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Theoretical Examination of Long-range Energy Propagation in Nano-Engineered Light Harvesting Antenna Arrays

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Abstract. Excitation energy transport in a biomimetic molecular nanoarray constructed from LH2 antenna complexes is investigated by a master equation approach including the effect of coherent hopping. Calculated stationary and transient fluorescence signals upon incidence of a diffraction-limited light pulse are compared with measurements. Energy transport was established from the influence of active energy-guiding layers on the observed fluorescence emission. Energy migration occurs as a result of efficient coupling between many hundreds of LH2 complexes. We obtain an analytical expression of stationary fluorescence distribution solving the master equations of the system. The time dependent fluorescence intensity is derived using the same formalism. The numerical results show a reasonable consistency with the experimental result in the engineered nanoarray of LH2 complexes. In addition, our results show that quantum coherence mechanism is necessary to explain the long distance energy transport. These results demonstrate the potential for long-range energy propagation in hybrid systems composed of natural light harvesting antenna molecules from photosynthetic organisms.

1. Introduction

Photosynthesis, one of the most essential energy-conversion processes on the planet, begins with the absorption of a photon of the incident light by light-harvesting pigments forming an electronic exciton, followed by excitonic transport to the photochemical reaction centre (RC), where charge separation occurs and the energy is finally converted into stable chemical bonds [1, 2, 3, 4]. Although there exists a large variety of photosynthetic organisms, distinguishable by their antennas of light harvesting and mechanisms of energy transfer, they share some basic transport principles. Recently, the unique capability of the light harvesting apparatus to guide electronic energy to the reaction centre with almost unity efficiency has been extensively investigated by spectroscopic and theoretical approaches, leading to important breakthroughs in our understanding of the photosynthesis physics [5, 6, 7, 8, 9, 10].

With the advance of protein crystallography and electronic microscopy, there emerges a wealth of structural information on individual photosynthetic units ranging from the peripheral light harvest antenna to the core complex and reaction centre [5, 6, 7, 8, 9, 10, 11, 12]. A natural next step is to study supra-molecular architecture formed from these individual photosynthetic units in ensemble machineries. Recently, submolecular-resolution images of various photosynthetic membranes have been obtained using atomic force microscopy, and structural organization of the pigment-protein aggregates on a large spatial scale has been measured directly [13, 14, 15, 16, 17]. Understanding architectural designs of the native supra-molecular structure such as photosynthetic membranes and their mechanisms for light harvesting and energy transfer is important to guide designs of future energy devices. It is a natural strategy to use the architectural information from photosynthesis to construct bio-inspired solar cells. A major open question is how we can design hybrid light converting constructs with superior optical properties, such as a broad spectral range, high absorption cross section and high photostability, while retaining high overall efficiencies and adaptation of light-harvesting in nature. With the advent of nanotechnology, biomolecules can now be manipulated with nanometer precision in a massively parallel fashion, and be combined with crystalline nanoparticles, nanowires, and surfaces into complex structures with new physical and chemical properties [18, 19, 20, 21, 22, 23, 24, 25, 26, 27], which opens the possibility to achieve the hybrid light converting devices.

Since the initial stage of photosynthesis, such as light harvesting and charge separation, involves pigments of sizes below 100 nm, assembling them into hybrid devices requires control and agile manipulation of structures on the nanoscale level. New venues to such designs have been opened up by chemical synthesis of nanostructures and their biochemical conjugation as well as the sustained improvements of nanotechnology machinery. Hybrid nanostructures comprising these biological photosynthetic systems and nanostructures, such as semiconductor nanocrystals, metallic nanoparticles or carbon nanotubes, can now be synthesized in the laboratory [21, 22, 23, 27]. Natural photosynthetic complexes that present excellent systems to study basic physical and

chemical processes underlying the conversion of sunlight energy, can be used to guide constructions of artificial nanoscale devices capable to perform either efficient energy transfer or charge separation or both. Quite possibly, photosynthetic complexes themselves could be used for fabrication of hybrid devices to convert light into electricity or chemical energy. Along this direction, recently, nanoscale patterns of functional light-harvesting LH2 complexes have been successfully fabricated [28, 29, 30, 31]. In the mean time, Escalante et al. [29] investigated the energy propagation in the engineered nanoarrays and found evidence of long-range transport of excitation energy within the biomimetic molecular nanoarrays constructed from LH2 antenna complexes. In the work of Escalante et al., two systems were investigated, a two-dimensional crystal of LH2 complexes, and an effectively one-dimensional nanofabricated array of the same complexes. They resonantly excited the LH2 assemblies with a diffraction-limited laser beam of 800 nm wavelength, and then imaged the fluorescence emission from the nanoarrays. For the case of the 2D-LH2-crystal, it is found that a full width of half maximum (FWHM) of the fluorescence emission was about 900 nm, compared with an FWHM of 400 nm for the diffraction limited spot size of the incident laser beam. The distance of energy transport is about 250 nm in one direction in the 2D crystal, and it becomes even larger for the one dimensional system. Actually, for the case of the nanopatterned line array of LH2 complexes, the FWHM of the intensity profile of fluorescence emission increases to 1200 nm with the same excitation laser beam. This means that the excitation energy migration distance reaches to about 400 nm. Compared with the less than 50 nm transport distance in a native bacterial photosynthetic system, the current transport distance is abnormally long [32]. In a real photosynthetic system, such long-range transport may not be necessary for light harvesting. For example, the photosynthetic membranes grown under low-light conditions contain a high LH2-to-LH1 ratio (up to 11) to enhance the efficiency of photon capture. In such a case, the estimated energy transfer distance from the farthest LH2 to a reaction centre is only about 40 nm [33]. However, in an artificial or a hybrid system, long-range energy transport may be necessary, and understanding its mechanisms is essential to help design artificial light-harvesting antenna. In this paper, we will analyze the long distance propagation of excitation energy in engineered LH2 assemblies by a master-equation approach, which is followed by discussions on quantum mechanical implications.

Traditionally, it is assumed that the energy transfer between photosynthetic units such as LH1 and LH2 complexes is incoherent while the excitation transfer within a given photosynthetic complex is at least partially quantum coherent[4]. Therefore, the dynamics of the excitation transfer on the photosynthetic membrane is usually described in terms of a probability master equation for a single excitation hopping from site to site[34, 35, 36]. However, this description of exciton transfer requires considerable modification in light of the recent experimental evidence on the existence of quantum coherence in photosynthetic systems [37, 38]. The measurement of transient fluorescence showed that the lifetime of a LH2 complex array is only about one third of the value of isolated LH2 complex [39], pointing to the cooperative superradiance that may play a

significant role in the excitation transfer in LH2 array. A recent theoretical estimate also demonstrates that the probability master equation method seems inefficient to explain this anomalous long distance energy transport[32]. As a first approximation of the energy transfer calculation, we examine the excitation dynamics based on the master-equation approach. A general analytical expression for the stationary fluorescence emission is also obtained for any excitation profiles. Given the available parameters in the literature for native photosynthetic antenna systems, estimated distances for energy transport are much less the experimental values both in 2D crystal and 1D nanowire cases. Therefore, the effect of quantum coherence is indispensable in an accurate theoretical description. Cooperative spontaneous emission between LH2/LH1 complexes, also known as superradiance, has to be taken into account. When a collection of LH2 transition dipoles oscillate in phase, their amplitudes add up coherently to form a large effective dipole. The oscillator strength, and consequently, the radiative decay rate, is proportional to the number of dipoles, which is defined as superradiance coherence size. The excitation transfer rate is enhanced as a result of the same coherence size. In the generalized master equation approach, only when the quantum coherence effect is included, the experimental results can be explained satisfactorily.

This paper is organized as follows. In Section 2, we outline the theoretical framework of probability master equation, and an analytical expression of the stationary fluorescence emission is derived for any excitation modes. In Section 3, the results of numerical simulation are compared with the experimental data. Superradiance effect is introduced to calculate the temporal and special fluorescence emission as the prediction of the theory. Some discussions and conclusions are presented in Section 4.

2. Structure of Light Harvesting Antenna Complexes Nanoarrays and Excitation Kinetics

In recent experiments probing long range energy transport, nanoarrays of light harvesting antenna LH2 complexes were fabricated using a combination of site-directed mutagenesis, nanoimprint lithography and multivalent host-guest interactions [28, 29, 30, 31]. They used two different LH2 assemblies for energy propagation experiments. The first type is LH2-only 2D crystals, selected from lipid reconstituted LH2 crystals of sufficient sizes, and the second is engineered quasi-1D 80 nm wide line arrays of LH2 complexes. Although no detailed arrangement of LH2 complexes was revealed, a hexagonal array is assumed to be a reasonable assumption for isotropic constructions [39]. As shown in figure 1, a hexagonal network is therefore adopted, which is consistent with the native structure in photosynthetic membrane [40], where one LH2 complex is surrounded by six others in a paracrystalline packing. The size of the LH2 complex was taken from the crystal structure in the Protein Data Bank (1KZU of Rps. Acilophia 10050). The inner diameter of a LH2 complex is 2.5 nm and the outer diameter is 7.5 nm as shown in the figure. Shown in figure 1a is a 2D array, and in figure 1b, a LH2 nanowire used for guided energy propagation. In the experiment,

Figure 1. Schematic representation of different LH2 substrates used for energy migration experiments: (a) A lipid reconstituted LH2 2D crystal; (b) A nanometer 1D array of LH2 complexes. A plausible model of the arrangement of LH2 and core complexes in the hybrid membrane.

the width of the nanowire is about 80 nm, which can accommodate 9 LH2 complexes chains since there are some gaps between these LH2 complexes. The centre to centre distance between two LH2 rings is set to 8.0 nm, consistent with structure data of natural photosynthetic membranes [33].

To investigate the long range energy propagation, we use a similar LH2-network model as in [34, 35, 36] but with spatial configuration. For simplicity, we start with a one-dimensional LH2 chain with N units, then move to a more realistic two-dimensional LH2 crystal and a LH2 nanowire system. In the one dimensional system, a LH2 complex is considered to be a two-level system since we are only interested in excitation kinetics. In the chain, any complex can be excited or de-excited, and a maximum of N excitations can exist in the system. In a dynamical picture, a picosecond flash creates i excitations within this chain, and these excitations decay in time by both radiative (fluorescence) and nonradiative processes. An initially excited donor complex can transfer its excitation to an acceptor complex. As dephasing occurs, the donor and acceptor phases become uncorrelated. Then the energy transfer can be modelled as an incoherent process, where excitation energy is first localized on a donor molecule(or complex) and is subsequently transferred to an acceptor via Förster mechanism under the assumption of a dipole-dipole electronic interaction.

To describe the excitation dynamics in the LH2 array with no quantum coherence effect, we can set up a set of master equations as follows

$$\frac{dp_i}{dt} = A_i - (K_i + \sum_j k_{ij})p_i + \sum_j k_{ji}p_j, \quad (1)$$

where the site index i runs from 1 to N , p_i is the (unnormalized) probability that complex i is excited, A_i is the rate of light absorption by complex i , K_i is the rate of local decay including florescence, and k_{ij} is the rate of transfer from complex i to j . The intensities of the laser field used in experiment are usually very weak, therefore it is assumed that the rate of light absorption is independent of the site states. We assume that the laser profile is of Gaussian $A_i = A_0 e^{-\frac{[(i-i_0)a]^2}{2\sigma^2}}$ with standard deviation σ , here a is center to center distance between two neighboring LH2s, and the center of the laser located at site i_0 . We consider the nearest neighbour interaction, and let $k = k_{ij} = k_{ji}$. The transfer rate k , measured from pump-probe experiments [41, 42], agrees with that calculated from by means of dissipative quantum mechanics, and the estimate transfer rate from LH2 to LH2 complex is about $k \approx 0.1 \text{ps}^{-1}$ from [43]. For each site, we assume the same decay rate $K = K_i$ for $i = 1$ to N . The dissipation rate is taken as the inverse of the singlet excited state lifetime of Bchl in [45, 46], i.e., $K = 10^{-3} \text{ps}^{-1}$. Then we have a triangular linear system of coupled equations

$$\frac{dp_i}{dt} = A_i - (K + 2k)p_i + kp_{i-1} + kp_{i+1}, \quad (2)$$

For the stationary case, $dp_i/dt = 0$, and let $\alpha = K + 2k$, we have the following matrix equation

$$\begin{pmatrix} \alpha & -k & 0 & \cdots & 0 & 0 \\ -k & \alpha & -k & 0 & \cdots & 0 \\ 0 & -k & \alpha & -k & \cdots & 0 \\ \cdots & \cdots & \cdots & \ddots & \cdots & \cdots \\ 0 & \cdots & 0 & -k & \alpha & -k \\ 0 & \cdots & 0 & 0 & -k & \alpha \end{pmatrix} \begin{pmatrix} p_1 \\ p_2 \\ \cdot \\ \cdot \\ p_{N-1} \\ p_N \end{pmatrix} = \begin{pmatrix} A_1 \\ A_2 \\ \cdot \\ \cdot \\ A_{N-1} \\ A_N \end{pmatrix} \quad (3)$$

This equation can be solved analytically [43]. By introducing $D = \alpha/k$, and letting $D = 2 \cosh \lambda$, we can have the following analytical solution

$$p_i = \frac{1}{k} \sum_{j=1}^N \frac{\cosh[(N+1-|j-i|)\lambda] - \cosh[(N+1-i-j)\lambda]}{2 \sinh \lambda \sinh[(N+1)\lambda]} A_j, \quad (4)$$

Since we will finally normalized p_i to $\tilde{p}_i$, which is unit at its center. It is clear seen from the above solution that $\tilde{p}_i$ only depends on the ratio K/k and the standard deviation σ , which is related to the FWHM of the laser profile via $FWHM = 2\sigma\sqrt{2\ln 2}$. We will set $A_0 = 1$ henceforth.

It would be helpful to consider the continuum limit of Eq. (1), in which case Eq. (1) becomes $\partial_t p(x, t) - a^2 k \partial_{xx} p(x, t) + K p(x, t) = A(x) = e^{-\frac{(x-x_0)^2}{2\sigma^2}}$, which is a 1D inhomogeneous diffusion equation. The laser has its maximum at $x = x_0$. Note that the system has inversion symmetry with respect to the origin such that the time dependent solution $p(x, t)$ is an even function of position x , so that $\partial_x p(0, t) = 0$.

Figure 2. (a) Calculated stationary fluorescence(normalized) of a 1D LH2 nanometer array (green, with $FWHM \sim 470nm$) and of LH2-only 2D crystal (red, with $FWHM \sim 450nm$) using the hopping model. The blue line is the profile of exciting diffraction limited laser beam with an FWHM of 400 nm.(b) Comparison between the discrete solution (Eq.(4)) and the continuum solution (Eq.(5))of the unnormalized stationary probability. Parameters: $a = 8nm$, $K/k = 0.01$, $FWHM_{laser} = 400nm$, $x_0 = a(i - i_0) = 4008nm$.

The stationary state $p_s(x)$ is determined by $a^2 k \partial_{xx} p_s(x) - K p_s(x) = -e^{-\frac{(x-x_0)^2}{2\sigma^2}}$, with boundary conditions $p'_s(0) = 0, p_s(\infty) = 0$. The solution therefore reads

$$p_s(x) = C_1 e^{\frac{x}{a} \sqrt{\frac{K}{k}}} + C_2 e^{-\frac{x}{a} \sqrt{\frac{K}{k}}} - \frac{a}{2} \sqrt{\frac{k}{K}} \cdot \left[e^{\frac{x}{a} \sqrt{\frac{K}{k}}} \int_1^x dy e^{-\frac{y}{a} \sqrt{\frac{K}{k}}} e^{-\frac{(y-x_0)^2}{2\sigma^2}} - e^{-\frac{x}{a} \sqrt{\frac{K}{k}}} \int_1^x dy e^{\frac{y}{a} \sqrt{\frac{K}{k}}} e^{-\frac{(y-x_0)^2}{2\sigma^2}} \right] \quad (5)$$

where the constants C_1 and C_2 are determined by the boundary conditions.

Calculated stationary fluorescence of the 1D nanowire according to the analytical expressions developed in the last Section is shown in figure (2a). The red line is the profile of the diffraction-limited laser beam with an FWHM of 400 nm, and the blue line is the calculated fluorescence emission profile with an FWHM of about 470 nm.

Before discussing the two dimensional array, we study how much will the continuum solution deviate from the exact discrete solution. Figure (2b) gives a comparison between the discrete solution Eq.(4) and continuum one Eq.(5). We can see that the two are almost the same. This suggests that we may also treat the 2D case with diffusion equations at very high accuracy.

Now we turn to the 2D LH2 array. Considering the rotational symmetry of the 2D array, the following master equation can be obtained

$$\begin{aligned} \frac{dp_{ij}}{dt} = & A_{ij} - (K + 6k)p_{ij} + k(p_{i-1,j} + p_{i+1,j} \\ & + p_{i,j-1} + p_{i,j+1} + p_{i-1,j+1} + p_{i+1,j-1}), \end{aligned} \quad (6)$$

where we used two indices i and j to assign a LH2 site on our hexagonal lattice, as shown in figure 1(a), and it is again assumed that hopping only occurs between nearest neighbors. The remaining part will be the same as that in the one dimensional case. Eq. (6), a set of coupled equations, cannot be solved analytically. However, its continuum limit is cylindrically isotropic and can be separated into a radial part and a trivial angular part. With the continuum approximation with cylindrical symmetry, the radial part of Eq. (6) can be written as

$$\frac{dp(r)}{dt} = A(r) - Kp(r) + \frac{a^2k}{r} \frac{d}{dr} \left(r \frac{dp(r)}{dr} \right), \quad (7)$$

where r denotes the radial coordinate, $A(r) = e^{-\frac{r^2}{2\sigma^2}}$ is the normalized profile of incident laser centered at the origin. For the stationary case, we have the probability density

$$\begin{aligned} p_s(r) = & C_1 J_0\left(\frac{r}{a}\sqrt{-\frac{K}{k}}\right) + C_2 Y_0\left(\frac{r}{a}\sqrt{-\frac{K}{k}}\right) + \frac{\pi}{2a^2k} \\ & \left[J_0\left(\frac{r}{a}\sqrt{-\frac{K}{k}}\right) \int_0^r Y_0\left(\frac{t}{a}\sqrt{-\frac{K}{k}}\right) e^{-\frac{t^2}{2\sigma^2}} t dt - Y_0\left(\frac{r}{a}\sqrt{-\frac{K}{k}}\right) \int_0^r J_0\left(\frac{t}{a}\sqrt{-\frac{K}{k}}\right) e^{-\frac{t^2}{2\sigma^2}} t dt \right] \end{aligned} \quad (8)$$

where $J_n(z)$ and $Y_n(z)$ represent the Bessel function of the first and the second kind, respectively. The constants C_1 and C_2 are determined by the boundary conditions $p'_s(0) = 0$ and $p_s(\infty) = 0$. The normalized steady probability distribution is plotted in figure (2a), with a FWHM around $450nm$. We see that our results agrees the experimental observation qualitatively. However, the calculated FWHMs using the incoherent model is far away from experimental values.

3. Superradiance and Supertransfer in LH2 Complex Nanoarray

In the preceding section, we calculated the stationary fluorescence of both the 1D LH2 nanometer array and a 2D LH2-only array using kinetic equations. In the assignment of energy transfer and dissipation parameters, values from native structure are borrowed for calculations of the artificial system. As a first approximation, we have taken the transfer rates as the inverse of the excitation transfer times computed or measured for

purple bacteria. In particular, for the LH2-to-LH2 transfer rate, a value of 10 ps^{-1} is used by taking in account the quantum chemical calculations in [43].

However, if we compare the simulated data with measurements, it is apparent that the current energy transfer distance of 35 nm (for 1D array) based on FWHM is much shorter than the actual observation of about 400 nm . The simulation for the emission fluorescence signal of the 2D lattice is similar, but yields an even shorter energy transfer distance. To eliminate the uncertainty in the choice of parameters, as an upper limit for the parameters such as the site decay rate and the transfer rate, we have tried out values that are 3 times the experimental or estimated ones for those rates during the course of simulation; the resultant width of the calculated fluorescent profile only reaches one half of the experimental value.

Therefore, the current incoherent hopping model needs to be revised. Two approaches might be considered for the revision. If the inter-LH2 transfer rate is increased tenfold from its value in [43], we can obtain a fluorescent intensity comparable with the experimental value, although the enhanced rate is much less than the value estimated by Lloyd and Mohseni [32]. However, it is hard to find a physical origin for such an enhancement. The silicon surface to support the nanoarray may be helpful to the increase of transfer rate, but such a huge increase seems not to be plausible. Noting the very close distances between the LH2 complexes (8 nm centre to centre distance and 0.5 nm separation between the outer rims), we can consider an alternative explanation for these anomalously long diffusion lengths, one that attributes such a significant enhancement to cooperative coherent effects. The light absorption frequencies and linewidths of the LH2 complexes in the crystal and nanofabricated arrays are essentially the same as in native LH2 complexes. The exact effect of cooperative behaviour depends on the precise arrangement of LH2 complexes in each array, and is difficult to assess precisely. As a first step, we can will treat a combination of coherent and incoherent hopping by using a toy model with an increased step size and an unchanged hopping rate (equal to the previous value). Such an arrangement can be justified by our quantum mechanical calculations of polaron dynamics in a few LH2 rings. The incoherent hopping model is known to be insufficient to describe long-lasting beating signals in a two-dimensional Fourier transformed electronic spectrum recorded from the reaction centre of green sulphur bacteria [37]. The coherence beatings in these measurements may be possibly explained by a strong correlation between protein-induced fluctuations in the transition energies of neighbouring chromophores, leading to conclusions that protein-correlated environments in fact preserve and support electronic coherence in photosynthetic complexes [37]. Recently, an ultrafast polarization experiment has revealed coherent intrachain (but not interchain) electronic energy transfer in conjugated polymers with various chain conformations as model multichromophoric systems at room temperature [38]. However, long-range quantum coherence between light harvesting complexes is an issue of contention. On one hand, some recent quantum calculations suggest that the excitation population for the donor LH2 ring decreases exponentially with time displaying little coherent features [47]. The probability master equation

method was used to explain the energy transfer in the light-adapted photosynthetic membrane [34, 35, 36]. On other hand, stationary and time dependent fluorescence measurements for LH2 array can not be satisfactorily explained by the incoherent hopping model [29, 32, 39]. Our calculation of master equation favours the latter viewpoint. Therefore, superradiance and supertransfer is needed for our generalized master equation model.

In order to get a reasonable estimate of the coherence size, we model LH2 complexes with the Holstein Hamiltonian written as [48, 49]:

$$\hat{H} = \hat{H}_{\text{ex}} + \hat{H}_{\text{ph}} + \hat{H}_{\text{ex-ph}} \quad (9)$$

with

$$\hat{H}_{\text{ex}} = - \sum_{r_1 \neq r_2} \sum_{nm} J_{nm}^{r_1 r_2} \hat{a}_n^{r_1 \dagger} \hat{a}_m^{r_2} - \sum_r \sum_{nm} J_{nm}^r \hat{a}_n^{r \dagger} \hat{a}_m^r, \quad (10)$$

$$\hat{H}_{\text{ph}} = \sum_r \sum_q \omega_q^r \hat{b}_q^{r \dagger} \hat{b}_q^r, \quad (11)$$

$$\hat{H}_{\text{ex-ph}} = -\frac{1}{\sqrt{N}} \sum_r \sum_n \sum_q g_q^r \omega_q^r \hat{a}_n^{r \dagger} \hat{a}_n^r (e^{iqn} \hat{b}_q^r + H.c.), \quad (12)$$

where $\hat{a}_n^{r \dagger}$ ($\hat{a}_n^r$) is the creation (annihilation) operator for an exciton at the n^{th} site (with total number of 16 sites in one ring) of the r^{th} ring (with total number of N_{ring} rings), $\hat{b}_q^{r \dagger}$ ($\hat{b}_q^r$) is the creation (annihilation) operator of a phonon with momentum $q = 2\pi n_q/16$ ($n_q = -7, -6, \dots, 7, 8$) and frequency ω_q^r in the r^{th} ring, and the Planck's constant is set as $\hbar = 1$. $J_{nm}^{r_1 r_2}$ is the exciton transfer integral between two pigments on different LH2 rings, and J_{nm}^r is the Frenkel exciton Hamiltonian for one LH2 ring [50]

$$J_{nm}^r = \begin{pmatrix} \varepsilon_1 & J_1 & W_{1,3} & \cdot & \cdot & \cdot & J_2 \\ J_1 & \varepsilon_2 & J_2 & \cdot & \cdot & \cdot & W_{2,2N} \\ W_{3,1} & J_2 & \varepsilon_1 & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \varepsilon_2 & J_2 & W_{2N-2,2N} \\ \cdot & \cdot & \cdot & \cdot & J_2 & \varepsilon_1 & J_1 \\ J_2 & \cdot & \cdot & \cdot & W_{2N,2N-2} & J_1 & \varepsilon_2 \end{pmatrix}, \quad (13)$$

In the equation above, ε_1 and ε_2 are the on-site excitation energies of an individual BChl-a (in this work we set $\varepsilon_1 = \varepsilon_2 = 0$ as the reference energy), J_1 and J_2 are the transfer integral between nearest neighbours, N equals 8 as the system is of C8 symmetry, and matrix elements $W_{i,j}$ are the dipolar coupling for the non-nearest neighbors. The dipolar coupling between site i and site j takes the form

$$W_{i,j} = C \left[\frac{\mathbf{d}_i \cdot \mathbf{d}_j}{|\mathbf{r}_{ij}|^3} - \frac{3(\mathbf{d}_i \cdot \mathbf{r}_{ij})(\mathbf{d}_j \cdot \mathbf{r}_{ij})}{|\mathbf{r}_{ij}|^5} \right], \quad (14)$$

where C is the proportionality constant, $\mathbf{r}_{ij}$ is the vector connecting the i th and j th monomers, and $\mathbf{d}_i$ are the unit vectors of the i th BChl-a. The following parameters are adopted[51]: $J_1 = 594\text{cm}^{-1}$, $J_2 = 491\text{cm}^{-1}$ and $C = 640725\text{\AA}^3\text{cm}^{-1}$. For simplification,

the exciton transfer integral between different rings could be confined on the nearest-neighbour case in the following discussion. $\hat{H}_{\text{ex-ph}}$ is the linear, diagonal exciton-phonon coupling Hamiltonian with $g_q^r = g$ the coupling constant. We can obtain the Huang-Rhys factor S from $\sum_q g_q^r \omega_q^r = S\omega_0$, where $\omega_0 = 1670\text{cm}^{-1}$ is the characteristic phonon frequency. For simplicity, ω_0 is set to unity in this work. Therefore, all other energies are rescaled by characteristic phonon frequency. It is noted that in our approach phonon dispersions in the Hamiltonian can have various forms to describe phonon branches of different origins. In this work, a linear optical phonon dispersion with $\omega_q = \omega_0[1 + B(2|q|/\pi - 1)]$ with $B = 0.1$ is adopted.

The temporal evolution of the photo-excited state in a 1D molecular aggregate follows the time-dependent Schrödinger equation. Just as in other many-body quantum systems, however, exact quantum dynamics is elusive for such multi-pigment aggregates with a phonon bath, and approximate techniques have to be borrowed. Here polaron dynamics in a multiple-ring LH2 system is studied using the Davydov D_1 Ansatz and the Lagrangian formalism of the Dirac-Frenkel time-dependent variational method [53, 54, 52]. The D_1 trial state can be written in a general form as

$$|\Psi_{D_1}(t)\rangle = \sum_{r,n} \alpha_n^r(t) \hat{a}_n^{r\dagger} \hat{U}_n^{r\dagger}(t) |0\rangle_{\text{ex}} |0\rangle_{\text{ph}}, \quad (15)$$

where $\alpha_n^r(t)$ are the variational parameters representing exciton amplitudes, and $\hat{U}_n^{r\dagger}(t)$ is the Glauber coherent operator

$$\hat{U}_n^{r\dagger}(t) \equiv \exp \left\{ \sum_q [\lambda_{n,q}^r(t) \hat{b}_q^{r\dagger} - \text{H.c.}] \right\}. \quad (16)$$

The reader is referred to Appendix A for detailed derivations of the equations of motion for the variational parameters. The multiple-ring system is initialized as follows: $\alpha_n^r(0) = \delta_{r,1} \delta_{n,8}$ and $\lambda_{n,q}^r(0) = 0$. After solving the coupled equations of motion, the reduced single-exciton density matrix $\rho_{mn}^{r_1 r_2}(t)$ can be obtained from

$$\rho_{mn}^{r_1 r_2}(t) = \text{Tr}[\rho(t) \hat{a}_m^{r_1 \dagger} \hat{a}_n^{r_2}], \quad (17)$$

where $\rho(t) = |\Phi(t)\rangle \langle \Phi(t)|$ is the full density matrix at zero temperature, and $|\Phi(t)\rangle$ is the total polaron wave function at time t after the photoexcitation takes place. Substituting the detailed form of the D_1 Ansatz into the polaron wave function, one obtains

$$\rho_{mn}^{r_1 r_2}(t) = \langle \Psi_{D_1}(t) | \hat{a}_m^{r_1 \dagger} \hat{a}_n^{r_2} | \Psi_{D_1}(t) \rangle = \alpha_m^{r_1*}(t) \alpha_n^{r_2}(t) S_{mn}^{r_1 r_2}(t), \quad (18)$$

where $S_{mn}^{r_1 r_2}(t)$ can be written as

$$S_{mn}^{r_1 r_2}(t) = \exp \left\{ \sum_q [\lambda_{mq}^{r_1*}(t) \lambda_{nq}^{r_2}(t) \delta_{r_1 r_2} - \frac{1}{2} |\lambda_{mq}^{r_1}(t)|^2 - \frac{1}{2} |\lambda_{nq}^{r_2}(t)|^2] \right\}. \quad (19)$$

From the reduced exciton density matrix, one can obtain an exciton coherence size L_ρ characterizing the size of a domain within which the chromophores emit coherently [55, 56]. All information relevant to the excitonic superradiance is contained within the reduced exciton density matrix $\rho_{mn}^{r_1 r_2}(t)$, the time dependence of which provides a

Figure 3. (a) Real space dynamics of the coherence size L_ρ s for 3 rings, 4 rings and 5 rings. (b) The reduced density matrix $|\rho_{mn}^{r1r2}|$ for 3 rings at τ_3 . (c) The long-time evolution of the coherence size L_ρ s for 5 rings, 6 rings and 7 rings. Multiple-LH2-ring systems are treated with a realistic transfer-integral matrix given by Eqs. (16) and (17). A moderate exciton-phonon coupling strength $S = 0.5$ and a narrow bandwidth $B = 0.1$ of phonon dispersion are adopted to calculate the exciton coherence size.

clear view of the relaxation process. Previously, for translationally invariant states, a definition of the characteristic coherence size L_ρ in terms of the density matrix was introduced by applying the inverse participation ratio concept commonly used in the theory of quantum localization,

$$L_\rho(t) \equiv \left(\sum_{r_1 r_2 mn} |\rho_{mn}^{r_1 r_2}(t)|^2 \right)^{-1} \left[L \sum_{r_1 r_2 mn} |\rho_{mn}^{r_1 r_2}(t)|^2 \right]^{-1} \quad (20)$$

where L is the total number of pigments in the system. In this work, the cases of 5 rings, 6 rings and 7 rings with a center-to-center distance of 8nm are considered. The multiple-ring system is assumed as a one-dimensional LH2 chain. The coherence size L_ρ , as a function of time, can be used to identify the number of rings over which excitonic coherence is maintained. Initially, L_ρ increases with increasing time for various system sizes until τ_1 is reached. For $t < \tau_1$, exciton transfer is confined to ring 1 (intra-ring) or between ring 1 and ring 2 (inter-ring). Plateau 1 occurs between τ_1 and τ_2 , and during this time, the exciton is mostly confined to ring 1 and ring 2. Additional inter-ring transfer, such as that from ring 2 to ring 3, is yet to develop for $\tau_1 < t < \tau_2$. As

inter-ring transfer can effectively increase the off-diagonal part of the reduced density matrix, L_ρ continues to increase due to exciton transfer from ring 2 to ring 3. After τ_3 , Plateau 2 is formed, suggesting that the exciton is mostly confined to ring 1, ring 2, and partially, ring 3, as shown in figure 3(a) and (b). If we evolve the dynamics further, a quasi-equilibrium can be reached for the exciton coherence size. The oscillation of the L_ρ is caused by the exciton-phonon-coupling and the exchange between homoentanglement and the heteroentanglement in the Holstein system [57]. As shown in figure 3(c), for various system sizes, the oscillation range of L_ρ is found to be about 32 pigments to 52 pigments, or about 2 rings to 3.3 rings with an average of 2.7 rings. The result is in agreement with those from recent reports[58], in which the time-resolved fluorescence was measured for separated LH2 complexes and LH2 arrays, and the fluorescence lifetime of the latter was found to be about 1/2.5 of the former.

By incorporating the superradiance effect, a cooperative hopping model can be established for the energy transport in the LH2 complex array. Let the excitonic lifetime of a separated LH2 complex be T , and the hopping rate in the absence of cooperative effects be k . Because of the presence of the cooperative effect, the coherence size increases to L_ρ , resulting in coherent exciton hopping through the array. Within the domain, the exciton is transferred quantum mechanically. Assuming that hoppings between the delocalized domains are coherent, the transfer rate is enhanced to $k' = L_\rho k$. Therefore, we use a combination of coherent and incoherent hopping as diffusive transport with an enhanced hopping rate and an increased step size of L_ρ , but the lifetime of the domain decreases to T/L_ρ due to superradiance. By including these modifications, we can again make use of the master equations to model the energy transport between photosynthetic units. We will show that the measured stationary fluorescence signal can be reproduced by the theory mixing coherent and incoherent hoppings. Following the approach laid out here, stationary fluorescence signals are calculated for a 1D nanometer array and a 2D LH2 lattice, and results are shown in figures. 4(a) and 4(b), respectively. For the 1D nanometer array case, the FWHM of fluorescence emission increases to 688 nm compared with an FWHM of 417 nm for the diffraction limited spot size of the incident laser beam. This means that the excitation energy migration distance reaches to about 135 nm, as demonstrated in figure 4(a). In addition, for the case of the 2D LH2 lattice, simulation shows that the FWHM of the fluorescence emission is about 575 nm, as displayed in figure 4(b). Therefore, by introducing superradiance and supertransfer in solving the master equation, we can indeed obtain results which are in accord with the measurements [31].

4. Transient fluorescence

A straightforward extension for experimentalists to pursue would be transient fluorescence. Here a prediction is presented for future experiments on transient fluorescence of LH2 arrays. For the LH2 chain, when the laser field is absent, the

Figure 4. (a) The calculated stationary fluorescence of 1D array of LH2 complexes from the hopping model when the supertransfer is included. The red line is the profile of exciting diffraction limited laser beam with an FWHM of 417nm. The blue line is the fluorescence emission profile with an FWHM of 688nm. (b) The corresponding case for 2D LH2 complexes crystal. The red line is the profile of exciting diffraction limited laser beam with an FWHM of 417nm. The blue line is the fluorescence emission profile with an FWHM of 575nm. The size of excitation delocalization takes 2.5 LH2 complexes in the above calculation.

dynamics is governed by Eq. (1) without A_i , and its solution reads[44]

$$p_m(t) = e^{-Kt} e^{-2kt} \sum_{i=-\infty}^{\infty} p_i(0) I_{m-i}(2kt)$$

Figure 5. The predicted transient fluorescence of 1D array of LH2 complexes. The red line is based the incoherent hopping model and the blue one is based on the supertransfer model, where The size of excitation delocalization is assumed to be 2.5 LH2 complexes.

where $I_n(x) = i^{-n}J_n(ix)$ and $J_n(x)$ is the Bessel function of the first kind. Suppose we can prepare an initial state of the chain in accordance with the laser profile by turning on the laser field and then switching it off immediately, i.e., $p_i(0) \propto \exp[-2a^2(i - i_0)^2/\sigma^2]$. Then the probability of excitation for a given site m is

$$p_m(t) = \frac{1}{Z} \sum_{i=-\infty}^{\infty} \exp[-2a^2(i - i_0)^2/\sigma^2] e^{-Kt} e^{-2kt} I_{m-i}(2kt) \quad (21)$$

where Z is a normalization constant. The time-dependent fluorescence intensity of the system can be written as

$$F(t) = \frac{1}{N} \sum_{i=1}^N p_i(t) \quad (22)$$

This intensity is normalized to unity at the maximum of the profile. If we are interested in the spatial dependent fluorescence, Eq. (10) can be used to calculate the intensity and its time evolution.

Figure 5 is the time dependent fluorescence intensities of 1D nanowire of LH2 complexes. For the case with no quantum coherence, the dominant decay (red line) has a time constant of 1100 ps, and we also see a weaker tail lasting several nanoseconds. The time constant is longer than the lifetime of an isolated LH2 complex because of energy diffusion in the chain. With the added quantum coherence, the fluorescence (blue line) decays much faster than the one predicted by a hopping model. The time constant for the dominant decay is decreased to about 450 ps from the 1100 ps of incoherent case. Similarly, the decay constant is slightly shorter than the lifetime (400 ps) of

Figure 6. The spatial dependence of the predicted transient fluorescences of 1D array of LH2 complexes.

superradiance of coherent domain (2.5 LH2 size). In the mean time, we can calculate the spatial distribution of the fluorescence, as shown in figure 6, where only the quantum coherent case is considered. It is remarkable to see fluorescence signal turning almost flat in the central domain as time evolves.

If we focus the domain far from the incident laser spot, we can see how the domain is excited and emits fluorescence. For example, for a spot at the distance $4 \mu m$ containing 10 LH2 units, the time dependent fluorescence is shown in figure 7. It is demonstrated that the fluorescent signal decay is much delayed in regions away from the central domain due to the energy transfer. We expect our prediction here to be tested in future experiments.

5. Conclusions

In summary, we have investigated the long-range excitation-energy transport properties within a biomimetic molecular nanoarray constructed from LH2 antenna complexes by using the master equation approach with the aid from a sophisticated simulation of polaron dynamics. Stationary and transient fluorescence signals after a local excitation with a diffraction-limited light beam are calculated and compared with the experimental results. The energy transport was established from the influence of active energy-guiding layers on the observed fluorescence emission. The energy migration occurs as a result of efficient coupling between many hundreds of LH2 complexes. We obtain an analytical expression of stationary fluorescence distribution by solving the master equations of the system. The time dependent fluorescence intensity is derived using the same formalism. The numerical results show a reasonable consistency with the experimental results in

Figure 7. Predicted transient local fluorescence signals at different measurement sites show the energy transport along the nanowire. The blue line is the transient fluorescence signal at $x = 4.08\mu\text{m}$ with a sampling size $= 0.8\mu\text{m}$, while the red line, at $x = 6.8\mu\text{m}$ with the same sampling size.

the engineered nanoarray of LH2 complexes. In addition, our results show that quantum coherence mechanism is necessary to explain the long distance energy transport.

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Appendix A. Detailed derivation of polaron dynamics in multiple-ring system

The system energies of the multiple-ring system can be obtained as follows by apply Davydov Ansätze to the modified Holstein Hamiltonian given in Eq. (10), (11) and (12):

$$E_{\text{ex}}(t) = - \sum_{r_1 r_2} \sum_{nm} J_{nm}^{r_1 r_2} \alpha_n^{r_1*}(t) \alpha_m^{r_2}(t) S_{nm}^{r_1 r_2}(t) \quad (\text{A.1})$$

$$E_{\text{ph}}(t) = \sum_r \sum_n |\alpha_n^r(t)|^2 \sum_q \omega_q^r |\lambda_{nq}^r(t)|^2 \quad (\text{A.2})$$

$$E_{\text{ex-ph}}(t) = -\frac{2}{\sqrt{N}} \sum_r \sum_n \sum_q g_q^r \omega_q^r |\alpha_n^r(t)|^2 \text{Re}[e^{iqn} \lambda_{nq}^r(t)] \quad (\text{A.3})$$

with Debye-Waller factor $S_{nm}^{r_1 r_2}(t)$ given by:

$$S_{nm}^{r_1 r_2}(t) = \exp\left\{\sum_q [\lambda_{nq}^{r_1*}(t) \lambda_{mq}^{r_2}(t) \delta_{r_1 r_2} - \frac{1}{2} |\lambda_{nq}^{r_1}(t)|^2 - \frac{1}{2} |\lambda_{mq}^{r_2}(t)|^2]\right\}, \quad (\text{A.4})$$

and the index r_1 and r_2 all runs over 1 to N_{ring} .

In the Hilbert space, for example, the time-dependent wave function $|\Phi(t)\rangle$ for the Hamiltonian $\hat{H}$ is parameterized by a set of time-dependent variables $\alpha_m^r(t)$ ($m = 1, \dots, M$):

$$|\Phi(t)\rangle \equiv |\{\alpha_m^r(t)\}\rangle. \quad (\text{A.5})$$

Assuming that $|\Phi(t)\rangle$ satisfies the time-dependent Schrödinger equation, one has

$$i \frac{\partial}{\partial t} |\Phi(t)\rangle = \hat{H} |\Phi(t)\rangle. \quad (\text{A.6})$$

Explicitly putting in the Hamiltonian $\hat{H}$ of Eq. (9) and writing $\partial|\Phi(t)\rangle/\partial t$ in terms of $\alpha_m^r(t)$ and their time-derivatives $\dot{\alpha}_m^r(t)$ ($m = 1, \dots, M$), one obtains

$$(i \frac{\partial}{\partial t} - \hat{H}) |\Phi(t)\rangle = |\{\alpha_m^r(t)\}, \{\dot{\alpha}_m^r(t)\}\rangle = 0. \quad (\text{A.7})$$

Projecting Eq. (A.7) onto M different states $|\Psi_m\rangle$ ($m = 1, \dots, M$), one obtains M equations of motion for the parameters $\alpha_m^r(t)$:

$$\langle \Psi_m | \{\alpha_m^r(t)\}, \{\dot{\alpha}_m^r(t)\} \rangle = 0. \quad (\text{A.8})$$

The approach we adopt in this work is the Lagrangian formalism of the Dirac-Frenkel time-dependent variational method [52], a powerful technique to obtain approximate dynamics of many-body quantum systems for which exact solutions often elude researchers. We formulate the Lagrangian L as follows

$$L = \langle \Phi(t) | \frac{i\hbar}{2} \left(\frac{\vec{\partial}}{\partial t} - \overleftarrow{\frac{\partial}}{\partial t} \right) - \hat{H} | \Phi(t) \rangle. \quad (\text{A.9})$$

From this Lagrangian, equations of motion for the M functions of time, parameters $\alpha_m^r(t)$, and their time-derivatives $\dot{\alpha}_m^r(t)$ ($m = 1, \dots, M$), can be obtained by

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{\alpha}_m^{r*}} \right) - \frac{\partial L}{\partial \alpha_m^{r*}} = 0. \quad (\text{A.10})$$

Therefore the equations of motions for the time-dependent variational parameters $\alpha_n^r(t)$ and $\lambda_{nq}^r(t)$ are written as:

$$\dot{\alpha}_n^r(t) = i[T_n^r(t) + \alpha_n^r(t) R_n^r(t)], \quad (\text{A.11})$$

and

$$\dot{\lambda}_{nq}^r(t) = i \left[\frac{\Omega_{nq}^r(t)}{\alpha_n^r(t)} + \frac{g_q^r}{\sqrt{N}} \omega_q^r e^{-iqn} - \omega_q^r \lambda_{nq}^r(t) \right]. \quad (\text{A.12})$$

Each collected term in Eqs. (A.11) and (A.12) is given as:

$$\varpi_{nq}^r(t) = i\dot{\lambda}_{nq}^r(t) + \frac{g_q^r}{\sqrt{N}}\omega_q^r e^{-iqn} - \omega_q^r \lambda_{nq}^r(t), \quad (\text{A.13})$$

$$R_n^r(t) = \text{Re} \sum_q [\varpi_{nq}^r(t) + \frac{g_q^r}{\sqrt{N}}\omega_q^r e^{-iqn}] \lambda_{nq}^{r*}(t), \quad (\text{A.14})$$

$$T_n^{r_1}(t) = \sum_{r_2} \sum_m j_{nm}^{r_1 r_2} \alpha_m^{r_2}(t) S_{nm}^{r_1 r_2}(t), \quad (\text{A.15})$$

$$\Omega_{nq}^{r_1}(t) = \sum_{r_2} \sum_m j_{nm}^{r_1 r_2} \alpha_m^{r_2}(t) S_{nm}^{r_1 r_2}(t) [\lambda_{mq}^{r_2}(t) \delta_{r_1 r_2} - \lambda_{nq}^{r_1}(t)]. \quad (\text{A.16})$$

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