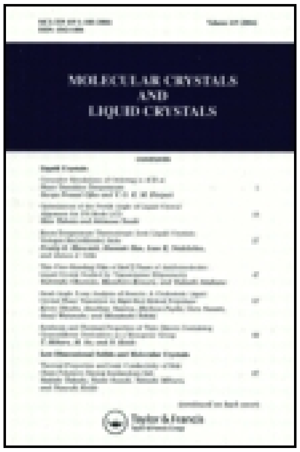

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Towards Nanophotonics: Temporal Patterns of Photons Create Spatial Patterns of Excitons in Molecular Dots and Wires

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TOWARDS NANOPHOTONICS: TEMPORAL PATTERNS OF PHOTONS CREATE SPATIAL PATTERNS OF EXCITONS IN MOLECULAR DOTS AND WIRES

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Abstract Time sequencing of laser excitation can control the microscopic patterns of molecular excitations (excitons) in nanometer scale molecular ensembles. This is demonstrated for isolated guest chains in polymer blends (P1VN/PMMA) and for molecular clusters in molecularly doped polymers (naphthalene/PMMA). The subwavelength exciton patterns are monitored via time resolved luminescence and fusion kinetics. The interpretation is aided by computer simulations.

INTRODUCTION

It is well known that spatial photon patterns can create spatial excitation (exciton) patterns in a condensed medium--the production of transient gratings[1] being one such example. We note that such patterns are no finer than $\lambda/2$, i.e., the optical diffraction limit for the given photon wavelength λ. On the other hand, reaction kinetics effects in restricted domains can produce patterns on the order of ρ^{-1} where ρ is the particle density.[2] Specifically, exciton reaction kinetics (fusion, trapping) is driven by the dynamics of exciton creation, which in turn is determined by the temporal patterns of the exciting radiation field. For instance, an ultrashort laser pulse will essentially create an instantaneous random distribution of excitons in a small domain (smaller than λ). On the other hand, a steady-state excitation may result in an ordered distribution.[2-4] This enables one to transform patterns from the time domain into the spatial domain (and vice versa).

An easy method for the detection of the ultrasmall spatial patterns is based on the "reverse transformation" of spatial patterns into temporal patterns. Exciton fusion kinetics and luminescence decay provides such a tool. For instance, on a molecular wire, a random exciton distribution results in the familiar second order exciton fusion kinetics.[2,3] On the other hand, an ordered distribution (e.g., superlattice) of excitons will result in third order kinetics.[2,5]

Experimentally, we follow the phosphorescence and delayed fluorescence decays of selected samples. The two examples discussed are: 1) The isolated poly-1-vinyl-naphthalene (P1VN) molecular chains in extremely dilute P1VN/PMMA blends. 2) The isolated clusters of naphthalene embedded in dilute naphthalene/PMMA glasses.

EXPERIMENTAL

The systems, procedures and instrumentation have been discussed in detail.[6,7] The same is true for the computer simulations.[2,8] We just give a schematic representation of the timing schematics for the laser excitation (Figure 1).

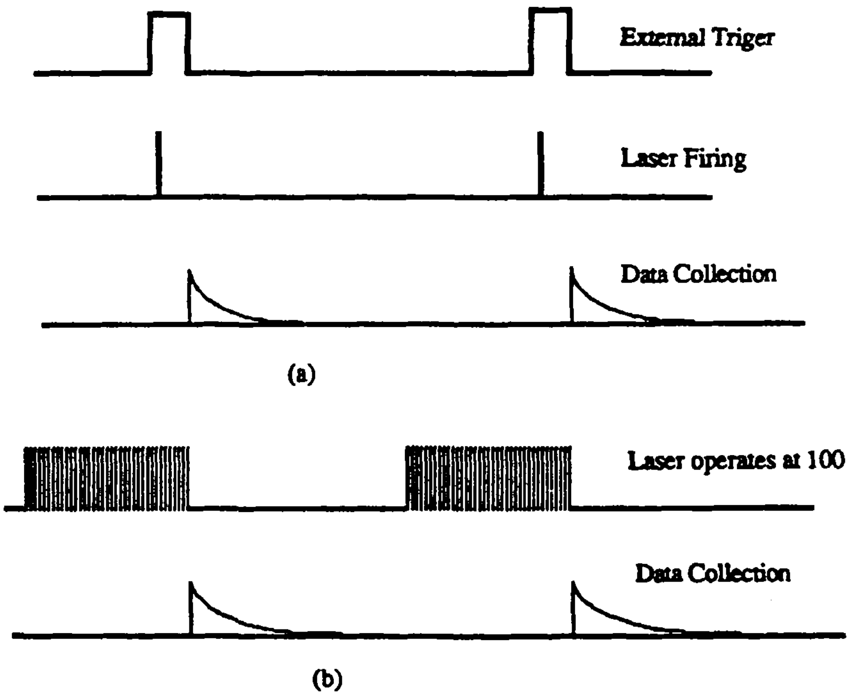

FIGURE 1 Timing schematics of decay data collections: a) the width of external trigger is 40 microseconds, 10 milliseconds, and 400 milliseconds, respectively, for early, medium, and adding delay time; b) is for the steady state excitation.

MOLECULAR WIRES

The most dilute blends (0.005% and 0.01% weight) show a kinetic behavior of the form

$$F \sim t^{-1/2}P \tag{1}$$

where F is the delayed fluorescence and P the phosphorescence, as can be seen from Figure 2. This is a case of exciton heterofusion,[2,6-8] involving free excitons and trapped excitons (at excimer sites).

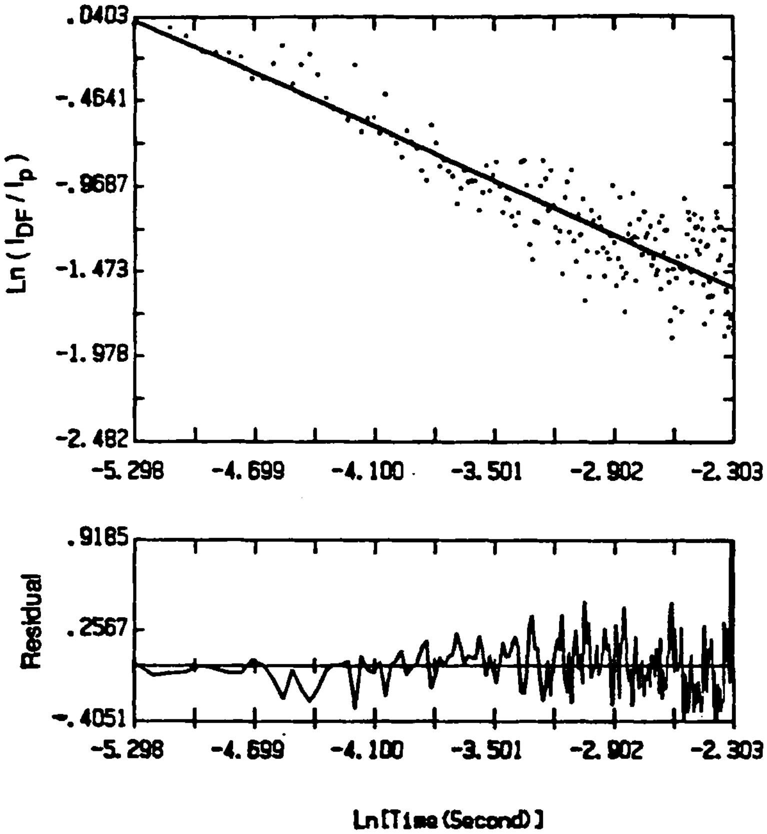

FIGURE 2 Ln(F/P) vs. lnt for 0.01% blend. Slope h = 0.53±0.03.

According to a recent theoretical analysis,[9,10] this means that there are gaps (depletion zones) around each trapped exciton with the nearest-neighbor distribution of distances r (between the free and trapped excitations) given by a "skewed-Gaussian" distribution:

$$f(r) \sim re^{-\gamma r^2} \tag{2}$$

rather than a Poisson (random) distribution of the form

$$f(r) \sim e^{-\beta r} \tag{3}$$

At long times, most chains will have at most two excitons per chain, with a "self-organized" distribution given by eq.(2).

MOLECULAR DOTS

An illustration of different spatial exciton distributions due to different temporal excitations is given for the 3% and 10% (by weight) samples of naphthalene doped poly-methyl-methacrylate (PMMA). Figure 3 shows the phosphorescence decays of the 3% and 10% samples with data collected 400 ms after the laser pulse.. Here the 10% sample shows a faster decay. Figure 4 shows the phosphorescence decays for the same two samples following a pulsed excitation. Here the 3% sample shows the faster decay! As these experiments are reproducible, this is a strong indication for different spatial exciton distributions resulting from the different temporal modes of photonic excitation. This conclusion is supported by detailed computer simulations.[11] A schematic picture (cartoon) of the different exciton distributions is given in Figures 5 and 6.

ACKNOWLEDGMENT

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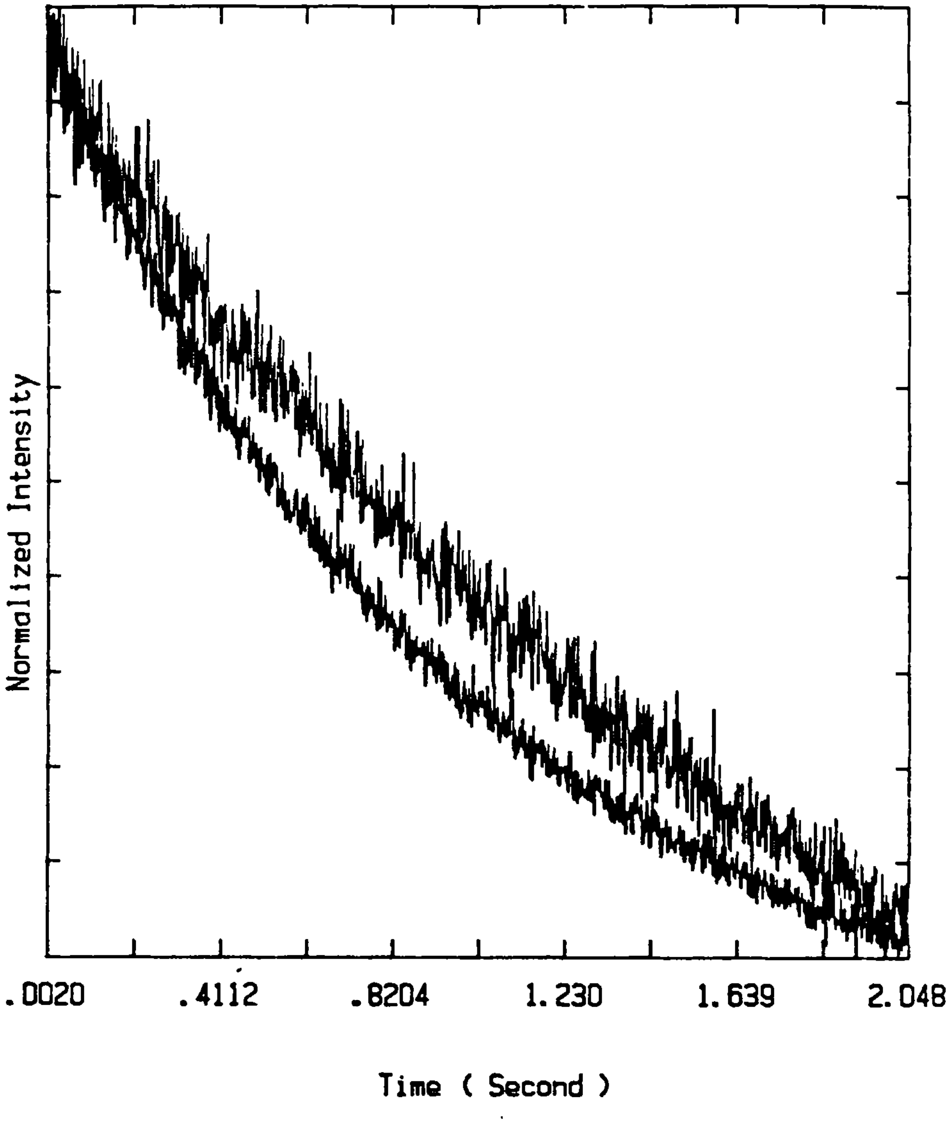

FIGURE 3 Phosphorescence decays for 3% (top) and 10% samples. Data are collected 400 milliseconds after laser pulse.

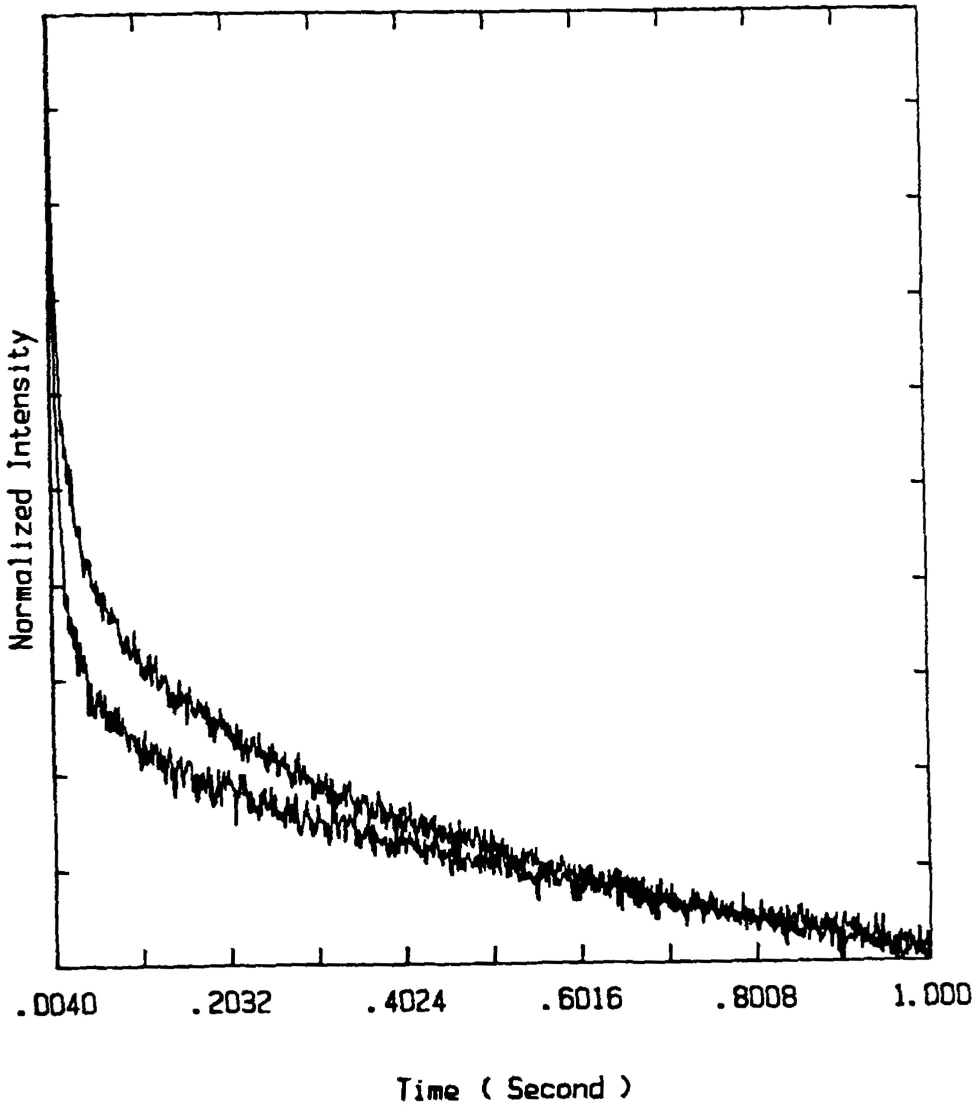

FIGURE 4 Medium time domain phosphorescence decays for 3% and 10% samples with pulse excitation. Note that 3% sample decays faster at early time (lower one).

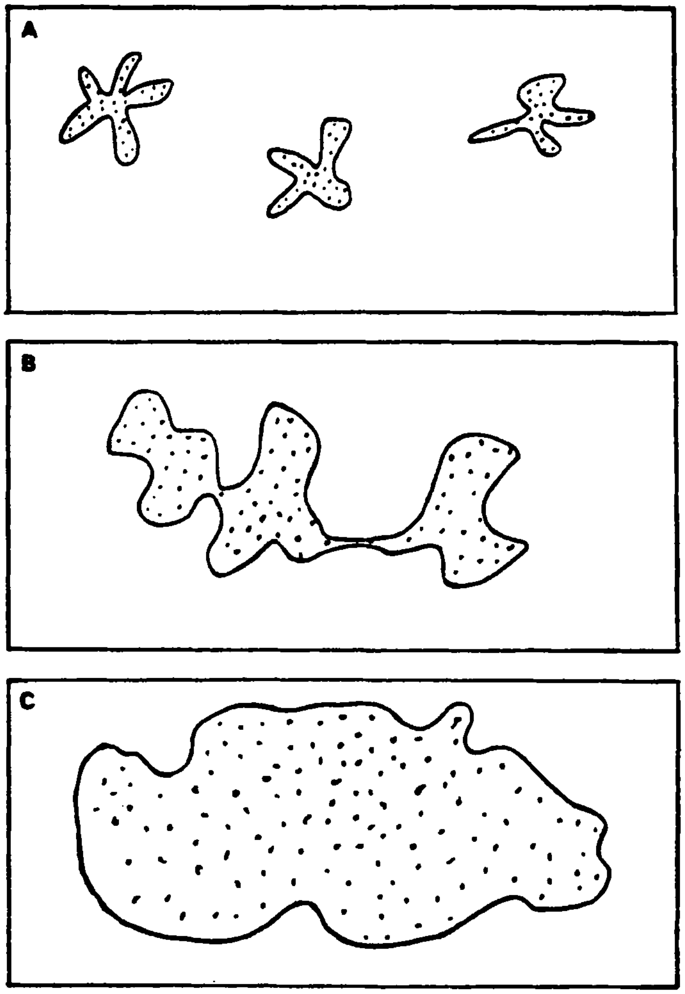

FIGURE 5 Schematics of various sizes and shapes at different dopant concentrations. The dots represent excited naphthalene molecules in their ^1T states.

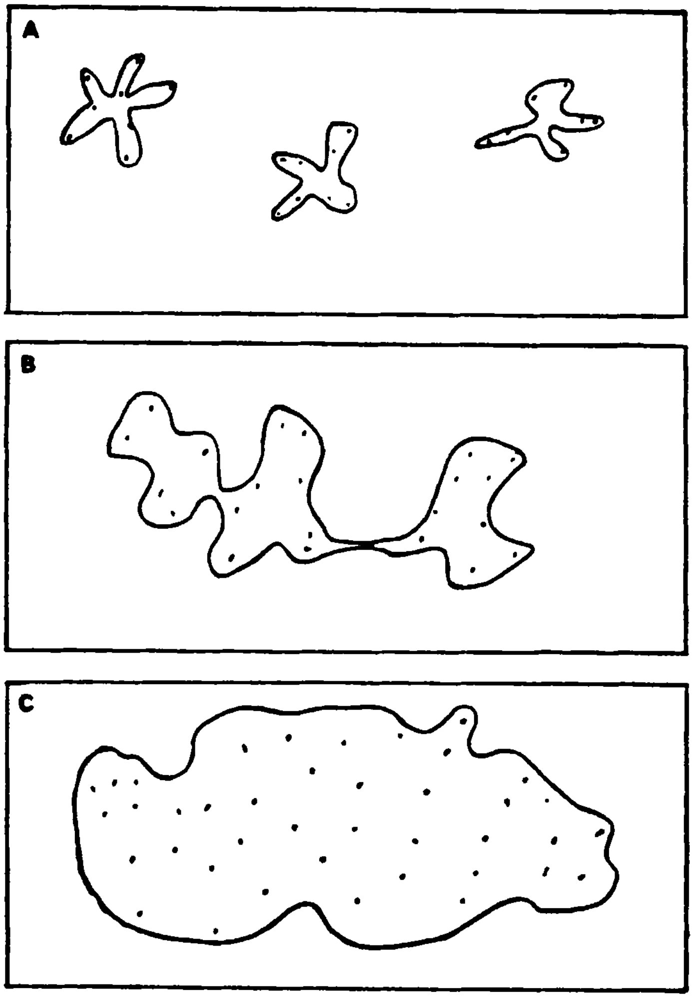

FIGURE 6 The redistribution of triplets at steady state or after amount of time delay while pulse excitation is used.

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