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Exciton and biexciton signatures in the femtosecond transient absorption of phenylene-based polymers and oligomers

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Abstract

The femtosecond transient-absorption of phenylene-based polymers at low intensities is dominated by singlet excitons. In films, inter-chain excitons are created at high intensities via two-exciton states. In solution, we observe signatures of stable biexcitons.

The photophysics of conducting polymers from the poly(*para*-phenylene vinylene) (PPV) family are studied using femtosecond (fs) transient absorption (TA) to address several issues: what are the primary photoexcitations; how do they interact under high excitation; what are the signatures of biexcitons? We have measured solutions and films of the PPV oligomer MEH-DSB, and several soluble PPV derivatives, with similar results. MEH-DSB results are representative of the entire family. The fs differential transmission (DT) spectra of MEH-DSB show: (1) a positive band due to stimulated emission (SE) around 2.4 eV; (2) a photoinduced absorption (PA) band extending from 1.3–2.0 eV. In solutions at low intensities, both features show exponential decay ($\tau \sim 650$ ps), indicating that both originate from singlet excitons. In films, the decay is much faster and strongly nonexponential, with a second PA band at ~ 1.8 eV. The 1.4-eV band (PA₁) shows *pronounced intensity-dependent* dynamics, while PA₂ exhibits slower *pump-independent* decay, indicating the creation of two species. The matching PA₁ and SE features both arise from singlet excitons. We assign PA₂ to interchain excitons (geminate electron-hole pairs on adjacent chains¹).

The intensity-dependent decay of PA₁ shows a slow component (A_s , $\tau \sim 5$ ps), and a fast component (A_f , $\tau \sim 450$ fs) with magnitude $A_f \propto A_p^2$ (Fig. 1). We infer that A_f originates from intrachain two-exciton states generated within the pump pulsewidth. The decay of the doubly-excited molecules leads to interchain species (PA₂), with a complementary 500 fs build-up time. The pump dependence of PA₁ and PA₂ also show a quadratic correlation. This nonlinear *generation* is distinct from the intensity-dependence predicted for exciton-exciton annihilation, involving nonlinear *decay*.

Biexcitons have been predicted in organic π -conjugated systems,² although not documented experimentally. In MEH-DSB films the doubly-excited molecules relax rapidly via charge separation to adjacent chains. These “hot” biexcitons should be stabilized in dilute solutions. Indeed, we find that at pump levels exceeding $1\text{--}2 \text{ mJ cm}^{-2}$, the solution SE decay deviates from a single exponential (~ 650 ps), showing an additional faster component (~ 200 ps), with $A_f \propto A_p^2$, similar to films (Fig. 2). However, the decay of biexcitons in solutions occurs on a much longer timescale of hundreds of ps.

In solutions the shorter lifetime of doubly-excited excitons is indicative of coherent interactions due to biexciton formation. Another signature is the superlinear increase of the SE at high pump levels, indicating a new species with enhanced oscillator strength. The ratio of the slow and fast SE decay times is around 3.3, an estimate of the enhancement factor for the biexciton oscillator strength. We independently estimate this factor by modeling the SE pump dependence, obtaining $S = 4$, using the measured magnitudes of A_f and A_s .

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FIGURES

FIG. 1. Pump-intensity dependent dynamics of PA₁ in MEH-DSB film. Inset: quadratic correlation of the fast (A_f) and the slow (A_s) components.

FIG. 2. Pump-intensity dependent dynamics of PA₁ in MEH-DSB solution. Inset: quadratic correlation of the fast (A_f) and the slow (A_s) components.

Fig. 1

Fig. 2

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