BIMOLECULAR DISPERSIVE RECOMBINATION PROCESSES OF PHOTOEXCITATIONS IN CONJUGATED POLYMERS

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We study the dynamics of the long-lived photoexcitations in a series of conjugated polymers using photomodulation spectroscopy. The dependence of the photoinduced absorbance on both the modulation frequency and exciting photon fluence is used as an identifying tool for the recombination process. We have concentrated in processes such as monomolecular, bimolecular and defect-limited recombination at saturation, as well as dispersive recombination where the lifetime distribution is extremely asymmetric. Studying the excitation intensity dependence away from steady state conditions, we are able to readily differentiate processes which, at near steady state conditions, look alike. For example, near steady state conditions, both bimolecular, defect limited monomolecular near saturation and dispersive mechanisms show sublinear intensity dependence. However, away from steady state conditions, a bimolecular process shows superlinear intensity dependence while dispersive reombination leads to sublinear dependence even under these conditions.

We have experimentally studied p-phenylene-vinylene based conjugated polymers including derivatives containing acid-sensitive bipyridine subunits, by following the dependence of the intensity of the photoinduced absorption bands on the laser modulation frequency and intensity. The photoinduced absorption spectra contain two broad bands, whose modulation frequency and excitation intensity dependencies are distinctly different. Whereas the higher-energy band follows the modulation frequency dependence expected for a "simple" (i.e. no lifetime distribution) bi-molecular recombination process, the lower-energy band shows a fractional power law frequency dependence at high modulation frequencies, strongly indicating a ``dispersive recombination'' process [1]. The value of the fractional exponent is sample dependent and is a quantitative measure for the distribution of lifetimes or recombination rates.

The bimolecular nature of the recombination of the high energy band is characterized by a sublinear dependence on the pump intensity at low frequencies and a superlinear dependence at high modulation frequencies. This is shown in Fig. 1, where the top panel shows the theoretical prediction and the bottom panel shows our experimental results for one of the samples.

We show that the dispersive nature can be quantified as a bimolecular recombination process augmented by an asymmetric lifetime distribution having an appreciable contribution at short lifetimes. The bimolecular nature of the recombination process is further corroborated by the sub-linear dependence of the photoinduced absorbance on the pump intensity at both low and high modulation frequencies.

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[1] O. Epshtein, G. Nakhmanovich, Y. Eichen and E. Ehrenfreund, Phys. Rev. B**63,** 125206 (2001).

Figure 1.
Top: Theoretical prediction of photoexcitation density for a bimolecular process. ω is the photomodulation frequency, b is the bimolecular recombination constant and g is the photoexcitation intensity. $g_0 = \omega^2/b$. Note that small values of g/g_0 correspond to high modulation frequencies, where the density is proportional to $g^{3/2}$ whereas at low modulation frequencies (large values of g/g_0) the photoexcitation density is proportional to $g^{1/2}$. Bottom: Experimental results at modulation frequencies of 140 Hz and 400 Hz, with $g^{0.7}$ and $g^{1.5}$ dependencies, respectively.