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Femtosecond Förster Energy Transfer over 20 Å in Phycoerythrocyanin (PEC) Trimers

L.O. Palsson[1], *T. Gillbro*[1], *A. Sharkov*[1], *R. Fischer*[2], *and H. Scheer*[2]

[1]Department of Physical Chemistry, University of Umea,
S-901 87 Umea, Sweden

[2]Botanisches Institut der Universität München,
W-8000 München, Fed. Rep. of Germany

Energy transfer between violobilin (α-84) and phycocyanin (ß-84) chromophores in phycoerythrocyanin trimers from *Mastigocladus laminosus* occurs in 400 fs indicating a Förster-type energy transfer over 20 Å.

Introduction.

Phycobilisomes constitute the antenna for capture of light enrgy and are active in the subsequent transfer of the excitaion energy to the reaction centers in red algea and cyanobacteria. The phycobilisome contains chromophores of several different types and thus have the capacity to absorbe light of different wavelengths. This enables the organism to harvest light energy and grow in different radiation environments. Thus far only a few photosynthetic antenna complexes have been crystallized and their structure determined. One example of a highly resolved structure is the phycoreythrocyanin antenna complex isolated from phycobilisomes of *Mastigocladus laminosus* [1]. In this work the positions and orientations of the three chrompohores (α-84, β-84 and β-155) were determined. The closest contact is between the α-84 (violobilin) and β-84 (phycocyanin) chromophores with a center-to-center distance of 19 Å. The α-chomophores is supposed to absorbe strongly about 572 nm, while the β-subunit absorbes at longer wavelengths, i.e. about 592 nm [2].

Results and discussion.

Exciting at 575 nm using cavity dumped compressed pulses, FWHM ~ 50 fs we resolve a very fast 400 fs partial recovery of the bleaching signal.This indicates an ultrafast energy transfer from α-84 to a red-shifted β-chromophore. The process we observe is actually an equlibration of the excitation energy between these chromophores. A

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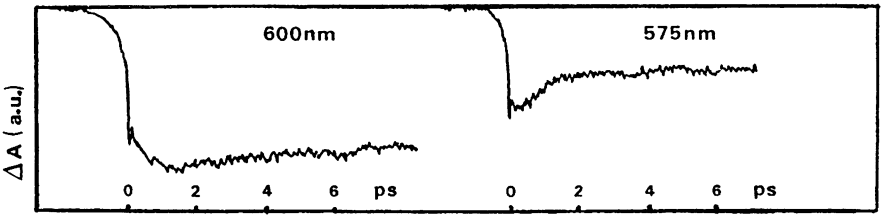

Fig. Absorption recovery at 575 nm and at 600 nm.

similar but reversed 400 fs process is observed if we excite at 600 nm (mainly β-chromophores). In this case a slow recovery of the transient bleaching is estimated to occur in about 50 ps is observed as well.
From the crystal structure and an estimated Förster radius (R_0) of 60-70 Å for this sub picosecondenergy transfer we calculate a transfer rate, k, of

$$k=\frac{\kappa^2}{\tau}\left(\frac{R_0}{R}\right)^6 = 978\ ns^{-1}$$

where τ = 2.0 ns, κ = -1.10, R_o = 65 Å and R = 19 Å. For the equilibration process $\Sigma k \cong 1950\ ns^{-1}$, giving a lifetime of about 500 fs in fair agreement with the experimental results.The results reported here are also consistent with recent work on allophycocyanin and c-phycocyanin trimers [3,4].

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