

Theoretical Study on the Excitation Energy Transfer Dynamics in the Phycoerythrin PE555 Light-Harvesting Complex

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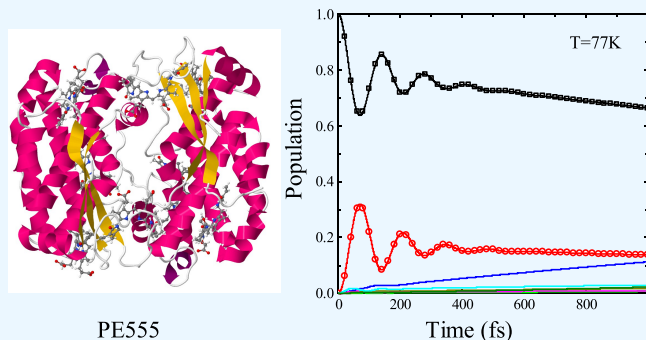
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ABSTRACT: Photosynthesis in nature begins with light harvesting. The special pigment–protein complex converts sunlight into electron excitation that is transmitted to the reaction center, which triggers charge separation. Evidence shows that quantum coherence between electron excited states is important in the excitation energy transfer process. In this work, we investigate the quantum coherence of the PE555 complex in exciton dynamics and its performance and significance in photosynthetic light harvesting. To elucidate the energy transfer mechanism of the PE555 complex, an exciton model is adopted with the full Hamiltonian obtained from structure-based calculations. We used quantum dissipation theory to investigate the excitation dynamic process. The results indicate the existence of long-lived quantum coherence phenomena. We then discuss the pathway of the excitation energy transfer process, which is when the PEB chromophore molecules absorb energy and then transfer the excited energy to the DBV50/61B molecule. To further discuss the effect of the initial coherent superposition of dimeric states on the excitation energy transfer process to the DBV50/61B chromophore molecule, the results indicate that the coherent superposition of initially excited states indeed promotes the transmission of excitation energy to the acceptor state. Furthermore, we investigate the optimization behavior of individual pigment molecules, and these results show that the local protein environment among chromophore molecules can affect the throughput of the system in a controllable manner.



PE555

INTRODUCTION

Natural photosynthetic biological significance is undeniable because it is essential for life on almost all of the Earth. Plants, bacteria, and algae obtain chemical energy through photosynthesis, but heterotrophs depend on these species as the source of their nutrients. The first step in photosynthesis is to harvest energy from sunlight. The light-harvesting complexes consist of special pigment–protein complexes that have evolved specifically for this process. The distinguishing feature of these pigment–protein complexes is that they have a near-unity quantum efficiency.^{1–5} Our work mainly focuses on how the excitation energy transfer process occurs in the PE555 complex, especially the role of quantum coherence. This theme is prominent in theoretical and experimental research.^{6–8} In recent years, interest in light-harvesting devices for some algae has increased, following the experimental results of long-lived quantum coherence of the phycoerythrin 545 (PE545) antenna from *Rhodomonas* sp. CS24 algae.^{9,10} After observing the long-lived quantum coherent oscillation phenomenon for the first time in the Fenna–Matthews–Olson (FMO) complex through two-dimensional electronic spectroscopy experiments (2DES),^{11,12} the electronic 2D spectra of the cryptophyte complexes PC645 and PE555 were obtained.¹³

Recently, some studies have shown that quantum coherence is crucial for achieving efficient light harvesting in photosynthesis. A lot of evidence suggests that the coherence effect is related to the dynamics of the light-harvesting process and therefore also to the mechanism. The existence of such high efficiency requires a better understanding of the balance between ultrafast (femtosecond to picosecond time scale) electron excitation transfer and relaxation to the ground state within and between antenna complexes, as well as the scaling of excitation diffusion time to antenna system size. Therefore, many biophysics research studies focus on clarifying the excitation energy transfer mechanism.^{14–17} The investigation into ultrafast transient absorption in photosynthetic proteins and other light-sensitive biological systems continues to captivate scientific interest. Previous reports have included studies on isolated bacterial reaction centers,^{18–20} Fenna–

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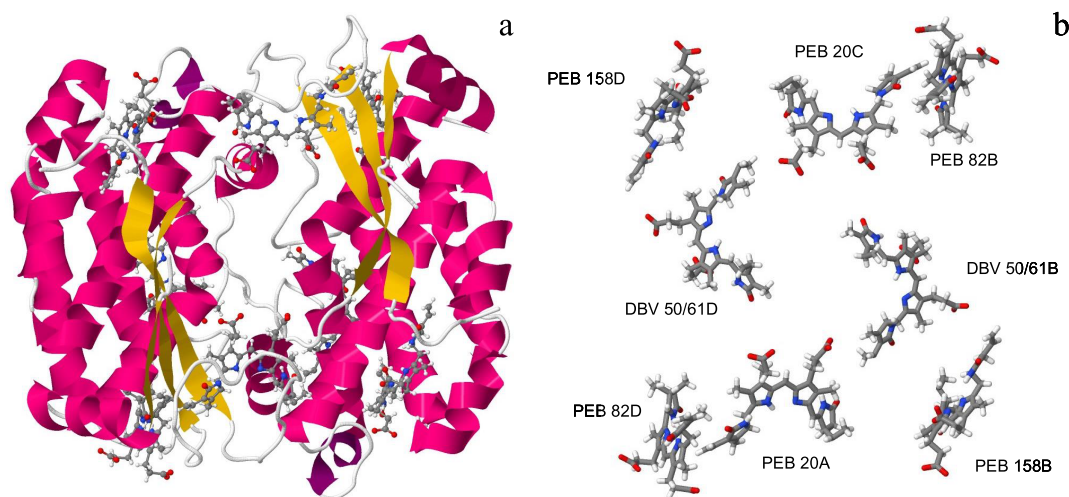


Figure 1. (a) PE555 complex structure with its protein scaffold, embedding eight chromophore molecules. (b) Eight chromophore molecules as depicted in the structural model of the PE555 complex.

Matthews–Olson complexes,^{21,22} bacterial rhodopsin,^{23,24} and light-harvesting complexes. These investigations have uncovered evidence of coherence in biological systems. Recent experiments adopting 2DES have provided further insights into the coherence of photosynthetic complexes. There is evidence for vibrational coherence and electronic coherence.^{9,11,12,25}

To better understand the interrelationships between protein structure and chromophore arrangement, the crystal structures of three cryptobiotic PBPs have been identified: from *Chroomonas* sp. phycocyanin PC645 (strain CCMP 270), PC612 (strain CCAC 1635B) from *Hemiselmis virescens*, and the PE555 complex.²⁶ In this study, we focused on phycoerythrin PE555, which has some similarities to the PE545 complex. The PE555 complex, originating from the marine algae *Hermiselmis Andersen* CCMP 644, serves as another system for light harvesting. The crystal structure of the PE555 complex has been identified with a resolution of 1.8 Å.²⁷ The structure of PE555 is illustrated in Figure 1. Within the PE555 complex, there are six phycoerythrobilin (PEB) chromophores along with two dihydrobiliverdin (DBV) chromophores. The PE555 complex is made up of four subunits (A, B, C, and D), creating a dimer that includes two $\alpha\beta$ monomers, of which the β subunit contains two phycoerythrobilins (PEBs) and one dihydrobiliverdin (DBV), denoted as β 82 (PEB82B, 82D), β 158 (PEB158B, 158D), and β 50/ β 61 (DBV50/61B, 50/61D). The first part of the α phycoerythrobilins (PEBs) is denoted α 20 (PEB20A, 20C). The PC645 dimer and PE545 complex have the same structure, which has a “closed” form. The two β 50/ β 61 pigments are physically in contact. However, the dimer configurations of the PC612 and PE555 complexes show substantial differences, with the $\alpha\beta$ monomers rotated by roughly $\sim 73^\circ$ in comparison to the closed form. This open formation features a water-filled channel that divides the central $\alpha\beta$ pigments. The β 50/ β 61 pigment in the PE555 complex is DBV, with the other three being PEBs. This is unlike the PE545 complex, where all PEB pigments are in the β subunit, and one DBV is in the α subunit. Both complexes have pigments individually attached to the α subunits and doubly attached to the β 50/ β 61 position, and the PEBs at the other two β positions are always individually attached.

In light-harvesting systems, the transfer of excitation energy is known as resonant energy transfer (RET).^{28–31} Historically,

this transfer has been thought to happen at the Förster³² limit within RET theory, where electronic excitation incoherently hops between localized states on different chromophores. The description of this energy transfer is primarily because electronic coherence between chromophores and quantum superposition of excited states on different chromophores can be quickly disrupted by the antenna molecules’ environment, especially by random energy fluctuations. These fluctuations originate from interactions between the vibrational freedom of the protein environment and the electronic excitation of chromophores, which is mainly driven by fluctuations in proteins and solvents surrounding the light-harvesting pigments. Electrostatic fluctuations are caused by physical fluctuations, which regulate the transition energy embedded in the chromophore.³³ Electronic coherence exists based on the coupling strength between chromophores. In light-harvesting systems, the importance of these couplings is elevated as chromophores are packed closely together to boost the antenna’s absorption cross-section. As a result, stable “excitons” frequently occur in light-harvesting antennas, making Förster theory generally less effective. Moreover, recent studies propose that electronic coherence can endure in biological environments since the electronic coupling is weaker than previously thought. As a consequence, it is necessary to go beyond Förster theory to provide a microscopic description of the RET mechanism to describe the light-harvesting system.³⁴ Attention to these subjects has drawn interest from multiple domains. The influence of quantum optical research has resulted in these deviations from the Förster incoherent energy transfer model being recognized as notable quantum effects in photosynthetic light-harvesting systems.

There has always been strong interest in whether the existence of the quantum coherence effect plays an important role in biology. This phenomenon was attributed to the discovery of persistent oscillations in two-dimensional electronic spectra within light-harvesting systems including phycobiliproteins in cryptophyte algae. A large amount of theoretical research on the light-harvesting system has been conducted on the FMO complex.^{35–38} However, there is little research on cryptophyte proteins. So far, the research has mainly focused on the PC645 and PE545 complexes. For the

Table 1. Site Energy Levels and Electronic Coupling Parameters among Chromophores in the PE555 Complex (in cm^{-1})^a

site	1	2	3	4	5	6	7	8
PEB20A	18,688	68	17	20	-13	5	26	-8
PEB158B	68	18,881	12	36	5	5	4	-2
PEB82B	17	12	18,494	-60	29	3	4	20
DBV50/61B	20	36	-60	17,921	-11	1	24	4
PEB20C	-13	5	29	-11	18,921	63	16	13
PEB158D	5	5	3	1	63	18,808	12	43
PEB82D	26	4	4	24	16	12	18,284	-56
DBV50/61D	-8	-2	20	4	13	43	-56	18,131

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PC645 complex, structural modeling was performed based on absorption and fluorescence spectra data to obtain the Hamiltonian and spectral density information of the complex. The density matrix calculation method was used to simulate the excitation energy transfer process.³⁹ Meanwhile, for the PE545 complex, the main focus is on the coupling between exciton transfer and environmental modes. By combining MD simulations and QM/MM calculations, the spectral density of this complex and its exciton dynamics process are determined.⁴⁰ There is a lack of research on the PE555 light-harvesting system. In this article, we primarily investigate the exciton dynamics in the PE555 complex, examine the role of quantum coherence in the excitation energy transfer process, and further elucidate its significance in photosynthesis.

In this work, we apply the DEOM method to explore the exciton dynamics of the PE555 complex. Through the use of the dissipation equation of motion (DEOM) theory, we calculated the population dynamic to study the excitation energy transfer pathway. Additionally, we discuss the best physical environmental conditions that are favorable for sustaining long-lived coherence in light-harvesting complexes. The interaction between the system and the solvent–protein environment significantly affects excitation dynamics. Our observations reveal long-lived quantum coherence oscillations in the population transfer process within the PE555 complex. For the PE555 complex, the calculation results show that the coupling of pigments and the protein environment is necessary to promote the efficient excitation energy transfer process.

MODEL AND THEORY

In our research on the exciton dynamics of the PE555 complex, we utilize an exciton model developed with the full Hamiltonian, which stems from the PE555 complex's structural calculations.^{27,41} The electronic coupling calculations for the PE555 complex are based on a previous study, which computed them using the transition dipole moments obtained from quantum mechanical/molecular mechanics (QM/MM) methods.^{41–43} Notably, the PE555 complex features a large average center-to-center distance between the bilin chromophores, as detailed by Chandrasekaran et al.⁴¹ By employing a nonpolarized force field, they⁴¹ carried out ground state molecular dynamics (MD) simulations, followed by excited state calculations along this trajectory using the ZINDO/S-CIS method (Zerner's intermediate neglect of differential overlap, customized for spectroscopic properties with single excitation configuration interactions).⁴⁴ Despite the inherent constraints of this semiempirical technique, the results along the trajectory are as good as TDDFT calculations.⁴⁵ The electronic structure calculations are based on previous research, and the authors adopted the QM/MM method.^{41,43} In the work done by

Chandrasekaran et al.,⁴¹ each chromophore molecule is subjected to quantum mechanical treatment one by one, while the environment is treated as background charges. To save calculation work, they⁴¹ chose the ZINDO/S-CIS method to calculate the excited state. Chandrasekaran et al.⁴¹ provided the site energies of the PE555 complex along the MD trajectory. As reported by Harrop et al.,²⁷ the excitonic couplings for the PE555 complex are determined using the transition density method at the CIS/cc-pvtz level. Consequently, Table 1 lists the exciton Hamiltonian for the PE555 complex.²⁷

For the PE555 complex, the average distance among chromophore molecules is large. Thus, the excited chromophore molecules are in a delocalized state, which can be utilized within the framework of the Frenkel exciton model. The complete Hamiltonian for the PE555 system can be represented as

$$H_{\text{tot}} = H_s + H_b + H_{\text{sb}} \quad (1)$$

The quantum subsystem component is represented by H_s , where H_s denotes the system Hamiltonian. The interaction between the system and the environment is defined by H_{sb} , which contains both the system and bath quantity. Approximately, the interaction H_{sb} can be described in a bilinear form as $H_{\text{sb}} = \sum m l m \rangle \langle m l B_m$, with B_m serving as the bath operator. The bath Hamiltonian H_b is used to model the vibration modes of the environment as a set of independent harmonic oscillators, which is $H_b = \sum_{\alpha} \hbar \omega b_{\alpha}^{\dagger} b_{\alpha}$, where b_{α} is the annihilation operator, and b_{α}^{\dagger} is the creation operator for the α th mode. The Hamiltonian of the system can be expressed as

$$H_s = \sum_{m=1}^N \varepsilon_m |m\rangle \langle m| + \sum_{m \neq n}^N J_{mn} |m\rangle \langle n| \quad (2)$$

Here, ε_m denotes the electronic excitation energy of the site m , the electronic coupling term between site m and n is presented as J_{mn} , and N is the total number of chromophore molecules.

The spectral density representing the interaction between the system and the bath can be described by $J(\omega) = (\pi/2) \sum_j c_j^2 \delta(\omega - \omega_j)$.⁴⁶ It determines all bath correlations related to the PE555 system. We use the Drude–Lorentzian correlation function $C(t)$ to stand for the bath correlation function. It is concerned with the bath spectral density $J(\omega)$ by the fluctuation–dissipation theorem, written as⁴⁷

$$C_j(t) = \langle \tilde{B}_j(t) \tilde{B}_j(0) \rangle \\ = \frac{1}{\pi} \int_0^{\infty} d\omega J(\omega) \frac{\exp(-i\omega t)}{1 - \exp(-\hbar\omega/k_B t)} \quad (3)$$

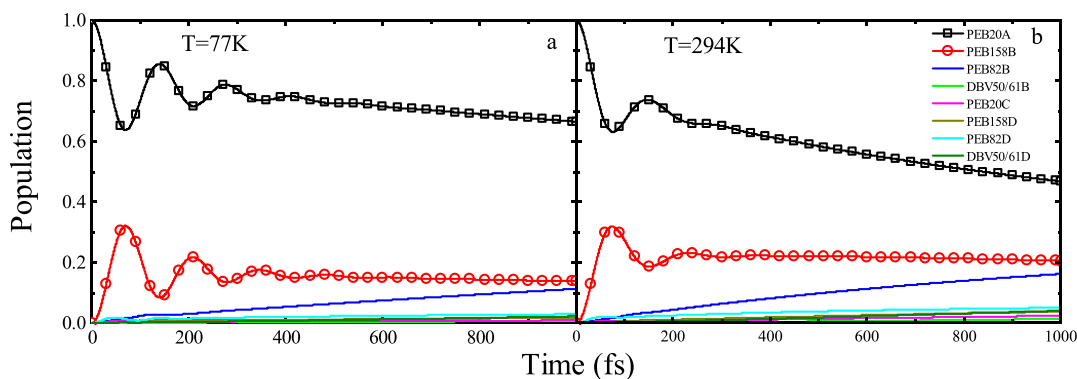


Figure 2. Population dynamics of the eight-pigment model at $T = 77$ K (a) and $T = 294$ K (b), with initial excitation on the PEB20A chromophore molecule.

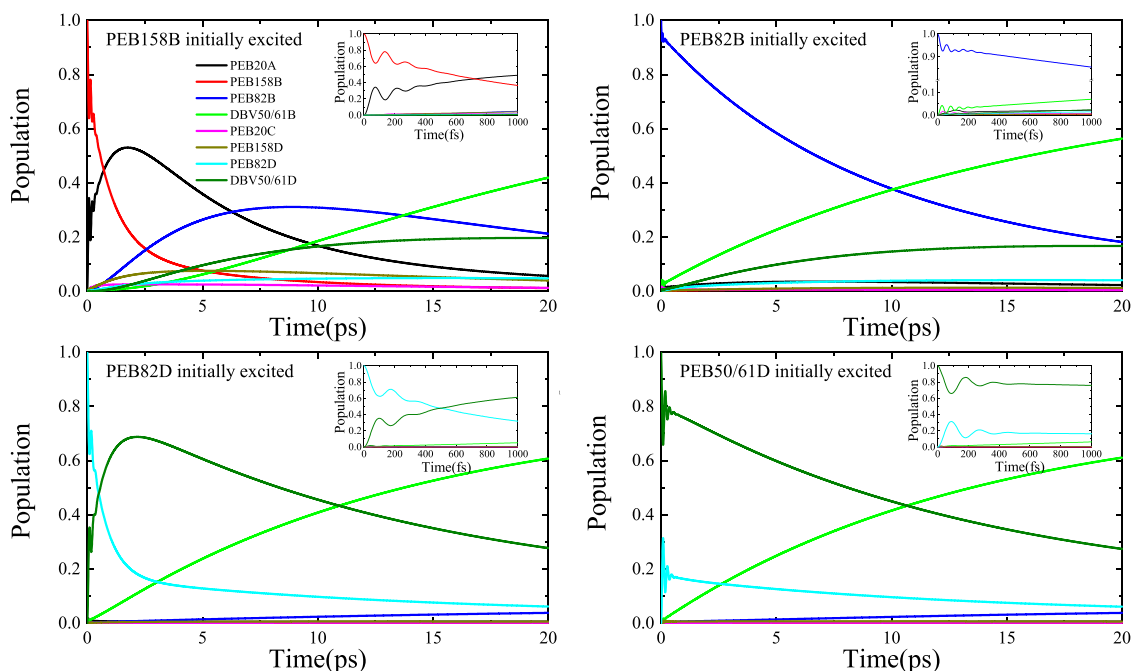


Figure 3. Population dynamics of the PE555 complex at $T = 77$ K, with initial excitation on PEB158B, PEB82B, PEB82D, and DBV50/61D chromophores.

Using DEOM theory, we investigate the processes involved in excitation energy transfer in the PE555 complex in this work. This theory was developed by Yan et al.,^{48–51} which has some differences between the DEOM theory and the traditional quantum dissipation theory. By using DEOM theory, the dynamic processes of reduction systems and baths can be described simultaneously. This method is practical for studying the dynamics of hybridization between systems and baths. This theory is an important method for investigating open quantum systems.

Dynamic variables in the DEOM approach are referred to as dissipation density operators, and they are expressed as^{52,53}

$$\rho_n^{(n)}(t) \equiv \rho_{n_1 \dots n_K}^{(n)}(t) \equiv \text{tr}_B[(\hat{f}_1^{n_1} \dots \hat{f}_K^{n_K})^\circ] \rho_T(t) \quad (4)$$

These dissipations inside $(\dots)^\circ$ are irreducible, and these dissipations satisfy the bosonic commutator relation, which is expressed as follows, $(\hat{f}_k \dots \hat{f}_k)^\circ = (\hat{f}_k \dots \hat{f}_k)^\circ$. In this eq 4, $n = n_1 + \dots + n_K$, where n_k is the specified number of dissipations, and $n_k \geq 0$, $n \equiv \{n_1 \dots n_K\}$. They assign the n -dissipative composite

structure $\rho_n^{(n)}$ of eq 4. The general formalism of the DEOM method is expressed as follows:

$$\dot{\rho}_n^{(n)} = -[iL(t) + \gamma_n^{(n)}] \rho_n^{(n)} + \{\rho_n^{(n-1)}\} + \{\rho_n^{(n+1)}\} \quad (5)$$

It is obtained by applying the quantum Liouville equation $\dot{\rho}_T(t) = -i[H(t) + h_B + H_{sb}, \rho_T(t)]$ to the total density operator of eq 4, and the total density operator defines L as the system Liouvillian superoperator. Generally, the system Hamiltonian generates L such that $L \cdot \equiv [H, \cdot]$, the H_b term is estimated via the generalized diffusion equation, and the H_{sb} term is evaluated using the generalized Wick theorem. This theoretical approach delivers precise numerical results, validating the long-lived quantum coherence dynamics of the PE555 complex at both ambient and low temperatures. It can be employed to reliably investigate the effect of system-bath coupling strength on the excitation energy transfer process. Additionally, it provides numerical data for the coherent density matrix elements, facilitating the exploration of the excitation energy transfer dynamics of the PE555 system.

Some researchers⁴¹ found that the width of the distribution of states (DOS) is similar to the width of the corresponding pigment in the PE545 complex. In comparison to the PE545 complexes, the average peak position of the PE555 pigment does not exhibit a significant difference. Viani and colleagues⁴⁰ utilized the following spectral density parameters to align experimental data with numerical fitting: reorganization energy $\lambda = 24.14 \text{ cm}^{-1}$ and bath cutoff frequency $\gamma = 56.82 \text{ cm}^{-1}$. Thus, we adopted the above data to simulate the exciton dynamics of the PE555 complex. The calculation results are presented using the DEOM method.

RESULTS AND DISCUSSION

In this article, we investigate the exciton dynamics process in the PE555 complex. First, we present the calculation results of the PE555 complex initial excitation on the PEB20A chromophore, as shown in Figure 2. The calculation results at low temperature 77 K and room temperature 294 K are shown on the left and right sides of the figure, respectively. For the PE555 system, the PEB20A chromophore molecule is located at the edge of the structure of the PE555 complex, which can promote excitation energy transfer to other chromophore molecules after relaxation within the PE555 complex. We utilized the Debye spectrum to characterize the spectral density of the environment. As is known to all, the coupling strength between the system and the environment is represented by the reorganization energy λ . Based on theoretical research,^{40,41} we utilize a reorganization energy of $\lambda = 24.14 \text{ cm}^{-1}$ and a cutoff frequency of $\gamma = 56.82 \text{ cm}^{-1}$. Moreover, we assume that all chromophore molecules of the PE555 complex have the same spectral density. When the PEB20A chromophore molecule is initially excited, in terms of protein structure arrangement, the PEB20A chromophore molecule and the PEB158B pigment molecule are close together in the structure arrangement. Due to the relatively large electronic coupling energy (68 cm^{-1}) between the PEB20A and PEB158B pigments, quantum coherent oscillations between the PEB20A and PEB158B molecules were observed. As shown in Figure 2a, notably, the quantum coherence time lasts for about 500 fs at a low temperature, and the electronic coherence time maintains ~ 300 fs at room temperature, as shown in Figure 2b. Our theoretical calculation results indicate that significant quantum coherence phenomena can be observed, with approximately several hundred femtoseconds of quantum coherence observed between the PEB20A and PEB158B pigments at low and room temperatures. These research results can provide some ideas for observing such quantum coherent oscillations in the experiment.

Figure 3 shows the population dynamics of four different initially excited chromophores at 77K. When the PEB158B chromophore is initially excited, PEB20A responds promptly. The population oscillations of PEB158B and PEB20A are noticeable in the first few hundred femtoseconds, and the population of PEB158B then decays to zero within 10 ps. Meanwhile, the excitation energy diffuses toward the surrounding chromophores and ultimately funnels to DBV50/61B. For the case where the PEB82B pigment molecule is initially excited, a certain degree of oscillation can also be detected, but the coherence time is relatively short. When the PEB82D or DBV50/61D molecule is initially excited, the duration and amplitude of the population oscillations are smaller. When initially exciting the PEB82D pigment, we observed the quantum coherence phenomenon.

Subsequently, the excitation state was transferred to the DBV50/61B pigment molecule. After 10 ps, the population of the DBV50/61B molecule surpasses the population of the initially excited PEB82D chromophore. In this case, the DBV50/61D pigment is initially excited, and the excitation energy is subsequently conveyed to the PEB82D chromophore. As time accumulates, the populations of the PEB82D and DBV50/61B pigments gradually increase. At last, the populations flow toward the DBV50/61B pigment. Obviously, the efficient pathway for excitation energy transfer involves the PEBs absorbing solar energy and conveying it to the DBV50/61B molecule. By adopting different initial excited states, the population will be redistributed, and the time scale of the excitation energy transfer is affected.

To further investigate the coherent oscillations of similar dimers that occur in the PEB20A and PEB158B pigment molecules, we conducted the following calculations. The strong coupling strength of 68 cm^{-1} between the PEB20A and PEB158B molecules quickly causes the population of the PEB20A and PEB158B molecules to oscillate synchronously similar to a dimer. In order to study how the initial coherent superposition of the dimer states affects energy transfer to the acceptor DBV50/61B states, we used exciton Hamiltonians to calculate the excitation dynamics, where a single excited state was used instead of the dimer state, and the single state's excitation energy was derived from the average energies of the PEB20A and PEB158B pigments. The single state, meanwhile, maintained coupling strength equivalent to that of the other pigment networks. Figure 4 illustrates the population of the

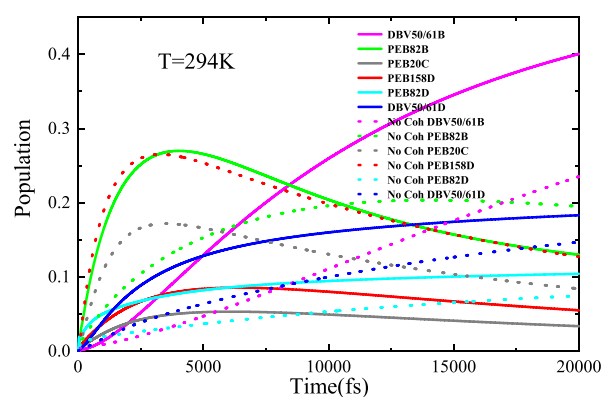


Figure 4. Comparison of populations of other chromophores when the dimer state is replaced by the single mean state in order to initially remove initial coherence. Solid curves show the chromophore populations observed with the coherently coupled dimer initially states; dashed curves give populations obtained when the mean state is excited.

acceptor pigment at ambient temperature over time, contrasting the coherent coupled dimer state (solid line) and the average single state with incoherent initial excitation. As depicted in Figure 4, the population of the DBV50/61B pigment (solid magenta curve) accumulates more under coherent conditions. This behavior can simply be explained by the fact that the coherent superposition of the initially excited dimer states indeed facilitates the energy transfer to the target acceptor DBV50/61B pigment, though the effect is weak.

We have redefined the Hamiltonian for our model system by substituting the initial coherent excited dimer structure with a

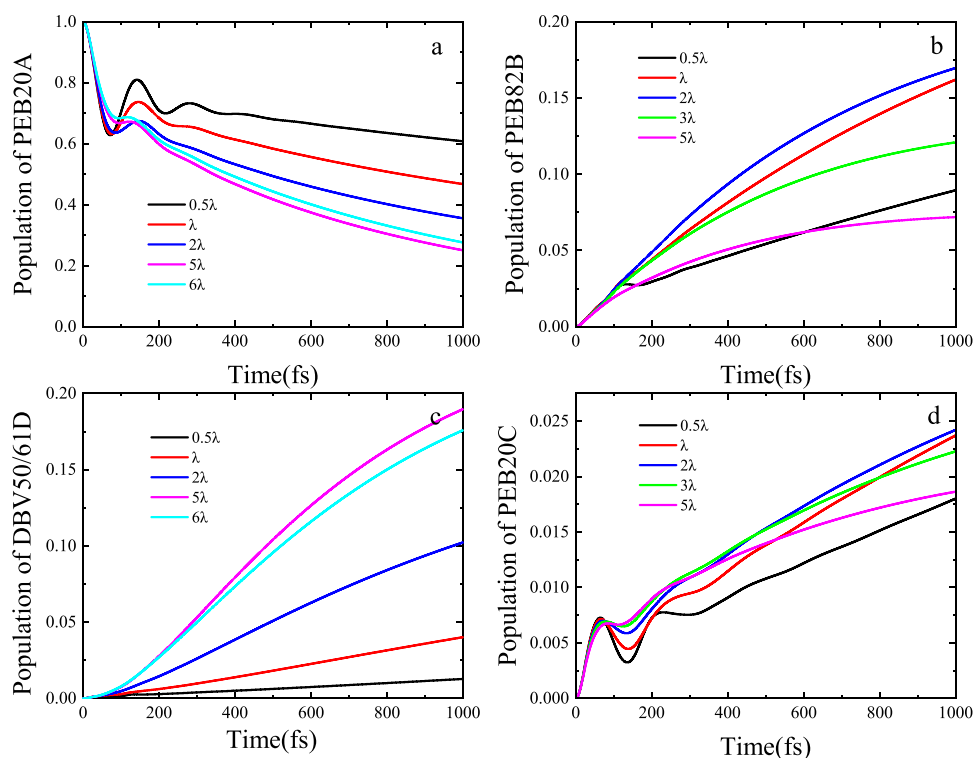


Figure 5. Population dynamics of various pigment states over time following initial excitation at the PEB20A site. Panels (a–d) each depict the outcomes for different system and bath coupling strengths for the PEB20A, PEB82B, DBV50/61D, and PEB20C chromophores within the network.

single “mean state,” thereby removing the initial excited coherence. Our research indicates that the model system’s Hamiltonian exhibits different capabilities in transferring excitation energy to its outer states, based on the coherence of the excited molecular structure. The results shown in Figure 4 indicate that excitation in a coherent form is more helpful in transferring the excitation energy to the lowest energy chromophore molecules. Therefore, we conclude that, at least for the PE555 complex model with an independent unrelated bath for the different chromophores, the initial excitation coherence in the theoretical calculations plays a certain role in the energy transfer characteristics of the network for different pigment molecules. By using two different Hamiltonian mechanisms, we calculated the entire excitation energy transport process for the PE555 complex and found that when a dimer Hamiltonian model is adopted, the population of the acceptor molecule is accumulated the most, that is, the energy transferred to the DBV50/61B molecule is the most. We believe that due to the strong coupling between dimers, the coherence between the two quantum states is significant, which further affects the process of excitation energy transport.

We discuss the coupling term between the system and the environment, which affects the excitation energy transfer process in the PE555 complex. We performed extensive theoretical analyses at room temperature by modifying the reorganization energy parameter in the Drude spectral density function. The scope of our discussion is within the scale range of a coherent time scale. In Figure 5, we provide the results of the time-dependent population dynamics for various chromophore molecules. The behavior observed on the panel of this graph indicates that population optimization within the coherent time scale can be monitored by adjusting the

reorganization energy parameter as a multiple of $\lambda = 24.14 \text{ cm}^{-1}$, as depicted in Figure 5a. With the initial excitation of the PEB20A chromophore molecule, the population oscillation value reaches about 0.7 at 300 fs in the case of the reorganization energy being 0.5λ (black line). As the reorganization energy λ continues to increase, such as λ , 2λ , 5λ , and 6λ , as demonstrated by the red and blue lines, we see that the coherence oscillations are gradually reduced. In this state, the population value is below 0.5λ . When considering larger reorganization energies such as λ and 2λ , the population value of the excited state decreases as the environmental coupling strength increases. When the coupling strength between the system and the environment is 5λ , we see that the population of this exciton state is at its minimum value. As the coupling strength increases, for example, 6λ , the population increases instead; therefore, for this exciton state, the ideal coupling strength between the system and the bath is determined to be 5λ , and the population decreases the fastest. In short, for the excited state PEB20A molecules, when the coupling strength between the system and the environment is equal to 5λ , it is most conducive to excitation energy transfer.

We also calculate the evolution of the populations of the PEB82B, DBV50/61D, and PEB20C molecules with the value of the reorganization energy. For instance, as depicted in Figure 5b, the PEB82B chromophore exhibits a decreasing population value with increasing reorganization energy. When the reorganization energy is 5λ , the population of the PEB82B molecules decreases over time. When the system-bath coupling strength reaches 2λ , the population of the PEB82B molecules is at its maximum. So, for the acceptor molecule, the optimal value for the PEB82B molecules is 2λ in the excitation dynamics process. Depending on their positions within the network, various chromophore molecules achieve population

maximization at different reorganization energy values. The population oscillation of the DBV50/61D pigment molecule under varying coupling intensities between the system and its ambient environment is depicted in Figure 5c. The population value reaches its peak at a reorganization energy of around 5λ . For the PEB20C molecule, the population oscillation behavior is asymptotic, as illustrated in Figure 5d. We note that the population value is maximized at a lower reorganization energy of 2λ .

The optimization behavior of increasing the coupling strength of the system and the bath can be observed in a simple model of the light-harvesting system.^{54,55} We used the principle of stochastic resonance to reveal this optimization behavior. When the coupling strength between the system and the environment changes, the populations of pigment molecules will be affected. For a pair of sites where the static excitation energy is separated by ϵ and the electronic coupling Δ is small, for example, if the solvent reorganization energy is weak, fluctuations in site energy due to bath dynamics will be minimal compared to the electronic excitation energy gap, and almost no population transfer will occur. Increasing the system-bath coupling leads to site energy fluctuations reaching the scale of the static excitation energy gap; in many cases, the fluctuation will cause the site energy to enter a resonance state, and limited electronic coupling will facilitate substantial particle population transfer, maximizing the energy transfer rate between sites at a specific system-bath coupling value. With stronger system-bath coupling, larger site energy fluctuations will frequently push the system out of resonance, resulting in a reduced level of population transfer across the network. The observations shown in Figure 5, which detail the stochastic resonance behavior in this model with precise quantum dynamics treatment, indicate that the fundamental ideas of stochastic resonance are robust in optimizing the behavior of nanostructured quantum dynamic light-harvesting systems.

CONCLUSIONS

In conclusion, we have comprehensively discussed the excitation energy transfer mechanism within the PE555 light-harvesting complex using theoretical methods. We conducted numerical calculations by the Drude spectral density form with the DEOM method at room temperature and low temperature. The calculation results show that quantum coherent beating signals can last for about 500 fs at low temperature, and the coherence time is about 300 fs even at room temperature. Additionally, we examined the population dynamics between distinct chromophores to investigate energy transfer pathways. Through the excitation of different chromophore molecules, we carried out the excitation dynamic calculations up to 20 ps for the PE555 complex. We observed that regardless of which chromophore molecule is excited, the excitation energy eventually flows to the DBV50/61B molecule, which is the closest to the reaction center as the final acceptor chromophore molecule. To put it differently, the excitation energy transfer process follows the pathway where PEBs chromophores absorb solar energy and convey the excitation energy to the DBV 50/61B molecule. To investigate the impact of the initial coherent superposition state of the dimer made up of PEB20A and PEB158B molecules on energy transfer to the final acceptor molecule DBV50/61B state, we conducted theoretical calculations using a Hamiltonian that replaces the dimer state with an average singlet state. The

energy of this singlet state is the average of the energies of the PEB20A and PEB158B molecules. In addition, the singlet state has the same coupling strength with other pigment molecules as before. The calculation results show that when PEB20A and PEB158B molecules form a dimer in the excitation energy transfer process, the population flowing toward the final acceptor molecule DBV50/61B state is the largest. This discovery indicates that excitation energy transfer in the form of coherence is helpful to improve the efficiency of excitation energy transfer.

We analyzed how the magnitude of the system-bath coupling strength affects the population dynamics of the PE555 complex. The scope of our discussion is within the coherent interval time, and we conducted a series of theoretical exciton dynamics calculations and found an optimal value that positively influences the exciton dynamics in individual chromophore molecules. These findings indicate that the local protein environment around pigment molecules can be adjusted, helping in the creation of artificial light-harvesting complexes and providing design guidelines for photovoltaic electronic devices.

At present, there is relatively little research on the excitation dynamics of the PE555 complex. We employed the DEOM method to analyze the dynamics of excitation energy transfer in the PE555 light-harvesting system. The calculation results show that there is a quantum coherence phenomenon in the exciton dynamics of the PE555 system, at either low temperature or room temperature. This discovery indicates that the excitation energy transfer process of the PE555 complex is carried out in the form of quantum coherence. In addition, by exciting other chromophore molecules, we found the excitation energy transfer pathway of the PE555 system. Research has shown that each pigment molecule has a certain optimization value for the excitation energy transfer process of the PE555 complex. We provide different optimization values for the stochastic resonance environment parameters for individual pigments, and these findings indicate that the surrounding pigment–protein microenvironments of different chromophore clusters can be regulated to control system throughput. Consequently, we speculate that integrating stochastic resonance effects with environmental modifications may yield crucial insights into developing efficient artificial photosynthesis systems.

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Notes

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