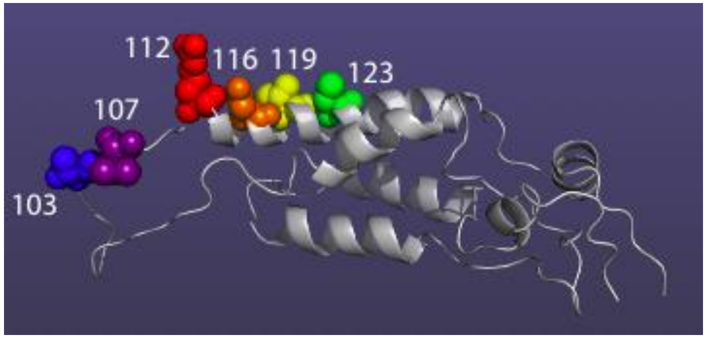
From Abraham, Jain & Goldberg, 2003

What are the trade-offs involved in light harvesting and sensing?. Need to formulate objectives -

Rational design: the optimization landscape for light harvesting

Example: compare two structures

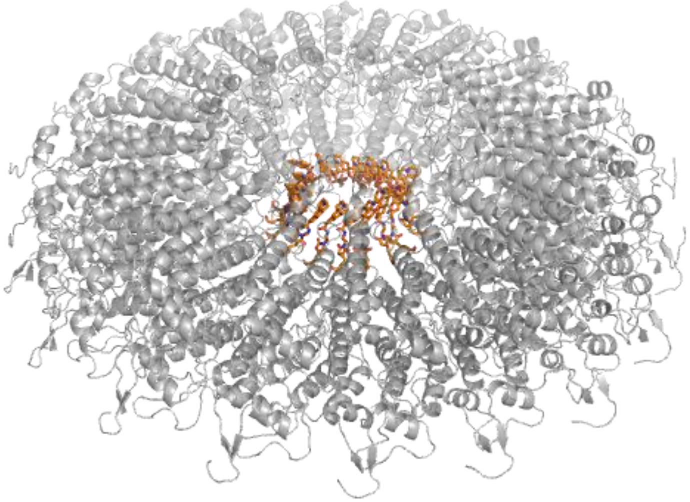
Want to maximize: efficiency of energy transfer and spectral width of absorption



<u>TMV103</u>

4.5 – 6 Å pigment separation

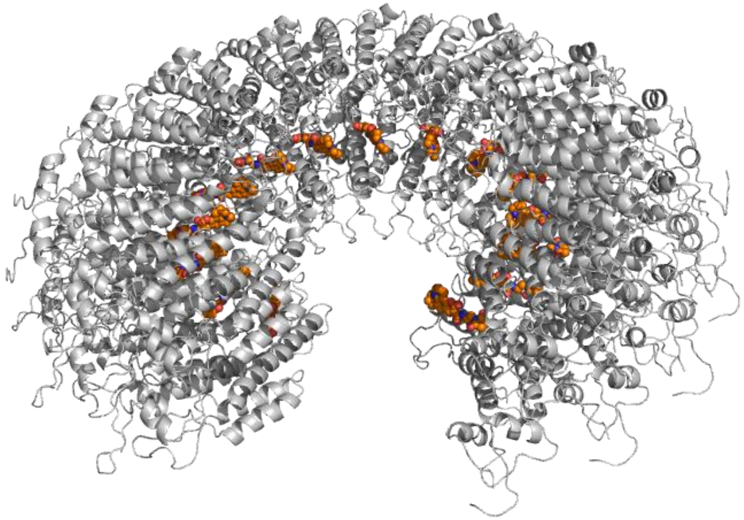
Strong coupling, quantum effects prominent



<u>TMV123</u>

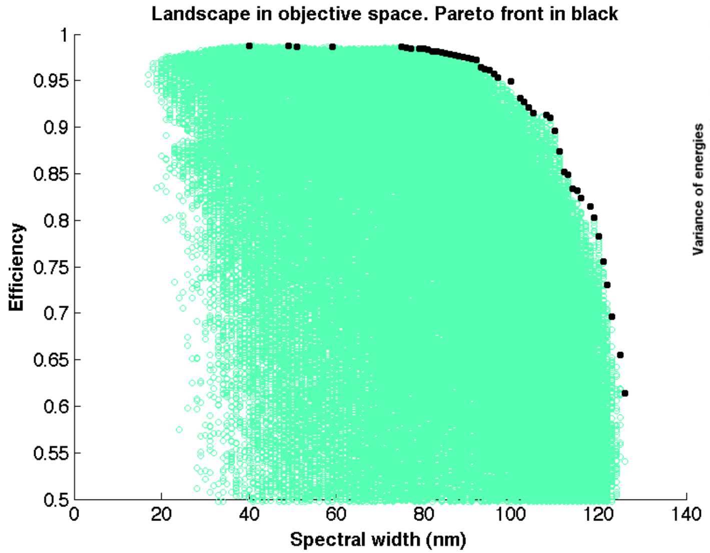
13-14 Å pigment separation

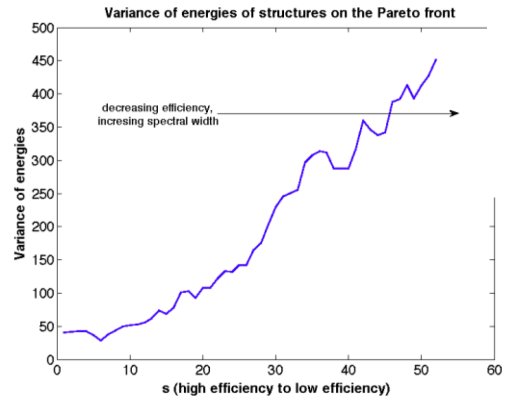
Weaker couplings, quantum effects less important

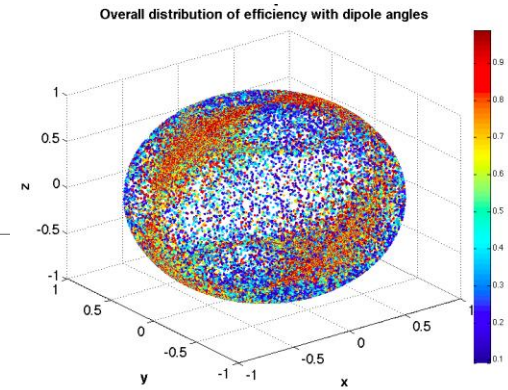


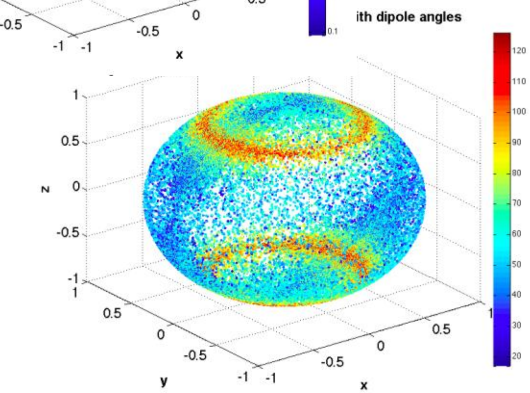
Rational design results:

TMV103 attachment (dense), without disorder

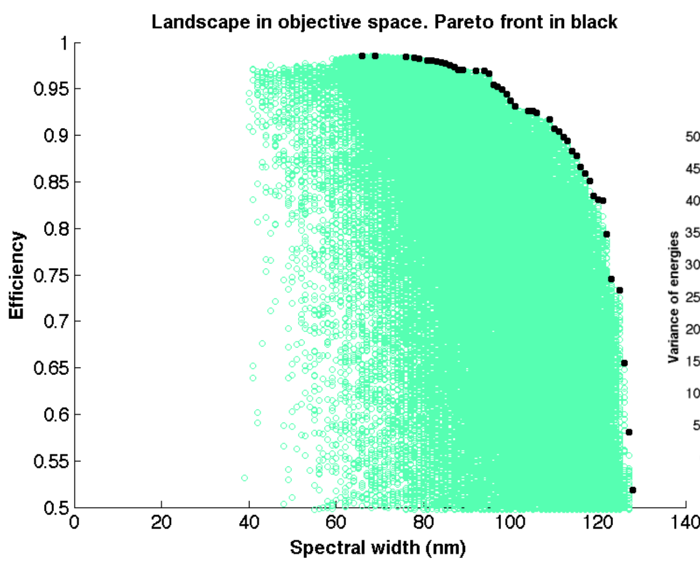


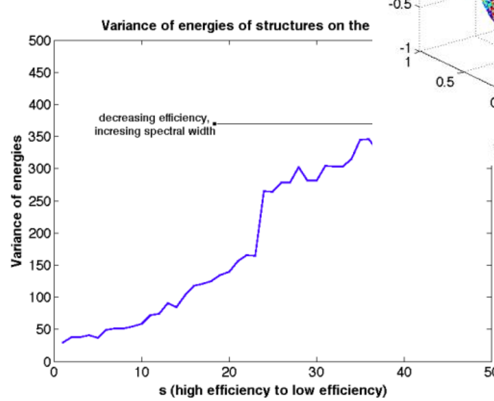


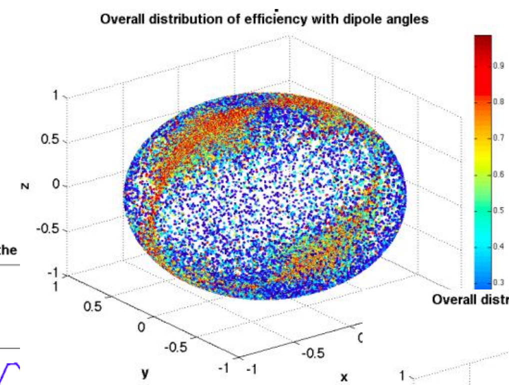


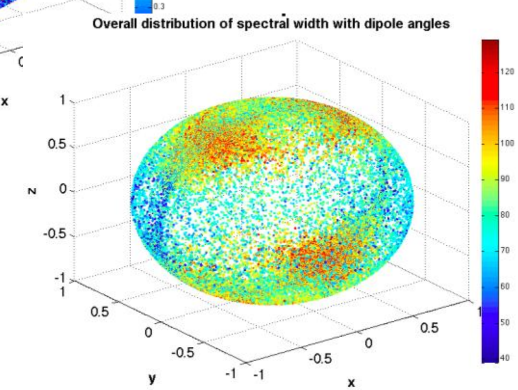


TMV123 attachment (sparse), without disorder



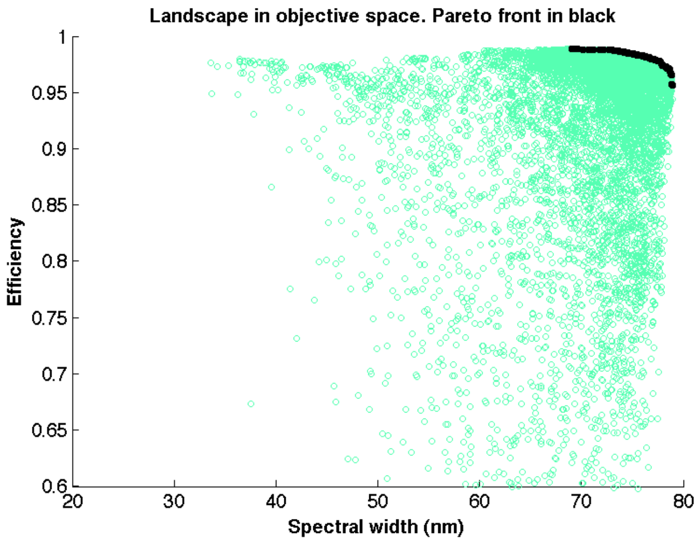


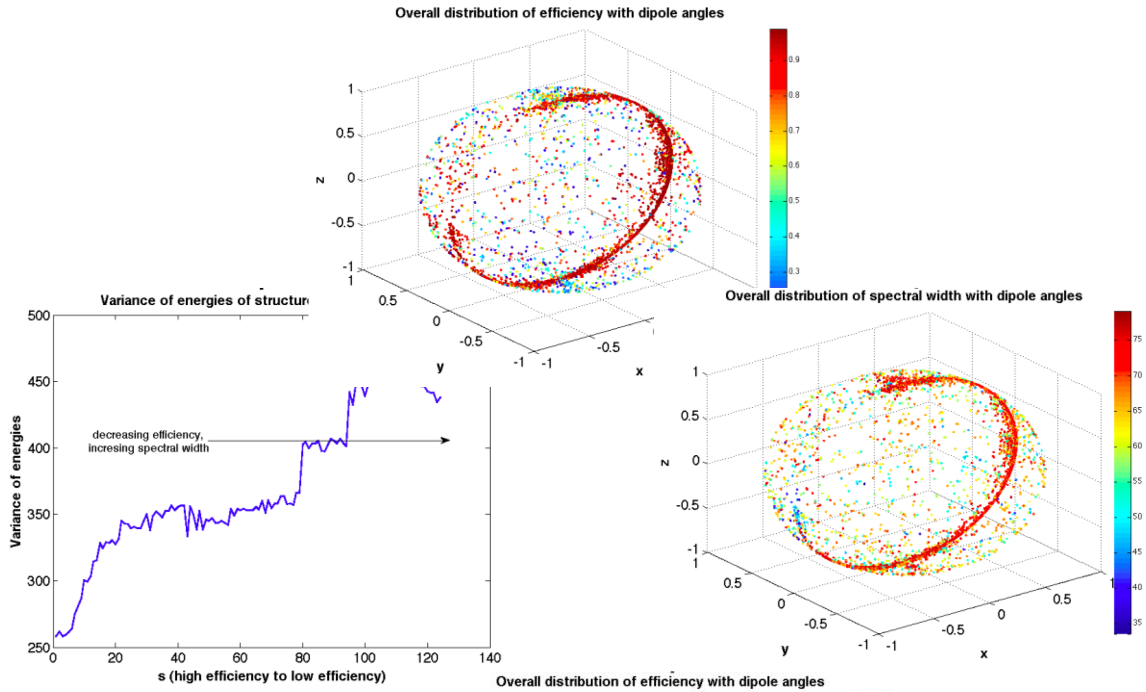




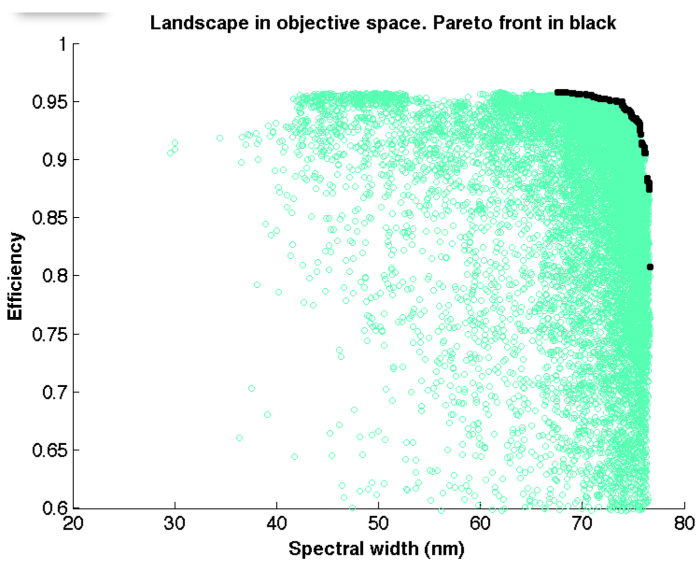
Rational design results:

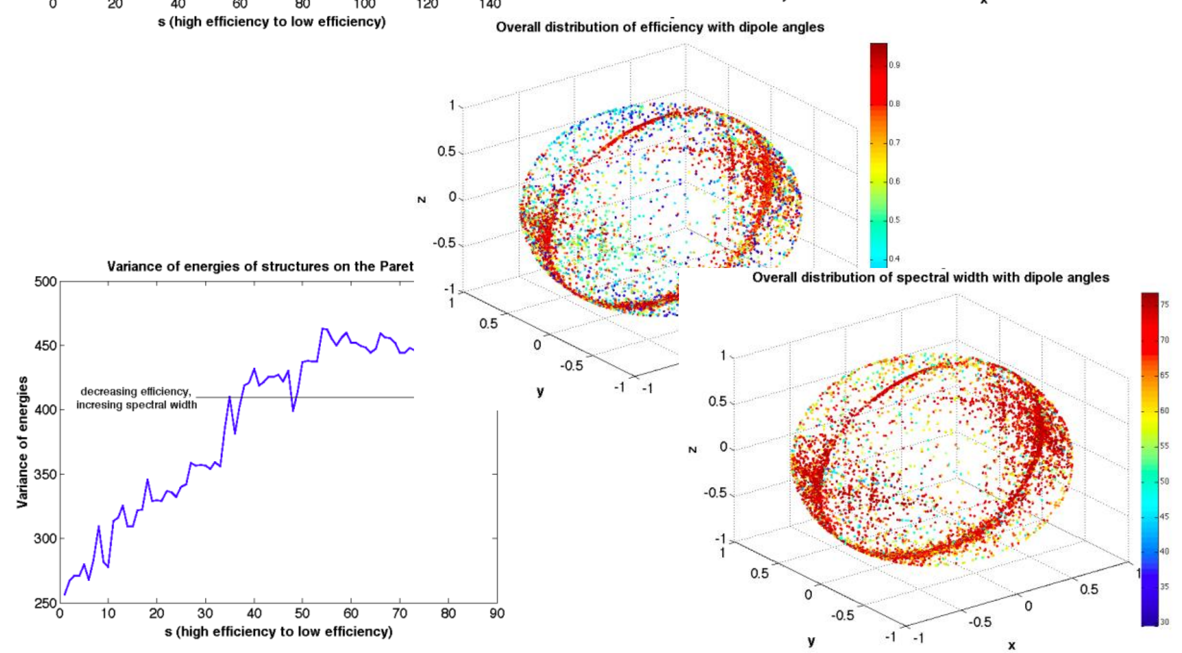
TMV103 attachment (dense), with disorder





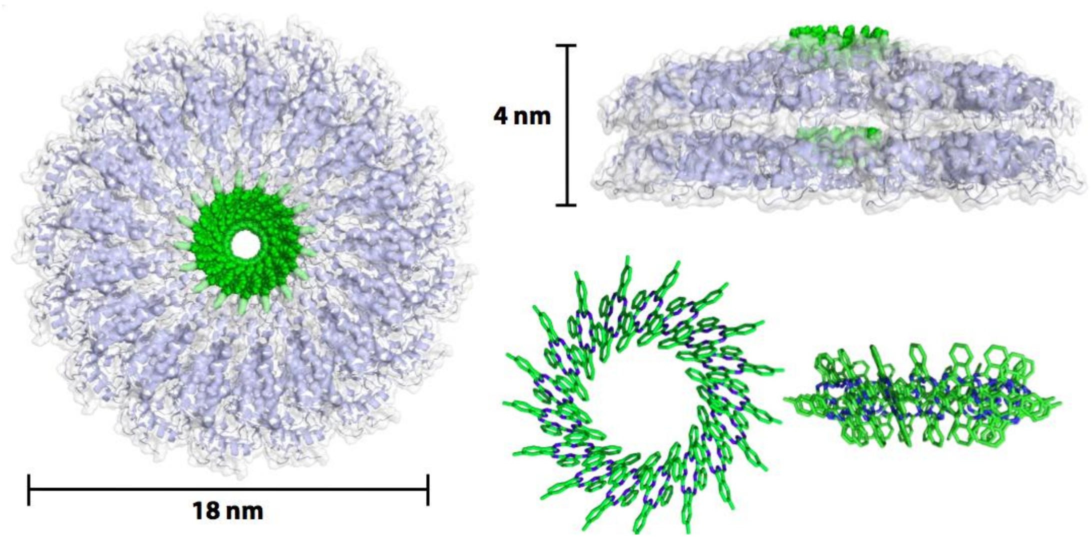
TMV123 attachment (coarse), with disorder

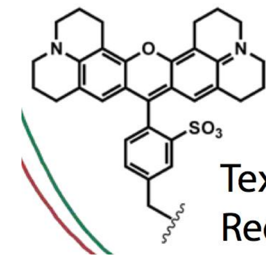


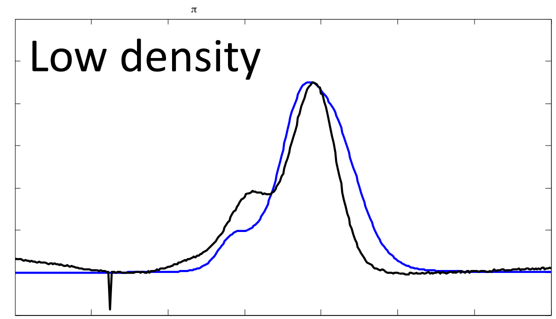


Rational design step 1: Choosing pigment/s

TMV modification with the Texas Red chromophore

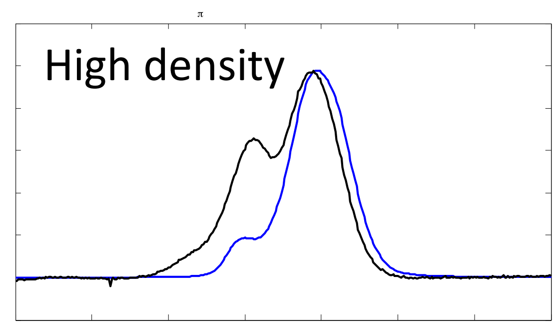






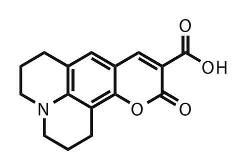
Black – experiment

Blue – theory



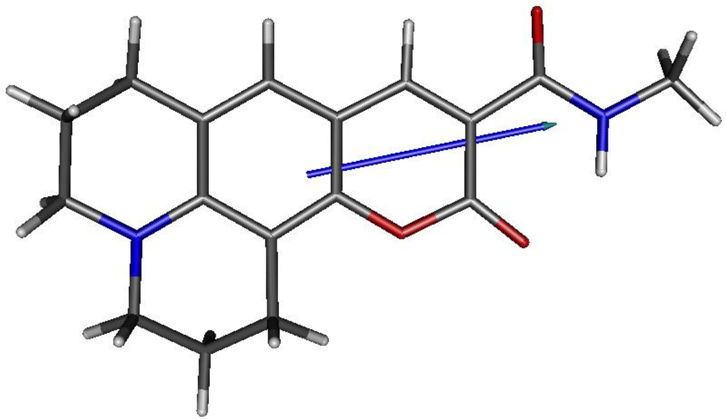
Problems with Texas Red:

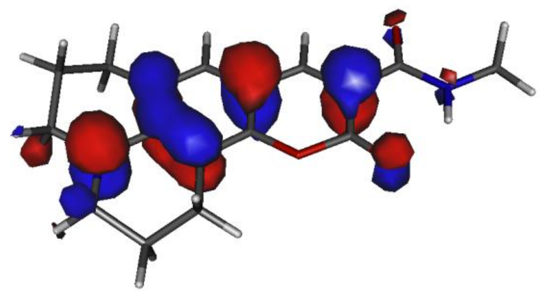
- Multiple dipoles, not taken into account in minimal model
- Too large, flexible, orientation uncertain
- interactions between chromophores not well known



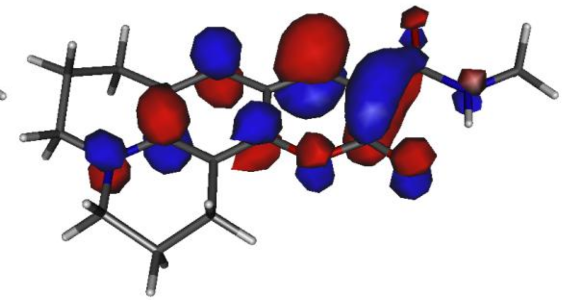
Coumarin 343

Rational design: microscopic analysis





HOMO

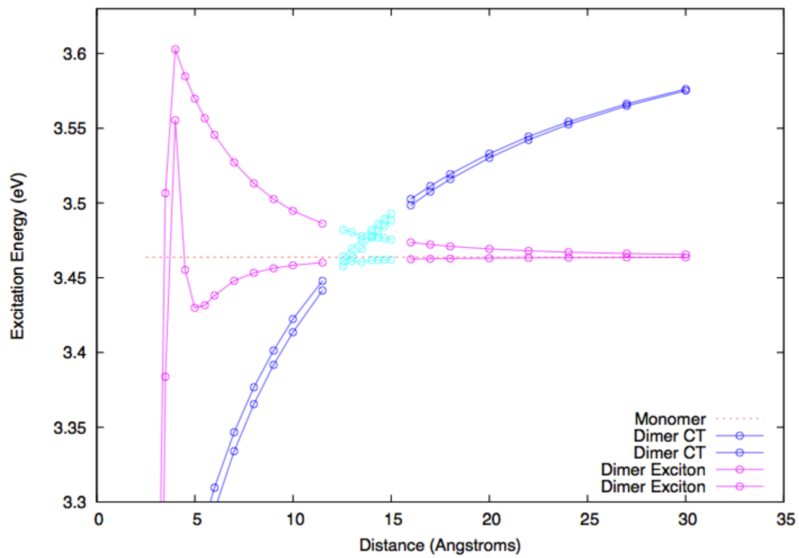


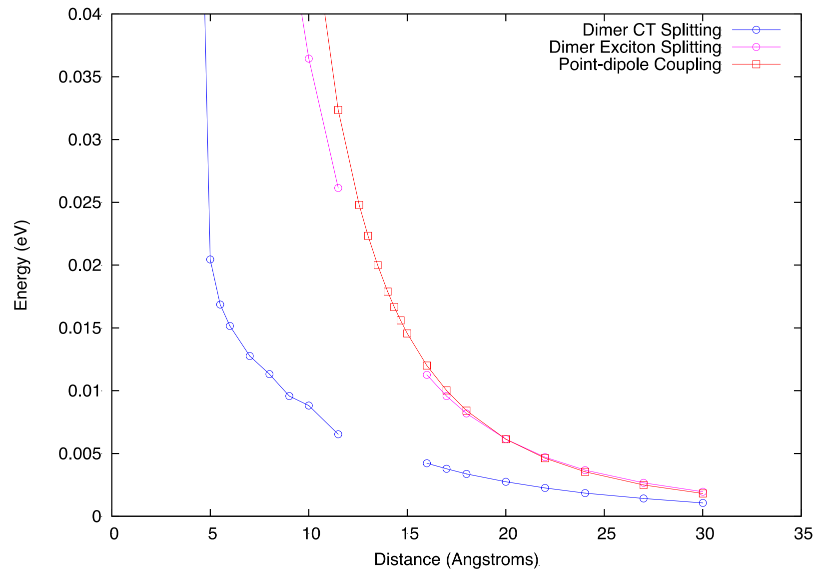
LUMO

- Time-dependent density functional theory has been used to determine the excitation energies and transition dipoles of coumarin-343
  - TD-B3LYP/6-31G* excited states for coumarin compared well with EOM-CCSD results.
  - Multiple functionals and basis sets were explored
- Coumarin-343 TDDFT results
  - Excitation energy – 3.465 eV (358 nm)
  - Transition dipole – 2.64 D (osc. str. 0.591)
  - PCM (implicit dielectric) water shifted results to
    - 3.199 eV (388 nm) and 2.99 D (osc. str. 0.703)
  - Experimental absorption at 446 nm in water
  - First bright state corresponds to HOMO – LUMO excitation

Rational design: microscopic analysis

Interaction of Two Coumarin Dyes

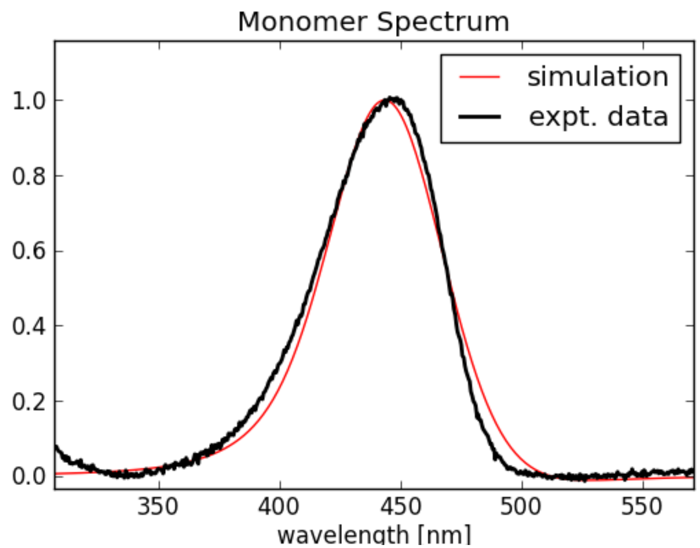


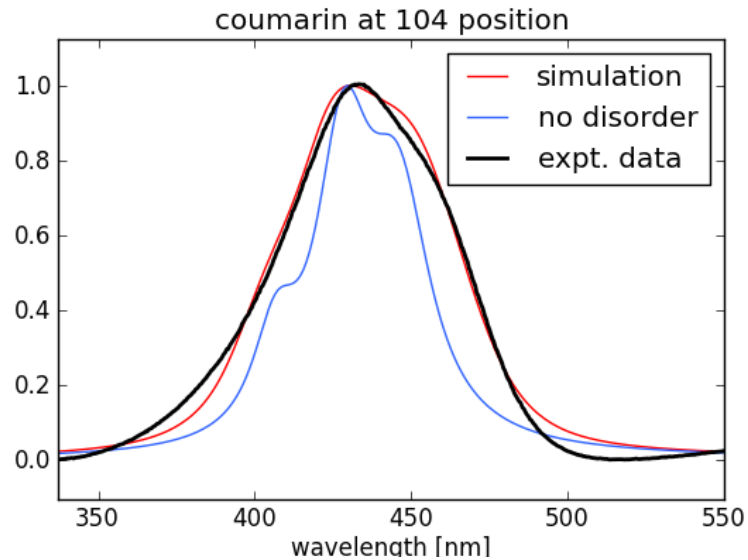


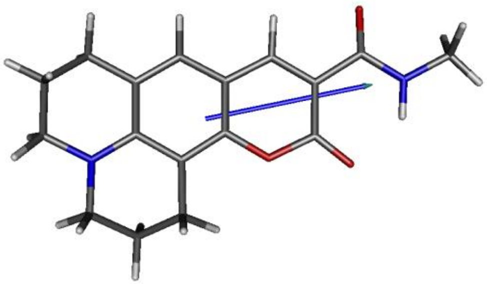
- TD-B3LYP was also used for the two-dye case (aromatic rings stacked parallel)
- Four states emerge, corresponding to the dipole-coupled exciton states and two charge-transfer states – bright state is higher exciton state
- According to TD-B3LYP the relative error for the point-dipole model falls below 10% at 15 Angstroms
- Mixing between CT and exciton states occurs between 12 and 15 Angstroms
- Higher level theory will be used to determine the accuracy of TDDFT for the CT states

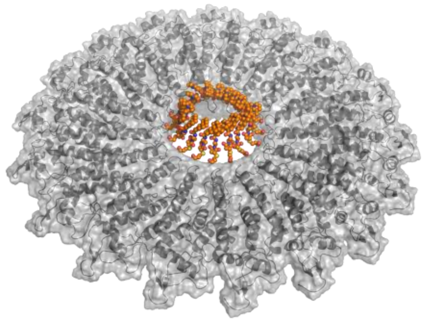
Rational design: microscopic analysis

Fits to experimental spectra





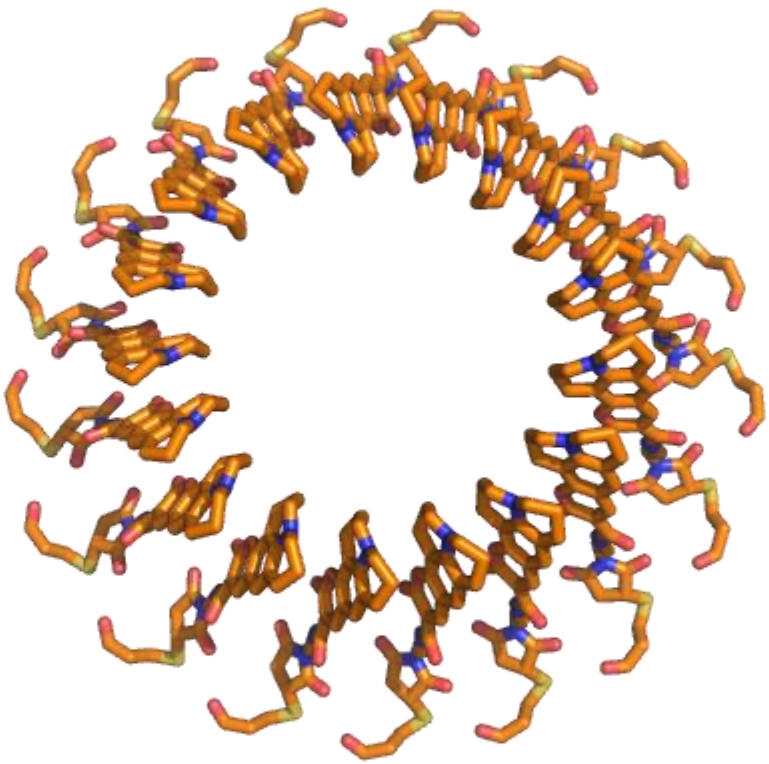




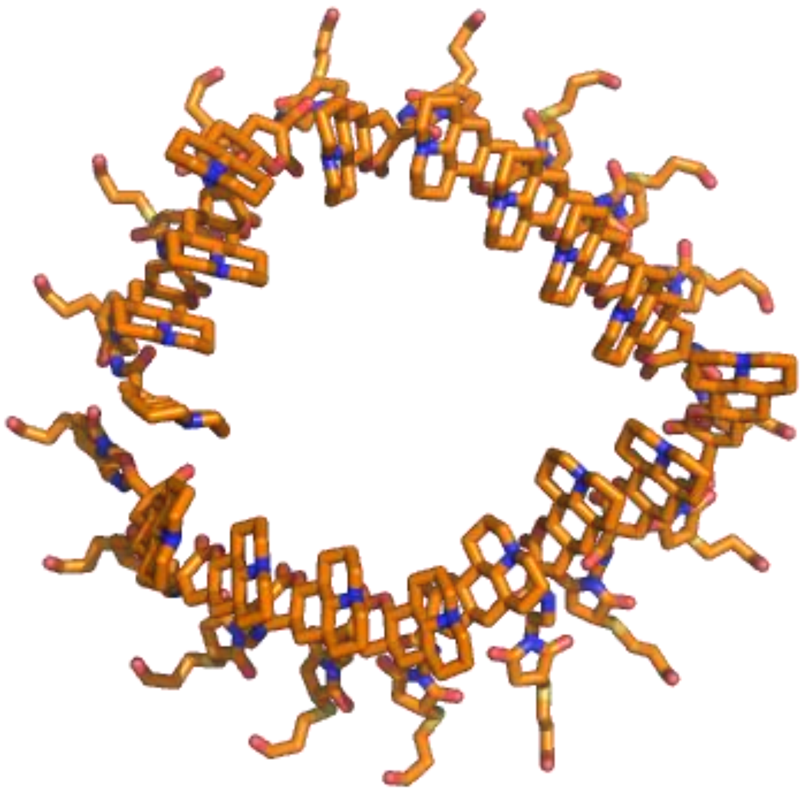
Rational design: microscopic analysis

TMV-templated assembly II:

Molecular Mechanics minimization of coumarin energy within the TMV pore



Initial condition



After energy minimization

Rational design: steps

Microscopic modeling

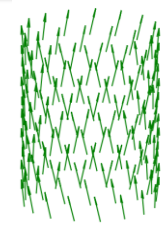
Electronic structure for individual and few coupled pigments

Molecular mechanics to describe aggregation and self-assembly

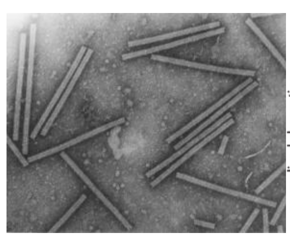
(Quantum informed) rational design

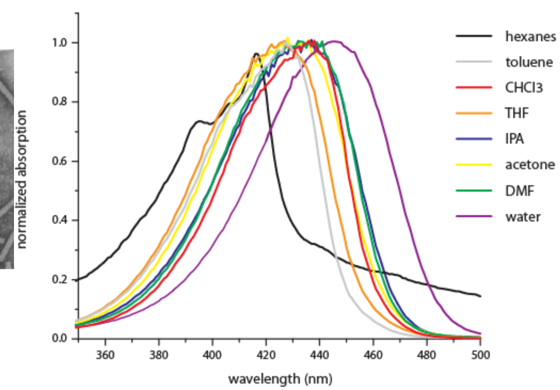
Effective theories, minimal models

Assess charge and energy transfer, and optical properties , match to experimental spectra



Experimental synthesis and characterization





Bottom-up approach: goals

(1) An understanding of the structure-function relationships, and how structure dictates quantum and functional properties

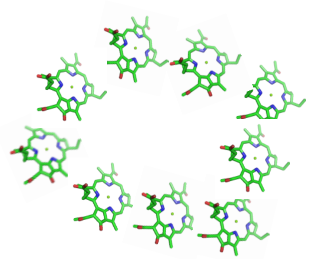
(1) Construct synthetic systems based on theoretical design principles. Goal is to create biomimetic light antenna that:

- mimics the fantastic efficiency (in light capture and excitation transport) of natural LHCs
- has tunable properties (e.g, absorption window)
- is stable in and suited to biological environments

Recipe

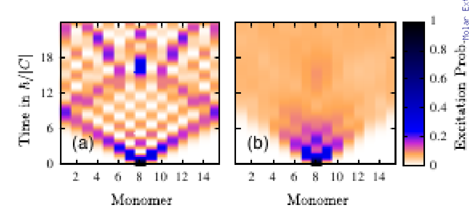
…

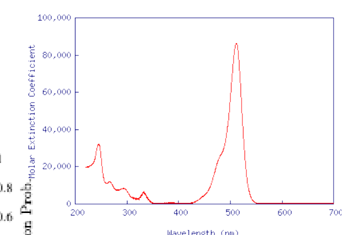
…



Tailored structure

Tailored optical and transport properties





Acknowledgements

Prof. K. Birgitta Whaley
Prof. Graham Fleming
Prof. Matthew Francis
Dr. Akihito Ishizaki
Stephan Hoyer
Donghyun Lee
Daniel Finley

QuBE and QuEST programs

Backup slides

Pigment-protein dynamics

A non-perturbative, non-Markovian treatment

THE JOURNAL OF CHEMICAL PHYSICS **130**, 234111 (2009)

Unified treatment of quantum coherent and incoherent hopping dynamics in electronic energy transfer: Reduced hierarchy equation approach

Akihito Ishizaki and Graham R. Fleming[a)]
Department of Chemistry, University of California, Berkeley, California 94720, USA and Physical Bioscience Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

A1) ***Linear Coupling*** of Protein Environment:

$$H_{\text{el-ph}} = \sum_{j=1}^{N} V_j^{\text{el}} u_j^{\text{ph}}$$

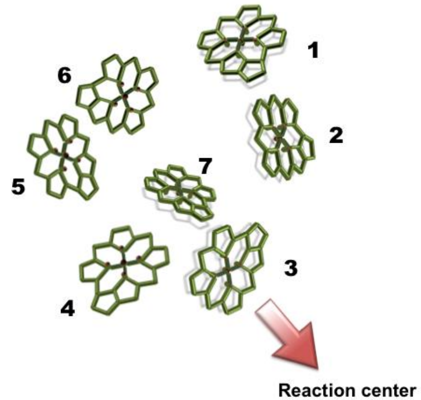
Typical photosynthetic systems

$$J \sim \lambda \sim \frac{\hbar}{\tau}$$

A2) ***Environmental fluctuations are Gaussian***

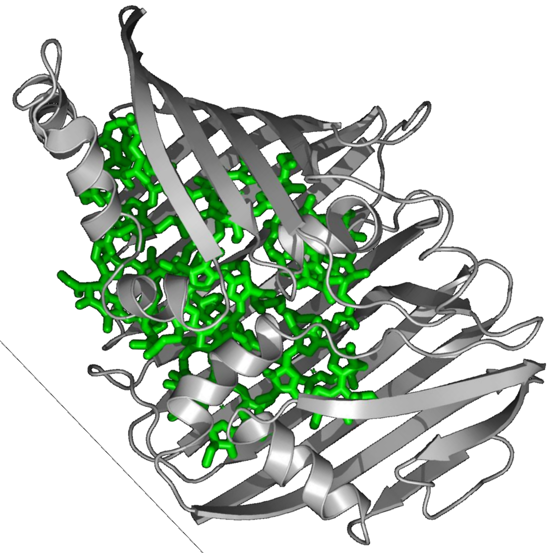
- Based on a cumulant expansion of full propagator
- Fluctuation-dissipation relation preserved
- Has successfully (quantitatively) modeled dynamical properties of light harvesting systems [A. Ishizaki & G. R. Fleming. PNAS **106**, 17255 (2009)]

Dynamics of Light Harvesting:



- Fenna-Matthews-Olson (FMO) is prototypical LH complex
- 7 chromophores (pigments), Frenkel excitons
- Well characterized from pump-probe experiments[1] and theoretical modeling[2].

- Closed system (excitonic) dynamics[2]: $H_{\rm el} = \sum_n E_n |n\rangle\langle n| + \sum_{n\neq m} J_{nm} |n\rangle\langle m|$



But pigment complex is an open quantum system:

Reorganization energy: $\lambda = 35\mathrm{cm}^{-1}$
(from exciton-phonon coupling)

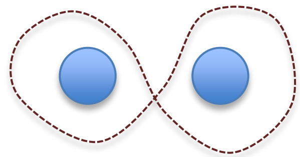
Phonon relaxation time: $\tau = 100fs \;\; (\hbar/\tau = 53cm^{-1})$

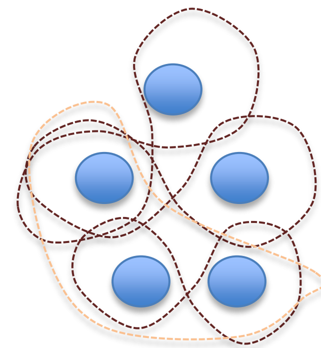
Reaction center trapping rate: $(4\mathrm{ps})^{-1}$

[1] A. Freiberg, S. Lin, K. Timpmann & R. E. Blankenship, J. Phys. Chem. B 101, 7211 (1997)
[2] J. Adolphs & T. Renger, Biophys. J. 91, 2778 (2006).

Quantifying entanglement

- An active field of study





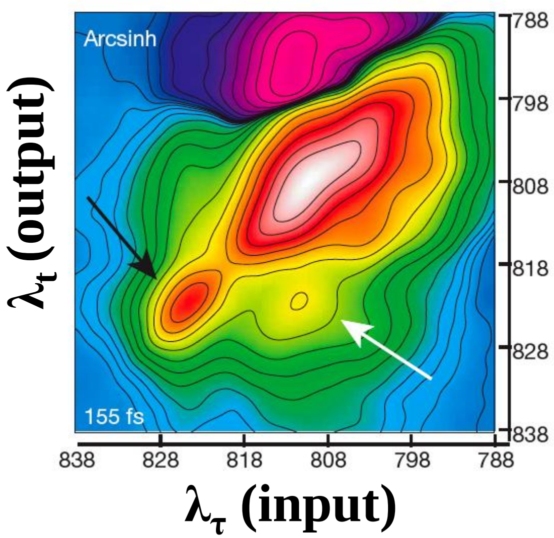
	2-body	many-body
Pure states $\lvert\psi\rangle_{abc\ldots}$	✔ •Unique, easily computable measure $$E(\lvert\psi\rangle_{ab}\langle\psi\rvert) = S(\mathrm{tr}_{\,a}\,\lvert\psi\rangle_{ab}\langle\psi\rvert)$$ $$S(\rho) = -\mathrm{tr}\,[\rho\log_2\rho]$$	? • No unique measure • Difficult to compute • Many classes of entanglement • Key to computational complexity of many-body states
Mixed states $\rho_{abc\ldots}$	? $$E_D, E_F, E_R$$ • No unique measure • Sometimes difficult to compute	? • No unique measure • Difficult to compute • Many classes of entanglement

Probing the ultrafast: ultrafast spectroscopy

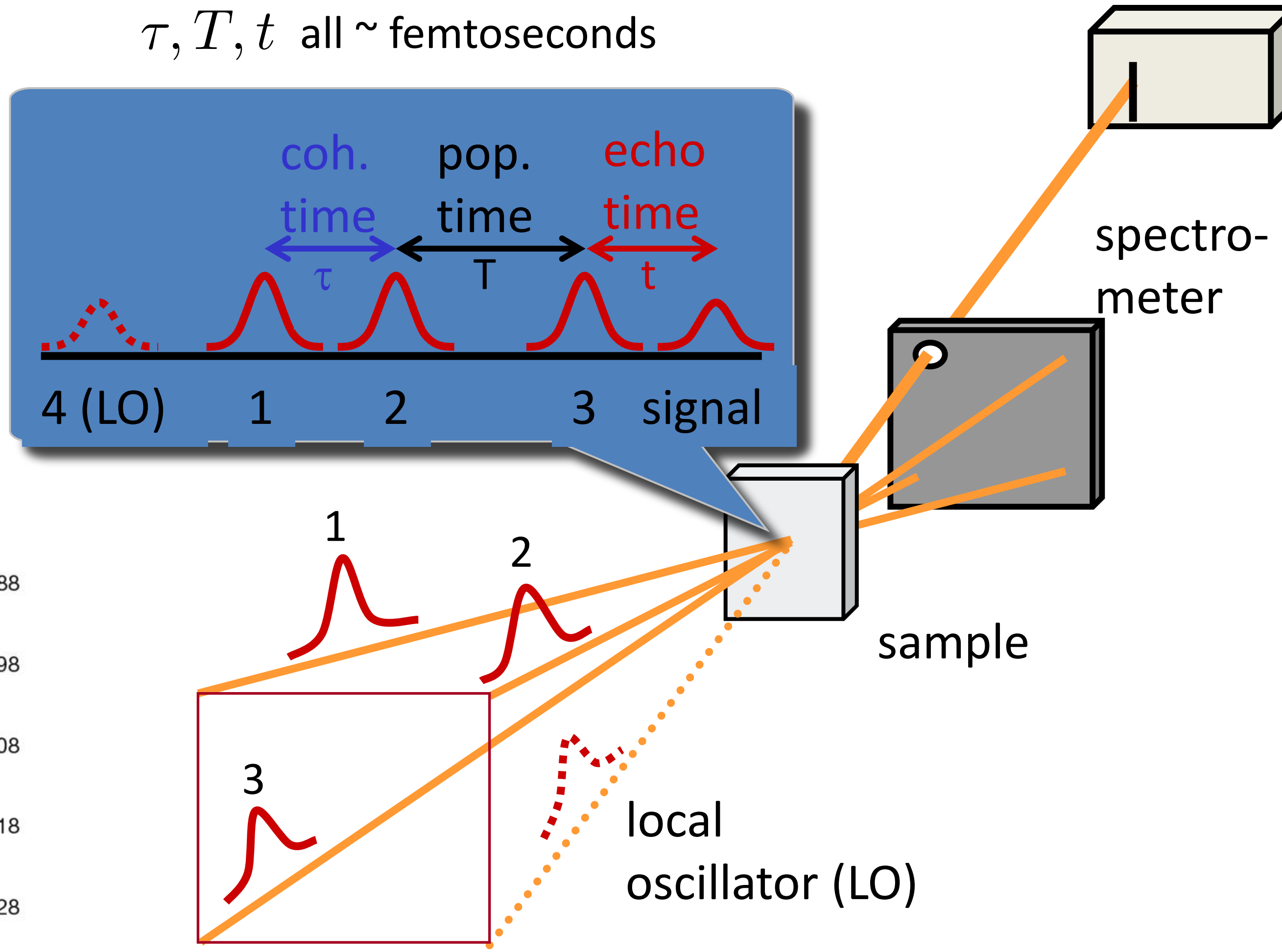
$E_s(\tau, T, \omega_t)$

Fourier transform along τ

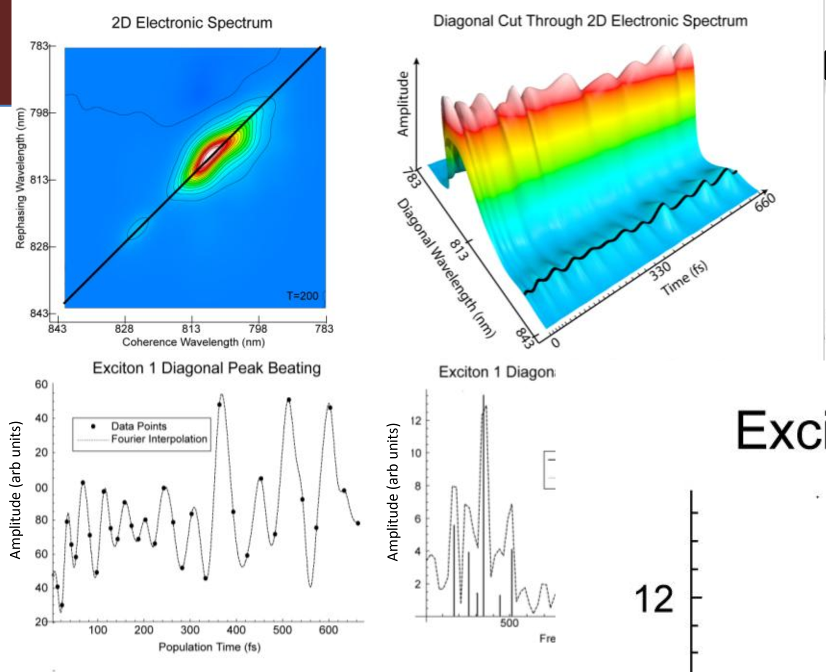
$E_s(\omega_\tau, T, \omega_t)$



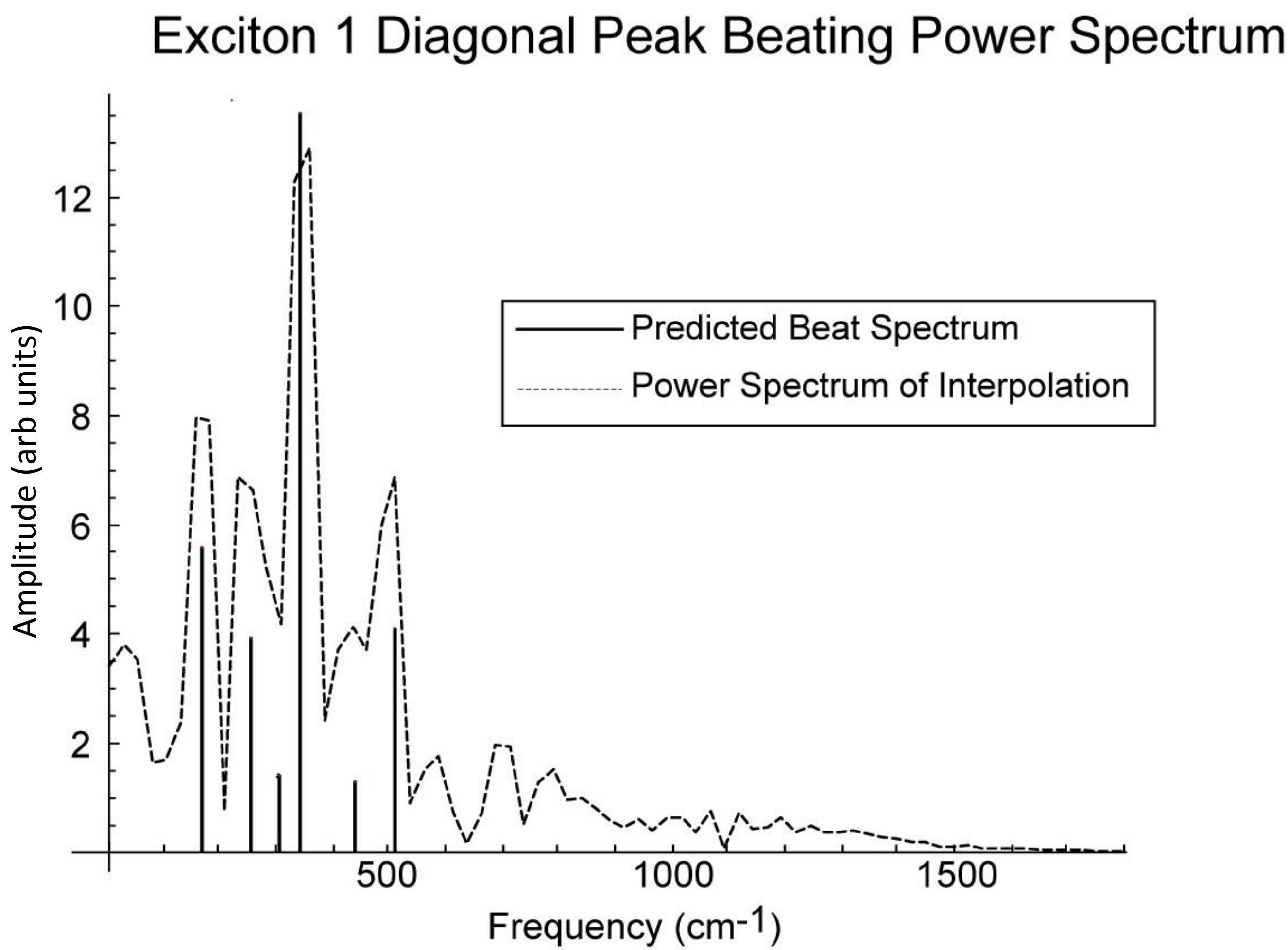
τ, T, t all ~ femtoseconds



ence in FMO (77K)



l Cut Through 2D Electronic Spectrum



- Oscillatory si coherence
- Electronic po persists: no s
- Strong evide

"Evidence for wavelike ene systems", G.S. Engel, T.R. Ca R.E. Blankenship, and G. R.

Quantum entanglement in the FMO complex

Entanglement

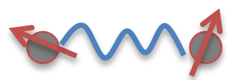
- Formal definition:

Entangled <=> Not separable

Separable state: $|\psi\rangle_{abc\ldots} = |\psi\rangle_a \otimes |\psi\rangle_b \otimes |\psi\rangle_c \otimes \ldots$

generalization: $\rho_{abc\ldots} = \sum_i p_i \rho_a^i \otimes \rho_b^i \otimes \rho_c^i \otimes \ldots$

e.g.



$$|\psi\rangle_{ab} = \frac{1}{\sqrt{2}}(|\uparrow\rangle \otimes |\downarrow\rangle + |\downarrow\rangle \otimes |\uparrow\rangle)$$

$$S[\rho] = -\mathrm{tr}(\rho \log \rho)$$

$$S(|\psi_{ab}\rangle \langle\psi_{ab}|) = 0$$

"Best possible knowledge of the whole does not include best possible knowledge of its parts"
– Schrödinger, 1935

$$\rho_a = \frac{1}{2}(|\uparrow\rangle\langle\uparrow| + |\downarrow\rangle\langle\downarrow|) \qquad \rho_b = \frac{1}{2}(|\uparrow\rangle\langle\uparrow| + |\downarrow\rangle\langle\downarrow|)$$

$$S(\rho_a) = S(\rho_b) = 1$$

"[Entanglement is] *the* characteristic trait of QM, the one that enforces its entire departure from classical lines of thought." -- Schrödinger, 1935

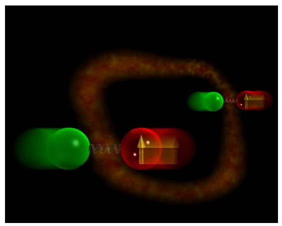
MAY 15, 1935 PHYSICAL REVIEW VOLUME 47

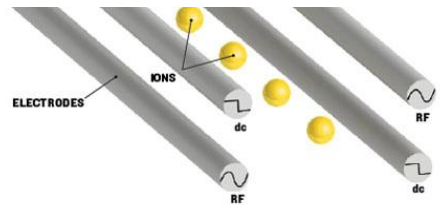
Can Quantum-Mechanical Description of Physical Reality Be Considered Complete?

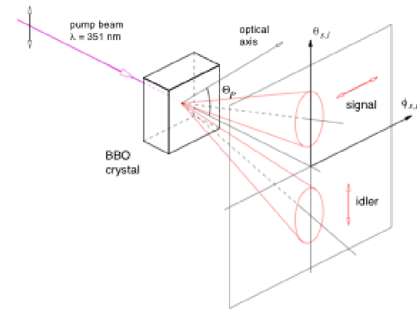
A. Einstein, B. Podolsky and N. Rosen, *Institute for Advanced Study, Princeton, New Jersey*

Manifestations of entanglement

- A resource for several tasks:
    - quantum information processing
    - quantum communication (teleportation, super-dense coding)
    - quantum cryptography
    - quantum metrology







Low temperature and/or low noise experiments. Even small deviations from ideal conditions rapidly degrades entanglement.

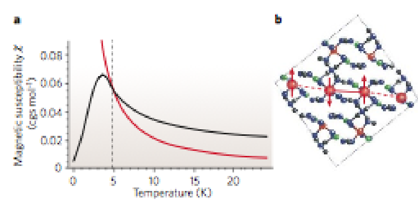


Figure 3 | Susceptibility as a macroscopic witness of entanglement. a, The

Entangled quantum state of magnetic dipoles

S. Ghosh[1], T. F. Rosenbaum[1], G. Aeppli[2] & S. N. Coppersmith[3]

Nature **425**, 48 (2003)

Can it exist in biological systems?
At physiological temperatures?

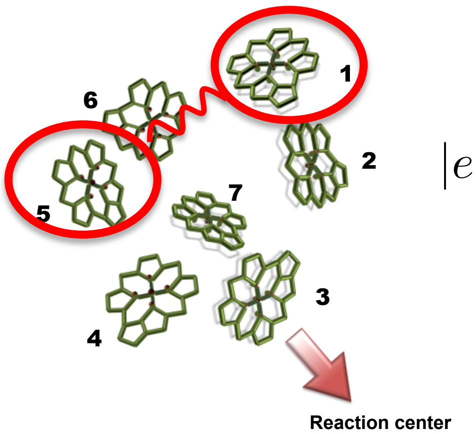
Quantifying entanglement in macroscopic systems

Vlatko Vedral[1,2,3]

Nature, **453**, 1004 (2008)

Quantifying entanglement in LHCs

- Entanglement = non-classical correlations between the electronic states of separated chromophores



$$|e_1\rangle = \alpha|\phi_g^1\rangle|\phi_e^2\rangle + \beta|\phi_e^1\rangle|\phi_g^2\rangle$$

Delocalization a sure sign of entanglement, but how long are excitons delocalized for?

- Multi-partite, mixed-state entanglement ?

- Simplification: single excitation subspace
- *In vivo* conditions for FMO: single excitation enters from baseplate

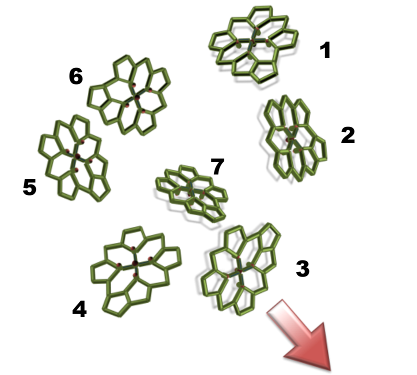
1. Multipartite, global entanglement measure: based on the *relative entropy of entanglement*

$$E[\rho] = -\sum_{i=1}^{N} \rho_{ii} \ln \rho_{ii} - S(\rho)$$

2. Bipartite entanglement measure: *concurrence* [Hill, Wootters , Phys. Rev. Lett. **79**, 5022 (1997)]

M. S., A. Ishizaki, G. R. Fleming, K. B. Whaley, Nature Physics **6**, 462 (2010)

Dynamics of FMO



- Well characterized from pump-probe experiments[1] and theoretical modeling[2].

- Closed system dynamics[2]:

$$H_{\mathrm{el}} = \begin{pmatrix} 200 & -96 & 5 & -4.4 & 4.7 & -12.6 & -6.2 \\ -96 & 320 & 33.1 & 6.8 & 4.5 & 7.4 & -0.3 \\ 5 & 33.1 & 0 & -51.1 & 0.8 & -8.4 & 7.6 \\ -4.4 & 6.8 & -51.1 & 110 & -76.6 & -14.2 & -67 \\ 4.7 & 4.5 & 0.8 & -76.6 & 270 & 78.3 & -0.1 \\ -12.6 & 7.4 & -8.4 & -14.2 & 78.3 & 420 & 38.3 \\ -6.2 & -0.3 & 7.6 & -67 & -0.1 & 38.3 & 230 \end{pmatrix}$$

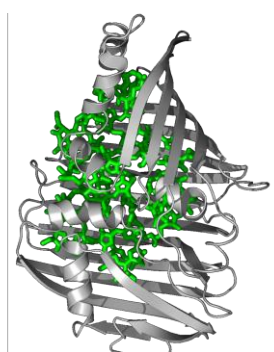
(in cm^{-1})

- The open system dynamics captured using the reduced hierarchy approach (no perturbative approximations)

THE JOURNAL OF CHEMICAL PHYSICS **130**, 234111 (2009)

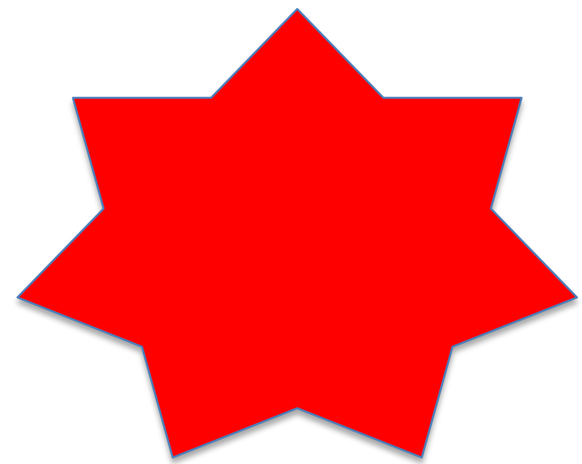
Unified treatment of quantum coherent and incoherent hopping dynamics in electronic energy transfer: Reduced hierarchy equation approach

Akihito Ishizaki and Graham R. Fleming[a)]
Department of Chemistry, University of California, Berkeley, California 94720, USA and Physical Bioscience Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA



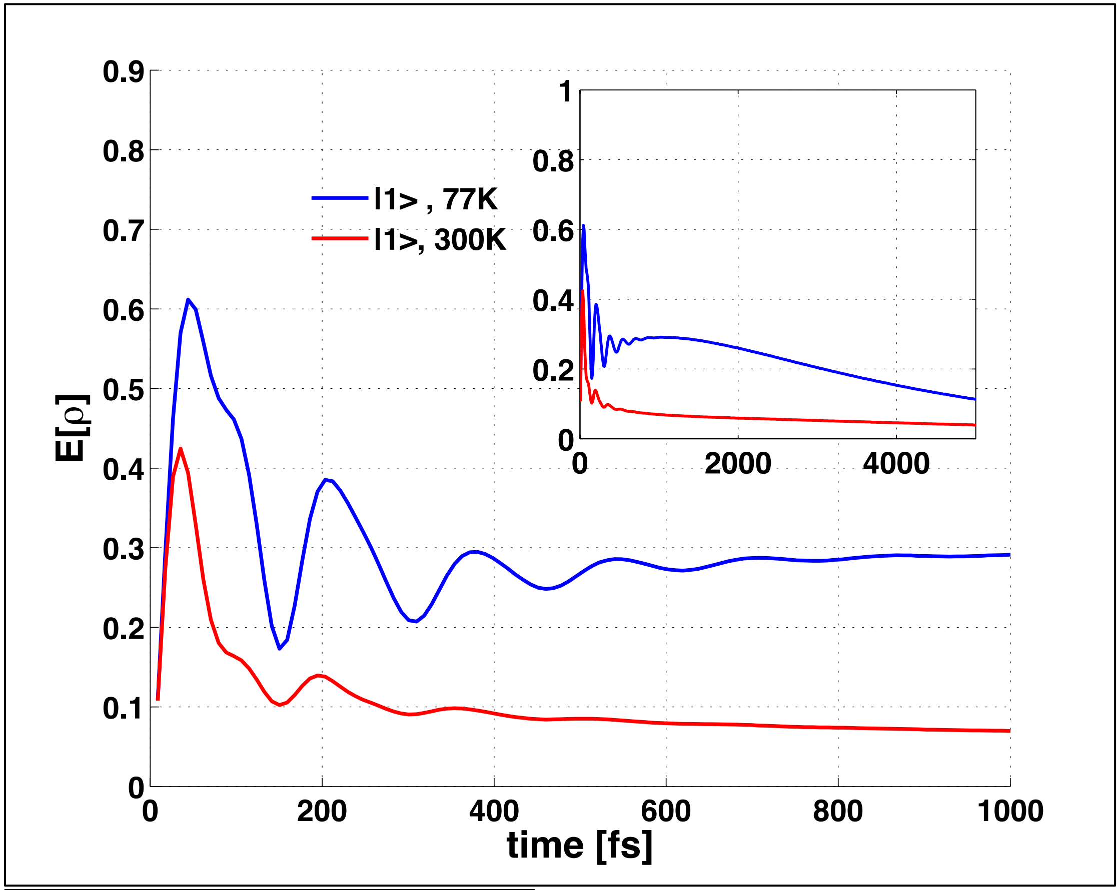
[1] A. Freiberg, S. Lin, K. Timpmann & R. E. Blankenship, J. Phys. Chem. B 101, 7211 (1997)
[2] J. Adolphs & T. Renger, Biophys. J. 91, 2778 (2006).

More about Aki's model

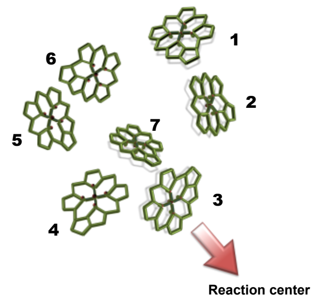


Entanglement in FMO

Global entanglement



Reorganization energy: 35 cm^{-1}
Phonon relaxation time: 100 fs
Reaction center trapping rate: $(4\ ps)^{-1}$

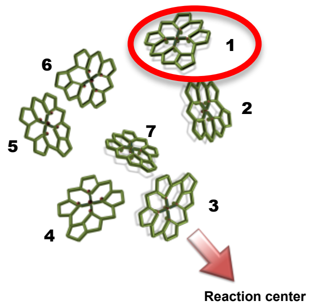


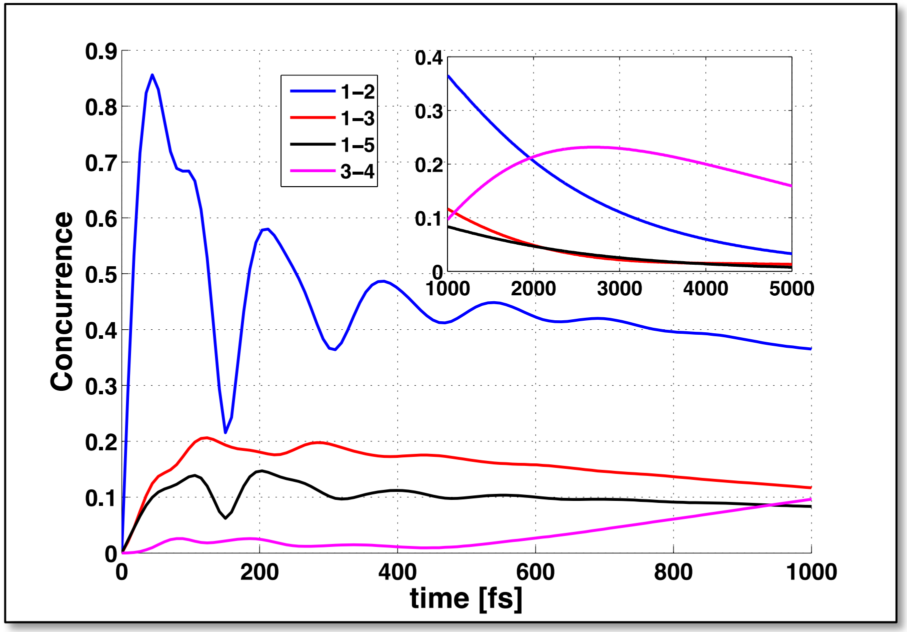
- Large amounts of global entanglement at short times (<500fs)
- Increasing temperature only scales entanglement by ~3/4
- Significant entanglement at long times (steady-state). Limited by trapping dynamics

M. S., A. Ishizaki, G. R. Fleming, K. B. Whaley. Nature Physics, **6,** 462 (2010)

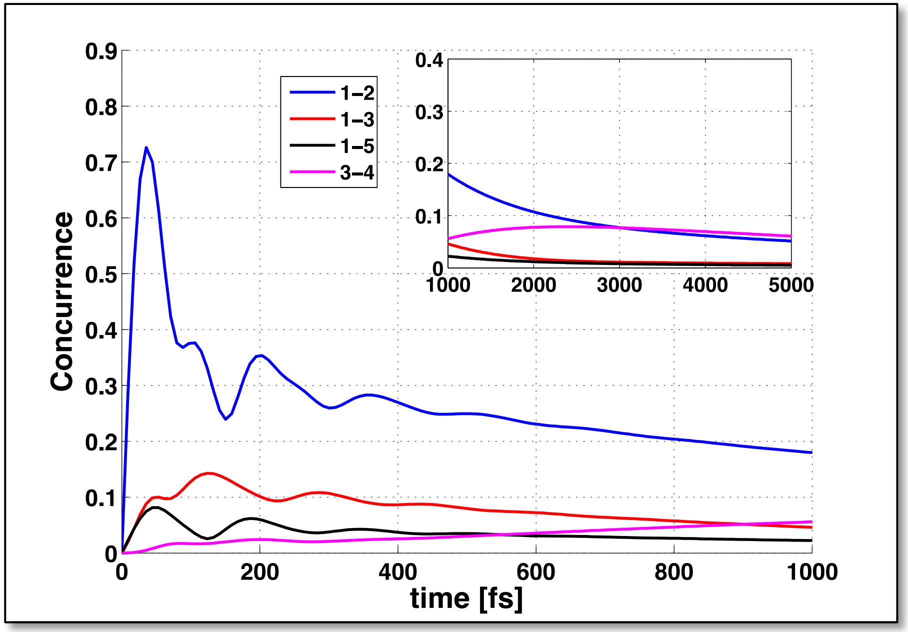
Entanglement in FMO

Bipartite entanglement – initial state: site 1





77K



300K

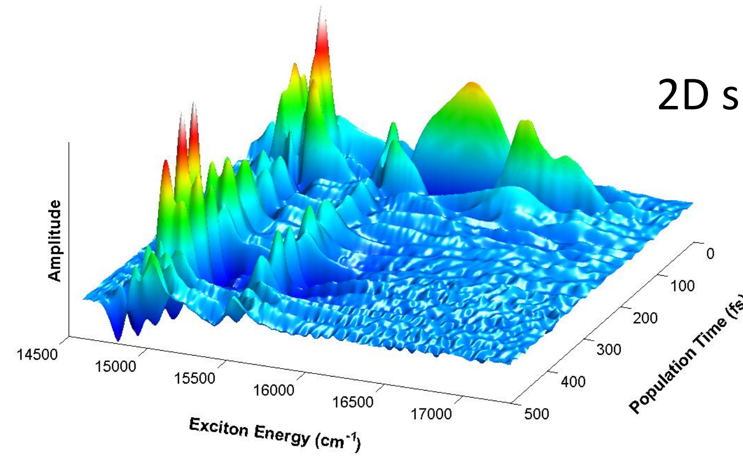
- Bipartite entanglement across multiple cuts → multipartite entanglement
- "Long-range" entanglement between sites 1 and 3 (~ 3nm separation)!
- Temperature damps entanglement, but not significantly at short times

M. S., A. Ishizaki, G. R. Fleming, K. B. Whaley. Nature Physics, **6,** 462 (2010)

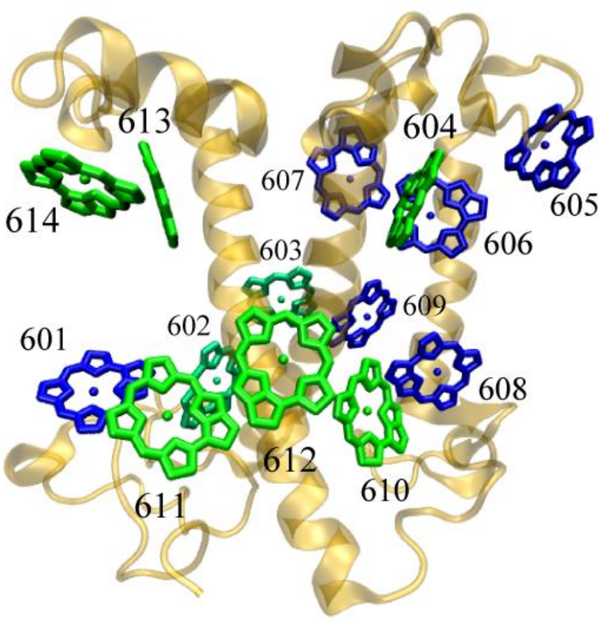
Entanglement dynamics in LHC-II

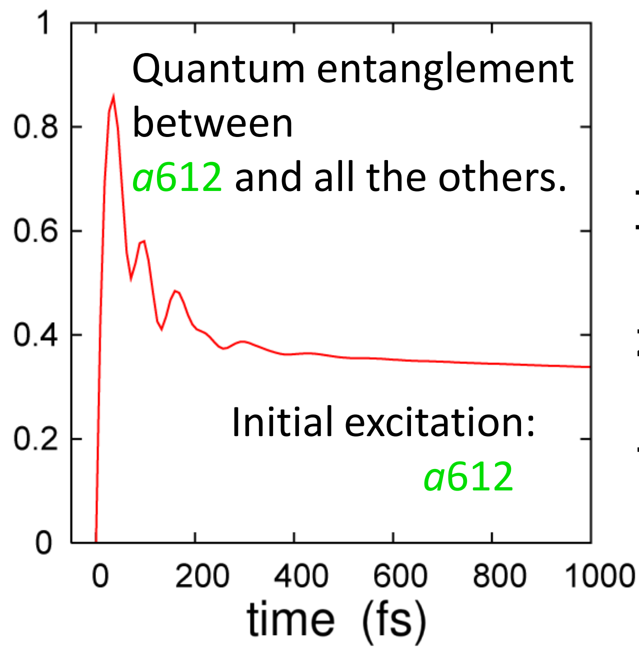
component of PSII,
~50% green matter
on earth

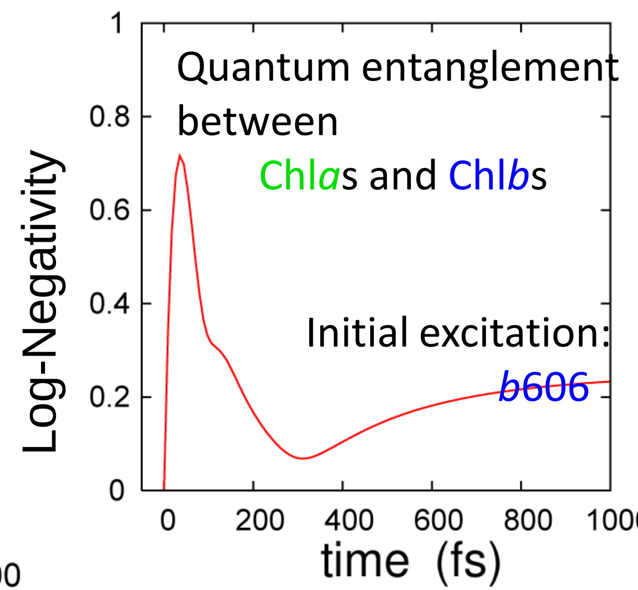
2D spectrum



Monomeric subunit of LHCII
isolated from spinach







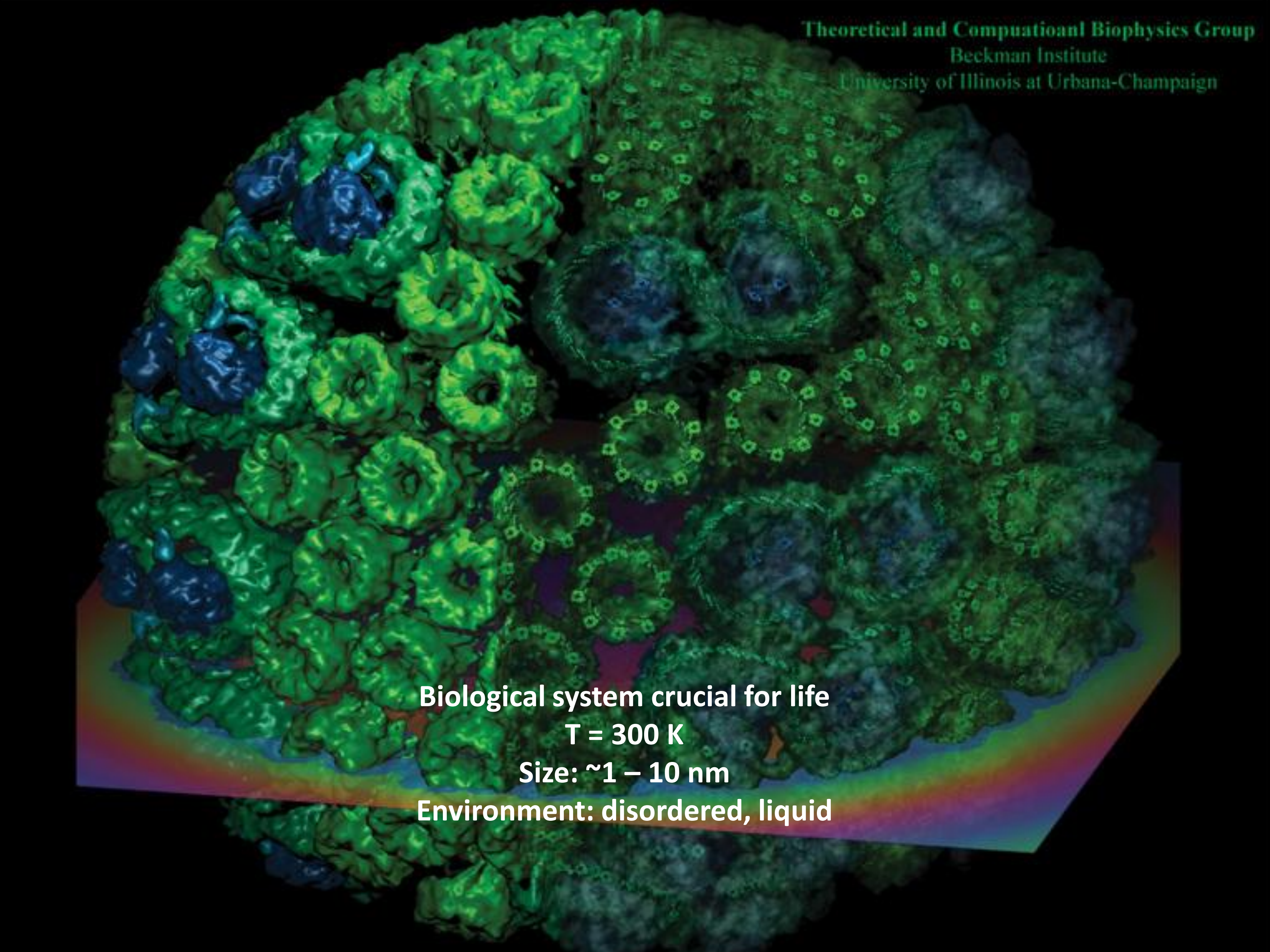
8 Chlorophyll *a* molecules (Chl*a*)
6 Chlorophyll *b* molecules (Chl*b*)

A. Ishizaki, G. R. Fleming, New Journal of Physics **12**, 055004 (2010)

Intermission

(1) **Experimental and theoretical evidence** for long-lived quantum coherence during energy transfer process in several light harvesting complexes

(1) **Entanglement**, *the* most remarkable and non-classical feature of quantum systems, manifested in a biological structure.


Theoretical and Compuatioanl Biophysics Group
Beckman Institute
University of Illinois at Urbana-Champaign
Biological system crucial for life
T = 300 K
Size: ~1 – 10 nm
Environment: disordered, liquid