

The Energy Transfer Processes between Carotenoid and Chlorophyll Regulated by Electron Exchange Mechanism

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Abstract: The energy transfer efficiency between carotenoids and chlorophyll depend on temperature and viscosity of the media. A 3.5 ps process was detected by the pico-second time-resolved spectra and the process was proved to be regulated by electron exchange mechanism.

Keywords: Carotenoid, chlorophyll, phycobilisomes, fluorescence.

Phycobilisomes, carotenoids and chlorophylls are the major pigments for photosynthesis of alga¹. But the exact mechanism for the excitation energy transfer between carotenoids and chlorophylls is not clear yet. Compared with the energy transfer process in the phycobilisome to photosystems, the overlap integral of emission spectra of carotenoid with the absorption spectra of the chlorophyll is small and the quantum yield of the carotenoid fluorescence is weak. This fact indicated that the mechanism is unlikely to be Förster dipole-dipole resonance transfer mechanism. Instead, it was believed that the process might be explained by Dexter electron-exchange mechanism²⁻⁴.

Spirulina platensis, a cyanobacterium, was grown in 10 L batch cultures at room temperature, and bubbled with air and illuminated with 40 W fluorescent lamps. It was harvested after two weeks. The two-week old *Spirulina platensis* cultures cells were harvested and suspended in either 0.75 mol/L or 10 mmol/L phosphate buffer. All steps of the membrane isolation were done at room temperature at pH 7.0 in the presence of 0.02% NaN₃. Cell was broken in a French pressure cell at 16,000 p.s.i. and then centrifuged at 60,000 rpm for 30 minutes in a Beckman 70 Ti rotor. The pellet in 0.75 mol/L phosphate buffer contained thylakoid membranes and phycobilisomes, which are referred to as “PBS-thylakoid membrane complex”. The pellet from the 10 mmol/L K-phosphate suspension was twice resuspended in the same buffer, homogenized and centrifuged as above. These membranes without phycobiliproteins are referred to as “thylakoid membrane⁵”.

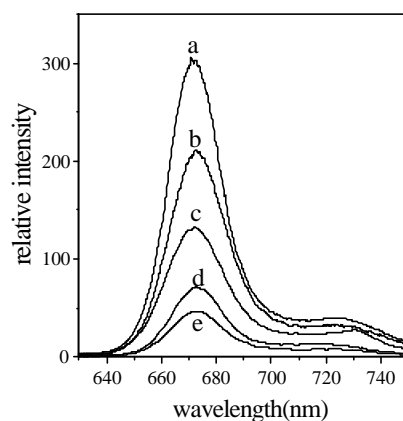
Absorption spectra were measured on a UV2001 UV spectrophotometer (Hitachi, Japan). Fluorescence emission spectra were measured on a F4500 spectrofluorimeter (Hitachi, Japan) at room temperature. The detailed setup to measure the fluorescence

decay dynamics of the dye was described elsewhere⁶.

Results and Discussion

Fluorescence spectra of thylakoid membrane at different temperatures or viscosities were shown in **Figure 1** and **Figure 2** respectively. In **Figure 1**, only carotenoid molecules are excited at the wavelength of 495 nm, while the 685 nm peak result from fluorescence emission of chlorophyll molecules. It is obvious that the intensity of fluorescence of chlorophyll molecules decrease with the increase of the medium viscosity. In **Figure 2**, it gives that the relative fluorescence intensity of chlorophyll molecules at different temperature and it clearly shows that the intensity of fluorescence of chlorophyll molecule decrease with the decrease of temperature. For the Förster dipole-dipole transfer mechanism, the prerequisite is that fluorescence emission spectra of donor and the absorption spectra of acceptor must be overlapped. It can not be affected by temperature and viscosity seriously. On the other hand, for Dexter's electron exchange mechanism, the interaction of the donor's orbital and acceptor's orbital of molecules is the prerequisite for energy transfer⁷⁻⁸. Therefore, the donor and acceptor molecules should be closed together. Obviously, temperature and viscosity may as the factors to affect the interaction of the donor's orbital and acceptor's orbital⁹, moreover, to change efficiency of energy transfer between donor's and acceptor's chromophores. In our experiments, the efficiencies of energy transfer increase with rising temperature or lowering viscosity. Therefore, the energy transfer processes between carotenoids and chlorophyll may regulate by electron exchange mechanism.

Figure 1 Relative intensity of fluorescence of chlorophyll molecules decreases with the increase of the medium viscosity



a, b, c, d, e represent 0.05 mol/L, 0.1 mol/L, 0.2 mol/L, 0.25 mol/L, 0.3 mol/L sucrose phosphate buffer respectively

Moreover, in **Figure 3**, it gave profile on the kinetic analysis of the energy transfers process detected by picosecond time-resolved spectra. The global analysis results of three components indicate the time constant of the fastest component is 3.5 ps. It is in

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well according with the calculated results of the Dexter model (3~4ps), based on a distance of about 4.5 Å reported recently for the antenna structure data¹⁰⁻¹¹. Therefore, the carotenoids may also play an important role in harvesting light and energy transfer. The mechanism of energy transfer can be reasonably described by electron exchange mechanism.

Figure 2 Relative intensity of fluorescence of chlorophyll molecules decreases with the decreases of temperature

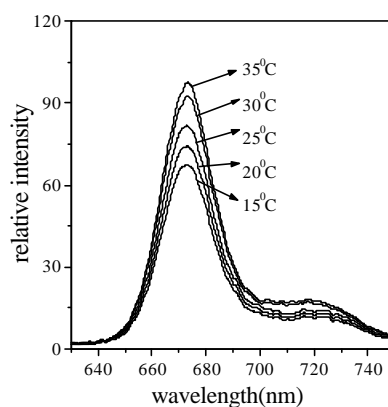
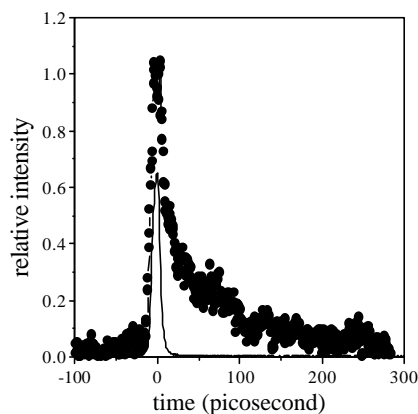


Figure 3 Kinetics of time resolved spectra of thylakoid membranes with excited wavelength of 459 nm observed at 685 nm



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References

1. R. MacColl, *J. Stru. Boil.*, **1998**, 124, 313.
2. A. P. Shreve, J. K. Trautman, H. A. Frank, T. G. Owens, A. C. Albrecht, *Biochim. Biophys. Acta*, **1991**, 1085, 283.

3. D. Siefermann-Harms, *Biochim. Biophys. Acta*, **1985**, *811*, 330.
4. K. R. Naqvi, *Photochem. Photobiol.*, **1980**, *31*, 524.
5. Y. Li, J. P. Zhang, J. Xie J. Q. Zhao, L. J. Jiang, *Biochim. Biophys. Acta*, **2001**, *1504*, 230.
6. Y. Li, Z. Y. Sun, Y. C. Ai, X. K. Zhang, J. Q. Zhao, L. J. Jiang, submitted to *J. Phys. Chem. (B)*.
7. N. J. Turro, *Modern Molecular Photochemistry*, Benjamin/Cummings Publishing Company press USA, **1987**, p.310.
8. T. Gillbro, P. O. Andersson, R. S. H. Liu, A. E. Asato, S. Takashi, R. J. Cogdell, *Photochem. Photobiol.*, **1993**, *57*, 47.
9. J. X. Shan, *Purification of photosystem II core antenna complexes CP43 and CP47 and studies on their spectroscopic properties*, Institute of Botany, Chinese Academy of Sciences, Ph. D dissertation, **1999**, p.68.
10. W. Kühlbrandt, D. N. Wang, Y. Fujiyoshi, *Nature*, **1994**, *367*, 619.
11. F. G. Zhang, T. Gillbro, R. van. Grondelle, V. Sundström, *Biophys. J.* **1992**, *61*, 700.

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