

A Cross-Species Comparison of Excitation Energy Transfer in Red-Lineage Photosystem I

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ABSTRACT

The Photosystem I supercomplex (PSI) is a central component of photosynthesis in plants and algae. Its antenna subunits absorb light and transfer the excitation energy through an interconnected pigment network to the reaction center (RC), where it is converted to chemical energy. Although the excitation energy transfer (EET) in photosystems has been well characterized for individual organisms, evolutionary variation and inconsistent modeling settings have obscured cross-species comparisons, and it remains unclear which common structural features sustain EET efficiency. To address this, we combined kinetic modeling and rate theories to simulate EET processes in multiple red-lineage PSI complexes, each consisting of hundreds of chlorophylls, using the same set of experiment-derived parameters. We performed network analysis to probe how their EET processes respond to structural variation across distinct species. The exciton becomes increasingly delocalized as it approaches the core region of the PSI complexes, creating a strong exciton-energy gradient (EEG) that funnels it to the RC. However, the EEG is effective only over a limited distance range from the core region. In large PSI complexes, the pigments farther from the RC are weakly coupled, thereby hampering EET. In the larger PSI complexes, the efficiency of long-range EET is maintained by additional features that complement the EEG, such as the pigment composition at the periphery of the antenna, which also broadens the energy range of light absorption. By comparing red-lineage PSI complexes with a common parameter set, we provide a framework for relating EET to structural rearrangements in the pigment network.

I. INTRODUCTION

The Photosystem I supercomplex (PSI) is a pigment-protein assembly central to photosynthesis in plants and algae. All PSI complexes share a structurally similar central region, namely the PSI core, which consists of two large protein subunits, PsaA and PsaB. The core subunits bind numerous pigments that convert absorbed light into electronic excitation (excitons), which is transferred through the pigment network until it reaches the reaction center (RC) located at the interface between PsaA and PsaB.¹ The RC then uses the energy of the exciton to drive charge separation, the primary photochemical step of the light-dependent reactions of photosynthesis. Surrounding the PSI core subunits are peripheral antenna subunits that bind additional pigments, which enlarge the light-harvesting cross section and transfer excitons inward to the core subunits and ultimately to the RC.

The number of antenna subunits, their structural arrangement, and their pigment composition vary widely from species to species. In the PSI of the green lineage (plants and green algae), the antenna is composed of light-harvesting complex *a* (Lhca) subunits that bind chlorophylls (Chl) *a* and *b*.² In the PSI of the red lineage, the antenna comprises Lhcr, Lhcf, Lhcq, and RedCAP subunits that bind Chl *a* and Chl *c*.³ Across different red-lineage species, the size of the antenna region of PSI ranges from five subunits binding slightly more than one hundred pigments to more than thirty subunits binding over five hundred pigments.⁴⁻⁸ This structural diversity raises the question of how the trade-off between light absorption and excitation-energy transfer (EET) efficiency is managed: a larger antenna captures more photons, but it also lengthens the path the excitation must travel to reach the RC,⁹ increasing the probability that it is dissipated before it arrives.

Nevertheless, PSI complexes from distinct species sustain quantum yields exceeding 95%.^{1, 6, 10}

The structure-function relationship of PSI complexes has been studied extensively, from their overall architecture to their individual protein subunits, and both experimental and theoretical investigations of their EET processes have advanced considerably.^{4-8, 11, 12} Recently, high-resolution structures of several red-lineage PSI complexes have been determined, including those of the unicellular red alga *Cyanidioschyzon merolae*,⁷ the diatoms *Thalassiosira pseudonana*⁵ and *Chaetoceros neogracilis*,⁸ the haptophyte *Isochrysis galbana*,⁴ and the coccolithophore *Emiliania huxleyi*.⁶ In parallel, theoretical modeling of EET in photosystems has matured over the past two decades. Kinetic modeling based on a combination of Redfield and generalized Förster theories¹³⁻¹⁶ has been applied extensively to EET in photosystems.^{10, 15-22} These studies enabled the visualization of EET pathways, kinetics, and bottlenecks. Such analyses have identified design principles for energy transfer in photosystems, including how excitation flows through the PSI and PSII supercomplexes,^{10, 20, 22} and why PSII employs both chlorophyll a and chlorophyll b.¹⁷

PSI complexes span a wide range of antenna sizes, and it has not been established how EET efficiency is preserved as the antenna grows or which structural features are shared across species to this end. Although EET has been modeled for individual PSI complexes using the theoretical framework described above,¹⁰ a systematic, comparative cross-species analysis has not been reported.

To address this gap, we model EET in the red-lineage PSI complexes listed above on the basis of their recently determined high-resolution structures. Applying a single parameter set to PSI complexes from distinct species places the comparison on a common basis and

separates the effects of the antenna architecture on EET from those of species-specific parameter choices: a uniform treatment fixes the model choices that influence the computed properties (such as exciton lifetimes) rather than fitting them separately for each species. Four parameter choices are particularly relevant: (1) the charge-separation rate constant at the RC, (2) the threshold of the clustering approach that assigns pigments to delocalized exciton domains, (3) the spectral density that models the coupling of electronic excitation to the vibrational modes of the pigments and the protein environments, and (4) the site-energy landscape, which includes site energy fluctuations within protein subunits, as well as inter-subunit variations. Because these choices have been made independently in single-species studies, the results have been difficult to compare directly across species. Fixing these choices removes this ambiguity and allows the trends across species, and the common features that preserve EET efficiency, to be identified.

Efficient EET to the RC relies on a funneling or ratcheting mechanism that directs energy toward the core and suppresses outward flux; otherwise, stochastic diffusion of excitons across a large antenna could lengthen the excited-state lifetime and lower the quantum yield. In previous studies, funneling has been attributed to redshifted, low-energy Chl dimers acting as gateways towards the RC,^{6, 10} and to a gradient of site energies or exciton energies decreasing towards the core.^{1, 23, 24}

These mechanisms remain an area of active research. Site-energy differences can be classified into two categories. The first is the intra-subunit variation; the site energies of the PSI Chls have been resolved in several first-principles studies, including electrostatic and quantum-chemical calculations,²³ QM/MM molecular dynamics,²⁵ and polarizable QM/MM calculations.²² The second is the inter-subunit variation, which includes a

possible systematic offset between the bulk Chls of the outer antenna and those of the core. Spectroscopic estimates from isolated core and antenna complexes suggest that their mean site energies may differ by several hundred cm^{-1} ;^{10, 11} however, this difference is found to be strongly attenuated in the assembled core–antenna complex.¹⁰

The spatial arrangement of the PSI pigments can also contribute to funneling through a radial exciton energy gradient (EEG) that arises from variations in domain size and coupling with distance from the core. Strong excitonic coupling and mixing with charge-transfer states can lower the exciton energy in tightly coupled Chl dimers, the so-called red forms.^{13, 26-30} Betti et al.²² reported that in plant PSI, the core contains extended domains of exciton delocalization, whereas the antenna domains comprise only a few pigments each, and suggested that these couplings may be instrumental in trapping the excitation.²² Whereas red forms are readily identified spectroscopically, it remains unclear how the domain-size contrast is spatially organized in PSI complexes with a large peripheral antenna, and in particular how far outward from the RC the domain-size-based EEG extends. This question is especially relevant for the larger PSI complexes, whose antenna can comprise several hundred Chls, because dissipation along the extended EET pathways can reduce the quantum efficiency. Analyzing the couplings and site energies of the peripheral pigments can therefore clarify how EET toward the core remains efficient as the antenna grows.

In the following sections, we describe the simulations of EET and the network analyses used to address these questions.

II. COMPUTATIONAL METHODS

A. Overview

A cluster of strongly coupled pigments can form an exciton domain that delocalizes the exciton. The entire EET process can be described as a combination of coherent transitions among the eigenstates of each domain (intra-domain component) and incoherent hopping between domains (inter-domain component). The intra-domain and inter-domain EET are treated with Redfield and generalized Förster theories, respectively.¹⁷⁻¹⁹ The effective inter-domain EET rate constants are calculated by combining both theories. These rates are then used in kinetic equations to model the time evolution of the exciton population across all exciton domains following initial excitation under varying conditions. During the EET process, the total exciton population can be dissipated at pigment sites via non-radiative decay or at the RC by inducing a charge-separation reaction. The time constants of the total exciton population decay are used to characterize the exciton lifetime. The quantum yield is defined as the fraction of the initial population that has undergone charge separation at the RC by the end of the simulation. Based on the time evolution of the exciton population in each domain, network analysis is then performed to characterize the flux of exciton population between domains and to compare it across species.

B. Structures of the PSI Complexes

The structures of the PSI complexes of the five species studied here are taken from the following PDB entries: 5ZGB for *C. merolae*, 8ZEH for *T. pseudonana*, 6LY5 for *C. neogracilis*, 8Z11 for *I. galbana*, and 9JJ8 for *E. huxleyi*. These structures are used to compute the parameters entering the Redfield³¹ and generalized Förster theories below.

C. Definition of Exciton Domains and Belts of Domains

The pigments are partitioned into exciton domains as follows. First, the Hamiltonian matrix of the whole system is constructed in the pigment-site basis, where the diagonal elements are the site energies of the pigments and the off-diagonal elements are the diabatic couplings V_{mn} between pairs of pigment sites m and n :

$$H_{mn} = E_m \delta_{mn} + V_{mn} (1 - \delta_{mn}) \quad \text{Eq 1}$$

where E_m is the pigment site energy of chlorophyll m , V_{mn} is the excitonic coupling between chlorophylls m and n , and δ_{mn} is the Kronecker delta. The site energies E_m depend on the pigment types. The Chl c site energy is set to $15,786 \text{ cm}^{-1}$ (633.4 nm).^{4, 32} The Chl b site energy, relevant only for the plant PSI-LHCI validation (Sec. III A), is set to $15,200 \text{ cm}^{-1}$.³³ The Chl a site energies are assigned by one of two treatments, both referenced to a mean core site energy of $14,800 \text{ cm}^{-1}$.¹⁰ In the stepwise site-energy bias treatment (SSB), following Akhtar et al.,¹⁰ all core Chl a share the value of $14,800 \text{ cm}^{-1}$ and the antenna Chl a are offset above the core by a uniform 65 cm^{-1} . In the binned site-energy bias treatment (BSB), the core Chl a pigments carry a radial profile obtained by binning the plant PSI landscape reported by Betti et. al.²² into $10 \text{ \AA}$ radial bins around the midpoint of the P700 special pair, each core Chl a taking the value of its bin; the antenna Chl a are set to the mean core value plus 51 cm^{-1} . The derivation of this profile, and the analysis of literature site-energy landscapes motivating both treatments, are presented in Sec. III A (Table 1). Static disorder is included by drawing every site energy from a Gaussian of standard deviation 100 cm^{-1} centered on these values. The two treatments, SSB and BSB, are compared in Sec. III A and Sec. III B.

The positions and orientations of pigments determine their couplings V_{mn} 's. The coupling between every pair of pigments is computed from the electrostatic interaction of their transition densities with the Transition Charges from Electrostatic Potentials (TrEsp) method.²⁶ To do so, the transition charges are first scaled to reproduce the full strength of the transition dipole of each chlorophyll type corresponding to the Qy 0–0 band in the vacuum.^{26, 33-35} Using these transition charges and the coordinates of pigments in the PSI structure, the site couplings are calculated and then scaled down. The details of the scaling process are described in Sec. II E. The surrounding protein is treated as a dielectric continuum, and all couplings are eventually scaled by the factor $(n^2+2)^2/9n^2 = 0.889$ for a refractive index $n = 1.4$.¹⁰

After constructing the pigment Hamiltonian, the pigments are grouped into exciton domains following the participation-ratio clustering of Betti et al.^{22, 36, 37} We use two different approaches to include site-energy disorder in the domain-partitioning process. In the first approach, we apply the same disorder-averaged domain-partitioning (described below) to each realization of the EET simulation. This is necessary for inter-domain flux network analysis since the domains need to be consistently defined for all realizations. In the second approach, each EET simulation realization has a distinct domain-partitioning pattern based on the site energies unique to that realization, and the domain partitioning varies across realizations. This domain-partitioning approach explicitly accounts for site-energy fluctuations at the domain level. All reported exciton lifetimes and quantum yields are averaged across all realizations based on the second approach. The results from these two approaches differ from each other by a few ps, as shown in Table S3.

The first domain-partitioning approach is performed as follows. For every pair of pigments m and n we compute the disorder-averaged participation ratio $PR_{mn} = \langle \sum_{\alpha} |c_m^{(\alpha)}|^2 |c_n^{(\alpha)}|^2 \rangle_{\text{dis}}$, where $c_m^{(\alpha)}$ is the amplitude of pigment m in exciton state α of the full, unpartitioned Hamiltonian, $|c_m^{(\alpha)}|^2$ is the corresponding probability, the sum runs over all exciton states, and $\langle \dots \rangle_{\text{dis}}$ denotes an average over 500 realizations of the site energies (Gaussian, $\sigma = 100 \text{ cm}^{-1}$). PR_{mn} is large when the two pigments repeatedly appear in the same exciton states across the disorder ensemble, and small when they do not mix. The co-participation is converted into a dissimilarity, $d_{mn} = 1 - PR_{mn} / \sqrt{PR_{mm}PR_{nn}}$, which ranges from 0 for pigments that always share exciton states to 1 for pigments that never do, and the pigments are grouped by average-linkage hierarchical clustering of d_{mn} , cut at a fixed threshold of 0.80 for all species. The resulting clusters are the exciton domains. Two constraints are imposed on the clustering: couplings between Chl a and Chl c (or Chl b) are omitted at this step, so each domain is homogeneous in pigment type, and the two P700 chlorophylls are always assigned to one domain, so that the charge-separation capacity of the reaction center is counted exactly once. The pigment Hamiltonian matrix is then block-diagonalized. The eigenvectors and eigenvalues of each block are the exciton states $|M\rangle$ and energy levels E_M of each domain:

$$|M\rangle = \sum_m c_m^{(M)} |m\rangle \quad \text{Eq 2}$$

where $c_m^{(M)}$ is the expansion coefficient of exciton state $|M\rangle$ on pigment site m . The frequency of intra-domain transition between states M and N , i.e., ω_{MN} , is calculated from the energy difference between the two states.

To analyze how the antenna's spatial organization affects EET, we group the antenna subunits into concentric belts according to their distance from the conserved core region. Belt 1 contains antenna subunits that have at least one chlorophyll within 30 Å of any core chlorophyll. Belt (k+1) contains the remaining subunits that are within 30 Å of any subunit in Belt k. Figure 1 illustrates the definition of the belts of *E. huxleyi* as an example. We assign each exciton domain to the belt that contains the majority of its constituent pigments. This classification is used to analyze the dependence of EET on the distance from the core.

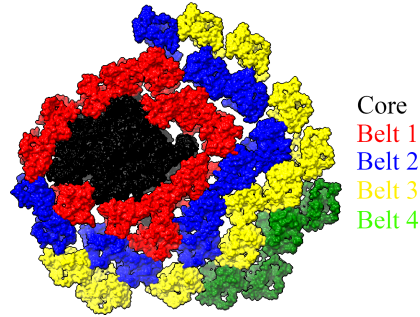


Figure 1. Definitions of belts across the PSI subunits of *E. huxleyi*.

D. Treatment of Vibronic Coupling

The electronic transitions of the chlorophylls are coupled to two classes of nuclear motions: the low-frequency vibrations (phonons) and the high-frequency intramolecular vibrations of the chlorophylls. Both couplings are described by one spectral density having both low-frequency and high-frequency components, $J(\omega) = J_{ph}(\omega) + J_{vib}(\omega)$.^{38, 39} For the low-frequency (phonon) component, we adopt the Renger–Marcus form:¹³

$$J_{ph}(\omega) = \frac{1}{s_1 + s_2} \sum_{i=1,2} \frac{s_i}{2 \cdot 7! \cdot \omega_i^4} \omega^3 \exp \left[- \left(\frac{\omega}{\omega_i} \right)^{1/2} \right] \quad \text{Eq 3a}$$

where $s_1 = 0.8$, $s_2 = 0.5$, $\omega_1 = 0.56 \text{ cm}^{-1}$, and $\omega_2 = 1.94 \text{ cm}^{-1}$. The prefactor $\frac{1}{s_1+s_2}$ normalizes the $J_{ph}(\omega) : \int_0^\infty d\omega J_{ph}(\omega) = 1$, with reorganization energy³⁸ $\lambda_1 = \hbar \int_0^\infty d\omega \omega J_{ph}(\omega) = 78.5 \text{ cm}^{-1}$.

The high-frequency (vib) component consists of the discrete, localized modes of chlorophylls:

$$J_{vib}(\omega) = \sum_k S_k \delta(\omega - \omega_k) \quad \text{Eq 3b}$$

with frequencies ω_k and Huang–Rhys factors S_k taken from the set of modes measured for Chl *a* by differential fluorescence line-narrowing.⁴⁰ The same set of modes is used for both Chl *a* and Chl *c*. The modes below 300 cm^{-1} are removed to prevent double counting, because in this range the vibronic structure has been reported to overlap the phonon sideband and the two cannot be separated unambiguously.⁴¹ The computed lifetimes depend only weakly on the position of this boundary: moving it between 100 and 500 cm^{-1} changes τ by less than 2%. The total vibrational Huang–Rhys factor is found to be $S_{vib} = \sum_k S_k = 0.344$ and the corresponding reorganization energy $\lambda_{vib} = \sum_k S_k \hbar \omega_k = 359.8 \text{ cm}^{-1}$.

E. Calculations of Rate Constants

The rate constants for intra-domain and inter-domain EET are calculated as in previous studies.^{10, 15, 17-19, 22} For intra-domain transitions between a pair of delocalized exciton states M and N of the same domain, we apply Redfield theory:^{22, 24}

$$k_{M \rightarrow N} = 2\pi\omega_{MN}^2 \sum_m |c_m^{(M)}|^2 |c_m^{(N)}|^2 [(1 + n_{BE}(\omega_{MN})) J_m(\omega_{MN}) + n_{BE}(\omega_{NM}) J_m(\omega_{NM})] \quad \text{Eq 4}$$

where $\hbar\omega_{MN} = E_M - E_N$ is the excitonic energy difference, $c_m^{(M)}$ are the expansion coefficients of Eq. 2, n_{BE} is the Bose–Einstein distribution at room temperature ($T = 300 \text{ K}$), and J_m is the spectral density of pigment *m*, defined only for positive frequencies

$J_m(\omega) = 0$ for $\omega < 0$). The site-energy fluctuations of different pigments are taken to be uncorrelated; in this limit exciton relaxation occurs only between states that share amplitude on the same pigments.^{22, 24} The spectral density of each pigment is¹⁰

$$J_m(\omega) = S_m J_{ph}(\omega) \quad \text{Eq 5}$$

where J_{ph} is the unit-normalized phonon spectral density of Eq. 3a and S_m is the Huang–Rhys factor of pigment m . Based on a previous study,¹⁰ we assign $S_m = 0.5$ to the bulk chlorophylls and $S_m = 1$ to the two chlorophylls of the P700 special pair.

Here, the intra-domain Redfield rates of Eq. 4 use the phonon component alone; the intramolecular modes enter only the inter-domain line shapes.³⁹ The rate of transfer from exciton state M_a of donor domain a to state N_b of acceptor domain b ($a \neq b$) is given by:

$$k_{M_a \rightarrow N_b} = \frac{2\pi}{\hbar^2} |V_{M_a N_b}|^2 \int d\omega F_{M_a}(\omega) A_{N_b}(\omega) \quad \text{Eq 6}$$

where $V_{M_a N_b} = \sum_{m_a, n_b} c_{m_a}^{(M_a)} c_{n_b}^{(N_b)} V_{m_a n_b}$ is the coupling strength between the exciton states of the two domains. The integral is the spectral overlap of $F_{M_a}(\omega)$, the fluorescence line-shape function of the donor state, with $A_{N_b}(\omega)$, the absorption line-shape function of the acceptor state. Below we detail the terms entering the line-shape functions:^{10, 13, 17, 18}

$$A_{N_b}(\omega) = \frac{1}{\pi} \text{Re} \int_0^\infty dt e^{i(\omega - \tilde{\omega}_{N_b})t - g_{N_b}(t) - \Gamma_{N_b}t} \quad \text{Eq 6a}$$

$$F_{M_a}(\omega) = \frac{1}{\pi} \text{Re} \int_0^\infty dt e^{i(\omega - \tilde{\omega}_{M_a})t - g_{M_a}^*(t) - \Gamma_{M_a}t} \quad \text{Eq 6b}$$

where the asterisk denotes complex conjugation. Each line shape is specified by three quantities: its center frequency $\tilde{\omega}_M$, its lifetime broadening Γ_M , and its line-broadening function $g_M(t)$. Both line shapes are normalized to unit area on the frequency axis. For each exciton state, the emission line shape differs from the absorption line shape only by the complex conjugation of $g_M(t)$, which makes it the mirror image of the absorption line

shape about $\tilde{\omega}_M$ — the sideband lies below the center frequency in emission and above it in absorption. Following previous work,^{10, 22} the center frequency is the excitonic energy corrected for the reorganization of the bath and for the dispersive part of the exciton–phonon self-energy; the effective energy is defined as¹⁰

$$\tilde{E}_M = \hbar\tilde{\omega}_M = E_M - \lambda_M + \Delta_M \quad \text{Eq 6c}$$

where E_M is the excitonic energy. The reorganization shift λ_M and the dispersive shift Δ_M entering it are

$$\lambda_M = \lambda_1 \sum m \left| c_m^{(M)} \right|^4 S_m \quad \text{Eq 6d}$$

where $\lambda_1 = 78.5 \text{ cm}^{-1}$ is the phonon reorganization energy at unit Huang–Rhys factor as defined after Eq. 3a, and S_m defined in Eq 5. Also,

$$\Delta_M = \hbar \sum_{N \neq M} \sum m \left| c_m^{(M)} \right|^2 \left| c_m^{(N)} \right|^2 S_m \cdot \mathcal{P} \int d\omega \frac{\Phi(\omega)}{\omega_{MN} - \omega} \quad \text{Eq 6e}$$

$\mathcal{P}$ denotes the Cauchy principal value, and $\Phi(\omega) = \omega^2 [1 + n_{BE}(\omega)] J_{ph}(\omega)$ for $\omega > 0$ while $\Phi(\omega) = \omega^2 n_{BE}(-\omega) J_{ph}(-\omega)$ for $\omega < 0$.

Γ_M is obtained from the intra-domain Redfield rates of Eq. 4 out of that state, as in previous studies,^{10, 17}

$$\Gamma_M = \frac{1}{2} \sum_{N \neq M} k_{M \rightarrow N} \quad \text{Eq 6f}$$

Both line shapes are constructed from a single line-broadening function, in which the phonon and intramolecular components enter with different weights,³⁹

$$g_M(t) = \sum m \left| c_m^{(M)} \right|^4 S_m g_{ph}(t) + g_{vib}(t) \quad \text{Eq 6g}$$

$$g_{ph}(t) = \int_0^\infty d\omega J_{ph}(\omega) \left(\coth\left(\frac{\hbar\omega}{2k_B T}\right) [1 - \cos\omega t] + i \sin\omega t \right) \quad \text{Eq 6h}$$

$$g_{vib}(t) = \sum_k S_k \left\{ \coth\left(\frac{\hbar\omega_k}{2k_B T}\right) [1 - \cos\omega_k t] + i \sin\omega_k t \right\} \quad \text{Eq 6i}$$

The scaling of the first term on the right-hand side of Eq. 6g by S_m 's applies only to the low-frequency, delocalized (phonon) modes. The vibronic transitions of the high-frequency intramolecular modes are treated as localized on the individual pigment, so these modes retain full molecular Huang–Rhys factors and are not scaled.^{39, 42, 43} This treatment — delocalized modes for 0–0 transitions with localized vibronic sidebands — follows the complex Redfield scheme with localized vibrations (cR loc. vib.) proposed by Saraceno et al.⁴⁴ Specifically, the line shapes of Eqs. 6d–6h follow their cR approach. Equation 6i follows their loc. vib. approach for the localized high-frequency vibrational modes, which are excluded from the calculation of Redfield rates in Eq. 4 and the dispersive shift in Eq. 6e.

The Qy 0-0 band's transition dipole strength is reduced by vibronic coupling to high-frequency modes. In the calculation of the inter-domain rate constants (Eq 6), since the formalism explicitly accounts for the high-frequency modes, the couplings need to reflect the full strength of the transition dipole and should not be scaled. Thus, the transition charges needed for calculating these couplings are parameterized to represent the full transition dipole of the pigments in the vacuum, which are scaled up from the measured transition dipoles of the Qy 0-0 band by a factor of $e^{S_{vib}}$: $\mu_{Chla}^2 = 21.0e^{S_{vib}} D^2 = 29.6 D^2$ for Chl a and $\mu_{Chlc}^2 = 8.4e^{S_{vib}} D^2 = 11.9 D^2$ for Chl c.^{42, 44} During the construction of the full Hamiltonian matrix (Eq 1), the couplings calculated from the transition charges representing the full-strength transition dipoles are scaled down by a factor of $e^{-S_{vib}}$ (~ 0.709), in accordance with the loc. vib. approach.

The spectral overlap in Eq. 6 is expanded as:

$$k_{M_a \rightarrow N_b} = \frac{2|V_{M_a N_b}|^2}{\hbar^2} \text{Re} \int_0^\infty dt e^{i(\tilde{\omega}_{M_a} - \tilde{\omega}_{N_b})t - g_{M_a}(t) - g_{N_b}(t) - (\Gamma_{M_a} + \Gamma_{N_b})t} \quad \text{Eq 6j}$$

The Redfield and generalized Förster rates are not constructed from the same equilibrium condition. The Redfield rates of Eq. 4 satisfy detailed balance with respect to the bare excitonic energies E_M . The generalized Förster rates of Eq. 6 would satisfy it with respect to the effective energies $\tilde{E}_M$ of Eq. 6c, except that the lifetime broadening Γ_M in their line shapes is symmetric in the transition frequency and contributes equally to the uphill and the downhill member of each pair. The assembled matrix therefore satisfies neither condition exactly. To enforce detailed balance, the downhill rate is retained and the uphill rate is reconstructed from it,²²

$$K_{M \rightarrow N} = K_{N \rightarrow M} e^{-(\tilde{E}_N - \tilde{E}_M)/k_B T} \text{ for } \tilde{E}_N > \tilde{E}_M \quad \text{Eq 7}$$

and the diagonal is then reset so that each column sums to zero.

F. Time Propagation of EET with Master Equations

With all exciton transfer rates defined above, the EET is propagated through time by integrating a network master equation, $dX(t)/dt = QX(t)$, where $X(t)$ is the population of each exciton state at time t and Q is the rate matrix assembled from the intra-domain rates of Eq. 4 within each domain and the inter-domain rates of Eq. 6 between domains, with detailed balance enforced as in Eq. 7. Its diagonal elements $q_{MM} = -\sum_{N \neq M} q_{NM}$ ensure that the overall exciton population is conserved in the absence of the sink sites introduced below. Integration of the master equation yields the time-dependent populations of all exciton states. The time evolution of the total exciton population is integrated to yield

the exciton lifetime τ , and the quantum yield QY for charge separation is the fraction of the initial population absorbed by the charge-separation sink.

Two absorbing sink states are added to the network. The first sink represents charge separation at the reaction center. Following Betti et al²², it is connected to the lowest exciton state of the RC domain. We adopt the charge separation rate constant $k_{CS} = 2.8\text{ps}^{-1}$, corresponding to the effective charge-separation time of approximately 1 ps from the thermally equilibrated RC domain. Reported charge-separation times range from 1 to 3 ps.⁴⁵⁻⁴⁸ The second sink represents intrinsic non-radiative decay of any chlorophyll to its ground state (dissipative loss) with a rate constant $k_{diss} = 2.5 \times 10^{-4} \text{ps}^{-1}$, corresponding to a 4 ns isolated-chlorophyll lifetime.

For the validation against the plant PSI-LHCI model of Betti et al²² (Sec. III A), the settings of that model are adopted instead: $k_{CS} = 2 \text{ps}^{-1}$, no RC-specific reorganization energy (uniform $S_m = 0.5$), and no dissipation channel.

Unless otherwise noted, the initial population of each exciton state is set proportional to its transition dipole strength, $x_{M_a}(0) \propto \left| \sum_m c_m^{(M_a)} \vec{\mu}_m \right|^2$.

G. Absorption Cross-section Calculation

The normalized absorption cross sections are calculated from the exciton states of all domains:

$$\sigma(\omega) \propto \sum_a \sum_{M_a} |\vec{\mu}_{M_a}|^2 \omega A_{M_a}(\omega) \quad \text{Eq 8}$$

where $\vec{\mu}_{M_a} = \sum_{m_a} c_{m_a}^{(M_a)} \vec{\mu}_{m_a}$ is the transition dipole moment of the exciton state M_a , and $A_{M_a}(\omega)$ is the absorption line shape of Eq. 6a.

H. Network Analysis

After the EET has been simulated with the master equation, the time-dependent domain populations and the inter-domain EET fluxes are analyzed by network analysis. Time-integrated cumulative flow parameters are defined to track the EET pathways through which the exciton is delivered to the RC.

The directional cumulative flow from domain i to domain j is defined as $F_{ij} = \sum_{M \in i} \sum_{N \in j} k_{M \rightarrow N} \int_0^\infty X_M(t) dt$,²² where the sums run over the exciton states of the two domains, $k_{M \rightarrow N}$ are the inter-domain transfer rates of Eq. 6, and $X_M(t)$ is the population of exciton state M . Because the master equation is linear, the time-integrated populations are obtained analytically as $\int_0^\infty X(t) dt = -Q^{-1}X(0)$, so the flows are evaluated at full convergence of the dynamics. The product $k_{M \rightarrow N} \int_0^\infty X_M(t) dt$ is the expected number of $M \rightarrow N$ transfers over the entire dynamics.

To delineate the net directional transport pathways, the bidirectional gross flows between each pair of domains are taken into account. To this end, the net cumulative flow (NCF) between the domain pair i, j is defined as the absolute difference between their gross forward and backward fluxes: $NCF(i, j) = |F_{ij} - F_{ji}|$. The resulting flow is assigned the direction of the larger gross flux. Selecting the links with the largest NCF values yields the backbone of the major transport pathways that route excitation from the peripheral antenna to the RC.

To identify the bottleneck and hub domains through which energy is routed, the cumulative input (CI) is computed for each domain j as the sum of its net incoming flows, $CI_j =$

$\sum_{i \neq j} \max(F_{ij} - F_{ji}, 0)$.²² Domains with large CI values are hubs located on the primary EET pathways.

I. Model Assumptions and Species Selection

To enable a consistent comparison of PSI supercomplexes differing in antenna size, the “red form” chlorophylls of PSI are not modeled explicitly for the following reasons. Red forms arise from the interaction between the lowest excitonic transition of closely packed Chl *a* dimers and their charge-transfer states.^{22, 28-30} Both defining properties of the red forms follow from this admixture: the transition energy shifts to the red, and, through the static dipole of the charge-transfer configuration, the coupling to the protein environment increases, giving the mixed state a reorganization energy well above that of bulk Chl *a* and making it a deeper trap than the energy shift alone implies.⁴⁹ A rigorous treatment of red forms therefore requires the explicit inclusion of the charge-transfer states in the Hamiltonian, with their own, much stronger bath coupling,^{22, 29} which is beyond the scope of our model.

A second assumption is that the PSI complexes correspond to their state under normal light conditions. Extreme low- or high-light conditions can substantially alter PSI lifetimes; under high light, this behavior has been ascribed a photoprotective role.⁵⁰ Analogous photoprotective quenching is well characterized in the antenna complexes of PSII.^{36, 51, 52} Under such conditions, some antenna subunits have also been proposed to decouple physically from the core.⁵⁰ Such states would confound a comparison intended to isolate the effect of antenna size on EET. The cross-species comparison is therefore restricted to species whose PSI, under normal light conditions, is reported to contain no deep red traps in the antenna. For example, the diatom *T. pseudonana* has been reported to lack the long-

wavelength Chls typical of plants and cyanobacteria;^{10, 53} the antenna sink of *C. neogracilis* (reported as *C. gracilis*) has been described as shallow;⁵⁴ for *E. huxleyi* the antenna landscape is reported to be flat and free of energy traps;⁶ and for the “medium-light” preparation of *C. merolae*, no long-wavelength Chl pools were detected in the antenna.⁵⁰

III. RESULTS AND DISCUSSION

A. Radial Site Energy Gradient in the PSI Core

The PSI core is reported to be highly conserved across species. To treat its site-energy landscape consistently across species, we examined the landscapes deposited in the literature and found that some of them exhibit a monotonic radial decrease in site energy toward the P700 special pair. As an example, we analyzed the site energies deposited by Betti et al.²² We renormalized these site energies so that the mean core Chl a site energy equals $14,800 \text{ cm}^{-1}$ and binned them in 10 Å radial bins about the midpoint of the P700 special pair. The energy reference (zero) is set to the mean site energy of the core. The binned offsets decrease monotonically toward P700 (Table 1).

Table 1. Mean site-energy offsets of the binned site-energy bias (BSB) profile: the core Chl a of plant PSI-LHCI are grouped into 10 Å radial bins about the midpoint of the P700 special pair, using the deposited site energies of Betti et al.²² The offsets are relative to the mean core Chl a site energy. The number of Chl a per bin is given in the middle column.

Bin (Å)	Number of Chl	$\langle E \rangle - \langle E \rangle_{core} \text{ (cm}^{-1}\text{)}$
0–10	2	–149.2
10–20	4	–76.4
20–30	14	–51.1

30–40	29	–28.7
40–50	25	+8.7
50–60	20	+46.7

Each core Chl *a* was then assigned the mean value of its bin, and each antenna Chl *a* was assigned the mean antenna value, which lies 51 cm^{–1} above the core mean. This core–antenna offset is close to the 50 cm^{–1} used by Akhtar et al. in their structural model of diatom PSI; their estimate of about 65 cm^{–1} is the value adopted in the SSB treatment (Sec. II C).

We compared the network analysis obtained with this coarse-grained landscape (the BSB treatment, Sec. II C) with that obtained directly from the landscape deposited by Betti et al.²² In both cases, and in agreement with Betti et al,²² the excitation converges on the RC domain in the “bikewheel” pattern described by them (Figure 2). The domain sizes follow the expected trend, being largest near the RC in the core and smaller in the antenna. A coarse-grained landscape from the BSB treatment may overestimate exciton delocalization relative to the fully resolved landscape; this effect can be compensated by tightening the domain-inclusion criterion, but the correction has a negligible effect on the lifetimes (see SI section “Sensitivity of the exciton lifetime to the domain-clustering threshold”).

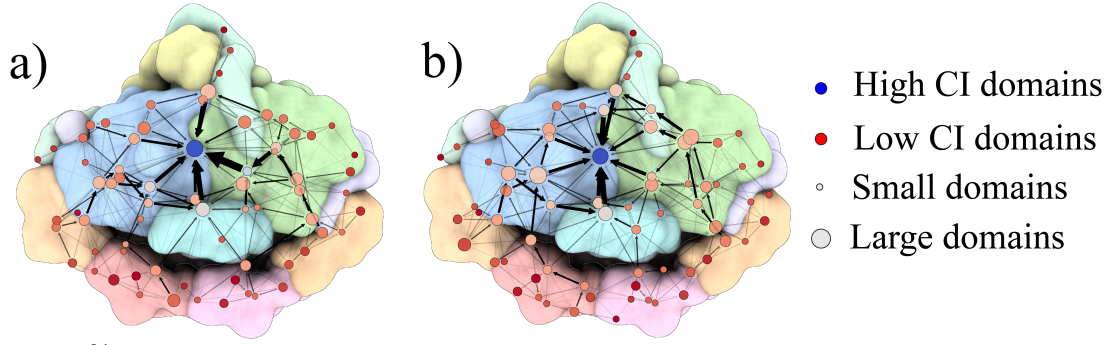


Figure 2. (a) Network analysis of plant PSI-LHCI with the site-energy landscape deposited by Betti et al.²² (b) The same analysis with the coarse-grained landscape built from the 10 Å binned values of Table 1. Symbol size is proportional to domain size, arrow thickness to the NCF magnitude, and color to the cumulative input (CI) of each domain.

Betti et al.²² noted a ring of low-energy chlorophylls near the RC²² that is not captured by our 10 Å binning. A finer, 5 Å binning resolves this feature, as well as the accessory chlorophylls lying below P700 in energy and a local energy maximum at the adjacent A₀ chlorophylls; a similar maximum was reported by Adolphs et al.²³ for cyanobacterial PSI. These features have little effect on the computed lifetime, which is 35.1, 33.8, and 34.9 ps for the deposited landscape of Betti et al.,²² the 10 Å binned landscape, and the 5 Å binned landscape, respectively. For a direct comparison with the lifetime of 33 ps reported by Betti et al.²², the plant PSI calculations adopt their values of $k_{CS}=2 \text{ ps}^{-1}$, no RC-specific reorganization energy ($S_m = 0.5$ for all pigments), and no dissipation channel. Setting all core and all antenna site energies to their respective mean values (antenna 51 cm^{-1} above the core) yields a lifetime of 45.2 ps.

A similar radial decrease in site energy within the core is found upon binning the core site energies deposited for *I. galbana* by He et al.⁵⁵ In the latter, the P700 pair lies approximately 200 cm^{-1} below the antenna mean, matching the pattern seen in Table 1 for the plant PSI landscape reported by Betti et al.²². In contrast, the cyanobacterial PSI site

energies reported by Adolphs et al.²³ and Reiter et al. show a relatively flat surface with no radial site energy gradient.

The structural model utilized by Akhtar et al.¹⁰ is the same as our SSB model. While this assumption might be suitable for cyanobacterial PSI landscapes, it is not as applicable to the sloped landscapes of the PSI core found in plant and *I. galbana* PSI. On this note, the absence of a peripheral antenna in cyanobacterial PSI suggests that the sloped site-energy landscape could be a unique feature of antenna-containing PSI complexes, facilitating the energy transfer from the antenna to the core. Consequently, the conclusion by Reiter et al. that thermal site-energy fluctuations tend to overpower the effect of a static site-energy funnel,²⁵ which applies to cyanobacterial PSI, might not hold for PSI complexes with antennas.

Explicit evaluation of site energies using quantum mechanical treatments may help clarify the above questions. However, our current study focuses on examining how the expansion of antenna sizes across species affects EET. For our purposes, we consider it sufficient to transfer the BSB profile (Table 1) to other species and compare the resulting lifetimes.

B. Exciton Lifetimes and EET Quantum Yields in PSI Complexes as a Function of Antenna Size

Figure 3 presents the network analysis of the five red-lineage PSI complexes. The bikewheel pattern of Figure 2 is reproduced in all five species, as is the contrast in domain size, with the core domains consistently larger than the antenna domains. This is expected, given the high conservation of the PSI core across species.⁵⁶⁻⁵⁸

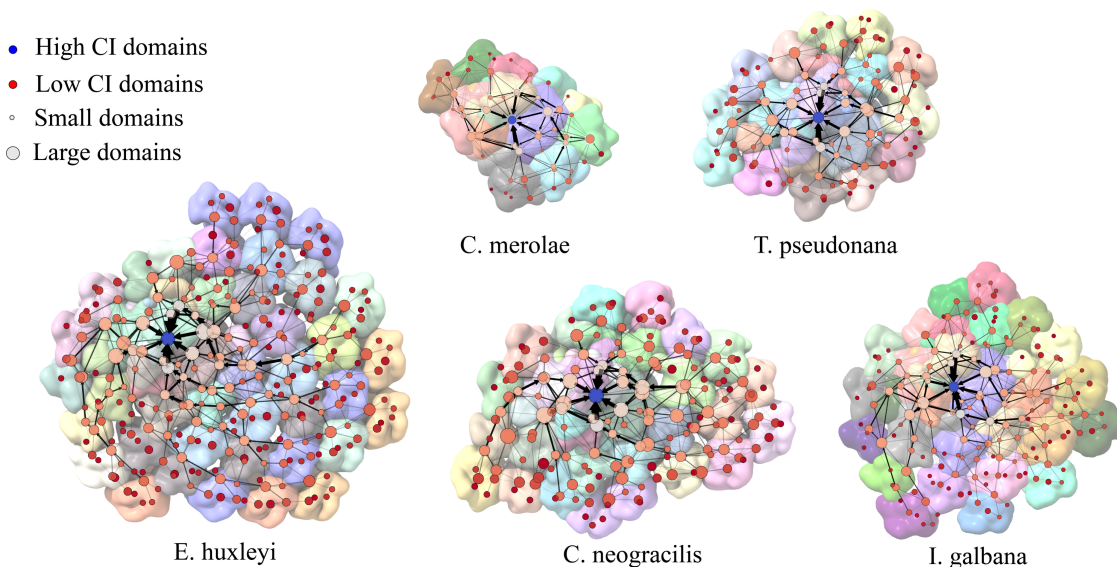


Figure 3. Net cumulative flow (NCF) analysis of the five red-lineage PSI complexes (species labeled), showing the flow of exciton population among exciton domains. Symbol size is proportional to domain size, arrow thickness to the NCF magnitude, and color to the cumulative input (CI) of each domain over the course of the simulation (see Methods for definitions). The BSB landscape was utilized for these computations.

Table 2 presents the calculated exciton lifetimes (τ) and EET quantum yields (QY) when an exciton is initially distributed across all exciton states in proportion to their transition dipole strengths (Methods). The computed lifetimes are compared with experimental values where available. As expected, the exciton lifetime increases and the QY decreases with antenna size (Table 2). For *C. merolae* and *T. pseudonana*, the BSB treatment gives closer agreement with experiment.

Table 2. The exciton lifetimes (τ) and quantum yields (QY) evaluated with SSB and BSB landscapes, at the RC charge-separation rate $k_{CS} = 2.8 \text{ ps}^{-1}$. These values are compared with the experimentally measured lifetimes where available. The experimental values are the amplitude-weighted mean lifetimes reported for *C. merolae* and *T. pseudonana* and the slowest decay component reported for *E. huxleyi*. The standard errors from disorder averaging are below 1 ps in τ and below 0.1% in QY in all cases.

Species	τ BSB (ps)	τ SSB (ps)	τ Exp. (ps)	QY BSB (%)	QY SSB (%)
<i>C. merolae</i>	28	40	25–30 ⁵⁰	99.3	99.0

<i>T. pseudonana</i>	43	60	38–42 ¹⁰	98.9	98.5
<i>I. galbana</i>	53	72	–	98.7	98.2
<i>C. neogracilis</i>	66	86	–	98.4	97.8
<i>E. huxleyi</i>	94	119	96–120 ⁶	97.7	97.0

C. The Effects of Exciton Energy Gradient (EEG) near the Core Region

We next examine the possible role of domain-size variations in EET efficiency across PSI species. As previously noted, Betti et al.²² reported that the PSI core forms extended domains, indicating high delocalization, while the antenna domains remain small.²² Our calculations reproduce this contrast in all five red-lineage species. In addition, we find that the domain size difference is graded rather than confined to the core–antenna boundary: the mean exciton-domain size decreases from the core through the inner antenna belts, so that antenna subunits nearer the core retain larger domains than those farther out (Table 3); only the outermost belt of *E. huxleyi* departs slightly from this trend.

Table 3. Mean size of exciton domains (chlorophylls per domain) per belt region, under the BSB treatment, as obtained from the disorder-averaged participation ratio (Sec. II C).

Species	Core	Belt 1	Belt 2	Belt 3	Belt 4
<i>C. merolae</i>	3.39	2.42	–	–	–
<i>T. pseudonana</i>	3.54	1.91	–	–	–
<i>I. galbana</i>	3.06	1.80	1.76	1.57	–
<i>C. neogracilis</i>	3.27	2.07	1.83	1.77	–

<i>E. huxleyi</i>	3.31	1.85	1.70	1.59	1.65
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The domain-size gradient contributes to the EEG. Excitonic coupling lowers the lowest exciton state of a domain below the site energies of its pigments, and the larger the number of strongly coupled pigments, the greater this lowering is on average; the large core domains therefore provide lower-lying acceptor states than the small antenna domains. Figure 4 shows the correlation between domain size and the mean lowest-exciton energy, obtained by averaging the energy of the lowest exciton state over all Chl *a* domains of a given size. The domain-size gradient therefore produces an EEG that funnels excitation into the core and limits the outflow of excitons toward the periphery of the antenna. The gradient is steepest at the core–antenna boundary and persists through the inner antenna belts in the three species with more than one belt (Table 3).

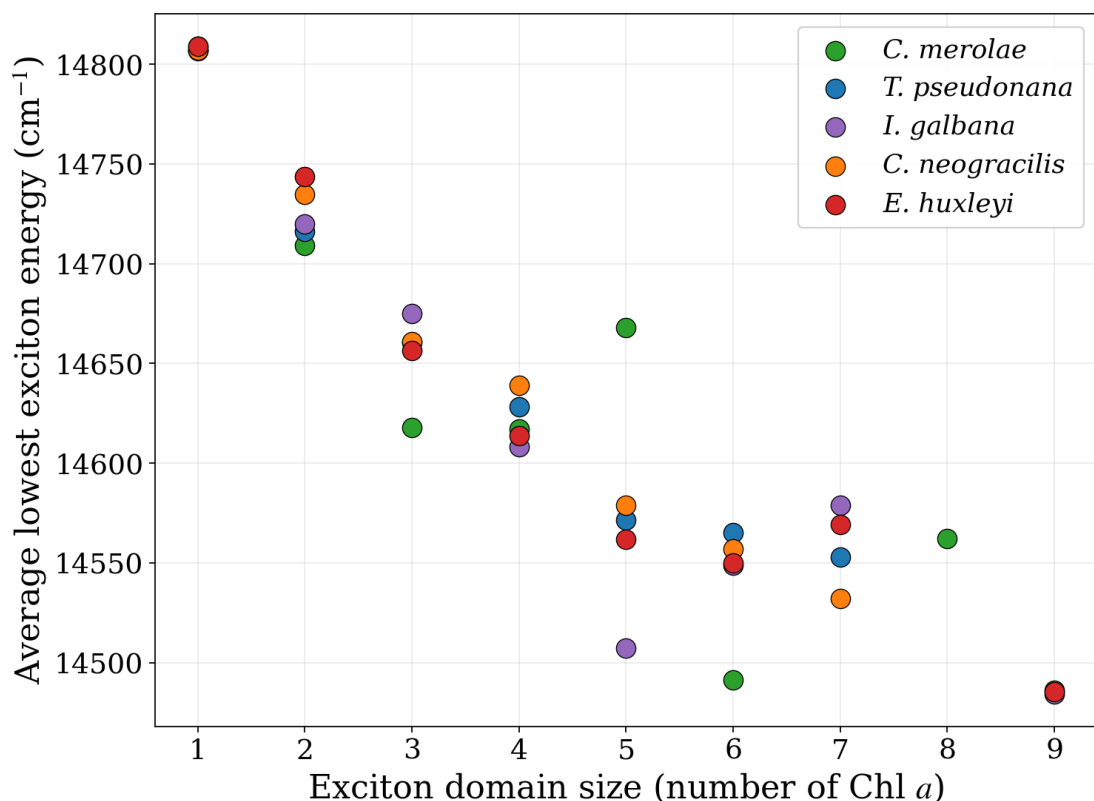


Figure 4. Average lowest-exciton energy of a domain as a function of domain size for the five red-lineage species studied. For each species, the mean lowest-exciton energy of all Chl *a* domains of each size is plotted. Larger domains have lower energies on average. The BSB landscape was utilized for these evaluations.

D. Role of Chl *c* in EET and Absorption Spectrum

The abundance of Chl *c* scales with antenna size, from none in the PSI of *C. merolae* to 152 of 563 chlorophylls in that of *E. huxleyi*. Because the transition dipole strength of Chl *c* in the model is smaller than that of Chl *a* ($11.9 D^2$ versus $29.6 D^2$), slower Chl *c*–Chl *c* transfer might be expected to lengthen the lifetime as the Chl *c* content increases. To test this, all Chl *c* were replaced by Chl *a*; the results are summarized in Table 4.

Table 4. Effect of Chl *c* → Chl *a* substitution on the exciton lifetime τ (ps) and QY (%) under the BSB treatment.

Species	$\tau(\text{Native}) \rightarrow \tau(\text{All Chl } a)$	QY
<i>T. pseudonana</i>	43→46 (+7%)	98.9→98.9

<i>I. galbana</i>	53→65 (+22%)	98.7→98.4
<i>C. neogracilis</i>	66→73 (+12%)	98.4→98.2
<i>E. huxleyi</i>	94→117 (+25%)	97.7→97.1

Contrary to this expectation, replacing all Chl *c* with Chl *a* lengthens the exciton lifetime (Table 4), with the largest increase in two of the larger species; in the PSI of *E. huxleyi*, Chl *c* accounts for 27% of the chlorophylls. This indicates that Chl *c* accelerates EET. This effect can be attributed to the higher site energy of Chl *c*, which outweighs its weaker coupling, and to its location at the periphery of the antenna: excitation is transferred downhill from the peripheral Chl *c* to the lower-energy Chl *a* in the inner antenna.

In addition to its role in EET, Chl *c* broadens the absorption band of the complex, allowing the absorption of additional wavelengths in optically crowded environments (Figure 5).

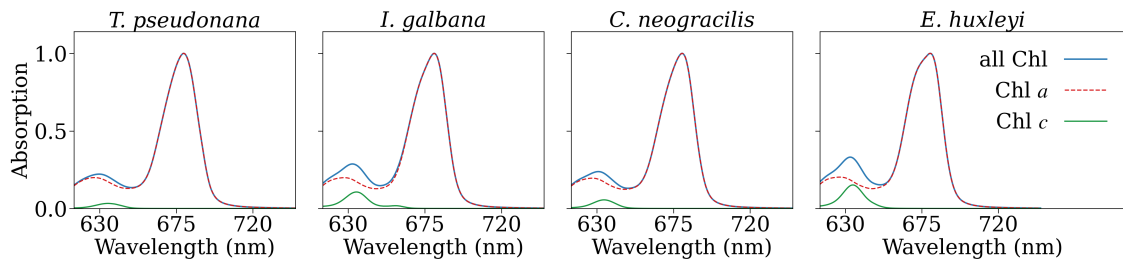


Figure 5. Calculated absorption spectra of the four Chl *c*-containing PSI complexes (solid blue line), decomposed into the contributions of Chl *a* domains (dashed red line) and Chl *c* domains (solid green line).

Figure 6 compares the computed absorption spectra with the experimental spectra of *C. merolae* and *T. pseudonana*.^{10, 59} The computed spectra are narrower than the experimental ones, because the uniform site energies are assigned to all antenna subunits, neglecting the heterogeneity among them.

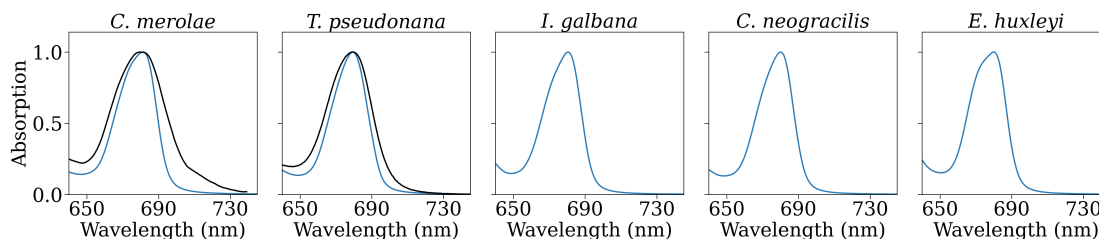


Figure 6. Computed absorption spectra of the five PSI complexes (blue). Experimental spectra of *C. merolae* and *T. pseudonana* (black) are shown for comparison.^{10, 59}

IV. CONCLUSIONS

In this study, we combined kinetic modeling, the Redfield and generalized Förster theories, and network analysis to simulate and compare EET across five red-lineage PSI complexes with a common parameter set. This comparison shows how the EET kinetics and quantum efficiency vary with the size, coupling, and energy landscape of the pigment network. The computed lifetimes are consistent with the available experimental values. We identified structural factors that maintain EET efficiency over long transfer pathways. Large, strongly coupled pigment clusters form low-energy exciton domains in the core region due to extensive exciton delocalization, creating an EEG that funnels excitation toward the reaction center; the same contrast between core and peripheral antenna has been reported for plant PSI.²² Across the red-lineage species examined here the contrast is graded, with domain size decreasing outward through the inner antenna belts. The EEG arises primarily from pigment packing and connectivity and does not require redshifted Chl dimers with low site energies, which suggests that the energy landscape for EET can be tuned by the spatial arrangement of the pigments. The peripheral antenna, in contrast, consists of small, weakly coupled exciton domains containing the higher-energy Chl *c*, which enables efficient downhill antenna-to-core EET. Where the antenna extends beyond the range over which the EEG is effective, the larger PSI complexes contain an increasing proportion of

Chl *c* in the peripheral antenna, which accelerates EET through fast downhill transfer of excitons into the Chl *a* network.

Although the overall exciton lifetimes increase with antenna size, all five complexes sustain average quantum yields above 97%, reflecting the effectiveness of the funneling mechanisms described above.

Several limitations of the model should be noted. As described in Sec. II I, the “red form” Chl dimers of PSI are not modeled here: they arise from mixing with charge-transfer states and carry a correspondingly larger reorganization energy, so their treatment requires explicit charge-transfer states.^{22, 29} Moreover, their formation is dynamic, induced under specific light conditions, often with photoprotective roles.^{37, 50, 51, 60} These effects are beyond the scope of the present study. The model also omits the carotenoids, which mediate nonphotochemical quenching (NPQ) in individual antenna complexes; these processes have been modeled explicitly in other studies.^{16, 22, 51, 61} Despite these limitations, the principles identified here may apply to other PSI complexes: the pigment network balances the competing demands of light absorption and EET through the combined effects of the domain-size variations, the site-energy bias, and the pigment composition. The accompanying code can be applied to model energy transfer in other red-lineage PSI.

SUPPLEMENTARY MATERIAL

The supplementary material discusses how the domain-clustering threshold affects exciton lifetimes, along with an analysis of different excitation patterns for each PSI system in our cross-species study. Table S1 compares exciton lifetimes obtained using different domain-clustering thresholds, and Table S2 compares exciton lifetimes for the initial excitation confined to the core region and to the antenna belts.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary information. Additional data are available from the corresponding author upon reasonable request. An example of our network analysis code is available at the following GitHub repository: <https://github.com/FysicsTeachr/psi-eet>

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