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LETTERS

Exciton Self Trapping in One-Dimensional Photosynthetic Antennas

Kõu Timpmann,[†,‡] Zivile Katiliene,[‡] Neal W. Woodbury,[‡] and Arvi Freiberg*[,†,‡]

Institute of Physics, University of Tartu, 51014 Tartu, Estonia, and Department of Chemistry and Biochemistry and Center for the Study of Early Events in Photosynthesis, Arizona State University, Tempe, Arizona 85287

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Experimental evidence is presented showing that excitons in circular antenna complexes from photosynthetic bacteria are dynamically self trapped in about 200 fs by coupling to nuclear vibrations. The induced deformation covers ~20% of the complex circumference at low temperature. This self trapping, the first of its kind observed in biological systems, results in a broad fluorescence spectrum and considerably improves energy resonance between heterogeneous antenna complexes. Exciton self trapping may thus be a part of nature's strategy, increasing the speed and efficiency of energy transfer in photosynthesis.

The peripheral light harvesting 2 (LH2) photosynthetic antenna complexes from purple nonsulfur bacteria are among the best-characterized protein complexes, both structurally and spectrally. The LH2 complex is made up of a ringlike arrangement of nine α-helical polypeptide heterodimers.[1] Each heterodimer contains three bacteriochlorophyll *a* (Bchl) molecules. Two of the three Bchls in each heterodimer are closely coupled. In the larger structure, a circular aggregate of strongly coupled dimers is formed promoting delocalization of the excited states over a substantial part of the aggregate. This one-dimensional Bchl aggregate absorbs at 850 nm and is labeled as B850. The remaining weakly coupled Bchls absorb near 800 nm. The delocalized excitons in the B850 aggregate have been studied in some detail.[2] Owing to the specific orientation of the transition dipoles of the Bchl molecules, which lay almost on the ring plane, the lowest ($k = 0$) exciton transition in perfect aggregates would be very weak. It is generally understood that in LH2 complexes this transition gains appreciable intensity because of disorder in the Bchl transition energies imposed by the protein environment.[3] Both low-temperature hole burning measurements[3] and single-complex fluorescence excitation spectra[4] have indicated that individual antenna complexes can have substantially different absorption spectra. Despite this, ultrafast energy transfer times on the order of a picosecond between the LH2 complexes have been observed not only at physiological temperature but also at low temperature.[5] Recent studies have also shown that the exciton size, which is almost delocalized over the whole ring of B850 at the moment of excitation, contracts significantly with time.[6,7] However, the nature of the relaxed emitting state of the complex is not yet well-understood.

Here, on the basis of steady-state and time-resolved absorption and emission spectroscopy studies of LH2 complexes isolated from the membrane of the bacterium *Rhodobacter sphaeroides* (*Rb. sphaeroides*), we present evidence that the absorbing and emitting states of this complex are qualitatively different. The free exciton created by light absorption becomes partially localized within (as an order of magnitude) ~10 fs by scattering on static disorder and further localizes dynamically by coupling with nuclear vibrations within ~100 fs to form a self-trapped exciton. Essential experimental details, including the isolation and characterization of LH2 complexes, have been described earlier.[5]

Figure 1a shows the low-temperature steady-state absorption and emission spectra of B850 aggregates together with the simulated absorption spectrum based on Frenkel exciton theory

* To whom correspondence should be addressed.
† University of Tartu.
‡ Arizona State University.

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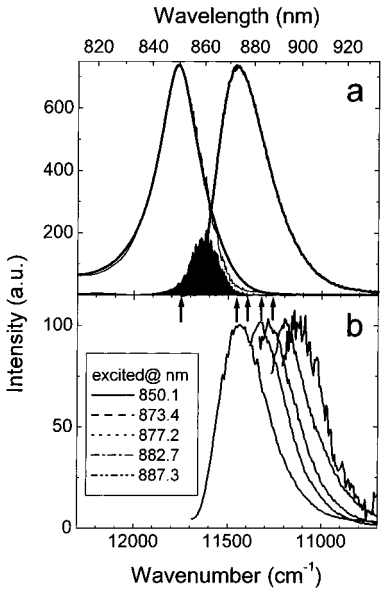

Figure 1. Peak-normalized absorption (left side, measured at 10 K) and emission (right side, measured at 5 K) spectra of the B850 aggregate in isolated LH2 complexes from *Rb. sphaeroides*. (a) The simulated absorption spectrum (dashed curve) is an average over 3000 disordered B850 aggregate spectra. The $k = 0$ absorption transitions are represented as the filled area under the curves. Fluorescence is nonselectively excited at 832 nm. Panel b shows emission spectra selectively excited within the inhomogeneously broadened B850 absorption band. The spectral position of a narrow-band (~0.3 nm) excitation laser is indicated with arrows.

including static diagonal disorder (according to the model described in ref 8). In the latter case, a Gaussian distribution of transition energies with a full width at half-maximum of $\Gamma_G \approx 430\ cm^{-1}$ was used. Although the red-side fit of the experimental band is not perfect, it is evident that the width of the distribution of the lowest $k = 0$ absorption transitions ($\sim 141\ cm^{-1}$) is strongly narrowed relative to Γ_G. This is a well-known manifestation of the excitation exchange between the neighboring pigments.[9] Unexpectedly, however, the emission spectrum is over 2 times broader ($\sim 331\ cm^{-1}$) than the $k = 0$ band. Involvement of higher exciton states in this broadening is excluded, because the exciton relaxation time is several orders of magnitude shorter than the exciton lifetime (see below) and the experimental temperature is very low relative to the energy gap between the relevant exciton states.[8]

Figure 1b shows the emission spectra obtained under resonant narrow-band excitation tuned over a wide ($>900\ cm^{-1}$) range and Figure 2 summarizes the main characteristics of these spectra. The position of the emission spectrum stays almost constant when excitation is on the blue side of the absorption spectrum maximum, while the emission maximum shifts together with the excitation wavelength on the red side (Figure 2a). The energy gap between the excitation frequency and the maximum of the emission spectrum decreases gradually with the excitation wavelength until at ~870 nm the gap saturates at $120-130\ cm^{-1}$ (Figure 2b). Both dependencies are characteristic of inhomogeneously broadened absorption spectra. In contrast, the overall shape and width (Figure 2b) of the emission spectrum change little suggesting that the emission spectrum is essentially homogeneously broadened. This is qualitatively consistent with the broad and featureless emission spectrum of LH2 complexes revealed by single molecule spectroscopy.[10]

Figure 3a presents the emission decay kinetics of the B850 excitons. The kinetics at 11 K is perfectly single-exponential over almost 4 orders of magnitude of decay and practically

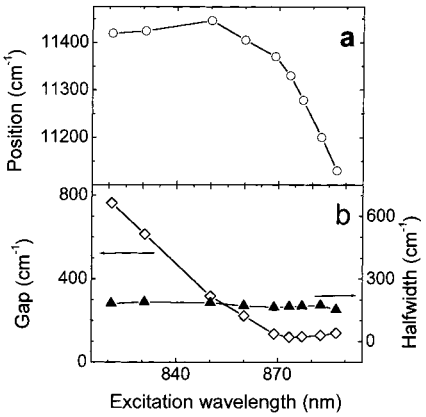

Figure 2. Characteristics of the selectively excited emission spectra as a function of excitation wavelength: (a) peak position; (b) gap between the excitation and emission light energies and red-side half bandwidth of the emission spectrum.

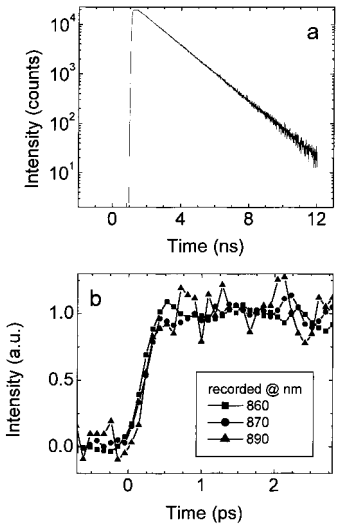

Figure 3. Emission decay kinetics of LH2 complexes at 10 K: (a) spontaneous emission recorded at 870 nm following excitation by ~5 ps laser pulses at 850 nm; (b) stimulated emission kinetics recorded at the different wavelengths indicated upon excitation with ~150 fs laser pulses at 840 nm.

(within ±4%) independent of emission wavelength. This again indicates the generally homogeneous nature of the emission spectrum. The decay constant of 1.53 ns remains unchanged with increasing temperature up to ~180 K, in qualitative agreement with ref 11. Further temperature increase leads to a gradual shortening of the lifetime (by ~20% at room temperature). According to ref 12, substantial temperature variations of the Frenkel exciton lifetime at or above 100 K are predicted, unless much stronger transition energy disorder is present than assumed in fitting the absorption spectrum in Figure 1a. However, in that case, the decay would necessarily be multiexponential,[12] again in apparent disagreement with the present experiment.

One may think of the statically disordered molecular aggregates as being built up from ordered segments including an effective number of molecular sites, N_{del}. A rough estimate of the exciton delocalization length can then be obtained from the absorption spectrum using the equation[9] $N_{del}^{A} = \sqrt{8\pi^2|J|/\Gamma} - 1$, where J is the nearest-neighbor interaction energy, Γ is the absorption bandwidth, and the superscript A denotes absorbance. Using $\Gamma \approx 275\ cm^{-1}$ and $J \approx 300\ cm^{-1}$ (these are the parameters obtained from fitting the low-temperature absorption

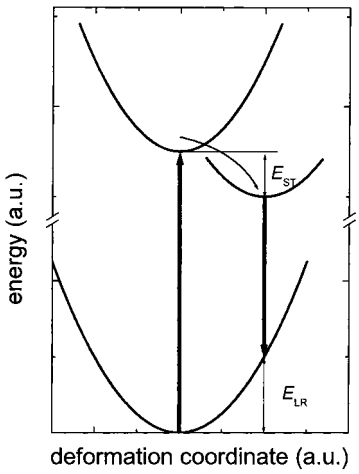

Figure 4. Configurations coordinate diagram illustrating self trapping of excitons in one-dimensional molecular aggregates. The straight and curved arrows represent optical and relaxation transitions, respectively. The deformation coordinate represents a linear combination of the real-space shifts of intermolecular coordinates from their equilibrium position.

spectrum in Figure 1a[8]), one calculates $N_{del}^{A} \approx 8$. This static-disorder-induced coherence length is almost 2 times shorter than that obtained from the nonlinear absorption data[6,7] but is still more than 2 times longer than the coherence length found from spontaneous emission quantum yield and lifetime studies,[11] $N_{del}^{E} = 3-4$ (the superscript E denotes emission). There are certain caveats in applying the above equation concerning the size of the aggregate and the correlated disorder that may both over- and underestimate the actual coherence size of the aggregate.[9] Therefore, we carefully inspected the spatial shape of the low-energy exciton wave functions simulating the B850 aggregate absorption spectrum.[8] It is revealed that the mean of the distribution of the segment sizes (defined as a double standard deviation of the distribution of the pigment site populations) for the lowest eigenstate is five to six sites.

Most of these apparently conflicting observations can be reconciled by assuming that in addition to virtually instantaneous localization due to exciton scattering on static disorder (as already mentioned before, the time scale of this process is on the order of $(c\Gamma_G)^{-1} \approx 10$ fs, where c is the speed of light), the exciton itself induces a slower structural reorganization of the B850 aggregate via exciton−phonon coupling, which further localizes the exciton. In one-dimensional structures, in contrast to systems of higher dimensions,[13,14] such exciton polaron self trapping is inherent and takes place for any nonvanishing exciton−phonon coupling strength,[13] because there is no energy barrier separating free exciton and self-trapped exciton states. The stimulated emission kinetics in Figure 3b allows estimation of the time scale of the B850 exciton self trapping. From the emission rise time, we obtain 180 ± 40 fs.

As seen in Figure 4, exciton self trapping generally leads to the loss of direct correspondence between exciton absorption and emission spectra and also separates them energetically. This explains most crucial observations of this work, such as the different nature of absorption and emission band broadening and an appreciable Stokes shift. The homogeneous nature of the emission spectrum and relative temperature insensitivity of the exciton polaron lifetime are both anticipated for strongly localized self-trapped excitons accounting for only a few pigment molecules. This is because hardly any mechanism can further squeeze the already strongly localized self-trapped exciton wave function. Our failure with the absorption line shape modeling based on disordered Frenkel exciton model (Figure 1a) becomes also understandable, because a modification of the spectrum due to self-trapping, especially in the red-band edge region, is expected.

Theoretical calculations of self-trapped exciton states in one-dimensional arrays by Higai and Sumi[14] allow estimation of some important parameters characterizing self-trapped excitons in the B850 aggregate. For example, on the basis of the Stokes shift of 146 ± 10 cm^{-1} between the $k = 0$ free exciton absorption band maximum and the peak of self-trapped exciton emission spectrum (Figure 1a) and assuming $J \approx 300$ cm^{-1}, we get the spatial extension of the lattice distortion in the self-trapped exciton state equal to $N_{ST} \approx 3.8 \pm 0.5$. This value, $\sim 1/5$ ring size of the B850 aggregate, is in fair agreement with N_{del}^{E} from ref 11 supporting the present interpretation. The same model[14] allows an estimation of the self-trapping binding energy relative to the free exciton band bottom, $E_{ST} \approx -48 \pm 6$ cm^{-1}, and the lattice relaxation energy released upon light emission (being the difference between the Stokes shift and E_{ST}), $E_{LR} \approx 98 \pm 10$ cm^{-1}. The diagram in Figure 4 explains the physical meaning of these terms.

In summary, we have shown that at low temperature the lowest energy photoexcitations in the LH2 complex are one-dimensional excitons self-trapped by coupling to nuclear vibrations rather than conventional disordered Frenkel excitons. Self trapping of excitons results in broader emission spectra considerably improving the energy resonance between heterogeneous antenna complexes in the membrane. The very weak temperature dependence of the emission properties of the LH2 complex implies that self trapping might also be relevant at physiological temperatures. The effect of self trapping is not limited to the LH2 antenna system. The spectral red shift induced by self trapping in LH2 antennas improves overlap with the absorption spectra of the core LH1 antennas surrounding the reaction center. The self trapping thus has an important biological function in promoting efficient energy transfer between individual photosynthetic antenna units with heterogeneous absorption spectra.

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