

# Quantum coherence controls the charge separation in a prototypical artificial light harvesting system

Sarah M. Falke<sup>1</sup>, Carlo A. Rozzi<sup>2</sup>, Nicola Spallanzani<sup>2</sup>, Angel Rubio<sup>2</sup>, Elisa Molinari<sup>2</sup>, Daniele Brida<sup>3</sup>, Margherita Maiuri<sup>3</sup>, Giulio Cerullo<sup>3</sup>, Heiko Schramm<sup>1</sup>, Jens Christoffers<sup>1</sup>, and Christoph Lienau<sup>1</sup>

1. Institut für Physik, Carl von Ossietzky Universität, 26111 Oldenburg, Germany

2. CNR, Centro S3, Centro S3, via Campi 213a, I-41125 Modena, Italy

3. IFN-CNR, Dipartimento di Fisica, Politecnico di Milano, 20133 Milano, Italy

In artificial light harvesting systems the conversion of light into charges or chemical energy happens on the femtosecond time scale and is thought to involve the incoherent jump of an electron from the optical absorber to an electron acceptor. Here we investigate the primary process of electronic charge transfer dynamics in a carotene-porphyrin-fullerene triad, a prototypical elementary component for an artificial light harvesting system combining coherent femtosecond spectroscopy and first-principles quantum dynamics simulations. Our experimental and theoretical results provide strong evidence that the driving mechanism of the photoinduced current generation cycle is a quantum-correlated wavelike motion of electrons and nuclei on a timescale of few tens of femtoseconds. We furthermore highlight the fundamental role played by the interface between the light-absorbing chromophore and the charge acceptor in triggering the coherent wavelike electron-hole splitting.

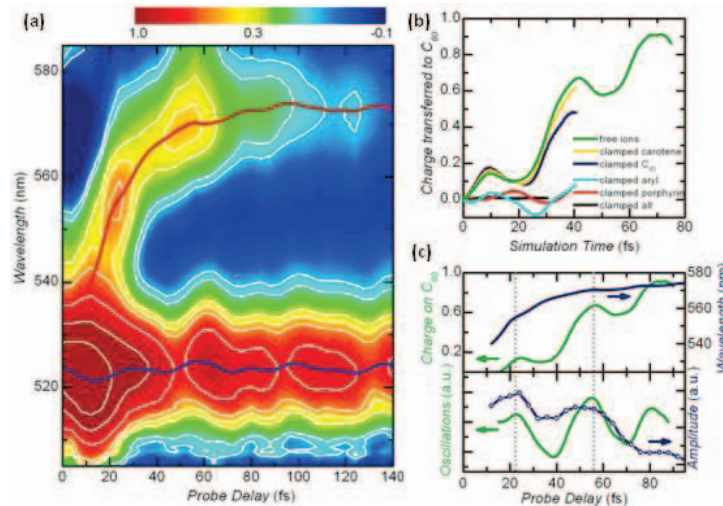


Fig. 1. Experimental (residual) differential transmission map recorded following impulsive excitation of the triad at around 550 nm (a). The blue and red lines highlight the time evolution of the center wavelengths of the porphyrin and charge transfer bands, respectively. Simulated charge transfer dynamics in the triad (b) under various conditions. Correlation between temporal oscillations (c) in the simulated transferred charge (green lines) and in the resonance wavelength (blue, upper panel) and the amplitude (blue, lower panel) of the differential transmission spectrum of the charge transfer band.

In order to probe the charge transfer dynamics in this triad, ultrafast nonlinear spectra were recorded using independently tunable ultrashort pump and probe pulses from two non-collinear optical parametric amplifier systems. Impulsive excitation of the porphyrin Q-band with a 7-fs pulse centered at 550 nm reveals rich transient transmission ( $\Delta T/T$ ) dynamics. This  $\Delta T/T$  map (Fig. 1a) displays two prominent features, (i) a long-lived photobleaching of the porphyrin Q-band absorption resonance around 523 nm and (ii) a short-lived and spectrally-red shifting transient emission band in the region between 540 nm and 580 nm. The red-shifting band shows both spectral and intensity oscillations and is assigned to stimulated emission of a photoexcited intermediate charge-transfer state displaying coherent population oscillations reflecting electronic wavepacket motion between the donor and acceptor state. This interpretation is supported by a detailed TDDFT quantum-dynamical simulation of the system. Photoexcitation of the porphyrin unit leads to an almost complete electron transfer to the fullerene moiety within about 70 fs, showing strong oscillations with a period of 30 fs (Fig. 1(b)). Both the time scale of the charge build-up and the oscillation period of the electronic wavepacket are in striking agreement with the experimentally observed dynamic evolution of the charge transfer band (Fig. 1(c)). The observed oscillation period matches that of carbon backbone vibrations, suggesting that nuclear motion delocalized across the porphyrin/fullerene region drives the charge transfer. This is confirmed by the observation of distinct changes in the transfer dynamics occurring when locking the positions of different (sub)-groups of the molecule (Fig. 1(b)). Especially nuclear vibrations in the porphyrin/linker region (aryl-group) of the molecule greatly influence the charge flow since even minor changes can suppress the charge accumulation on the fullerene.