Coherent polaron pair formation in a semiconducting polymer

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Combining high-time resolution two-dimensional electronic spectroscopy with detailed theoretical simulations, we investigate the initial dynamics of excitons and polaron pairs in a semiconducting polymer thin film. We show that coherent vibronic coupling promotes charge delocalization and results in long-lasting coherent oscillatory dynamics of strongly coupled excitons and polaron pairs.

Semiconducting polymers combine remarkable optoelectronic properties with ease of processing and low fabrication costs. They are therefore suitable candidates for flexible optoelectronics devices, such as transistors and solar cells [1-2]. Because of their low dielectric constants compared to inorganic semiconductors, electron-phonon interactions cannot be neglected in the description of the optical excitations [3]. Hence, excitons, polarons, and polaron pairs contribute to the optical and transport properties. The latter are of fundamental importance for application in optoelectronic devices, since they are thought to be the precursors of free charges. Here we use two-dimensional electronic spectroscopy (2DES) with sub-10-fs time resolution to study a reference conjugated polymer for solar cells applications. We show experimental evidence for ultrafast coherent polaron pair formation on a sub-100-fs time scale and pronounced peak splittings of the 2DES maps at early waiting times. These observations are explained in terms of the interplay between electronic coupling of excitons and polaron pairs and their mutual coupling to an underdamped vibrational mode.

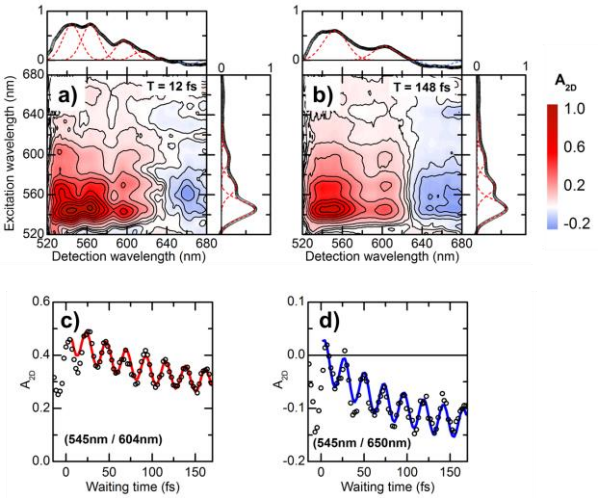

Fig.1 Absorptive 2DES maps of P3HT thin films at room temperature at a waiting time of 12 fs (a) and 148 fs (b). At early times we detect spectral splittings of all peaks. The dynamics of both the positive (c) and negative cross peaks (d) show long-lived temporal oscillations with a dominant period of 23 fs. Remarkably, the negative cross peak signal, corresponding to excited state absorption of polaron pairs, builds up on a sub-100-fs time scale. Both the spectral splittings and the fast rise time of the dynamics are signatures of strong vibronic coupling between exciton and polaron pair states.

[1] G. Li et al, Nature Photonics 6, 153 (2012)
[2] T. Sekitani et al, Nature Materials 9, 1015 (2010)
[3] S. Kilina et al, Chemical Reviews 115, 5929 (2015)