ULTRAFAST ENERGY TRANSFER IN AN ARTIFICIAL PHOTOSYNTHETIC ANTENNA

Global and target analysis of femtosecond transient absorption spectra

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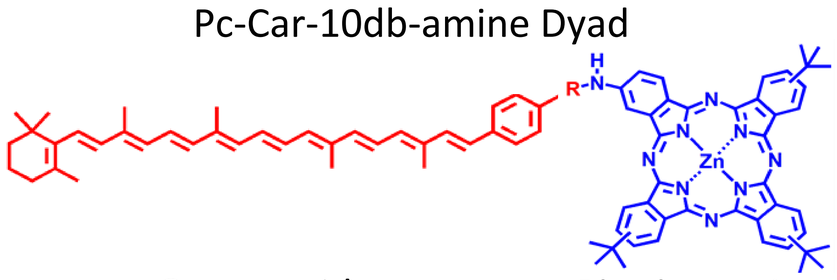
Abstract

Photosynthesis relies on light harvesting from peripheral antennas –typically performed by carotenoids (Car) and (bacterio)chlorophylls– and subsequent energy transfer (ET) to the reaction center, which can occur with almost 100% efficiency in some organisms [1]. In this work we studied a prototypical artificial supramolecule mimicking the natural photosynthetic unit [2]. It is composed of a Car with 10 conjugated double bonds (serving as light harvester) linked to a phthalocyanine (Pc, acting as energy acceptor) through a phenylamino group [3]. We excite the sample in resonance with the maximum of the first vibronic band of Car and we monitor the ultrafast rise of the Pc population. The Car->Pc ET process occurs from the bright Car S2 excited state and competes with an internal conversion (IC) process towards the lower-lying dark Car S1 excited state. To establish the relative weight of these two deactivation pathways, we compare the excited state dynamics of the isolated Car (where only the IC process occurs) with that of the dyad (where also the IC channel is active). Both these processes occur with sub-100-fs time constants, thus challenging the time resolution of conventional transient absorption (TA) systems. Using a combination of high-resolution pump-probe spectroscopy and exhaustive global and target analysis we overcome this limit. We were able to determine a 52% energy transfer efficiency, one of the highest values so far recorded for artificial complexes.

Introduction

Artificial Photosynthetic Antenna

Pc-Car-10db-amine Dyad



Carotenoid Phtalocyanine

Goal

Understanding photo-excited dyad properties on the ultra-fast timescale:

- Energy Flow Pathways
- Electronic coupling between Car and PC
- Improving the efficiency of the artificial leaf

Method

•Time-resolved pump probe TA spectroscopy

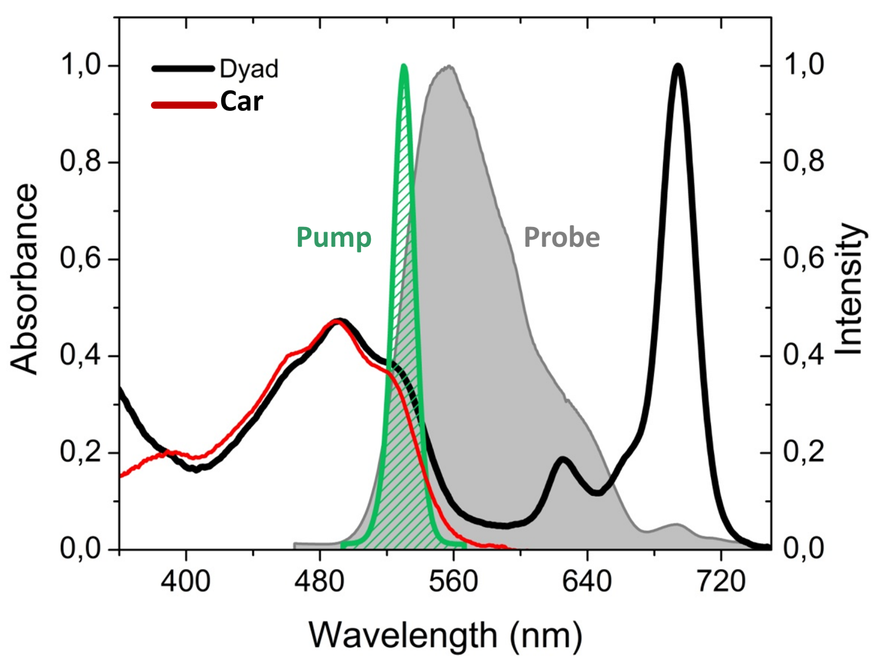
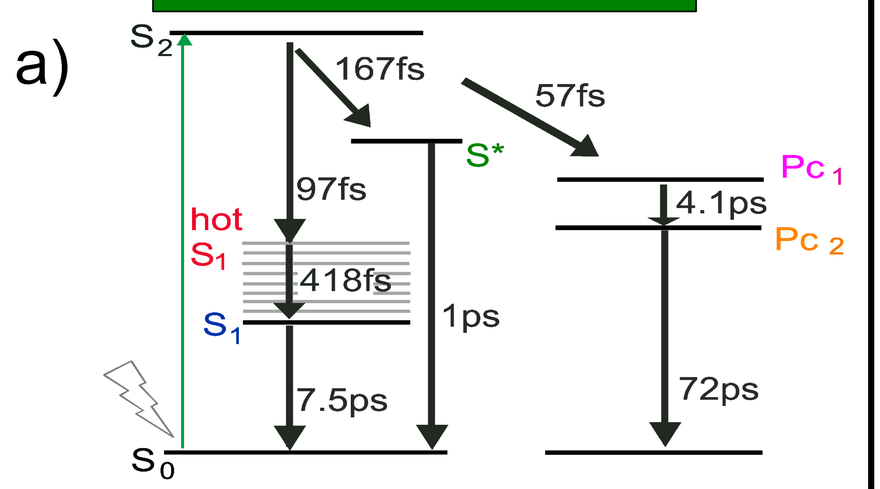


Figure 1: Absorption spectrum of the Car moiety and the Pc-Car Dyad as well as the pump and probe spectra used in the experiments.

Model + Results



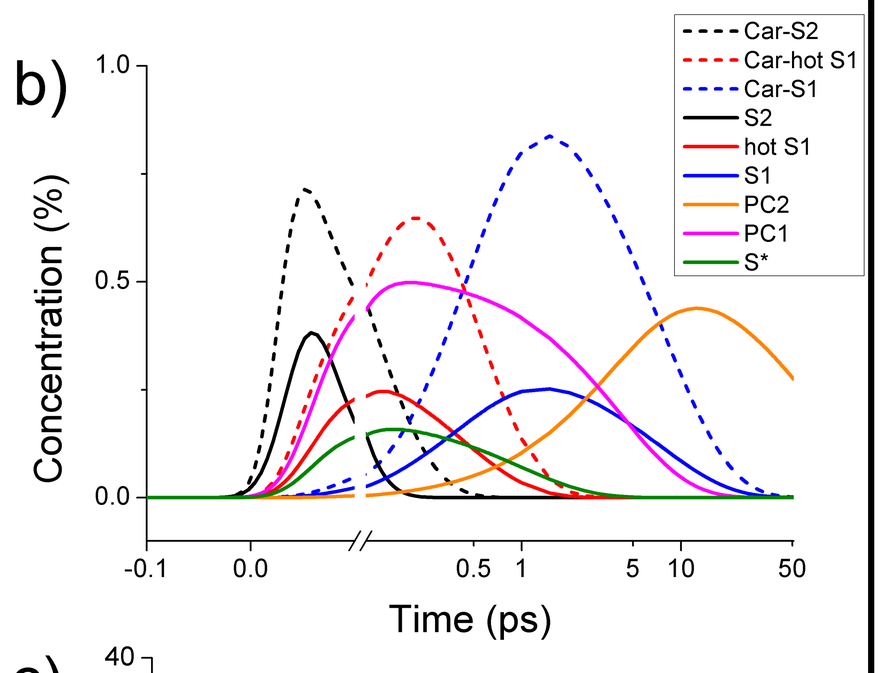


Figure 2: a) Energy level diagram with lifetimes (reciprocal of rate constants) estimated from target analysis. b) The concentration profiles and c) estimated SADS for the compartmental model as depicted in (a). Note that the time axis is linear until 0.1 ps and logarithmic thereafter. The dashed concentration profiles correspond to the isolated Car and the solid to the Car-PC dyad.

Data + Fit

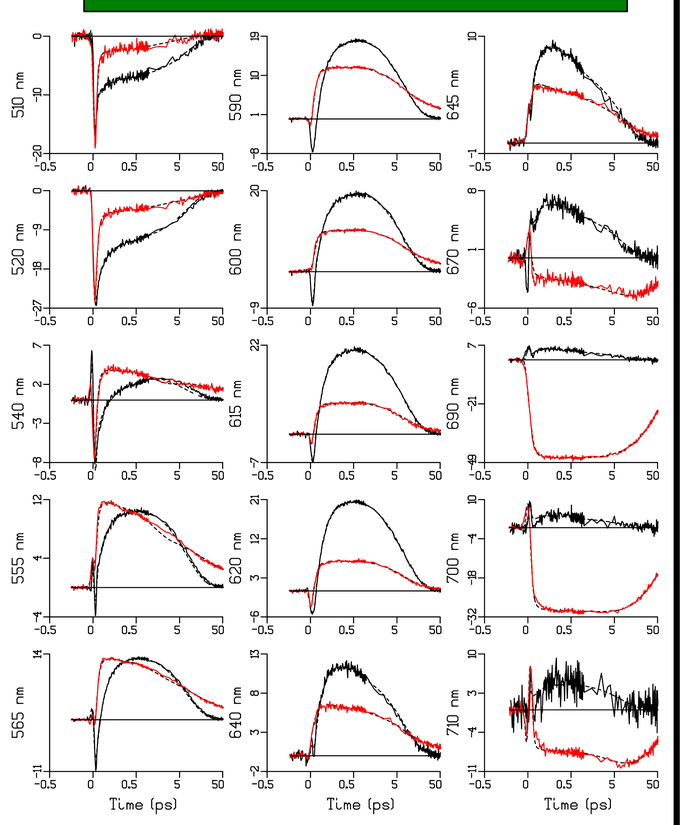
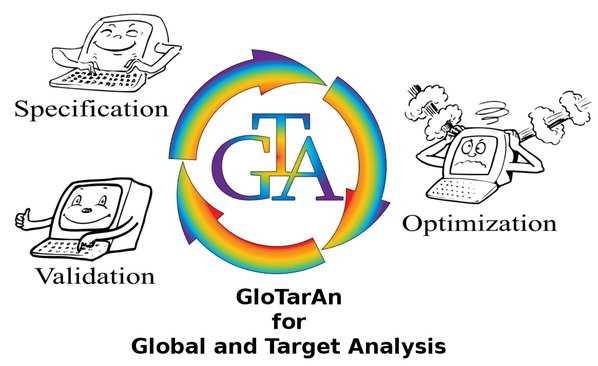


Figure 3: selected traces from the 530nm excitation experiment, here the solid line represents the data and the dahsed line represents the fit; the Car dataset is in black, the Dyad dataset is in red.

Method

•Global and target analysis

Glotaran is a free software program developed for global and target analysis of time-resolved spectroscopy and microscopy data [4]. It serves as a graphical user interface (GUI) to the R-package TIMP and facilitates easier model specification and interactive results inspection. It can be downloaded for free from glotaran.org (see QR code).



Glotaran:

- **Interactive data exploration**
- **Flexible model specification**
- **Interactive results inspection**

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