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Study of the broad-band saturable absorption of indocyanine green J-aggregates in polymeric films using 10-fs laser pulses

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ABSTRACT Thin films of indocyanine green J-aggregates in polymers have been prepared and their saturable absorption properties studied in a high intensity regime using a unique ultrashort pulse Ti:sapphire laser (10 fs) with a very broad bandwidth (over 200 nm at –20 dB). The samples showed a surprisingly high stability to irradiation, strong absorption bleaching, and wavelength dependent differential absorption spectra.

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1 Introduction

The J-aggregates are systems which have had a growing interest since its discovery by Scheibe and Jelly in 1934, especially in the field of nonlinear optics. Their properties are given by the excitonic nature of their identifiable J-band. Among the nonlinear properties of the J-band is its saturable absorption which has been extensively studied in many J-aggregates in solution, as well as in thin films. This property has been applied to optical switches [1, 2] and for passive mode-locking in lasers [3]. The J-band of indocyanine green (ICG) aggregates in water solution lies in the infrared zone (890 nm) [4] and its saturable absorption properties have already been studied [5]. Part of the interest in this compound is that the central absorption wavelength of its J-band can be reached for certain operation conditions of a Ti:sapphire laser, and thus the nonlinear properties can be thoroughly studied. Previous studies were made using with ultrafast lasers with typically 80 fs pulse durations, corresponding approximately to a spectral range of only 4 nm for transform limited pulses. The unusual characteristics of the Ti:sapphire laser used in this work, namely a much broader spectra and few-cycle pulse durations [6] are adequate for the study of the nonlinear optical properties of the J-aggregates in a broad spectral zone around their absorption band. Since the solid state media is much more convenient than liquid solutions and, to our knowledge, no studies in the solid form of ICG have been performed, this work is focused on the broad-band saturable

absorption characteristics of ICG J-aggregates embedded in polymeric thin films.

2 Experimental

2.1 Sample preparation

J-aggregates of ICG in water were prepared departing from 1.5×10^{-3} M solutions heated at 70 °C in an electric oven during 72 h [4]. In order to carry out the study in thin films, different polyvinyl-alcohol polymers (PVA) were selected as matrices. The PVA polymer was chosen because both polarity and solubility were appropriate to mimic water as the solvent. The preliminary results obtained in the preparation of thin films with ICG showed that the most suitable among them was a PVA with an average molecular weight number of $M_n = 17\,200$, corresponding to a polymerization degree of 350 and a hydrolysis degree of 87–89 mol %. The PVA is obtained by hydrolysis of polyvinyl acetate. Thus the hydrolysis degree in PVA represents the number of hydroxyl groups per one hundred repetition units in the polymer, that is, the percentage of repetition monomer units (vinyl alcohol) in the final polymer. The water solution was mixed in $a : b$ proportions with a solution of 0.4 g/20 cm³ of this PVA (a = volume of J-aggregate solution, b = volume of PVA), and some drops were deposited in a Petri cell. The film resulted from evaporation of the solvents at room temperature and air atmosphere and thus the resulting J-aggregates are not expected to be oriented. Two different series of samples were prepared with the aim of reaching the highest possible absorbance in the J-band. In the first series, concentration was changed and hence we shall call it series C. It was performed with volume proportions $a : b = 0.75 : 9$ for sample C1 and $1 : 9$ for sample C2. The second series was done with different thicknesses and hence we shall call it series T. We used proportions $a : b = 1 : 9$ and made samples having 1, 2, 3 layers (samples T1, T2, T3), where each consecutive layer was fabricated after the previous one had dried up. The thickness of the film was not controlled during fabrication and was later measured with a non contact confocal imaging profiler using a 50× microscope objective. Series C had thicknesses ranging from 1 μm to 10 μm, while series T had from 10 μm to 25 μm. Figure 1 shows a picture of the films in series C for the two different concentrations, and in series T for the three different

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FIGURE 1 Phot

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son along the whole spectral range. For all samples it can be clearly seen how the nonlinear transmitted power is higher in the zone where the J-band lies (800–900 nm).

An even more informative picture is given by Fig. 8 where we plot the ratio of the nonlinear transmitted intensity vs. linear transmitted intensity (NLTP/LTP). This ratio is clearly wavelength dependent, except for the sample with the polymer alone. Wavelength dependent nonlinear properties in J-aggregates under high peak intensities (100 MW/cm²) have been previously observed by other authors [8, 9]. Specifically, a blue-shift of a few nanometers was observed in the differential absorption spectrum (DAS is the change of optical density ΔOD , and hence the relationship with our measurements is $DAS = \Delta OD = OD_{NL} - OD_L = -\log_{10}(\frac{NLTP}{LTP})$).

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