Recombination of photoexcitations in conjugated polymers: dispersive processes

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We study the dynamics of the long-lived photoexcitations in p-phenylene-vinylene based conjugated polymers containing acid-sensitive bipyridine subunits, and in poly(5,5'-vinylene-2,2'-bipyridylene), by following the dependence of the intensity of the photoinduced absorption bands on the laser modulation frequency and laser intensity. The photoinduced absorption spectra contain two broad bands, whose relative intensities strongly depend on the protonation state of the polymers [1] and whose modulation frequency dependence is distinctly different. Whereas the higher-energy band follows the modulation frequency dependence expected for either mono- or bi-molecular recombination process, the lower-energy band shows a fractional power law frequency dependence at high modulation frequencies, strongly indicating a dispersive relaxation process. The value of the fractional exponent is sample dependent and is a quantitative measure for the distribution of the relaxation centers [2].

We show that the dispersive nature can be quantified as an elementary recombination process (e.g. mono- or bi-molecular) augmented by an asymmetric lifetime distribution having an appreciable contribution at short lifetimes. The sub-linear dependence on the pump intensity at low modulation frequencies and the super-linear dependence at high modulation frequencies both indicate a bi-molecular recombination mechanism.

In addition, we connect this dispersive behavior with a stretched exponential relaxation in the time domain. Our results indicate that the dispersive relaxation process in our films may be interpreted as a diffusion process, taking place in a fractal configuration space with reduced effective dimensionality.

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[2] O. Epstein, G. Nakhmanovich, Y. Eichen, and E. Ehrenfreund, Synthetic Metals (Proceedings of ICSM 2000, in press, 2001); Phys. Rev. B. **63,** (15 March 2001).