

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

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Abstract. Ultrafast spectroscopy and quantum-dynamics simulations of an artificial supramolecular light-harvesting system – a supramolecular triad - provide strong evidence that the quantum-correlated wavelike motion of electrons and nuclei on a timescale of few tens of femtoseconds governs the ultrafast electronic charge transfer.

1 Introduction

In artificial light harvesting systems the conversion of light into electrical or chemical energy happens on the femtosecond time scale [1], and is thought to involve the incoherent jump of an electron from the optical absorber to an electron acceptor [2]. Here we investigate the primary dynamics of the photoinduced electronic charge transfer process in a carotene-porphyrin-fullerene triad, a prototypical elementary component for an artificial light harvesting system. Our approach combines coherent femtosecond spectroscopy and first-principles quantum dynamics simulations. Our experimental and theoretical results provide strong evidence that the driving mechanism of the primary step within the 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 flexible interface between the light-absorbing chromophore and the charge acceptor in triggering the coherent wavelike electron-hole splitting.

2 Details

The supramolecular triad studied consists of three functional units, a porphyrin ring acting as the primary light absorber in the center of the molecule, a fullerene (C₆₀) electron acceptor and a carotene unit serving as hole stabilizer. The triad has been synthesized by slightly modifying existing protocols [3]; in brief the individual functional units were prepared separately and finally linked together via cycloaddition and an amidation step.

It is known that upon photoexcitation of the porphyrin ring an ultrafast electron transfer from the porphyrin to the fullerene unit occurs with a charge separation yield of up to 95% [3]. A long-lived charge separated state is formed by a subsequent electron transfer from the carotene to the porphyrin unit on a 100 ps timescale. The optical properties of the triad were first experimentally investigated

and then numerically modeled using large-scale first-principles simulations within time-dependent density functional theory (TDDFT). Both the experimental and the simulated steady-state absorption spectra of the supramolecular triad are well approximated by a superposition of the individual subunit spectra, thus no signature of ground-state interaction was observed.

In order to probe the charge transfer dynamics ultrafast nonlinear spectra were recorded using a two-color pump-probe spectrometer providing independently tunable ultrashort pump and probe pulses from two non-collinear optical parametric amplifiers [4]. Impulsive excitation of the porphyrin Q-band with a 7-fs pulse centered at 550 nm reveals rich transient transmission ($\Delta T/T$) dynamics. Besides a slowly-rising long-lived photoinduced absorption band from the S_1 state of carotene, induced by weak coupling of the carotene S_2 state to the spectrally broad pump pulse and a subsequent internal conversion step, the impulsive excitation leads to a pronounced oscillation pattern originating from coherent ground-state vibrations. To gain insight into the charge-transfer dynamics in the triad, we have analyzed these known oscillations [5] using well-established density matrix formalism and subtracted them from the original data to obtain the $\Delta T/T$ shown in Figure 1(a).

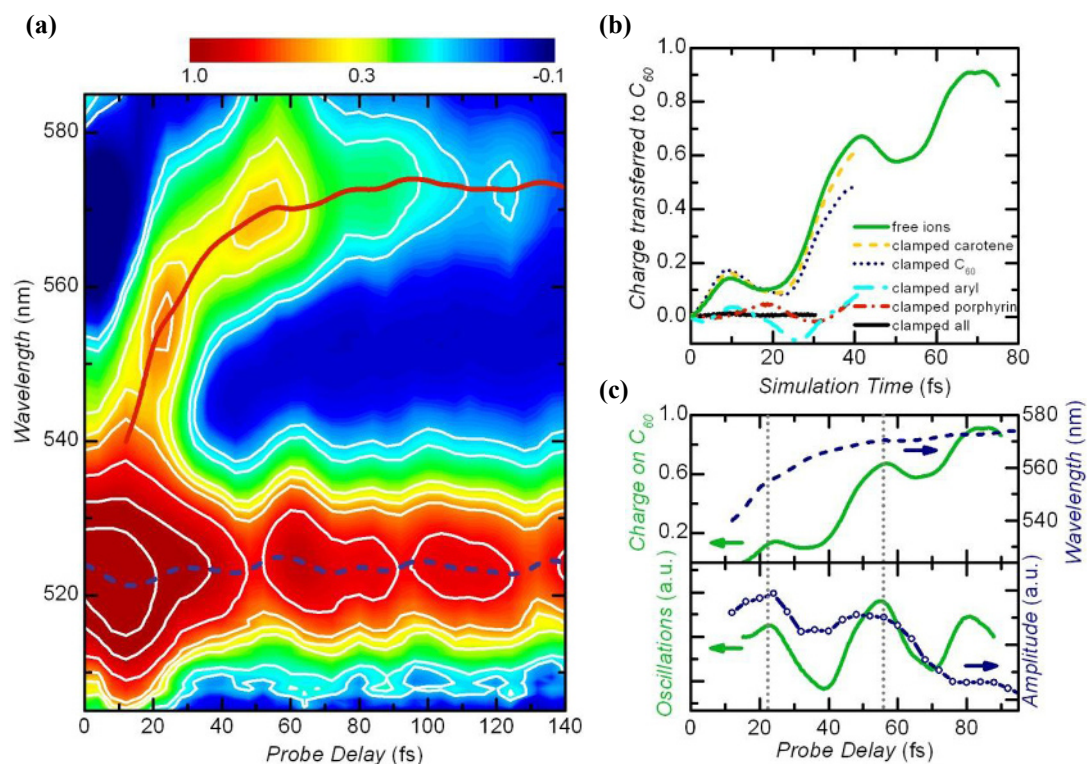


Fig. 1. Experimental (residual) $\Delta T/T$ map following impulsive excitation of the triad at around 550 nm (a). The dashed blue and solid red lines highlight the time evolution of the center wavelengths of the porphyrin and charge transfer bands, respectively. Simulated charge transfer dynamics in the triad (b) under various conditions. Correlation between temporal oscillations (c) in the simulated transferred charge (solid green lines, in lower panel the slow exponential rise was subtracted, and a time shift of 15 fs was applied) and in the resonance wavelength (dashed blue, upper panel) and the amplitude (blue symbol and line, lower panel) of the $\Delta T/T$ spectrum of the charge transfer band.

This residual $\Delta T/T$ map 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, which is attributed to stimulated emission from a photoexcited intermediate charge-transfer state,

displays both temporal and intensity oscillations indicating that the population coherently oscillates between donor and acceptor state.

This interpretation is supported by a detailed TDDFT quantum-dynamical simulation of the system, where the initial photoexcitation of the molecule was modeled as a sudden change in the charge density localized on the porphyrin moiety, and the resulting motion of charges and ions was tracked in space and time. Photoexcitation of the porphyrin unit leads to an almost complete electron transfer to the fullerene moiety within about 70 fs displaying moreover strong oscillations with a period of 30 fs (Figure 1(b)) suggesting that the launched wavepacket oscillates a few times back and forth between the carotene-porphyrin group and the fullerene moiety. Both the time scale of the charge build-up and the oscillation period of the electronic wavepacket derived from the simulation are in striking agreement with the experimentally observed dynamic evolution of the charge transfer band (Figure 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 (Figure 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.

3 Conclusions

Taken together, our experimental and theoretical data provide strong evidence that the correlated, quantum-coherent motion of ions and electrons not only governs the first steps of the photoinduced electron dynamics but also the yield of the charge separation in this prototypical molecular photovoltaic system, in stark contrast to prevailing statistical models for electron transfer reactions. Specifically our results suggest that the carbon backbone motion promotes coherent charge oscillations while rapid geometric rearrangements of the donor-acceptor structure are crucial in stabilizing the separated charges. This implies that not only the geometric and electronic structure of a photosynthetic/photovoltaic system, but also the flexibility of its molecular structure is an important parameter for optimizing its yield. It seems interesting to explore this new optimization parameter and to further test interface quantum coherence effects in technologically relevant devices.

References

1. C. J. Brabec, G. Zerza, G. Cerullo, S. De Silvestri, S. Luzzati, J. C. Hummelen, S. Sariciftci, *Chem. Phys. Lett.* **340**, 232 (2001)
2. R. A. Marcus, *Rev. Mod. Phys.* **65**, 599 (1993)
3. G. Kodis, P. A. Liddell, A. L. Moore, T. A. Moore, D. Gust, *J. Phys. Org. Chem.* **17**, 724 (2004)
4. C. Manzoni, D. Polli, G. Cerullo, *Rev. Sci. Instrum.* **77**, 023103 (2006)
5. D. Polli, M. R. Antognazza, D. Brida, G. Lanzani, G. Cerullo, S. De Silvestri, *Chem. Phys.* **350**, 45 (2008)