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Ultrafast Energy Transfer in an Artificial Photosynthetic Antenna

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Abstract. We temporally resolved energy transfer kinetics in an artificial light-harvesting dyad composed of a phthalocyanine covalently linked to a carotenoid. Upon carotenoid photo-excitation, energy transfers within ≈100fs (≈52% efficiency) to the phthalocyanine.

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 (Fig. 1(a)) mimicking the light harvesting process in natural photosynthesis [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 S_2 excited state and competes with an internal conversion (IC) process towards the lower-lying dark Car S_1 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 ET channel is active). Both these processes occur with sub-100-fs time constants, thus challenging the time resolution of conventional transient absorption (TA) systems. We overcome this limit by exploiting a state-of-the-art pump-probe system with 10-fs temporal resolution. We were able to extract a ≈52% ET efficiency, one of the highest values so far recorded for energy transfer from the S_2 state in artificial complexes.

Our experimental apparatus is based on two synchronized non-collinear optical parametric amplifiers (NOPAs). The first NOPA generates 10-fs pulses in the green, resonant with the $S_0 \rightarrow S_2$ transition of the Car, while the second NOPA provides ultra-broadband probe pulses with ≈7-fs duration spanning the 500-700 nm wavelength range, thus covering both the Car and Pc absorption bands [4]. A spectrometer with single-shot detection capability at 1 kHz is used to acquire 2-dimensional TA maps as a function of probe wavelength and delay [5].

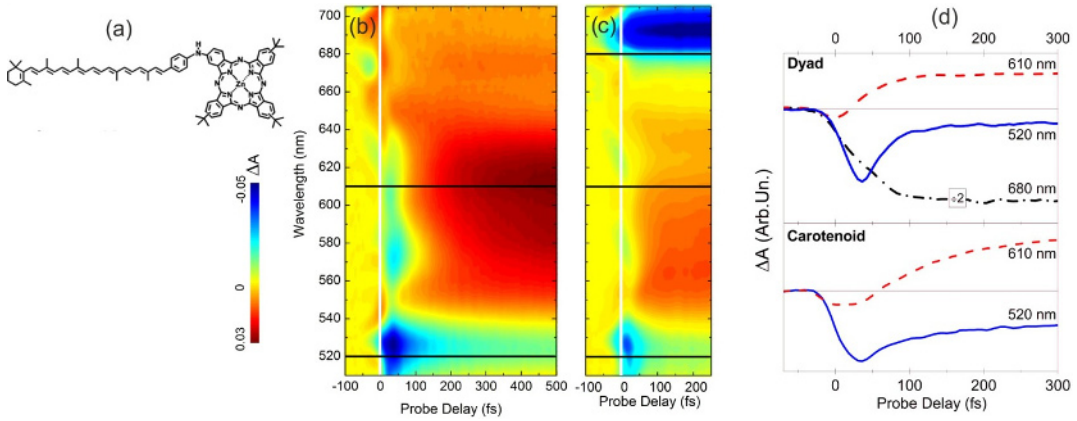

Fig. 1. (a) molecular structure of the dyad; (b) and (c) ΔA maps as a function of probe wavelength and delay for the isolated carotenoid and the dyad respectively; (d) temporal time traces at selected probe wavelengths for the isolated carotenoid (bottom panel) and dyad (upper panel).

Fig. 1(b) shows the ΔA map of the isolated Car in solution: we observe the prompt rise of a negative signal, which we assign to ground state photobleaching (PB) and stimulated emission (SE) from S_2 to S_0. This signal rapidly decays, giving rise to the formation of a positive photoinduced absorption (PA) band peaking at 610 nm, which is completed within ≈400 fs. This PA band is well known in Cars and assigned to a transition from S_1 to an higher-lying S_n state, thus providing a signature of the population in the S_1 state through the IC process. The PA band shows a faster build-up in the red compared to the blue, and undergoes spectral narrowing within the first 500 fs. These effects are due to intermolecular vibrational relaxation within S_1 associated with dissipation of excess energy deposited as a result of the IC process.

In the dyad (Fig. 1(b)) the temporal evolution of the TA signals occurs on a significantly shorter time scale as compared to the isolated Car, indicating a much faster decay of the population from the initially excited Car S_2 state. In particular, the resulting TA spectrum, completed within ≈100 fs, displays not only the expected $S_1 \rightarrow S_n$ PA from the Car but also: (i) a peaked negative PB signal around 690 nm, reflecting the Pc ground state absorption spectrum and thus indicating Car→Pc ET; (ii) an increased PA shoulder in the blue (peaking at ≈555 nm), representing a new deactivation pathway within the Car manifold towards an additional intermediate excited state denoted S*. This state, which was not participating in the IC process for the isolated Car, had already been observed for other Cars when embedded in light-harvesting systems in the same spectral region [6].

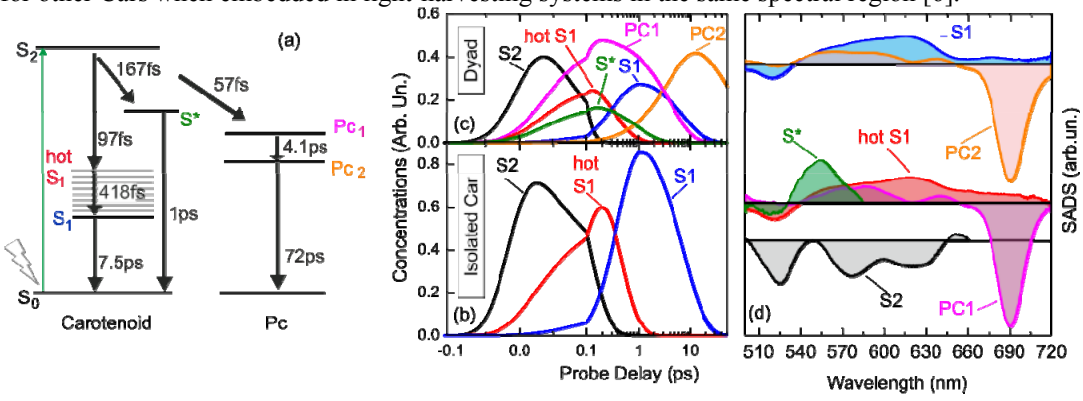

Fig. 2. (a) Energy level diagram in the target analysis; the numbers on the thick arrows indicate the inverse of the rate constants of the deactivation pathways involved; (b-c) Temporal evolution of the concentration profiles for the isolated Car (b) and for the dyad (c); the time axis is linear until 0.1 ps, then logarithmic; (d) Estimated SADS.

The two datasets for Car and the dyad were analyzed simultaneously using a combination of global and target analysis [7]. The compartmental model used is depicted in Fig. 2(a). $S_1^{hot} \rightarrow S_1$ and $Pc_1 \rightarrow Pc_2$ spectral evolutions were taken into account in order to include vibrational relaxation processes within the two species. $S_2 \rightarrow S_1^{hot} \rightarrow S_1$ IC rate constants and associated SADS were constrained to be equal for the isolated Car and the dyad. The result is a combination of concentration profiles (Fig. 2 (b-c)) and their respective spectral amplitudes. In Fig. 2 (d) these estimated species associated difference spectra (SADS) are shown. The first SADS can be identified as the S_2 of the Car with a PB at 525 nm and SE from 550 until 650 nm. From the S_2 state of the Car three different species are populated: the hot S_1 of the Car, the first state of the Pc species, and a clear Car S* state. The S* state is populated by the S_2 state and subsequently decays again in about 1 ps to the ground state, presumably via an IC processes. The Car S* state is restricted to only contribute to the fit below 580 nm. The hot S_1 state evolves in roughly 400 fs into the S_1 state which subsequently decays to the ground state in 7.5 ps. The resulting ET efficiency from the Car S_2 state to the Pc molecules is then calculated as $\eta_{ET} = \frac{1/57}{1/57 + 1/97 + 1/167} = 51.8\%$.

In conclusion, using our state-of-the-art spectroscopy system with ≈10-fs temporal resolution it was possible to completely time resolve the ultrafast excited-state dynamics of the isolated Car and of the dyad system, occurring on the ≈100-fs time scale. Their simultaneous comparison by means of global and target analysis enabled the evaluation of ET pathways and efficiency (as high as ≈50%) from the Car to the Pc.

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