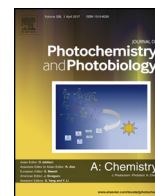




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Invited paper

Singlet and triplet excited states dynamics of photosynthetic pigment chlorophyll *a* investigated by sub-nanosecond pump-probe spectroscopy

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ABSTRACT

Singlet and triplet excited states dynamics of the photosynthetic pigment chlorophyll *a* in various solvents have been investigated by sub-ns pump-probe spectroscopic measurements with a sub-ns time resolution and a temporal window up to 400 μ s. The singlet and triplet lifetimes of chlorophyll *a* were determined respectively to be 5.2–7.0 ns and 1.2–12 μ s, depending on solvents. On a basis of a global analysis of time-resolved spectroscopic data, we estimated an yield of the intersystem crossing from the singlet to triplet excited states chlorophyll *a* to be about 30% depending not on surrounding environments. The value is much lower than the previously reported values.

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1. Introduction

Chlorophyll *a* (Chl *a*, Fig. 1(A)) is an essential pigment for natural oxygenic photosynthesis of higher plants and algae [1,2]. It acts as a major light-harvesting (LH) pigment in antenna systems and as a redox pigment enabling light-induced charge separation in photosynthetic reaction centers (RC) with a very high quantum yield [1,2]. Based on the molecular orbital models of tetrapyrroles, the excited states of a monomeric Chl molecule are characterized by linear combinations of the four lowest allowed one electron $\pi \rightarrow \pi^*$ excitations [3–6]. The two lowest-lying singlet excited states, which are designated as the Q_x and Q_y states, play key roles by acting as acceptors of highly efficient energy transduction from excited states of carotenoid in the primary stages of photosynthetic light-harvesting of aquatic algae [7–11]. The other crucial excited state is the triplet T_1 excited state. The T_1 state of Chl *a* safely dissipates excess light energy to carotenoid in photosynthetic

systems of higher plants in order to avoid a generation of harmful singlet oxygen [12–16].

It is widely accepted that following excitation to the lowest singlet excited state Q_y of Chl, an efficient intersystem crossing process generates the T_1 state on a time scale of several nanoseconds, competing with the radiative and nonradiative decay to the ground state [17]. Although the intrinsic T_1 lifetime of Chl is longer than several ten microsecond [17], the energy stored in T_1 is easily transferred to surrounding oxygen molecules in aerobic condition. Redmond and Gamlin summarized singlet oxygen generation yields sensitized by various dye molecules [18]. For Chl *a* in organic solvents, the T_1 generation yield is more than 50%, resulting highly efficient singlet oxygen generation because a triplet energy transfer efficiency between Chl *a* and oxygen is almost unity. On the other hand, our recent spectroscopic investigation on light-harvesting complex 2 (LH2) from purple bacteria suggested that the triplet generation yield of bacteriochlorophyll (Bchl) *a* is significantly lower (<20%) [19] than the reported value (35–70%) [18].

The electronic excited state and vibrational dynamics of Chl have been investigated by means of steady-state or time-resolved spectroscopic measurements [20–29]. A flash photolysis method has been widely utilized to observe chemical reactions in organic

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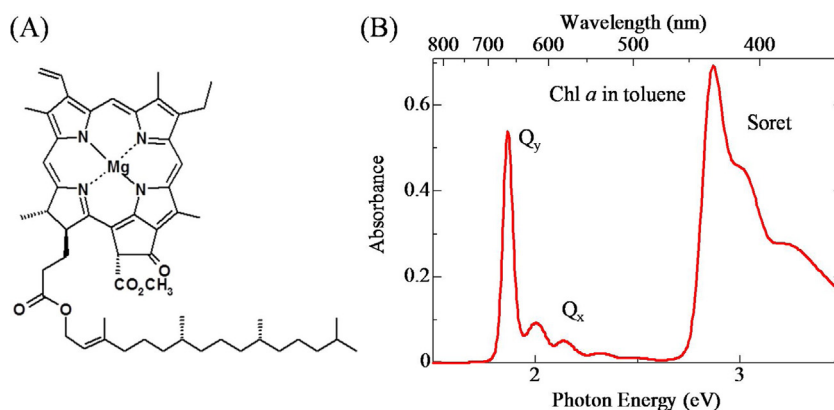


Fig. 1. (A) Chemical structure of Chl *a*. (B) Steady-state absorption spectra of Chl *a* in toluene.

materials even though this procedure was usually limited in a temporal resolution of several ten nanoseconds. Thus, this measurement has been applied to observations of triplet decay kinetics of Chl *a* in solution or bound to photosynthetic systems [30,31]. A time-resolved fluorescence measurement using a streak camera or a time-correlated single-photon counting system is also a powerful tool with a higher temporal resolution (<100 ps) and a wide temporal window ($>\mu\text{s}$) [32–34]. However, fluorescence spectroscopy is suitable only to detect optically allowed states. Femtosecond pump-probe measurements were performed on Chl or Bchl to observe excited state dynamics taking place up to several nanoseconds with a femtosecond temporal resolution [35–38]. A temporal window up to several nanoseconds is not sufficient to observe formation kinetics of triplet Chl. These situations have made difficult to determine a quantum yield of triplet generation of Chl or Bchl. We recently introduced a novel method which covers a wide temporal range from ps to sub-ms with a sub-ns temporal resolution [19,39]. This spectroscopic procedure enables us to observe the singlet decay and triplet formation/decay kinetics of Chl *a* without a temporal gap. In this study, we performed sub-ns pump-probe measurements on monomeric Chl *a* in solution to clarify a singlet-triplet intersystem crossing process following excitation to the lowest lying singlet Q_y excited state.

2. Experimental

Sub-ns pump-probe spectroscopic measurements were performed based on combination of a 1 kHz Ti:Sapphire regenerative amplifier (Hurricane-X, Spectra-Physics) and a commercial time-resolved spectrometer (EOS Vis-Nir, Ultrafast Systems) [19,39]. The excitation pulse at 665 nm, to excite the Q_y absorption band of Chl *a*, was generated by the second harmonic generation of a signal pulse from an optical parametric amplifier (OPA-800CF, Spectra-Physics). Excitation intensity was set to 50 nJ/pulse and the excitation beam was focused on to the sample with a diameter of 200 μm . The zero time delay and the instrumental response function at each probe energy of the system were determined by the pump-probe measurement on Chl *a* in toluene. The instrumental response function of the system was estimated to be about 700 ps.

Chl *a* was purchased from Fuji SLI Co., Ltd. Chl *a* was dissolved in some organic solvents (acetone, toluene, and diethyl ether) and was also solubilized in a 20 mM cetyltrimethylammonium bromide (CTAB) micellar medium containing potassium phosphate buffer (pH 7.0) [40,41]. The sample was packed in a static cuvette with 2.0 mm optical path length. The sample was bubbled with Ar gas before the measurements and stirred by a micro magnetic bar in the cuvette to avoid optical damage during the measurements.

The absorbance of the sample was set to 0.5 at the Q_y absorption band. All measurements were performed at room temperature.

3. Results and discussion

Fig. 1(B) shows the steady-state absorption spectrum of Chl *a* in toluene. The absorption band at 660 nm is owing to the one-photon transition from the ground state to the lowest singlet Q_y excited state of Chl *a*. Additional peaks appear at 578 and 616 nm originates both from the Q_x state and the higher vibrational levels of the Q_y state [27]. The absorption band below 450 nm has been assigned to the Soret band.

The photo-induced absorption spectra of Chl *a* in toluene at different delays in the time regime from sub-ns to μs are presented in Fig. 2. The photo-induced absorption spectra were recorded after excitation into the Q_y absorption band at 665 nm. The transient signals owing to Chl *a* appeared immediately after excitation. Negative changes around 430 and 660 nm reflect a mirror image of the steady-state absorption, thus these signals are assigned to the bleaching signals of Chl *a* due to the depletion of the ground state. In addition, the negative signal around 660 nm slightly extends to longer wavelength due to the stimulated emission from the Q_y state at early delay times (<3.0 ns). A broad positive change is assignable to the transient absorption of the Q_y state at early delay time or the T_1 state at longer delay time.

Fig. 3(A) and (B) plots the kinetic traces of the photo-induced absorption signals of Chl *a* in toluene. The thin solid lines are the best fits using exponential decay and rise components convoluted with a Gaussian instrumental response function of the system. The

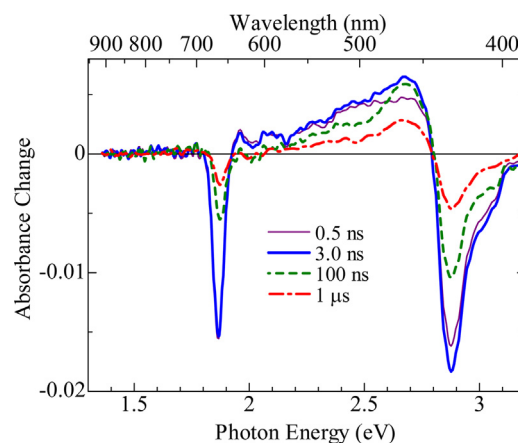


Fig. 2. Photo-induced absorption spectra of Chl *a* in toluene taken at various delay times after excitation at 665 nm.

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