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A theoretical study on the dynamics of light harvesting in the dimeric photosystem II core complex: regulation and robustness of energy transfer pathways†

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Here we present our theoretical investigations into the light reaction in the dimeric photosystem II (PSII) core complex. An effective model for excitation energy transfer (EET) and primary charge separation (CS) in the PSII core complex was developed, with model parameters constructed based on molecular dynamics (MD) simulation data. Compared to experimental results, we demonstrated that this model faithfully reproduces the absorption spectra of the RC and core light-harvesting complexes (CP43 and CP47) as well as the full EET dynamics among the chromophores in the PSII core complex. We then applied master equation simulations and network analysis to investigate detailed EET plus CS dynamics in the system, allowing us to identify key EET pathways and produce a coarse-grained cluster model for the light reaction in the dimeric PSII core complex. We show that non-equilibrium energy transfer channels play important roles in the efficient light harvesting process and that multiple EET pathways exist between subunits of PSII to ensure the robustness of light harvesting in the system. Furthermore, we revealed that inter-monomer energy transfer dominated by the coupling between the two CLA625 molecules enables efficient energy exchange between two CP47s in the dimeric PSII core complex, which leads to significant energy pooling in the CP47 domain during the light reaction. Our study provides a blueprint for the design of light harvesting in the PSII core and show that a structure-based approach using molecular dynamics simulations and quantum chemistry calculations can be effectively utilized to elucidate the dynamics of light harvesting in complex photosynthetic systems.

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1 Introduction

Photosynthetic systems utilize complex structures composed of pigment–protein complexes (PPCs) to harvest sunlight and convert the energy into chemical potentials that can be used to drive subsequent chemical reactions.^{1–4} In particular, oxygenic photosynthetic organisms employ the photosystem II (PSII) supercomplex in their photosynthetic machinery.^{5–9} The PSII supercomplex utilizes several hundreds of chlorophylls to perform light harvesting and charge separation at almost unity quantum efficiency. This remarkable process, called the light reaction, is at the core of photosynthesis, yet many aspects of its fundamental molecular mechanisms remain elusive due to the vast complexity of photosynthetic systems.^{7,8}

Previous studies indicated that the PSII supercomplex exhibits a variety of different forms in natural photosynthesis^{10–15} that nevertheless share the same basic functional unit, the PSII core complex (PSII-cc). The atomistic structure of the PSII-cc is available in high resolution.^{6,9,15,16} The PSII core complex consists of several pigment–protein complexes assembled in a dimeric structure with near C2 symmetry. In each monomer, it consists of two antenna complexes (CP43 and CP47) and one reaction center (RC). The location of the antenna complexes and reaction centers are shown in Fig. 1. In the past few decades, the excitation energy transfer (EET) and charge separation in PSII-cc have been investigated extensively using various spectroscopic techniques.^{10,17–25} In addition, with the availability of the high-resolution structures, theoretical models with detailed descriptions of the dynamics of light harvesting in the PSII-cc have also been constructed.^{10,23,24,26–29}

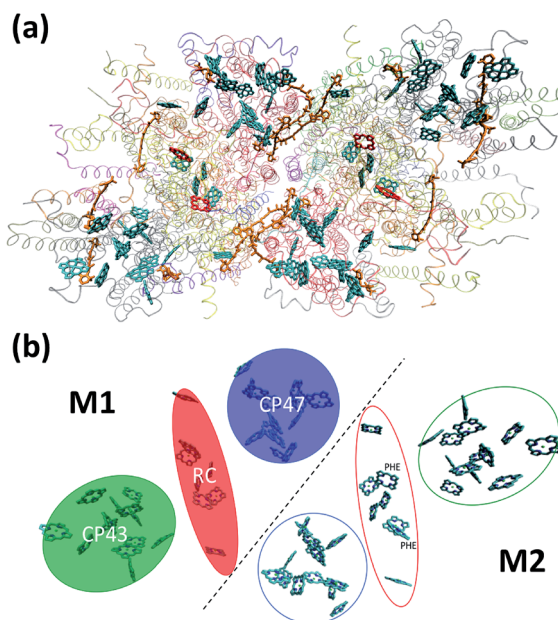


Fig. 1 Pigment arrangement in the dimeric PSII-cc. (a) The top view of the PSII core complex. The illustration is based on the crystal structure from *T. vulcanus* at a resolution of 1.9 Å (PDB: 3ARC). (b) The chlorophyll arrangement in the PSII-cc. The chlorin rings of chlorophyll a and pheophytin molecules are shown. Furthermore, we depict the two monomers (M1 and M2) as well as the respective subunits (CP43, RC, and CP47).

The accumulated data have allowed the elucidation of many mechanistic aspects of the light reaction in PSII, yet some key questions regarding the energy landscapes, the relative time scales of EET and charge separation processes, and energy regulation in PSII remain to be answered.^{7,8,30,31} In particular, previous theoretical studies have largely overlooked the dimeric nature of the PSII-cc and almost exclusively focus on dynamics within a single monomeric unit. It remains unclear, however, whether the dimeric form serves only a structural role to stabilize the assembly on the thylakoid membrane, or it also provides a functional role to offer more advantages in light harvesting. To this end, an accurate molecular-level understanding of the dynamics of light harvesting in the dimeric PSII-cc is crucial for revealing the design principles underlying the efficient light reaction in the system.

In recent years, molecular dynamics (MD) simulations have been utilized as powerful tools to elucidate detailed pigment–protein interactions crucial in the mechanistic of light harvesting in PPCs.^{29,32–35} Here, we follow the MD simulation approach published previously³⁶ to obtain key parameters that govern EET dynamics in the dimeric PSII-cc system. Our goal is to construct an accurate effective model for light harvesting in the dimeric PSII-cc system. This model would allow us to focus on the role of the inter-monomer EET pathways and to elucidate whether the dimeric structure of PSII-cc contributes to the function of the system.

2 Theoretical methods

2.1 Effective Frenkel exciton model

For a pigment–protein complex, it is conventional to adopt the Frenkel exciton model to describe the photo-excitations in the system.^{1,2,37} The Frenkel exciton Hamiltonian for a system with N pigments (sites) is given by

$$H_s = \sum_{n=1}^N E_n |n\rangle \langle n| + \sum_{n \neq m} J_{nm} |n\rangle \langle m|, \quad (1)$$

where $|n\rangle$ represents a local excitation on the n th pigment, E_n is the transition energy (site energy) of $|n\rangle$, and J_{nm} is the excitonic coupling between $|n\rangle$ and $|m\rangle$. The effective Hamiltonian describes electronic excitations in a pigment–protein complex, and in this work we determine the site energies and excitonic couplings based on structures obtained in MD simulations.

2.2 Molecular dynamics simulation and excitonic parameters

Our effective excitonic model for EET in the PSII-cc is constructed based on MD simulations of the PSII-cc embedded in a lipid-bilayer membrane. Details about the structure model and MD simulations were published previously,³⁶ and here we only present essential information in order to make this work self-contained. The structure model is based on the crystal structure of PSII-cc from *T. vulcanus*.¹⁶ To capture the dynamical effects, 30 snapshots sampled with equal time intervals (1 ns) from the last 5 ns of five independent 20 ns equilibrium MD runs at 300 K were used as initial conditions to carry out equilibrium MD simulations, resulting in an ensemble of 30 50 ps MD trajectories for the PSII-cc system. Instantaneous structures in these MD trajectories were saved every 4 fs to obtain structure dynamics of the PSII-cc in high temporal resolution.

To estimate site energies based on the MD trajectories, the charge density coupled (CDC) method^{27,38,39} is used. In this approach, the time-dependent site energy shift of a pigment in a PPC is calculated by considering Coulomb interactions between the pigment and the background atomic partial charges of the protein, water, and all other molecules. Thus, for the n th site

$$\begin{aligned} \Delta E_n(t) &= \frac{1}{\epsilon_{\text{eff}}} \sum_i \sum_j \left(\frac{q_{e,i}^n q_j^{\text{bg}}}{|r_i^n(t) - r_j^{\text{bg}}(t)|} - \frac{q_{g,i}^n q_j^{\text{bg}}}{|r_i^n(t) - r_j^{\text{bg}}(t)|} \right) \\ &= \frac{1}{\epsilon_{\text{eff}}} \sum_i \sum_j \frac{\Delta q_i^n q_j^{\text{bg}}}{|r_i^n(t) - r_j^{\text{bg}}(t)|}, \end{aligned} \quad (2)$$

where i runs over all heavy atoms on the n th site, and j includes all the charged atoms in the background. ϵ_{eff} is an effective dielectric constant, $q_{e,i}^n$ and $q_{g,i}^n$ are the atomic partial charges on atom i for the excited state and ground state, respectively, of the n th pigment. $r_i^n(t)$ and $r_j^{\text{bg}}(t)$ are the instantaneous positions of atom i and atom j , respectively. Δq_i^n is the charge difference due to electronic excitation, $\Delta q_i^n = q_{e,i}^n - q_{g,i}^n$. Following the treatment detailed in ref. 36, the atomic charges for the excited state and ground state of the pigment are obtained by fitting to TDDFT electrostatic potential distributions, and the background partial charges are obtained from the AMBER03 force field.^{40,41} We apply eqn (2) to calculate site energy shifts for all the structural snapshots sampled by the MD simulations, resulting in a total of 30 50 ps trajectories of site energy shifts for each site. We then calculate the site energy of each site by averaging over all the MD snapshots:

$$E_n = E_0 + f \langle \overline{\Delta E_n(t)} \rangle, \quad (3)$$

where E_0 is an empirical total energy shift that depends on the type of pigments, $\overline{A(t)}$ denotes the time average of the observable $A(t)$ over a single trajectory, and $\langle \cdot \rangle$ denotes the average over all the trajectories. f is an empirical scaling factor used to compensate for the errors in the CDC scheme, and it will be determined by comparing to experimental data.

We applied the transition charge from electrostatic potential (TrEsp)⁴² method as described in ref. 36 to calculate excitonic couplings between excitations on each pair of pigments. Our results indicate that the structure fluctuations at 300 K do not significantly affect the excitonic couplings. In general, the couplings do not fluctuate more than 5% from the values calculated using the crystal structure. Thus, in order to simplify our model, we choose to neglect the time-dependence of the excitonic couplings by using the excitonic couplings calculated from the crystal structure of PSII-cc. In addition, since most exciton states in PSII-cc are localized at pigments no greater than 30 Å apart, we consider the excitonic coupling only if the center-to-center distance between the two pigments is less than 30 Å in order to avoid unphysical delocalization among pigments with a large spatial separation due to accidental energy degeneracy.

2.3 System-bath interactions from MD data

The description of quantum dynamics for excitons in PPCs is well established.^{4,27,37,43–45} The standard Hamiltonian used to study energy transfer in a PPC contains three parts:

$$H = H_s + H_b + H_{sb}, \quad (4)$$

where H_s is the system Hamiltonian (eqn (1)), H_b is the bath Hamiltonian, and H_{sb} describes the system–bath interactions. The bath Hamiltonian is represented by a set of harmonic oscillators:

$$H_b = \sum_{\alpha} \hbar \omega_{\alpha} \left(b_{\alpha}^{\dagger} b_{\alpha} + \frac{1}{2} \right), \quad (5)$$

where $\hbar \omega_{\alpha}$ is the energy of the vibrational quanta in the α th bath mode. The system–bath Hamiltonian is described by

$$H_{sb} = \sum_{\alpha} \sum_n \hbar \omega_{\alpha} g_{\alpha,n} (b_{\alpha}^{\dagger} + b_{\alpha}) |n\rangle \langle n|, \quad (6)$$

where $g_{\alpha,n}$ is the system–bath coupling constant between $|n\rangle$ and the α th bath mode. We also assume that the fluctuations of site energies are linearly coupled to the displacement of nuclei from their equilibrium positions. Therefore, the system–bath couplings lead to fluctuations in the site energies of the pigments, which can be calculated from the MD data.

To evaluate the system–bath couplings from the MD data we calculate the time-correlation function (TCF) of the energy gap fluctuations for each pigment in the PSII-cc system using the time-dependent site energy shifts (eqn (2)) obtained from the MD trajectories. For each trajectory, we average the site energy shift within a 10 ps window to yield the time-averaged shift $\overline{\Delta E_n(t)}$, and then evaluate the site-energy fluctuations around this average:

$$\delta E_n(t) = \Delta E_n(t) - \overline{\Delta E_n(t)}. \quad (7)$$

Then, we can calculate the TCF for the site-energy fluctuations on the n th site as:

$$\begin{aligned} C_n(\tau) &= \langle \delta E_n(\tau) \delta E_n(0) \rangle \\ &= \frac{1}{T} \int_0^T \langle \delta E_n(\tau + t) \delta E_n(t) \rangle dt, \end{aligned} \quad (8)$$

where the window of time average is $T = 10$ ps. We emphasize that the division into 10 ps windows allows us to separate the fast dynamical disorder from the slow static disorder, therefore $C_n(\tau)$ calculated here would not be significantly affected by inadequate sampling of slow protein dynamics in the MD simulation.

In principle, one can calculate the TCF of site energy fluctuations for each site and model the full PSII-cc system using all of the MD details of dynamical fluctuations. Nevertheless, we further assume that the system–bath couplings of different sites are independent and identical. As a result, we use the same averaged quantum TCF for all of the sites to describe the system–bath couplings.

$$C_{MD}(\tau) = \frac{1}{M} \sum_n C_n(\tau), \quad (9)$$

where M is the total number of sites in the system.

The classical TCF calculated based on MD data does not satisfy the detailed balance condition. Therefore, we adopt a harmonic quantum correction to

calculate the quantum time-correlation function for the site-energy fluctuations.^{46,47} The quantum correction is performed in the frequency domain. Given a classical TCF, $C_{\text{MD}}(\tau)$, we can calculate its Fourier transform:

$$\tilde{C}_{\text{MD}}(\omega) = \int_{-\infty}^{\infty} e^{i\omega\tau} C_{\text{MD}}(\tau) d\tau, \quad (10)$$

where ω is the angular frequency. Then, the quantum TCF in the frequency domain can be obtained by multiplying the classical TCF with an harmonic quantum correction factor:

$$\tilde{C}_{\text{qc}}(\omega) = \frac{\beta\hbar\omega}{1 - e^{\beta\hbar\omega}} \tilde{C}_{\text{MD}}(\omega), \quad (11)$$

where $\beta = \frac{1}{k_{\text{B}}T}$ is the inverse temperature. Finally, the inverse Fourier transform is applied to $\tilde{C}_{\text{qc}}(\omega)$ to obtain the quantum TCF in the time domain, $C_{\text{qc}}(\tau)$.

2.4 Simulation of the absorption spectrum and EET dynamics

The above-mentioned system-base Hamiltonian for a pigment-protein complex can be used to calculate EET dynamics and spectra. To this end, we diagonalize H_{s} in order to obtain the exciton states. The exciton state $|\alpha\rangle$ satisfies $H_{\text{s}} |\alpha\rangle = E_{\alpha} |\alpha\rangle$, where E_{α} is the exciton energy of $|\alpha\rangle$, and can be represented as a linear combination of localized excitations, $|\alpha\rangle = \sum_n c_n^{\alpha} |n\rangle$, where c_n^{α} is the coefficient for the excitation on site n .

To simulate the linear absorption spectrum and the EET dynamics, we adopt the modified-Redfield approach.^{43,48,49} We define the TCF of energy fluctuations in the exciton basis:

$$C_{\alpha\beta\gamma\delta}(\tau) = \sum_n c_n^{\alpha} c_n^{\beta} c_n^{\gamma} c_n^{\delta} C_{\text{qc}}(\tau), \quad (12)$$

where $C_{\text{qc}}(\tau)$ is the quantum TCF for site-energy fluctuations calculated from the MD data. Furthermore, we define the line shape function in the exciton basis,

$$g_{\alpha\beta\gamma\delta}(t) = \int_0^t d\tau C_{\alpha\beta\gamma\delta}(\tau)(t - \tau), \quad (13)$$

and the reorganization energy function,

$$\lambda_{\alpha\beta\gamma\delta} = - \int_0^{\infty} \text{Im}(C_{\alpha\beta\gamma\delta}(\tau)) d\tau. \quad (14)$$

Using the exciton Hamiltonian and the quantum TCF, the optical density (OD) of linear absorption can be calculated:

$$\text{OD}(\omega) = \omega \sum_{\alpha} \mu_{\alpha}^2 \text{Re} \int_0^{\infty} dt e^{i(\omega - \omega_{\alpha})t - g_{\alpha\alpha\alpha\alpha}(t) - R_{\alpha\alpha\alpha\alpha}t}, \quad (15)$$

$$R_{\alpha\alpha\alpha\alpha} = - \sum_{\beta \neq \alpha} R_{\beta\beta\alpha\alpha}, \quad (16)$$

where $\mu_{\alpha} = \sum_n c_n^{\alpha} \mu_n$ and $\omega_{\alpha} = E_{\alpha}/\hbar$ denote the transition dipole moment and frequency of the α th exciton state, respectively. $R_{\beta\beta\alpha\alpha}$ is the transition rate

constant from the α th exciton state to the β th exciton state based on the modified Redfield theory:

$$R_{\beta\beta\alpha\alpha} = -2\text{Re} \int_0^\infty dt \hat{W}(\omega_{\beta\alpha}, t) \left\{ \ddot{g}_{\beta\alpha\alpha\beta}(t) - \{ \dot{g}_{\alpha\beta\alpha\alpha}(t) - \dot{g}_{\alpha\beta\beta\beta}(t) + 2i\lambda_{\alpha\beta\alpha\alpha} \} \right. \\ \left. \times \{ \dot{g}_{\alpha\alpha\beta\alpha}(t) - \dot{g}_{\beta\beta\beta\alpha}(t) + 2i\lambda_{\alpha\alpha\beta\alpha} \} \right\}, \quad (17)$$

where

$$\hat{W}(\omega_{\beta\alpha}, t) = \exp\{-i\omega_{\beta-\alpha}t - g_{\alpha\alpha\alpha\alpha}(t) - g_{\beta\beta\beta\beta}(t) + 2g_{\alpha\alpha\beta\beta} + 2i(\lambda_{\alpha\alpha\beta\beta} - \lambda_{\alpha\alpha\alpha\alpha})t\}$$

and

$$\omega_{\beta\alpha} = \omega_\beta - \omega_\alpha. \quad (18)$$

The rate constants given in eqn (16) and (17) can also be used to construct a master equation describing the full EET dynamics in the exciton states of the PSII-cc. In addition to energy transfer, we phenomenologically include fluorescence decay with $k_{\text{FL}} = 1 \text{ ns}^{-1}$ for all exciton states, and the two charge separation pathways for primary charge separation in each RC are also included in our rate matrix. The two pathways are the P_{D1} pathway and the Chl_{D1} pathway, with rate constants of 0.33 ps^{-1} and 1.43 ps^{-1} , respectively. We can then propagate the master equation with given initial populations on the exciton states to obtain the full EET dynamics.

3 Results and discussions

3.1 Quantum time correlation function

We have performed a MD simulation of the PSII-cc system and calculated the TCF for site energy fluctuations using the MD data. To justify our choice of using a single TCF to describe system–bath couplings of all of the chlorophyll *a* molecules (CLAs) and pheophytins (PHEs), we have separately calculated TCFs for CLAs in different subunits of the PSII-cc (Fig. S1†), and the results confirmed that different CLAs do not show significantly different site energy fluctuations. Fig. 2 shows the averaged quantum TCF of site energy fluctuations ($C_{\text{qc}}(t)$) in PSII-cc. The TCF decays rapidly, showing a correlation time of $\sim 50 \text{ fs}$, which is in agreement with the time scales of bath relaxation in empirical TCFs normally used for photosynthetic PPCs. However, the variance of fluctuations ($C_{\text{qc}}(0)$) is only $\sim 830 \text{ cm}^{-2}$, which is more than an order of magnitude smaller than the normal empirical TCFs used for PPCs at 300 K . We thus conjecture that while the classical force fields properly describe the molecular dynamics and time scales of site energy fluctuations, the magnitude of the fluctuations were described poorly by the atomic partial charges, which is not surprising since these partial charges were not fitted to describe couplings to the excited state of the pigments. Therefore, we propose to use a scaled quantum TCF in order to correct for the deficiency in the partial charge model:

$$C_{\text{qc}}^{\text{s}}(\tau) = f^2 C_{\text{qc}}(\tau), \quad (19)$$

where f is a scaling factor. This approach is also consistent with the scaling factor proposed for site energy shifts (eqn (3)). The scaled quantum TCF will be used to

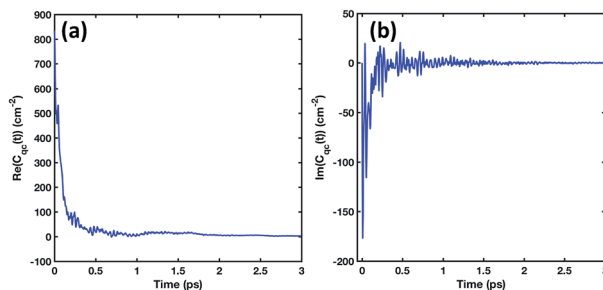


Fig. 2 The averaged quantum time-correlation function of site energy fluctuations calculated based on the PSII-cc MD trajectory. (a) The real part of the quantum time-correlation function. (b) The imaginary part of the quantum time-correlation function.

calculate spectra and EET dynamics presented in this work, and the scaling factor will be determined by comparing to experimental spectral data.

3.2 Linear absorption spectra

We first focus on the linear absorption spectrum of the RC of the M1 monomer. In our spectral simulation study, we found that the scaling factor f , the transition energy in vacuum E_0 , the two pheophytin site energies, the site energies of the special pair CLAs and the excitonic coupling between the special pair CLAs have to be adjusted in order to achieve a reasonable fit to the experimental spectrum. These fitting parameters are well justified because they are precisely where the CDC scheme for site energy shifts and the TrESP approach for excitonic couplings are expected to perform poorly. Moreover, since the simulation time of each MD trajectory is only 50 ps, the inhomogeneous broadening is not captured by the MD trajectories. Therefore, we apply an additional diagonal Gaussian disorder with $\sigma_{\text{static}} = 70 \text{ cm}^{-1}$ to capture the static disorder effects.^{23,26} Fig. 3 shows the comparison between the optimized theoretical absorption spectrum and the experimental spectrum for the RC in 300 K. There, we found that a scaling factor of $f = 5$ together with the MD structure-based data yield an excellent fit to the absorption spectrum. The resulting exciton Hamiltonian is shown in the RC block in Table S1.† Fig. 4 shows the labeling of the pigments used in this work.

We also simulated the absorption spectra for the CP43 and CP47 subunits of the PSII-cc (Fig. 5). In these two light-harvesting complexes, we found that if we use the site energies obtained from the MD structures and a scaling factor of $f = 5$ for the quantum TCF, the experimental spectra can be nicely reproduced.

Overall, we have demonstrated that the MD structures together with the CDC scheme for site energy shifts and the TrESP approach for excitonic couplings can be used to obtain effective models of PSII-cc that reasonably reproduce the linear spectra of each subunit in the PSII-cc. The universal scaling factor $f = 5$ for the TCF of site energy fluctuations confirm our conjecture that the MD trajectory captures the essential dynamics of site energy fluctuations. Note that the comparison between the experimental spectrum and the theoretical spectrum is utilized as a means to correct for the effective electronic screening and local field effects in the scaling factor f , and we do not consider the agreements unequivocally prove that the MD structure and the CDC scheme yields correct site energy

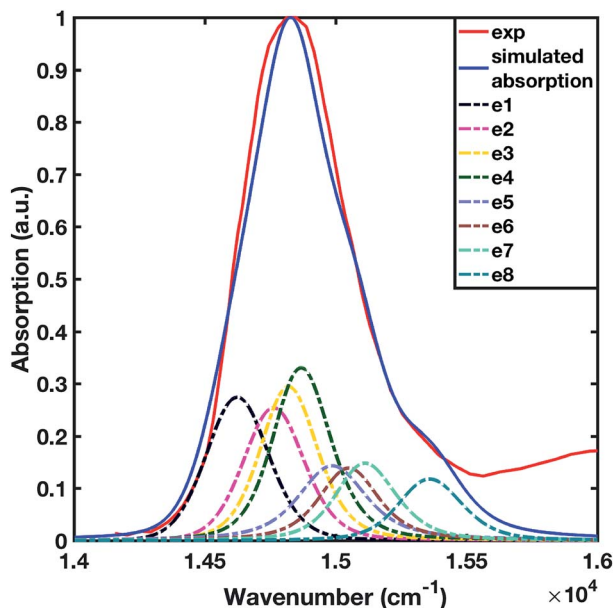


Fig. 3 The comparison of the simulated and experimental absorption spectra of the PSII RC. The red curve depicts the experimental result at 297 K.⁵⁰ The blue peak is the simulated spectrum based on our PSII-cc exciton model. Curves depicted with dashed lines are contributions from each individual exciton states.

values. Instead, our goal is mainly to show that the MD structure-based models can be made consistent with available experimental data with a minimal number of adjustable parameters. To further and unbiasedly validate the model, it is necessary to compare it to additional spectral data and available time-resolved spectroscopic measurements. For PSII-cc, that would present a formidable challenge since clean experimental data that could be directly compared to simulations are still not available. As a result, we choose to not carry out a detailed comparative study. Instead, we would go on to carry out simulations of EET dynamics, and see how far the MD data could take us. Intriguingly, we found that

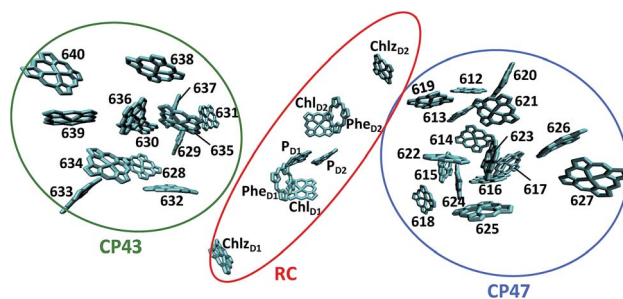


Fig. 4 Labeling of pigments in a monomer of the PSII-cc. The blue ellipse represents the location of the CP47 antenna complex, and the red ellipse represents the location of the RC. The green ellipse represents the location of the CP43 antenna complex.

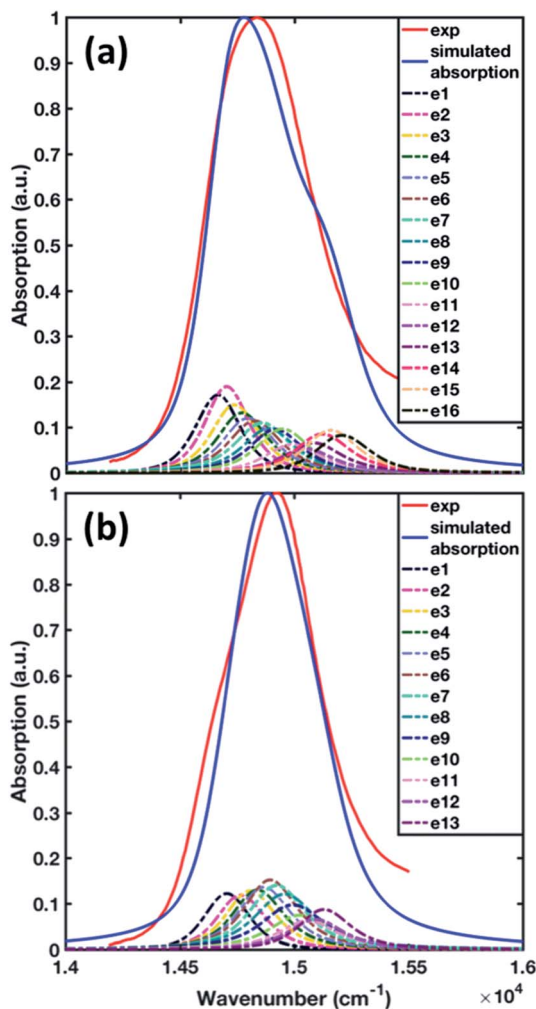


Fig. 5 Simulated absorption spectra of CP47 and CP43. (a) The simulated absorption spectrum of CP47 compared to the experimental spectrum. (b) The simulated absorption spectrum of CP43 compared to the experimental spectrum. The experimental spectra at 297 K was taken from ref. 51. Contributions from each individual exciton states are depicted in colored dashed lines.

the MD based model could semi-quantitatively reproduce most of the results presented in previous studies, and furthermore allowed us to explore new aspects of the dynamics of light harvesting in the PSII-cc.

3.3 Exciton states in the PSII-cc

Before we present simulations of EET dynamics in the PSII-cc, we examine the model Hamiltonian. The full excitonic Hamiltonian for the PSII-cc system is presented in Tables S2 and S3.[†] We see that the Hamiltonian exhibits a blocked form, where significant couplings only exist between CLAs in the same subunit. Moreover, this model Hamiltonian shows that the lowest energy site is Chl_{D1} in

the RC, which is in agreement with previous work.³⁶ Aside from Chl_{D1}, several CLAs in the CP47 subunit represent a group of low energy sites in the PSII-cc, causing the averaged site energy of the CP47 to be significantly lower than that of CP43 and the RC. Again, this is in agreement with previous experimental observations and theoretical calculations.^{23,26,30,31} We note that the assignments of low-energy sites in CP47 are still controversial,^{23,30,52} yet the overall key features in our model Hamiltonian are consistent with previously published effective models for the PSII-cc.

The exciton states that diagonalize our model Hamiltonian are illustrated in Fig. S2.† To quantify the degree of delocalization, we calculated the delocalization length (Fig. S3†) as well as the spatial delocalization distance (Fig. S4†) for all the exciton states. We found that most exciton states exhibit a delocalization length between 1–3 across a distance shorter than 15 Å. The average delocalization length for the 74 exciton states is 2.3, meaning that most of the exciton states are delocalized among 2 CLAs. The average spatial delocalization distance for the 74 exciton states is 9.5 Å, whereas the average distance between nearest-neighbor CLAs is 10.6 Å. Therefore, the spatial delocalization shows that in general excitons are delocalized among nearest-neighbor CLAs, which confirms the average value of the delocalization length.

Our data also revealed that exciton states e12 and e13 have especially large values of spatial delocalization. These states are contributed by Chl_{D2} and CLA627 in the CP47 of the M2. Interestingly, these two CLAs do not strongly couple to each other. The delocalization is due to excitonic couplings between these pigments and CLA621 and CLA619. In this case, EET from Chl_{D2} to CP47 is mediated by a cluster of CLAs.

3.4 EET dynamics in the PSII-cc

Our MD-structure based exciton model and scaled quantum TCF allows us to simulate full EET dynamics in the PSII-cc. Previous studies have established that excitation energy from the peripheral light-harvesting complexes could enter the PSII-cc through two pathways in the PSII supercomplex:^{13–15} one into CP43 and the

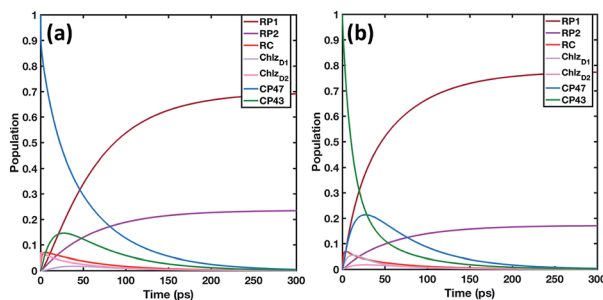


Fig. 6 EET dynamics in the M1 monomer of the PSII-cc. (a) EET population dynamics when CLAs in the CP47 subunit are uniformly excited initially. We depict aggregated population for each subunit as a function of time. In addition, we show the populations of the excited Chl_{D1} and Chl_{D2}, respectively. The populations that reach the two radial-pair states (RP1 and RP2) are shown as well. (b) EET population dynamics when CLAs in the CP43 subunit are uniformly excited initially.

other into CP47. Therefore, we will focus on EET dynamics with either CP43 or CP47 excited initially. Furthermore, to investigate the efficiency of light harvesting, fluorescence decay of CLAs and the charge separation pathways leading to the two radical-pair states, RP1 and RP2, respectively, are also included in all the subsequent dynamical simulations (Tables S3 and S4†).

We first study the EET dynamics in a single monomer (M1) of the PSII-cc by inspecting the aggregated excitation population in each subunit of the M1 monomer as a function of time. Fig. 6a shows the EET dynamics when the exciton states in CP47 are initially excited. In this case, the aggregated population of CP47 decays in a 50 ps time scale, and at the time scale the two radical pair states are populated, showing rapid EET from CP47 to the RC and the subsequent charge separation dynamics. The quantum efficiency of charge separation in this case is about 0.93, which is also in agreement with previous studies. Noticeably, transient population of CP43 is observed, and it reaches a maximum of about 0.15 at ~ 30 ps. This EET from CP47 to CP43 occurs presumably through the RC because CP47 and CP43 are not adjacent in space and all excitonic couplings between CP47 and CP43 pigments are effectively zero. This indicates that regardless of the much faster (~ 1 ps) charge separation dynamics in the RC, EET between the two antenna complexes could still occur rapidly. Thus, EET dynamics in the PSII-cc shows significant non-equilibrium effects and a multiple-pathway nature, which can not be described by a hopping rate from the antenna to the RC.

In Fig. 6b, we show EET dynamics in the M1 monomer when the exciton states in CP43 are initially excited. Similar to the case when CP47 is initially excited, rapid charge separation and EET to CP47 are both observed. The time scale of population decay in CP43 is ~ 20 ps, slightly faster than the population decay in CP47, which could be a result of CP47 containing the low-energy CLAs. The quantum efficiency of charge separation in this case is about 0.94.

To investigate the role the peripheral chlorophylls (Chl_{D1} and Chl_{D2}) play in EET to the core of RC, we also plot the population of excitation on Chl_{D1} and Chl_{D2} , respectively, in Fig. 6. We observe that the population decay on either Chl_{D1} or Chl_{D2} does not cause a corresponding population increase on the RC. Therefore, excitation energy transfer from CP43 and CP47 to RC can be achieved without passing through either Chl sites. In addition, the EET dynamics shown in Fig. 6 indicate that Chl_{D2} is more closely connected to CP47, whereas Chl_{D1} is more closely connected to CP43. This is also in agreement with previous theoretical studies.^{23,26}

It is interesting to compare our simulation results with experiments. Generally speaking, our model predicts 30–50 ps EET from CP47 and CP43 to the RC and 15 ps EET from RC to the antenna complexes (Tables S3 and S4†). Note that EET in the PSII-cc does not proceed through a single energy funnel, therefore these timescales should be considered as coarse-grained averaged values over a range of multiple pathways. Nevertheless, these numbers are in reasonable agreement with EET parameters obtained in previous combined theoretical-experimental studies,^{23,26} despite the differences in the site energies and couplings between our models. Moreover, in the recent 2D electronic spectroscopic study by Pan *et al.* at 77 K,⁵³ multiple time scales of energy relaxation dynamics were resolved by applying global data analysis on 2D spectra. Although the ultrafast sub-ps energy transfer dynamics reported in this 2D study are intentionally ignored in our study because of the setup of the initial conditions, the 7 ps and 36 ps relaxation

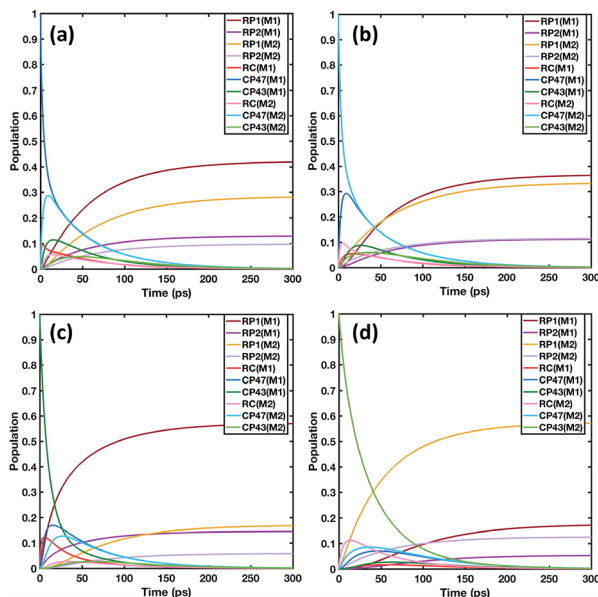


Fig. 7 EET dynamics in the dimeric PSII-cc. Here we show EET dynamics in a full dimeric PSII-cc with different initial excitation conditions. (a) EET dynamics with initial excitation at CP47 of M1. The quantum efficiency of charge separation: RP1(M1) is 0.42; RP2(M1) is 0.13; RP1(M2) is 0.28; RP2(M2) is 0.10. Total QE = 0.93. (b) EET dynamics with initial excitation at CP47 of M2. The quantum efficiency of charge separation: RP1(M1) is 0.37; RP2(M1) is 0.11; RP1(M2) is 0.34; RP2(M2) is 0.12. Total QE = 0.94. (c) EET dynamics with initial excitation at CP43 of M1. The quantum efficiency of charge separation: RP1(M1) is 0.57; RP2(M1) is 0.15; RP1(M2) is 0.17; RP2(M2) is 0.06. Total QE = 0.95. (d) EET dynamics with initial excitation at CP43 of the M2. The quantum efficiency of charge separation: RP1(M1) is 0.17; RP2(M1) is 0.05; RP1(M2) is 0.58; RP2(M2) is 0.13. Total QE = 0.93.

kinetics are in good agreement with the <10 ps intra-subunit relaxation and 30–50 ps CP43 to RC EET, respectively. Therefore, our simulation results show a good level of consistency with previous experimental data. We should emphasize that direct comparison between theoretical model and experimental data is highly non-trivial in this case because of the disordered nature of the PSII-cc system and the sensitivity of the EET dynamics to the experimental conditions (sample preparation, temperature, form of the aggregations... *etc.*) More detailed comparisons of the model parameters and EET kinetics between our model with previous theoretical and experimental studies is a work in progress and will be published later.

The EET dynamics in the dimeric PSII-cc system is investigated by performing simulations with four different initial conditions (Fig. 7). In Fig. 7a, we show the EET dynamics when initially the CP47 of the M1 monomer is excited. Following photo-excitation, the excited population in the CP47 of the M1 decreases rapidly, and at the same time the population of excitation in the CP47 of the M2 increases. Excitation energy in the two CP47s reach an equal value at ~15 ps, which indicates that excitation energy can equilibrate rapidly among the two CP47 subunits. In addition, the energy also rapidly flows to the RC of the M1 as well as the CP43 of the M1 within a 15 ps time scale. Remarkably, although the CP47 of the M1 is

initially excited, a significant portion of the excitation energy ends up in the radical-pair states in the M2. This indicates that inter-monomer EET enables excitation energy to be utilized in both RCs. Moreover, Fig. 7b shows the EET dynamics when initially the CP47 of the M2 monomer is excited. The dynamics are qualitatively the same as those shown in Fig. 7a (when the CP47 of the M1 is initially excited), confirming that rapid EET between the two CP47s allows a quasi-equilibrium of excitations among the two CP47s to be established before EET to the RCs. It is interesting to note that rapid energy pooling to the CP47 subunits can also be observed in previous studies of EET dynamics in the PSII super-complex,^{24,28} however the significance of this phenomenon was not explicitly investigated before.

In contrast, when initially the CP43 in one of the monomers is excited, most of the excitation energy goes to the nearest RC and the population dynamics on the two monomers show a significant difference (Fig. 7c and d). Therefore it is confirmed that the inter-monomer EET in the dimeric PSII-cc must occur through the two CP47 subunits.

Croce and co-workers investigated PSII samples with different peripheral antenna sizes.⁵⁴ The results show that the quantum efficiency of charge separation in the PSII often exceeds 0.84, whereas in the PSII with smaller antenna size, the quantum efficiency can be as high as 0.91. Because excitation energies in PSII samples with larger antenna would need more time to reach a RC, it is reasonable that the quantum efficiency increases as the size of antenna decreases. Our theoretical simulations predict that the total quantum efficiency of charge separation in the PSII-cc is about 0.93, in good agreement to the experimental data.

3.5 Inter-monomer EET between CP47s

The rapid inter-monomer EET between the two CP47s revealed in our full EET dynamics of the dimeric PSII-cc system deserves a more detailed investigation. A recent study clearly showed the existence of inter monomer EET in dimeric PSII core,⁵⁵ yet the detailed molecular mechanism and time scales of such process is still unclear. Published structure-based models for EET in the PSII-cc mostly overlooked the inter-monomer EET because the two CP47s are well separated spatially, with the

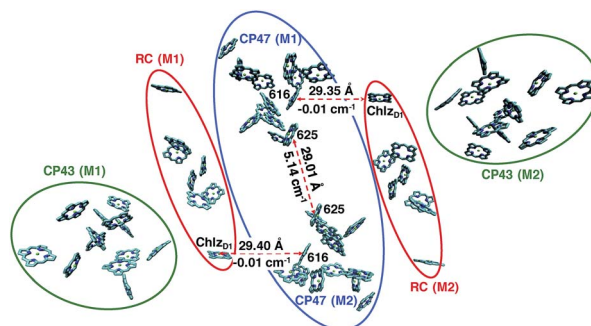


Fig. 8 Illustration of the inter-monomeric excitonic coupling between the two CLA625s. The inter-pigment distances and excitonic couplings between two other representative pairs of CLAs are also shown.

closest inter-CP47 CLAs located at a distance of 29.0 Å apart from each other. So how could excitation energy flow so rapidly between the two CP47s? In Fig. 8, we show the inter-CLA distances as well as the excitonic couplings calculated in this work for three representative CLA pairs that have a CLA–CLA separation of about 29.0 Å. It is clear that the coupling between the two CLA625 sites, which is located in the interface of the two CP47s, is anomalously large. The value of $J_{\text{CLA625(M1)}-\text{CLA625(M2)}}$ is two orders of magnitude greater than those of the other two pairs. Clearly, the large $J_{\text{CLA625(M1)}-\text{CLA625(M2)}}$ plays an important role in the efficient inter-monomer EET between CP47s. A close inspection indicates that the large coupling is a consequence of the near parallel transition dipoles of the two CLA625 molecules. This favorable molecular orientation is due to the C2 symmetry of the PSII-cc system. As a result, the two CLA625s serve as an efficient energy bridge that conducts excitation energy rapidly between the CP47s. Furthermore, we found that CLA625 is also located closely to several CLAs within the same CP47 subunit (Fig. 4). In particular, CLA624 and CLA623 are strongly coupled to CLA625. $J_{\text{CLA625-CLA624}}$ is about -59 cm^{-1} , and $J_{\text{CLA625-CLA623}}$ is about 119 cm^{-1} . These values indicate that CLA625 is well connected to CLAs within the same CP47, which also facilitates the efficient EET between the two CP47s.

To demonstrate the importance of CLA625s in the inter-monomer EET of the PSII-cc, we investigated the dynamics of EET in a mutant PSII-cc, in which the two CLA625 sites are deleted from the model Hamiltonian. The EET dynamics for this mutant PSII-cc are presented in Fig. S5.† Clearly, when the two CLA625s are deleted, the inter-monomer EET can no longer be observed, and the EET dynamics resemble those observed in the monomeric PSII-cc (Fig. 6). We conclude that the EET pathway between the two CLA625 sites plays a crucial role in the inter-monomer EET in the PSII-cc. Nevertheless, the mutant PSII-cc still exhibits a high quantum efficiency for light harvesting since the two monomers could function independently.

3.6 EET in the PSII-cc with a closed RC

The significance of inter-monomer EET in the light harvesting of the PSII-cc is not obvious in normal circumstances. We conjecture that the inter-monomer EET could play a significant role in maintaining the efficiency of light harvesting when

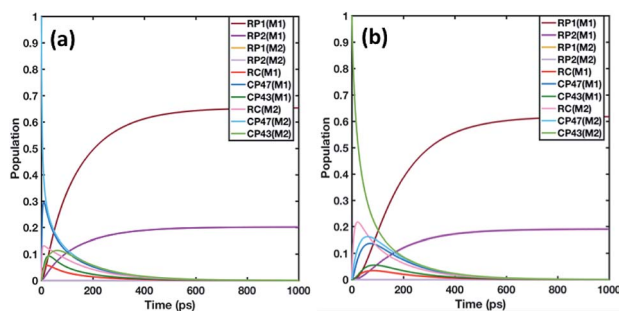


Fig. 9 EET dynamics in PSII-cc when the RC of the M2 is closed. (a) EET dynamics with initial excitation at CP47 of M2. The quantum efficiency of charge separation: RP1(M1) is 0.65; RP2(M1) is 0.20. Total QE = 0.85. (b) EET dynamics with initial excitation at CP43 of M2. The quantum efficiency of charge separation: RP1(M1) is 0.62; RP2(M1) is 0.20. Total QE = 0.82.

one of the RCs is closed. Under ambient conditions for photosynthesis, it is highly likely that one of the RCs in a dimeric PSII-cc is oxidized and only one RC remains active for charge separation, due to the vast mismatch of the time scales between light harvesting (<1 ns) and the recovery of the neutral ground state of the special pair (>1 μ s).¹ To mimic the dynamics when one of the RCs is closed, we simulated EET dynamics of the PSII-cc system while removing the two radical-pair generation pathways in the RC of the M2 monomer. In this case, excitation energy can flow into and out of the RC of M2, but charge separation can not take place in the closed RC of M2.

The EET dynamics in the PSII-cc with the RC of M2 closed are shown in Fig. 9. There, we examine the worst-case scenarios when the core light-harvesting complex belonging to the M2 monomer is initially excited. Because the RC of M2 is closed, we expect that the quantum efficiency of charge separation would be very low if the EET is limited to a single monomer. Nevertheless, EET dynamics shown in Fig. 9 exhibit rapid EET to the CP47 of M2, followed by inter-monomer EET to the CP47 of the M1, and then finally reach the RC of M1, leading to successful charge separation in M1. The quantum efficiency is still greater than 0.8. Our simulations indicate that even with one of the RCs closed, the dimeric PSII-cc still maintains a high quantum efficiency. Thus the inter-monomer EET enhances the robustness of the PSII-cc.

To elucidate the importance of the two CLA625s in the robustness of the light harvesting in the PSII system, we simulated EET dynamics in the mutant PSII-cc (without the CLA625s) with the RC of M2 closed. Fig. 10 shows the simulated EET dynamics when both CP47s are initially populated. The EET dynamics within the M1 monomer (Fig. 10a) are not very different from the corresponding case in a normal monomeric PSII-cc (Fig. 6a), because the RC in M1 is still open. In contrast, the EET dynamics within the M2 monomer are drastically different due to the closed RC. The fluorescence decay dominates the longtime dynamics in M2. As a result, the mutant PSII-cc with the RC of M2 closed shows a significantly reduced total quantum efficiency of ~ 0.47 . Therefore, we have clearly demonstrated that the inter-monomeric EET in the PSII-cc mediated by the two CLA625s play an important role in the robustness of the light reaction in the PSII system.

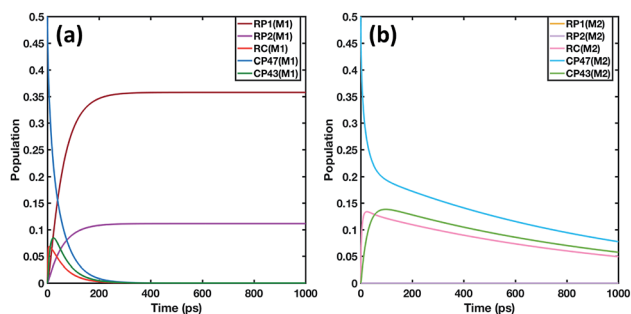


Fig. 10 EET dynamics in mutant PSII-cc with the RC of the M2 closed. (a) EET dynamics in the M1 monomer. (b) EET dynamics in the M2 monomer. The initial condition is that both CP47s are equally populated. The quantum efficiency of charge separation: RP1(M1) is 0.36; RP2(M1) is 0.11.

3.7 Minimum-cut network analysis

To further elucidate the EET dynamics in the PSII-cc system we carried out an analysis of the EET network in the PSII-cc based on a minimum cut approach for network clustering.^{56–58} A minimum cut in a flow network is the division that separates the network into two clusters of nodes, a source cluster and a target cluster, and minimizes the total flow from the source to the target.⁵⁶ The concept is in line with the idea of finding bottlenecks in EET networks and we have successfully adapted the minimum cut method and applied it to study energy transfer in several photosynthetic pigment–protein complexes.⁵⁹

To apply the minimum cut approach to the PSII-cc system, we consider EET network in the PSII-cc. In this network, nodes comprised of exciton states and edges weighted by the calculated rates are used as a weighted network representation for the EET dynamics. We then apply the minimum cut algorithm to locate the bottleneck in the EET network and divide the network into two clusters. When this procedure is applied recursively, a binary minimum-cut tree is obtained.

Fig. S6† shows the minimum-cut tree of the PSII-cc EET network. The minimum-cut tree depicts the source cluster and the target cluster for each cut as well as the corresponding maximal flow. These cuts represent bottlenecks of EET dynamics within the PSII-cc system, and the maximum flows are the sum of the rate constants from the source cluster to the target cluster. The maximum-cut tree also enables us to develop a efficient kinetic clustering method that can be used to generate effective coarse-grained model for EET dynamics. We can start from the bottom of the tree and regroup clusters when maximum flows between them is greater than a selected cut-off value to yield a clustering model for the network.^{57,58} Furthermore, we can control the number of clusters in the reduced model by varying the cut-off value. Once the clustering is determined, we can calculate a coarse-grained (CG) effective energy transfer rate between each two clusters:

$$R_{TS} = \sum_{\beta \in T} \sum_{\alpha \in S} k_{\beta\alpha} \frac{e^{-E_{\alpha}/k_{\text{B}}T}}{Z_S}, \quad (20)$$

where T and S denote the target cluster and the source cluster, respectively. R_{TS} is the effective EET rate from S to T , E_{α} is the energy of the exciton state $|\alpha\rangle$, $k_{\beta\alpha}$ is the rate constant of EET from $|\alpha\rangle$ to $|\beta\rangle$, and $Z_S = \sum_{\alpha \in S} e^{-E_{\alpha}/k_{\text{B}}T}$ is a partition function.

Eqn (20) assumes rapid thermal equilibrium of excitation energy among the exciton states in the source cluster, therefore the effective rate is a sum with Boltzmann weights. To validate the effectiveness of the CG scheme, we can simulate EET dynamics using the CG model and compare the results to those calculated from the full dynamics. A quantitative comparison can be achieved using the integrated absolute population difference between the CG dynamics and the exact dynamics as an error function for a given CG model.

In Fig. S7a,† we plot the integrated absolute population difference for CG models constructed with different numbers of clusters. Clearly, the 7-cluster model yields an excellent description of the EET dynamics, while still keeping the number of clusters in the model minimal. Fig. S7b† shows the excellent agreement between the CG dynamics calculated using the 7-cluster model and the dynamics from the full simulation. Fig. 11 depicts the 7-cluster CG model as well

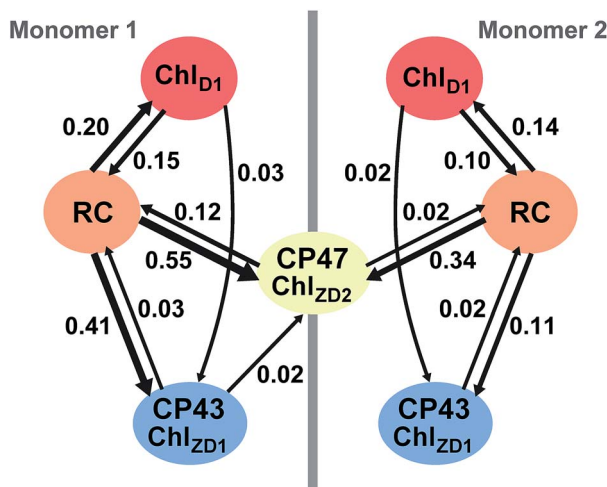


Fig. 11 The 7-cluster kinetic CG model for the PSII-cc obtained from a minimum-cut tree based cluster scheme. The effective inter-cluster rates are also labeled in the network model (unit: ps^{-1}).

as the effective inter-cluster EET rates. It is interesting to note that this CG model basically follows the subunit divisions in the PSII-cc system. However, the minimum-cut scheme places Chl_{D1} in the CP43 cluster and Chl_{D1} in the CP47 cluster, respectively, which is in agreement with our dynamical simulations (Fig. 6) and previous structure-based model for EET in the PSII.^{23,26} The minimum-cut clustering scheme also successfully identified the lowest energy Chl_{D1} sites and separates them from the RC. Moreover, the two CP47s are considered as a large cluster in the CG model, reflecting the rapid inter-monomer EET through CLA625s discussed above. The CG model also indicates that the two PSII core monomers are very similar but not exactly the same, which is a result of the sampling of heterogeneity by the MD simulation.

The CG model for EET in the PSII-cc presented in Fig. 11 suggests that the dimeric PSII-cc is specifically designed to perform light harvesting with high efficiency and robustness. The two CP47s, locating in the center of the PSII-cc structure, could serve as an effective energy pool that collects energy efficiently from the antenna. In this regard, the fact that the CP47 complex contains several low energy sites could be a design feature to facilitate directional and rapid energy transfer by providing an energy gradient. In addition, since CP47 is lower in energy compared to the RC, the energetics also favor energy pooling in CP47, which could be beneficial when the RC is closed. The dimeric form of the PSII-cc also provides the extra redundancy such that the excitation energy could be utilized even when one of the RCs is closed. It seems that nature adopted this design of pooling excitation energy into the CP47s of PSII-cc to enable efficient light harvesting as well as the mitigation of the mismatch in the time scales of light harvesting and the recovery of a closed RC.

Very recently, the entire pigment network and punitive energy transfer pathways in the PSII supercomplex have been elucidated based on high-resolution structural models.^{9,13,15} On the basis of these structural data, it was proposed that energy transfer from the major light-harvesting complexes to CP29 and then

to CP47 is likely the dominant pathway for conducting energy from the outer antenna to the PSII RC. It is interesting to note that our CG model indicates that the PSII-cc with CP47 pooling the excitation energy is well positioned to take advantage of this EET pathway.

4 Conclusions

In this work, we present a structure-based effective model for the dimeric PSII core complex. The model was constructed based on MD simulations of the PSII core complex in combination with the charge density coupled method for site energies and the transition charge from electrostatic potential approach for excitonic couplings. We demonstrated that with proper separation of dynamical and static disorders and rescaling of the site energy fluctuations, system–bath couplings evaluated by our method describes the absorption spectrum of CP47, CP43 and the RC at 297 K as well as the full excitation energy transfer dynamics among the 74 pigments in the PSII core complex.

Simulation of EET dynamics in the monomer of PSII core complex shows that our model describes highly efficient light harvesting in the system. Sites important for EET from CP43 and CP47 to the RC can be identified, and we found that the Chl_z sites do not mediate EET into the RC. In addition, we observe that EET between two antenna complexes takes place through the RC, despite the rapid charge separation dynamics in the RC. Thus, EET dynamics in the PSII core complex exhibit strong dynamical heterogeneity and is conducted by multiple pathways. We conclude that the EET dynamics can not be describe by a single hopping rate and a reasonable description of light harvesting in the complex must take into account the detailed non-equilibrium dynamics. In this regard, the long-lasting debate regarding the validity of the exciton radical pair equilibrium model and the transfer-to-the-trap limited model in the PSII^{7,8,10,26} is partially a result of the overly-simplified nature of gross kinetic models. When the detailed geometry and disordered energy landscape of the PSII-cc are considered, the dynamics become intrinsically heterogeneous and can not be described by a single hopping time.

In the EET dynamics of dimeric PSII core complex, we reveal that the two CP47s can mediate rapid EET between the two monomers, and the two CLA625 sites in the CP47s play crucial role in the inter-monomer EET. The relatively strong excitonic coupling between the two CLA625s is achieved by the parallel orientation of the two molecules due to the C₂ symmetry of the core complex. We showed that after removing the two CLA625s in the system Hamiltonian, the inter-monomer EET is totally suppressed.

We further investigate EET dynamics in the PSII core complex when one of the RCs is closed. In normal PSII core complex, the closed RC does not significantly affect the overall quantum efficiency of the system, since rapid inter-monomer EET can transfer the excitation energy to be utilized by the RC that is still open. However, the quantum efficiency is drastically reduced when the inter-monomer EET is suppressed. We conclude that the dimeric form of the PSII core complex could significantly enhance the robustness of the system, which suggests that the evolution did not make the dimeric PSII core complex just for a structural reason.

Finally, we applied a minimum-cut clustering method to analyze the complex EET network of the 74 exciton states in the PSII core complex. The network

analysis approach produces a 7-cluster coarse-grained model that captures the key EET pathways in the PSII core complex. Furthermore, the coarse-grained model provides a clear blueprint for the design of the PSII core complex. The CP47 subunits, with their favorable energetics and location, serve as a energy pool to collect and distribute the excitation energy to both RCs within the dimer. We suggest that this design allows the high efficiency and robustness of light harvesting in the PSII system, especially when the large time-scale mismatch between the dynamics of light harvesting and the recovery of the radical-pair state back to the neutral state is considered. Furthermore, we suspect that the energy pooling in the CP47s could also contribute to the regulation of excess energy *via* non-photochemical quenching.⁶⁰

Our model shows that the method based on MD simulations and quantum chemistry calculations can be effectively utilized to elucidate the dynamics of light harvesting in complex photosynthetic complexes. Furthermore, the minimum cut based clustering method provides a powerful approach to generate accurate CG models for EET dynamics in large EET networks. This framework should be applicable to general organic molecular aggregates and useful for the design of efficient light-harvesting materials. We believe this approach is likely to bring significant breakthrough towards the understanding of geometrical factors and functional design principles of photosynthetic light reactions.

Conflicts of interest

There are no conflicts to declare.

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