

## Third-harmonic generation in *J*-aggregates of a cyanine dye immobilised in a polymer matrix

K.A. Kuznetsov, T.V. Laptinskaya, Yu.B. Mamaeva, E.A. Mamchits, E.E. Makhaeva, A.P. Khokhlov, B.I. Shapiro

**Abstract.** Third-harmonic generation is obtained for the 1245-nm laser radiation in monolayers of *J*-aggregates of a cyanine dye in a diallyldimethylammonium chloride polymer matrix. The third-order susceptibility of *J*-aggregates is two orders of magnitude higher than that of fused silica. The wavelengths of fundamental and third-harmonic radiation lie in the transparency region of the material.

**Keywords:** third-harmonic generation, *J*-aggregates, polymers.

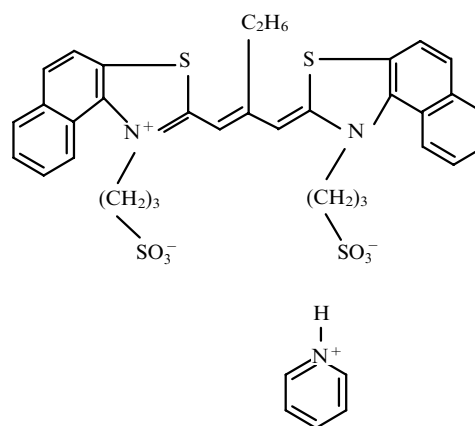
The optical properties of materials containing cyanine dyes attract the attention of researchers because these materials can be used for changing the spectral range of photosensitivity of silver halide emulsions employed in optical switchers, for optical data recording and storage [1]. An important property of such dyes is their ability to form highly ordered molecular associates (*J*-aggregates) in solutions, on the surface of crystals and in polymers [1, 2]. It is assumed that *J*-aggregates consist of dye molecules packed to form the brickwork structure [1, 3], the number of molecules in each *J*-aggregate varying from several to  $10^6$ .

The monomers of cyanine dyes have a broad absorption band in the visible region, usually between 400 and 600 nm. The absorption band of *J*-aggregates is shifted to the red compared to that of monomers and is quite narrow, indicating the presence of excitons. The optical properties of *J*-aggregates were theoretically described by the model of delocalised Frenkel excitons [4]. The calculation within the framework of this model shows that the third-order susceptibility of a *J*-aggregate consisting of  $N$  molecules greatly exceeds the susceptibility of the same number of monomers, which is confirmed by experimental studies. The absolute value of the third-order susceptibility  $|\chi^{(3)}|$  near the exciton resonance, determined by the method of four-wave mixing upon biharmonic pumping, is  $\sim 10^{-7} - 10^{-5}$  esu with the time response  $\sim 10^{-12}$  s [5]. Measurements of nonlinear

absorption for the same frequency range by the  $z$ -scan method [6, 7] also give  $|\chi^{(3)}| \sim 10^{-5}$  esu.

In this paper, we found and studied the third-harmonic generation in monolayers of *J*-aggregates of a cyanine dye immobilised in a polymer matrix. The third-order susceptibility  $\chi^{(3)}(-3\omega, \omega, \omega, \omega)$  was measured for the case when the fundamental radiation frequency  $\omega$  and the third-harmonic frequency lie in the transparency region of the material.

We measured samples of three types. Samples of the first type were prepared by the method of layer-to-layer adsorption [8–10] of polycations of polydiallyldimethylammonium chloride (PDADMAC) and anions of the cyanine dye (pyridine salt of 3,3'-di( $\gamma$ -sulfopropyl)-4,5,4',5'-dibenzo-9-ethylthiacarbocyanine betaine) synthesised at the 'NII-KHIMPROEKT' Research Center. The structural formula of the cyanine dye is presented in Fig. 1.



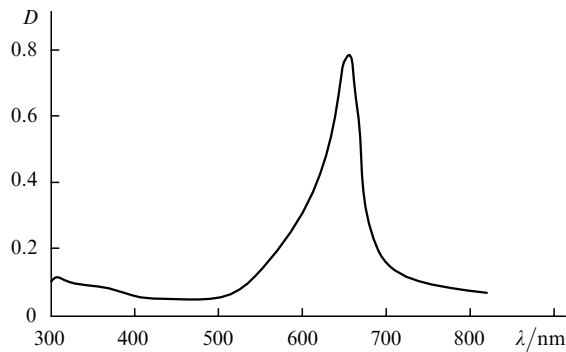
**Figure 1.** Structural formula of a cyanine dye (pyridine salt of 3,3'-di( $\gamma$ -sulfopropyl)-4,5,4',5'-dibenzo-9-ethylthiacarbocyanine betaine).

The thickness of a dye–polymer layer estimated by the ellipsometry method was  $\sim 60$  nm. The number of layers was varied from 2 to 10. The absorption spectra, of which one (for a sample containing five layers) is shown in Fig. 2, were measured with an HP-8452A spectrophotometer. The optical density at the maximum of the 656-nm exciton absorption band was directly proportional to the number of polymer–dye layers.

A sample of the second type, of thickness  $\sim 70$   $\mu\text{m}$ , was prepared by drying the PDADMAC hydrogel with the immobilised dye. The optical density at 656 nm was 1.23. The third harmonic was also generated in dry gelatine 20-

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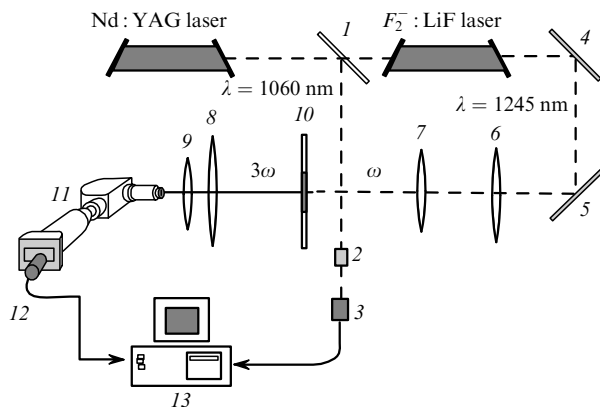
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**Figure 2.** Absorption spectrum of a sample containing five dye layers. The optical density at 1245 nm does not exceed 0.01.

$\mu\text{m}$  thick films containing the same dye and prepared at the 'NIIKHIMPROEKT' Research Center.

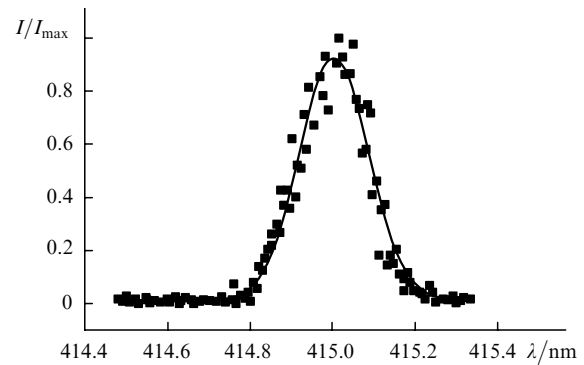
The scheme of the experimental setup is shown in Fig. 3. A  $F_2^-$ :LiF laser emitting 1245-nm, 10-ns, 0.2-mJ pulses with a pulse repetition rate of 10 Hz was pumped by a 1060-nm Nd:YAG laser. Radiation from the LiF laser was focused by lenses (6) and (7) into a 0.01-mm spot on a sample. The third-harmonic radiation was focused by lenses (8) and (9) (the collection angle was  $60^\circ$ ) on the entrance slit of an ISP-51 spectrograph equipped with a photomultiplier.



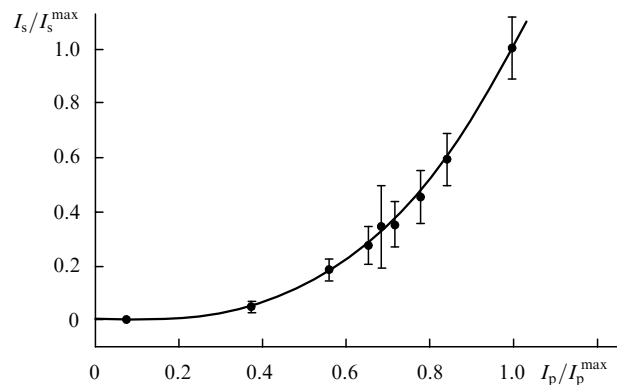
**Figure 3.** Principal scheme of the experimental setup: (1) beamsplitter; (2) LiNbO<sub>3</sub> crystal (second harmonic of a Nd:YAG laser is used to control intensity); (3) photodiode; (4, 5) mirrors; (6–9) lenses; (10) sample; (11) ISP-51 spectrograph; (12) photomultiplier detecting signal radiation; (13) PC.

The maximum of third-harmonic radiation was detected at a wavelength of 415 nm, which lies within the transparency region. The spectrum of the third-harmonic signal is shown in Fig. 4. Note that the second-harmonic signal, whose wavelength (623 nm) lies near the exciton resonance, was not detected.

The dependence of the third-harmonic intensity on the incident radiation intensity (Fig. 5) was measured using calibrated neutral filters to attenuate laser radiation. One can see that this dependence is cubic. We also studied a polymer matrix without the dye. Because no third-harmonic generation was observed in this sample, we believe that the third harmonic is generated due to the presence of *J*-aggregates.

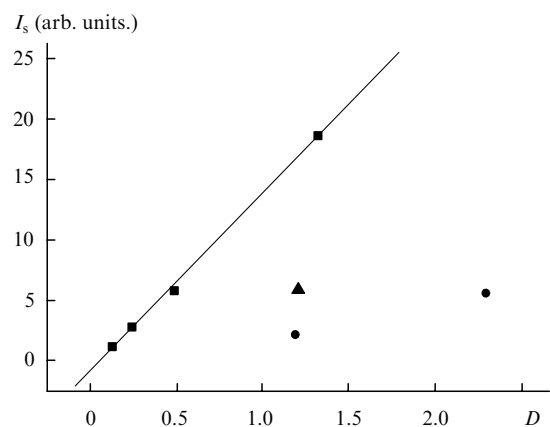


**Figure 4.** Spectrum of third-harmonic radiation of the 1245-nm LiF laser.



**Figure 5.** Dependence of the normalized third-harmonic intensity  $I_s/I_s^{\text{max}}$  on the normalized pump intensity  $I_p/I_p^{\text{max}}$  (circles). The solid curve is the dependence  $I_s/I_s^{\text{max}} = (I_p/I_p^{\text{max}})^3$ .

We studied third-harmonic generation in several samples containing different numbers of dye monolayers. Figure 6 shows the dependence of the third-harmonic intensity on the optical density of the sample at 656 nm. The optical density of the sample is directly proportional to the number of monolayers. It follows from our experiments that the third-harmonic intensity linearly depends on the number of dye monolayers. Figure 6 also shows the conversion efficiency



**Figure 6.** Dependences of the third-harmonic intensity  $I_s$  on the optical density  $D$  of the sample for the sample consisting of dye monolayers (■), the sample containing the dye in a gelatine matrix (●), and the sample prepared by absorption of the dye by the polymer (▲). The straight line is a linear approximation.

for samples of the second type, in which the dye is distributed inside the gelatine film of thickness 20  $\mu\text{m}$ , and for samples prepared by adsorption of the dye by gel. In both cases, for the same optical density (i.e., for the same number of *J*-aggregates in the interaction volume), the third-order susceptibility of the sample consisting of mono-

layers was 3–5 times higher. We estimated the third-order susceptibility by comparing the signal from a sample of the first type with the optical density  $D \sim 1.3$  and the third-harmonic signal obtained from an amorphous silica plate [11]. The coherence length for third-harmonic generation in silica did not exceed 0.035 mm and the plate length was 0.7 mm. The position of the plate with respect to the focus of the system of lenses (6) and (7) (Fig. 3) and its tilt were chosen so that the signal at 415 nm would be maximal. Because several angular third-harmonic radiation modes fall within a broad aperture of the detection system, the signal intensity changed no more than by 15% when the plate was rotated within 18°. As a result, we found that the third-order susceptibility of *J*-aggregates in the polymer matrix was  $\chi^{(3)} \sim 10^{-11}$  esu.

Therefore, *J*-aggregates of the cyanine dye immobilised in the polymer matrix have a significant third-order non-linear susceptibility also in the case when the pump and signal frequencies lie away from the exciton resonance.

It is known that the third-order susceptibility in the region of exciton resonance depends on the dye concentration and the ordering of molecules in the *J*-aggregate [12]. It follows from our experiments that the radiation conversion efficiency depends considerably on the method of sample preparation, being higher for samples prepared by assembling monolayers than for samples prepared by adsorption of the dye by gel. In the latter case, molecules and aggregates enter the gel during diffusion, and one can assume that the third-order susceptibility is smaller because dye aggregates are distributed over the film thickness less homogeneously.

The radiation power that can be converted in a non-linear-optical element is usually limited due to absorption, which changes the optical properties of the medium, causes heating and destruction of the sample if the optimal heat sink is not provided. The fundamental radiation and third-harmonic frequencies in our experiments lie within the transparency region. We hope that polymer films prepared by assembling monolayers will find applications for intense laser radiation frequency conversion.

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