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Design of an artificial light harvesting system that may spontaneously evolve toward greater efficiency

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Abstract

The design principles for a light harvesting system that may spontaneously evolve toward greater efficiency for energy transfer are discussed and a new system based on these principles is introduced. The system consists of a tetraphenylchlorin as the antenna and a phthalocyanine as the energy acceptor in a poly(vinylpyridine) matrix. Excitation of the antenna leads to strong emission from the acceptor. Long term illumination of the film leads to increasing quantum efficiency for the energy transfer process. Some possible mechanisms for this evolution are discussed as are some possible improvements of the system.

Keywords: Light harvesting system; Energy transfer; Excitation

1. Introduction

Nature employs a light harvesting system that funnels energy to the photosynthetic reaction center where charge separation takes place [1–4]. Without this concentrated flux of excitation, the reaction center would be idle most of the time since it undergoes direct excitation only about once per second under normal terrestrial illumination [2]. Most artificial photosynthetic systems model only the reaction center [1,5–7] and do not include a light harvesting function. Ultimately, however, realistic artificial photosynthetic systems will probably include a light harvesting system to make efficient use of the rapid charge transfer capabilities of their reaction center analogs. Similarly, catalysts in homogeneous photoconversion systems, for example, platinum and ruthenium oxide colloids for the reduction and oxidation of water, respectively, [8–10] can usually support reaction fluxes orders of magnitude higher than those provided by the unconcentrated flux from the photoconversion system. Efficient use of these catalysts would require coupling to some light harvesting system. Semiconductor-based photoconversion systems, [11,12] on the other hand, contain an inherent light harvesting function that converts light energy absorbed throughout the bulk material into a flux of electrons and holes directed toward opposite electrodes. This is one of the reasons for their high efficiency. One aspect of the present work is the introduction and preliminary characterization of a new artificial light harvesting system. Such systems may eventually become models for the light harvesting antennae of natural photosynthetic membranes, and may allow experimental verification of theories of exciton transfer processes [2,13,14].

Another aspect of the research described here is the introduction of some design criteria for light harvesting systems that may spontaneously improve with time. Natural systems tend to evolve over time (aeons) toward greater efficiency at their particular function, while man-made systems, in general, deteriorate. So far, little effort has been directed toward designing artificial systems that can self-optimize under appropriate conditions. We describe here an initial attempt to design such a light harvesting system. This work was inspired by K.K. Rebane's recent suggestion of the possibility of self-organization in light harvesting antennae [15], which he proposed as a possible physical mechanism for the evolution of the primordial photosynthetic antenna system. Our system was designed with Rebane's criteria in mind: besides the usual requirements for efficient, multi-step singlet energy transfer (high concentration of chromophores, high extinction coefficient

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for the lowest energy absorption band, small Stokes shift, relatively high quantum yield for fluorescence in the isolated chromophore) we sought a chromophore that would undergo slow photodecomposition. If the decomposition reaction occurs only from the excited state, it provides a mechanism to distinguish molecules that participate in an efficient energy transfer pathway (and therefore have short excited state lifetimes) from those that are energy traps or are on dead-end pathways (and have relatively long-lived excited states). The photodecomposition reaction should tend to preferentially eliminate the long-lived excited molecules, thus selecting for the more efficient energy transfer pathways. One might call this "survival of the fastest".

The system described here shows an energy transfer efficiency that increases with illumination time. The underlying mechanisms responsible for this evolution, however, are not yet fully understood. The design, fabrication, and preliminary characterization of this light harvesting system are described. To our knowledge, this is the first report of the evolution in time of a light harvesting system.

2. Experimental section

Poly(vinylpyridine) (PVP) (Polysciences, MW 50 000) and free base tetraphenylchlorin (TPC) (Midcentury) were used as received. Free base phthalocyanine tetrasulfonate (PcTS) (Midcentury) was converted to the tetrabutyl ammonium salt by dissolving it in water containing tetrabutyl ammonium bromide, and then extracting the product into dichloromethane. After evaporation of the solvent, the PcTS was dissolved in pyridine and filtered through a 0.2 μm filter. The concentration was determined by measuring the absorption maximum at 698 nm and assuming an extinction coefficient of $\epsilon = 162,180$ [16]. The TPC was similarly dissolved in pyridine, filtered, and its concentration determined at 654 nm assuming $\epsilon = 42,000$ [17]. A number of films of varying concentrations were examined; we will discuss primarily films made from a solution containing 7.8 mg TPC, 1.92 mg PcTS and 100 mg PVP in 7.8 mL pyridine. The density of the final film was assumed to be approximately 1.0 g cm^{-3}, leading to approximate concentrations of TPC and the PcTS of 115 mM and 10 mM, respectively.

The films were prepared by applying several drops of solution to a clean microscope slide and spinning it off at 250–1000 rpm leading to films 0.1–1 μm thick. The ratio of approximately 12 chlorin molecules per phthalocyanine molecule is apparent from the absorption spectrum of the dry film. Except when spectra were being taken, the films were illuminated by a 60 W tungsten bulb from a distance of 45 cm. The film temperature was not more than 2 °C above ambient. Both the long-term illumination and the spectral measurements were performed in air. Control experiments showed that the spectral properties of films kept in the dark did not change with time. Also, attempts to exclude oxygen during the irradiation lead to markedly slower rates of change.

Fluorescence emission and excitation spectra were measured with an Aminco Bowman AB2 spectrofluorometer employing a front face cell holder for solid samples. The emission spectra were measured at 4 nm resolution with excitation at 520 nm (16 nm bandpass) through a 500 nm long pass and a 600 nm short pass filter to ensure that no stray light reached the sample. The emission spectra were not corrected for the instrument response since only relative measurements were important. The excitation spectra were measured at 2 nm resolution while monitoring the emission at 711 nm (4 nm bandpass) through a 700 nm long pass filter to eliminate scattered excitation light. Excitation spectra were corrected for the lamp profile. Absorption spectra were measured at 2 nm resolution with a Hewlett Packard 8452A diode array spectrophotometer. All absorption spectra were normalized to an absorbance of 0 at 800 nm; no further attempt was made to correct the baseline for scattering.

3. Design of the light harvesting system

A light harvesting system must absorb energy and transfer it to an acceptor before the excitation is lost by competing processes such as fluorescence or internal conversion [15,18]. A problem in most artificial systems is the presence of dead-end energy transfer pathways and energetic traps [15,18,19]. In nature, the molecules responsible for energy transfer (primarily chlorin derivatives) exhibit a precise spatial and energetic order [2,3,15,20]. However, it has not been possible to make realistic experimental models of these systems because we cannot imitate nature's positional control of the chromophores. Spatially random systems, [13,19] on the other hand, are easy to prepare but have a relatively low efficiency for energy transfer, because they usually contain traps and dead end pathways [15]. Our ultimate goal is to discover the conditions under which illumination of a random system will lead to progressively increasing efficiency of the energy transfer process by "burning out" traps and dead-end pathways.

The detailed mechanism of energy transfer in photosynthetic membranes is still somewhat controversial, [2,21] but the general requirements for such a process are well-understood. Singlet energy transfer (incoherent Förster-type transfer) [2,19,21] involves coupling between the transition dipole moments of the two molecules. The coupling between identical molecules, such as those involved in the single component antenna system described here, increases with increasing extinction coefficient of the lowest energy band, with increasing quantum yield for fluorescence, and with decreasing Stokes shift [2,15,19]. Energy transfer from the antennae to the acceptor occurs by a similar mechanism, but is exergonic and often irreversible.

Some of the criteria used in designing an energy transfer system that could spontaneously evolve towards greater efficiency upon illumination are listed here: The antenna molecules must have a high efficiency for exchanging energy amongst themselves, be soluble in the polymer film in high concentration with minimal "concentration quenching", and must slowly undergo a decomposition reaction from the excited state that removes the chromophore from further optical interactions with the antennae. The acceptors must have strong overlap between their absorption spectrum and the emission spectrum of the antenna. Furthermore, in order to observe the energy transfer process and to excite the donor without exciting the acceptor, the latter should have a high quantum yield for fluorescence and emit at energies substantially lower than the antenna while having minimal absorption over some wavelength range where the antenna absorbs strongly. Finally, the acceptor should be chemically inert. The polymer should be a good "solvent" for the antenna and acceptor, and should be transparent and inert. The system described here meets many, but not all, of these criteria, as discussed below. Fig. 1 shows the absorption spectra of TPC and PcTS in thin films of PVP.

The meso phenyl groups of the tetraphenylchlorin tend to inhibit somewhat the formation of aggregates (that are often energy traps) in concentrated solutions or films. TPC has similar spectral properties to its natural cousins, and therefore is expected to have similar energy transfer properties. Chlorins are known to undergo slow photo-oxidation by oxygen with the production of a weakly absorbing yellow mixture of products [22,23]. Thus, the photoreaction of chlorin with oxygen will remove the reaction product from the energy transfer chain. Phthalocyanine is a chemically robust compound with a high fluorescence quantum yield ($\Phi_f = 0.62$) [16]. The emission maximum of the PcTS is 54 nm (0.14 eV) to the red of the TPC emission (Fig. 2) thus the two chromophores can be independently monitored and the endergonic transfer of excitation energy from the PcTS back to the chlorin can be neglected. Also the PcTS absorbs only weakly over much of the chlorin's absorption spectrum (Fig. 1). Although most phthalocyanines are practically insoluble in organic solvents, the tetrabutyl ammonium salt of PcTS is moderately soluble in polar organic media.

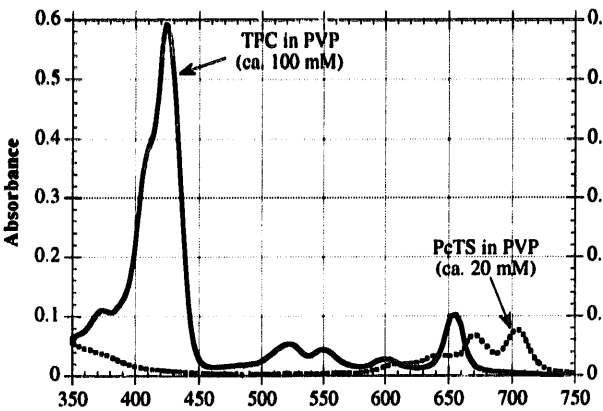

Fig. 1. Absorption spectra of the antenna chlorin, TPC, and the acceptor phthalocyanine, PcTS, in solid films of poly(vinylpyridine), PVP.

Films were made using a number of different polymers including poly(styrene), poly(carbonate) and poly(vinyl-alcohol). Poly(vinylpyridine) was found to be superior to the others in its ability to solvate high concentrations of TPC and PcTS without inducing substantial changes in the absorption and emission characteristics of the chromophores. The absorption spectra shown in Fig. 1 are almost identical to the spectra of the species in dilute pyridine solution, showing only a slight broadening of the absorption bands relative to solution and a slight tilt of the baseline indicative of scattering. Both these effects are somewhat more pronounced in the mixed film shown in Fig. 2.

4. Results and discussion

Fig. 2 shows the emission from a film as-prepared (i.e., before the long-term illumination) when illuminated at 520 nm. The emission at 711 nm is almost completely due to the phthalocyanine as seen from a

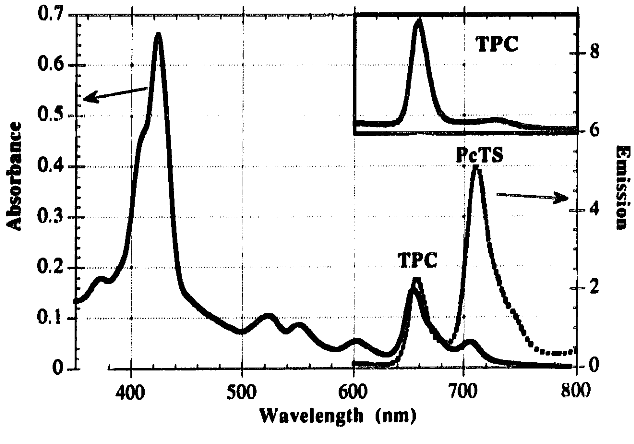

Fig. 2. Absorption spectrum of a new (before illumination) PVP film containing both chlorin (ca. 115 mM) and phthalocyanine (ca. 10 mM), and the fluorescence spectrum of the film when excited at 520 nm where the phthalocyanine does not absorb. The direct fluorescence from the chlorin and the sensitized fluorescence from the phthalocyanine acceptor are labeled. The insert shows the emission spectrum of the pure chlorin in a PVP film.

comparison of the emission spectra of the mixed film and the pure chlorin in PVP (inset, Fig. 2). The phthalocyanine emission at 711 nm is markedly stronger than that from the chlorin although practically all (>99%) of the light absorbed at 520 nm is absorbed by the chlorin. This suggests that the excited state of the chlorin transfers its energy to the phthalocyanine. Further evidence that the emission at 711 nm is caused by energy transfer from the chlorin to the phthalocyanine is given by the fluorescence excitation spectrum (Fig. 3) taken while monitoring the emission at 711 nm. This spectrum is essentially identical to the TPC absorption spectrum showing that excitation of the TPC leads to emission from the PcTS.

After the spectra in Figs. 2 and 3 were taken, the film was illuminated with a 60 W tungsten lamp for a number of hours and the changing absorption and emission spectra were periodically measured. Figs. 4 and 5 show several of the absorption and emission spectra, respectively, taken at different total illumination times. It is apparent that the absorbance of the TPC at the excitation wavelength used in the fluorescence measurements (520 nm) decreases monotonically with illumination time. This is expected from the known lability of photoexcited chlorins in the presence of oxygen. Other spectral changes are not yet clearly understood, such as the greater-than-expected decrease in the 656 nm band of the TPC and the narrowing of its Soret band.

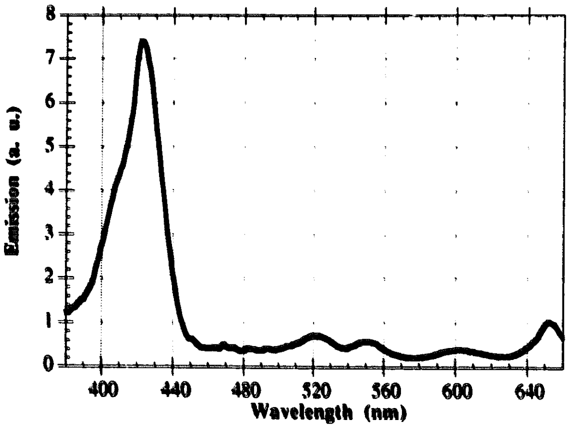

Fig. 3. Fluorescence excitation spectrum of the film while monitoring the phthalocyanine emission at 711 nm.

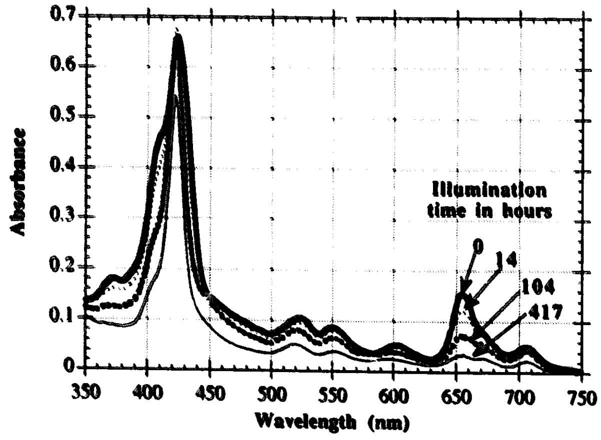

Fig. 4. Absorption spectra as a function of illumination time.

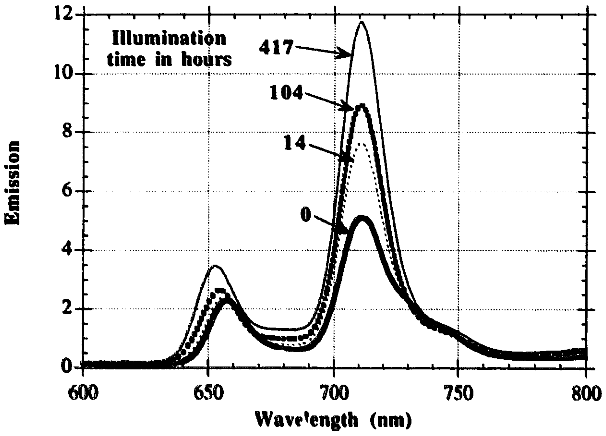

Fig. 5. Emission spectra as a function of illumination time. Excitation at 520 nm. The spectra have not been corrected for the decreasing absorbance at 520 nm.

The emission spectra (Fig. 5) show a monotonic and substantial increase in the phthalocyanine emission as well as a slight increase and gradual blue-shifting in the chlorin emission. The spectra have not been corrected for the decreasing absorbance at 520 nm.

The relative efficiency for energy transfer as a function of illumination time, $\Phi(t)$, was calculated as the emission intensity of the phthalocyanine divided by the fraction of the incident light absorbed at 520 nm. $\Phi(t)$ was set equal to 1 at the beginning of the experiment. The fraction of the incident light that is absorbed at 520 nm is

$$I(t) = \frac{I(t)_{\mathrm{abs}}}{I_0} = 1 - 10^{-A(t)_{520}}$$

where $A(t)_{520}$ is the absorbance at 520 nm as a function of time. The relative efficiency for energy transfer is then

$$\Phi(t) = \frac{\mathrm{Em}(t)_{\mathrm{PcTS}}}{I(t)}$$

where $\mathrm{Em}(t)_{\mathrm{PcTS}}$ is measured at the peak of the phthalocyanine emission. Using this definition, the relative efficiency for energy transfer can be calculated as a function of illumination time. Fig. 6 shows that $\Phi(t)$ increased by about a factor of 5 during 530 h of illumination.

The decrease in PcTS concentration with time (Fig. 4) was unexpected and complicates the interpretation of the results. In control experiments with only PcTS in the film, the concentration of the PcTS, and its emission intensity, did not change significantly with time

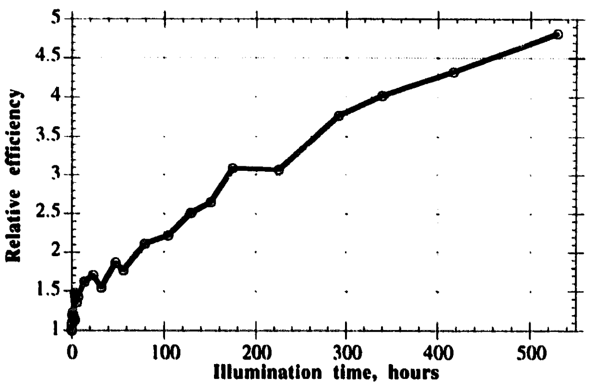

Fig. 6. The relative efficiency for energy transfer, $\Phi(t)$, defined in the text, as a function of illumination time. $\Phi(t)$ is normalized to 1 at the beginning of the experiment.

during long-term irradiation. However, an unavoidable complication to an exergonic energy transfer process (e.g., TPC → PcTS) is the possibility of the competing electron transfer process. If the excited state redox potentials are similar to the ground state redox potentials, as is usually the case for singlet state processes, then exergonic energy transfer implies that either electron transfer or hole transfer from donor to acceptor must also be exergonic. In our system, the excited chlorin may reduce the phthalocyanine, leading to the PcTS radical anion and the TPC radical cation. The PcTS radical anion is expected to be less stable than either the ground state or excited state phthalocyanine, and it may be this species that is responsible for the decrease in the PcTS concentration with time.

The emission from the chlorin increases by about 50% over 530 h of illumination, and that of the PcTS increased by about 250%, even while the concentrations of both species decreased to less than half their original values. There are several mechanisms that should be considered to explain these results: (1) Both the chlorin and the phthalocyanine are present in such high concentrations that their emission intensities are somewhat diminished by concentration quenching. (These high concentrations are required for efficient energy transfer.) It is possible that a random, rather than targeted, decrease in chromophore concentration could explain the increases in emission intensities. Control experiments show that the sensitized PcTS emission does increase with decreasing random PcTS concentration over the concentration range observed in the illuminated films. However, the chlorin emission from films with decreasing random concentrations of chlorin decreases, although less than linearly because of concentration quenching. Thus the concentration quenching effect alone cannot explain the observed results. (2) The chlorin emission is inversely proportional to the phthalocyanine concentration. A decrease in (randomly dispersed) PcTS concentration by a factor of 2.6, similar to the total concentration decrease seen in the film during illumination, causes an increase in chlorin emission by the same factor of 2.6. Thus this factor alone would result in an increase in chlorin emission much larger than that observed. Furthermore, randomly dispersed films containing the concentrations of TPC and PcTS observed at various times along the evolution of the illuminated film do not correspond to the observed emission from the illuminated film. For example, in these random films the ratio of emission intensities of the PcTS to that of the TPC remain approximately constant, while this ratio increases substantially with time in the illuminated films (Fig. 5). Thus, a combination of mechanisms (1) and (2), by themselves, cannot account for the observed results. (3) If the film is evolving according to the mechanism proposed by Rebane, the emission from the chlorin should decrease with time as the inefficient molecules are photo-oxidized, while the emission from the phthalocyanine may increase with time as the energy is more efficiently funneled to the PcTS rather than to dead end pathways. However, such mechanisms cannot be perfect, even some efficient molecules will be photo-oxidized. This can counteract the general trend: for example, if energy is being efficiently transferred down a chain of *n* chlorins to a phthalocyanine and, by chance, the chlorin adjacent to the PcTS becomes photo-oxidized, the emission from the remaining *n*-1 chlorins in the chain will increase while the sensitized emission from the PcTS will be eliminated.

Although the third mechanism alone could qualitatively account for the observed results, it seems clear that the other two mechanisms also play a role in the evolution of the film properties. Thus, the observed results are most likely a combination of the random and the targeted evolution of the film.

Concentration quenching is a serious problem in artificial energy transfer systems, especially those that are expected to evolve toward greater efficiency. An aggregate of chromophores, say of TPC, almost invariably has a shorter excited state lifetime than the corresponding monomers, unless the aggregate is highly ordered [24]. Thus, the aggregates involved in concentration quenching in these films presumably imitate the effects of an efficient energy transfer pathway by decreasing the excited state lifetime of the antenna molecules that transfer energy to them. Since we can only monitor energy transfer to the phthalocyanine acceptor, the existence of other acceptors (aggregates) with short lifetimes can obscure some of the evolutionary processes taking place in the films.

Although the present system meets many of the criteria for a self-organizing light harvesting array, the self-quenching of the chromophores at the high concentrations required for energy transfer makes an unambiguous interpretation of the results problematic. We are presently modifying this system in an effort to minimize both the concentration quenching effects and the photodestruction of the phthalocyanine. When this system is in hand, a more detailed investigation will be undertaken.

5. Conclusions

Some design principles for light harvesting systems that may evolve in time toward greater efficiency have been enunciated. One system based on these principles has been introduced and it was shown that its efficiency for energy transfer increases with time when illuminated. The lability of the phthalocyanine acceptor, and the concentration quenching of both chromophores, complicate the quantitative interpretation of the results from this system.

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