



## Research Article

# Transient optical properties, laser induced avalanche effect, and all optical switching in molecular aggregates

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## ABSTRACT

Organic dyes have attracted expressive research interest in recent years due to their wide range of applications. Self-aggregation occurs in a variety of organic molecules, a phenomenon that changes the photochemical and photophysical properties of dyes. Laser beams with wavelengths of 663 nm and 532 nm were used for thermal modulation of the aggregation states of the methylene blue dye, which led to the discovery of a novel avalanche phenomena in the molecular/supramolecular level and observations of not yet reported material optical behaviors. The obtained experimental data reveals the existence of asymmetric optical responses of aggregated dyes under laser excitation with wavelengths at the monomer or at the dimer absorption bands. The observed optical behaviors, resulting from the laser modulation of the molecular aggregation states, may find applications in the field of organic electronics and devices, such as optical logical gates and optical power limiters. A dual mechanism all optical switching driven by the simultaneous action of the cooperative effects of the laser induced disruption of dimeric dye units and thermal lensing was achieved.

## 1. Introduction

Self-aggregation is a well-known phenomenon that occurs in a variety of organic molecules [1–4]. Driven by electrostatic forces, dye molecules may aggregate following three basic arrangements: head to tail (J-aggregates), parallel molecular stacking (H-aggregates), or a geometry that is intermediate between the J and H (oblique aggregates) [5–7]. Upon aggregation, dimers, trimers, and higher order aggregates may be formed [8–11]. The dimeric species is usually dominant and the presence of the higher order aggregates, commonly at very low concentrations, may be neglected in many studies. In the present work, only the presence of the monomeric and dimeric species will be considered, and higher order aggregates will be neglected. An important consequence of aggregation is the shift of the optical absorption band of the aggregated species, as compared to the monomer. For instance, the parallel (H) aggregation leads to a shift of the optical absorption band towards shorter wavelength (blue shift) with respect to the monomer [12,13], while the J-type aggregation leads to a red shift of the absorption band [14–16].

For the development of the rationale of the present research, it is interesting to highlight the fact that, for a dye solution at a given concentration, if the concentration of the monomer falls due to monomer-to-dimer conversion, the intensity of the monomer absorption peak decreases, while the intensity of the shifted dimer absorption peak increases. Conversely, if dimer disaggregation is somehow induced, the intensity of the monomer absorption peak increases at the expense of a decrement in the dimer absorption peak. Such interchange in the amplitudes of monomer and dimer optical absorption bands is the point of interest for the present investigation.

A liquid solution of an organic dye susceptible to self-aggregation presents the monomer and dimer concentrations in dynamic equilibrium. The mole fractions of monomer and dimer in the solution depend strongly on temperature. Many thermodynamic studies are published in the literature for a variety of dyes [17–21]. In those studies, the samples are heated in an oven or in a heated water bath. In our research work we propose to use a laser beam as a heat source to modulate the relative mole fractions of dimers and monomers. Because the laser deposited heat will induce dimer to monomer conversion, asymmetric dynamic

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