

Coherent ultrafast charge transfer in an organic photovoltaic blend

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Abstract: Combining high-time resolution pump-probe spectroscopy and time-dependent density functional theory calculations, we show that coherent vibronic coupling is of key importance in triggering charge transfer in a technologically relevant organic photovoltaic blend.

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1. Introduction

Polymer:fullerene blends are reference material systems for organic solar cells [1, 2]. Light-induced charge transfer from the photoexcited polymer donor to the fullerene acceptor represents the key process in organic photovoltaic (OPV) devices [3, 4]. It is now accepted that charge separation is an ultrafast process occurring on a sub-100-fs time scale. However, still very little is known about the initial quantum dynamics of this process in technologically relevant OPV materials.

Here we study the ultrafast optical response of a model OPV material system, the conjugated polymer *poly-3-hexylthiophene* (P3HT) and its blend with the fullerene derivative [6,6]-phenyl-C61 butyric acid methyl ester (PCBM), combining high-time resolution pump-probe spectroscopy and time-dependent density functional theory (TDDFT) simulations.

Our experimental and theoretical results provide strong evidence that the driving mechanism in the primary steps of the current photogeneration cycle is a quantum-correlated wavelike motion of electrons and nuclei on a timescale of few tens of femtoseconds [5, 6].

2. Results

We have performed ultrafast spectroscopic studies on P3HT:PCBM films, as well as on the single components, using a two-color pump-probe spectrometer providing independently tunable pulses [7]. The overall time resolution of the setup is better than 15 fs. Pump pulses centered at 540 nm resonantly excite the polymer moiety, whereas the transient absorption is monitored by broadband probe pulses in the blue-to-green wavelength range.

For both the pristine P3HT and the P3HT:PCBM blend (Fig. 1 a), the transient absorption map shows a pronounced oscillatory contrast throughout the entire visible range [5]. Fourier transform analysis (Fig. 1 b and c) reveals that such oscillations correspond to the symmetric C=C stretching mode of the polymer at 1450 cm^{-1} , in the 500-520 nm wavelength region in both samples. For shorter probe wavelengths, we detect, in the blended film, additional oscillatory components: a stronger one at 1470 cm^{-1} and a weaker one at 1289 cm^{-1} . Both these frequencies correspond to vibrational modes of the fullerene [8, 9]. Control experiments on PCBM films [5] rule out direct excitation of the acceptor as a cause for the observed fullerene oscillations. These results provide evidence for a coherent charge transfer mediated by strong vibronic coupling between polymer and fullerene.

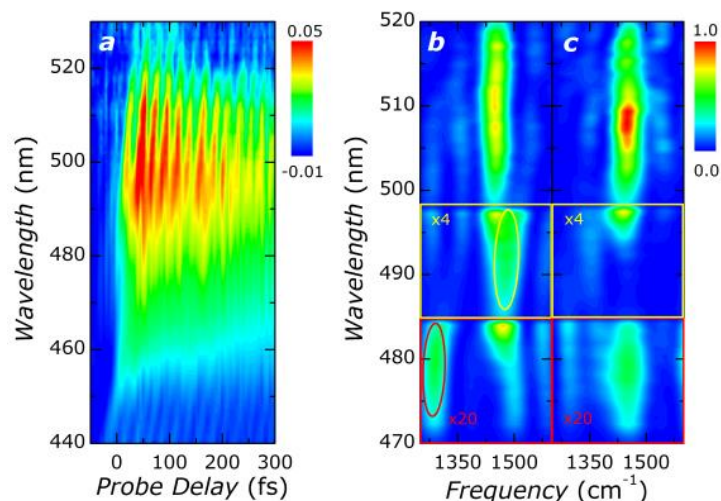


Fig. 1. Differential transmission map (a) of the P3HT:PCBM blend after impulsive excitation of the polymer with 8-fs pump pulses centered at 540 nm. Fourier transform maps of the P3HT:PCBM blend (b) and of a pristine P3HT (c) film.

TDDFT simulations [5] point out coherent electron transfer between donor and acceptor, and oscillations of the transferred charge with a period of about 25 fs, which matches the oscillation frequency observed in the experiments. The simulations thus predict that vibronic coupling is necessary for charge transfer to occur. Moreover they indicate that vibronic coupling is responsible for dynamically driving donor and acceptor LUMOs in resonance, explaining the coherent charge oscillations [5].

3. Conclusions

We show that strong vibronic coupling between electronic and nuclear degrees of freedom promotes delocalization of the photoexcited electronic wave packet across the interface. Both the electronic density and the nuclei display correlated oscillations on the same time scales, which are essential for an ultrafast charge transfer from the donor to the acceptor. The observation of coherent electron-nuclear motion in this non-covalently bound artificial light harvesting complex is strong evidence for the dominant role of quantum coherences in the early stages of the charge transfer dynamics in this class of OPV materials.

4. References

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