

LETTERS

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Optical orientation of azo dye molecules in a thin solid film upon nonlinear excitation by femtosecond laser pulses

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***Abstract*. The orientation of molecules in an amorphous pure azo dye film upon nonlinear excitation is detected for the first time. The simultaneous increase and decrease in the film transmission by a factor of 2.5 for orthogonal polarisations of probe radiation indicated the appearance of orientation order in the film caused by the reorientation of azo dye molecules. Due to a high photostability of the AD-1 azo dye demonstrated in single-photon experiments and a high efficiency of nonlinear orientation obtained in experiments with femtosecond pulses, this dye can be widely used in three-dimensional nanophotonic devices such as photonic crystals, optical computers, and optical memory.**

Keywords: *nanophotonics, nonlinear absorption, femtosecond pulses, photoorientation.*

The class of azo dyes having a strong photoinduced optical anisotropy is of interest for applications in nanophotonic devices. Optical anisotropy can be induced by the selective photochemical change in molecules (the Weigert effect [1]) or the appearance of an orientation order in a medium due to reorientation of molecules [2]. The latter effect is the most interesting for applications because it can provide the maximum optical anisotropy.

While the orientation effects of azo dye molecules upon single-photon excitation are still being discussed in detail in the literature [3], the orientation of molecules upon nonlinear excitation is poorly studied at present (see, for example, [4, 5]). As far as we know, no reliable experiments on the photoinduced optical anisotropy caused by the reorientation of molecules upon nonlinear excitation have been reported in the literature so far.

The aim of this paper is to produce efficiently the orientation ordering of the AD-1 azo dye molecules in thin amorphous films with the limiting concentration of the dye upon nonlinear excitation.

To study the orientation ordering of molecules in a submicron film upon nonlinear optical excitation, we selected the AD-1 azo dye (4,4′-bis(4-N.N-diZ(n-butyl)aminophenylazo)biphenyl). The absorption spectrum of the AD-1 dye in benzene is presented in Fig. 1.

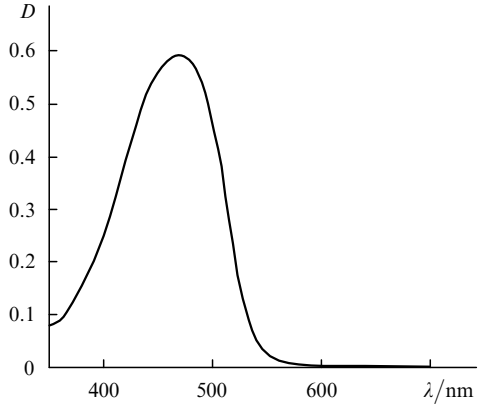

Figure 1. Absorption spectrum of the AD-1 azo dye in benzene (*D* is the optical density).

This dye was successfully used so far for fabricating optically oriented film polarisers and for optical orientation of lithotropic liquid crystals [6], where the degree of orientation ordering of molecules with an order parameter of 0.86 was achieved, which is almost limiting for such systems. Unlike most dyes, AD-1 had two azo groups, which indicates to its potential permanent photostability [7]. Our studies have confirmed that this is indeed the case. Thus, films prepared from this azo dye preserved their characteristics in the disordered state at room temperature and at day light for more than 20 years. As for the highly ordered state, our observations have shown that this state is preserved for more than 15 years.

Films were prepared by dissolving the dye in dichloroethane, centrifuging (3000 rev min^{-1}, 30 s) the solution to pure glass substrates, and drying it in air at 100 °C for 30 min. The film thickness in the region studied was 210 nm and its optical density was 0.6.

Films were activated by linearly polarised cw radiation or 60-fs, 0.6-nJ, 800-nm pulses from a Ti : sapphire laser with a pulse repetition rate of 80 MHz focused to a spot of diameter ~ 15 μm on a film. Probing was preformed with 450 – 470-nm LED arrays equipped with film polarisers.

After exposing the film to 50-mW cw radiation for 1 min, no changes in the optical properties of the film were observed. After irradiation of the film by femtosecond pulses at the same parameters, anisotropic variations in its optical properties were observed (Fig. 2). Figure 3 shows the profile of variation in the optical density of the film in

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the irradiated region. The optical density at the beam centre for probe radiation with polarisation orthogonal to the pump polarisation increased by 0.4 (transmission decreased correspondingly by factor of 2.5), while for parallel polarisations, the optical density decreased by the same value. Profiles of variation in the optical density in the vertical direction (the y axis) shown in Fig. 3 were obtained by the line averaging of the spatial distribution of variations in the optical density within a narrow vertical stripe selected in Fig. 2.

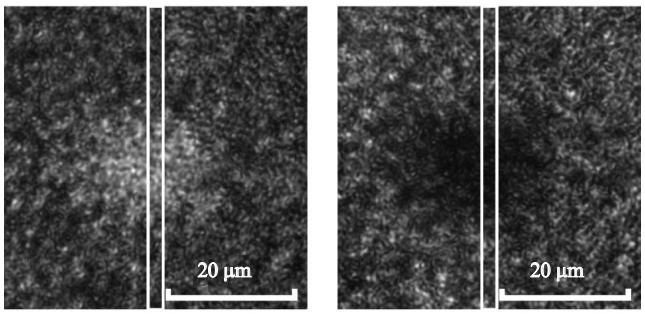

Figure 2. Photographs of a sample surface obtained after irradiation by femtosecond pulses for parallel (a) and orthogonal (b) polarisations of pump and probe beams.

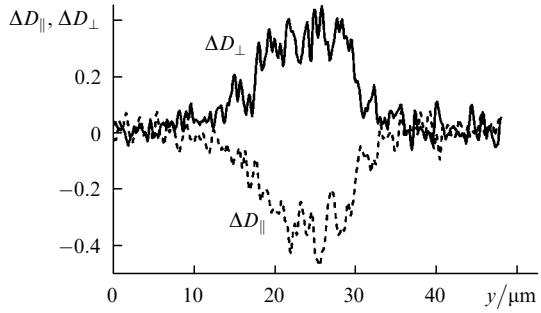

Figure 3. Spatial profiles of variations in the optical density of a sample for parallel ($\Delta D_{\parallel}$) and orthogonal ($\Delta D_{\perp}$) polarisations of pump and probe beams.

We found that AD-1 submicron films had a high nonlinear optical sensitivity. The irradiation of the film by ~ 2 GW cm^{-2} femtosecond laser pulses for 1 min (the total energy density was ~ 800 kJ cm^{-2}) produced a strong polarisation dichroism of its transmission: the dichroic ratio was ~ 6.

Thus, we have detected for the first time the dichroism of transmission of amorphous azo dye films caused by the nonlinear absorption of light. Variations in the optical densities obtained for two orthogonal polarisations of radiation suggest that the spatial reorientation of dye molecules makes a considerable contribution to the induced dichroism, whereas in previous papers the photochemical bleaching and orientation hole burning mainly occurred.

The absence of variations in the optical density upon exposing to cw radiation proves that the observed effect is nonlinear.

A high stability of the AD-1 azo dye together with the possibility of efficient nonlinear optical orientation of the AD-1 molecules in amorphous films with the limiting dye concentration opens up the outlook for applications of this dye in modern photonics.

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