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Upconversion of He-Ne Laser Light in Xanthene Dye-Doped Polymer Waveguides[*]

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We report on generation of yellow light emission (peak intensity at 577 nm) from a low power red He-Ne laser beam (1 mW, 632.8 nm) propagating in dye-doped planar polymer waveguides. Upconversion of He-Ne light (higher energy photons created by lower energy photons) was observed in planar slab waveguides made of poly(*N*-vinylpyrrolidone) (PVP) doped with Phloxine B. The films viewed from the side show a characteristic streak of yellow light. Monitoring it with a CCD camera we find that logarithm of intensity decays linearly with propagation distance, the slope giving the total loss factor. The loss factor at 632.8 nm depended linearly on the dye concentration providing the decadic absorption coefficient of 54 cm^{-1} for neat Phloxine B. The upconverted yellow luminescence can be regarded as a convenient indicator of waveguide losses. Monitoring fluorescence instead of the scattered guided light provides much more noise-free waveguide loss data.

We measured spectral and temporal response of the upconverted fluorescence as well as the dependence of luminescence on the intensity of the He-Ne beam to learn about the nature of the observed emission. The spectra excited with He-Ne laser as well as with 488 nm from cw Ar ion laser were similar. The lifetime of the luminescence in films of Phloxine B and Ethyl Eosin in PVP was of the order of 1 ms. The intensity of upconverted emission was found to vary linearly with the input intensity. We postulate that the mechanism of upconversion in the materials involves the first triplet state of the dye and generation of delayed fluorescence by these states.

Key words: optical waveguide, thin film, light upconversion, delayed fluorescence

The phenomenon of upconversion, *i.e.* generation of higher energy photons by two or more lower energy photons is most often associated with the use of relatively high light intensities available from pulsed lasers. Higher energy photons can be produced by second harmonic generation, *i.e.* simple doubling of the photon energy by a second-order nonlinear process. The third-order nonlinear process of two-photon absorption can also be responsible for generation of upconverted fluorescence photons (see *e.g.*[1,2]). Simultaneous absorption of two low energy photons may lead to the generation of a fluorescing excited state decaying with emission of fluorescence photons, which can be of higher energies than the original excitation photons.

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[*] Dedicated to the memory of Professor Krzysztof Pigoń.

Upconversion fluorescence can also be produced in cases when the higher energy excited state is generated by a multistage absorption process (*i.e.* involving absorption to an intermediate state followed by absorption of another photon). Such cases are, however, relatively rare in the domain of organic molecules because of the predominance of the Kasha's rule stating that the fluorescence proceeds most often from the lowest excited state even if higher lying states are generated on excitation of the molecules.

We report in this paper on a rather spectacular phenomenon of generation of upconverted fluorescence higher energy "yellow" photons from a relatively low intensity, 1 mW power, "red" He-Ne laser beam at 632.8 nm. The observation of this phenomenon is possible due to special spectroscopic features of the xanthene dyes used by us and to the fact that the local intensity of the He-Ne beam is increased by confining it in a planar polymer waveguide.

We have been interested in nonlinear optical phenomena, like dark spatial solitons (a self-guided dip in the intensity profile of an optical beam) and self-phase modulation (a change of the refractive index of the medium due to intensity of light beam which, in turn, modifies the properties of the beam) in materials such as dye-doped polymers, π-conjugated polymers, and composites thereof. These materials are among interesting candidates for future photonic media. A variety of nonlinear optical phenomena of potential use in future photonic devices require propagation of a laser beam for a certain distance in a nonlinear medium, so that the effects due to the material nonlinearity can be accumulated. Both from the basic research point of view and from that of prospective applications one needs to consider planar waveguide structures. We have investigated a large number of dyes of various chemical structures in various media (solutions, doped polymers, sol-gel silica glasses) to select systems with negative nonlinearity useful for dark spatial soliton propagation [3]. A negative nonlinearity (a reduction of refractive index with light) can be induced thermally by a change of density following absorption of light, by photochemical transformation, which leads to a transient or permanent bleaching of absorption, and by electronic third-order nonlinear response. We found that the refractive index change necessary to create dark soliton and the associated waveguide can by obtained by bleaching. In particular many xanthene dyes, belonging to the family of fluoresceine dyes, could be bleached to high transparency in the visible when exposed for a few minutes to high power cw Ar ion laser beam at 514.5 nm or UV light [3]. We have studied propagation of light beams in films of poly(*N*-vinylpyrrolidone) (PVP) doped with various dyes. An unexpected behaviour was observed [4] when investigating propagation of a red beam from a low power, 1 mW, He-Ne laser in PVP films doped with some of these dyes, for example Phloxine B or Ethyl Eosine. The films viewed from the side show a characteristic streak of yellow light. The emission did not decay even when the film was excited continuously for several hours. This paper reports results of our studies undertaken to identify the nature of the phenomenon in PVP films doped with Phloxine B and an example of application of the upconverted emission of the dye for waveguide loss determination.

EXPERIMENTAL

Materials and instrumentation. This family of xanthene dyes incorporates, among others, such dyes like Fluoresceine, Eosine (a few different eosines are commercially available), Rose Bengal and Erythrosine. Properties of this class of dyes have been described in many reports. The molecular structure of Phloxine B is shown in Figure 1a. The commercial dye was available from Sigma-Aldrich. The compound (min. 80% dye content) was used without further purification.

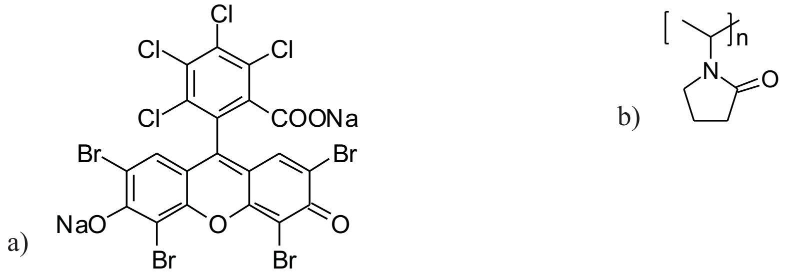


Figure 1. Molecular structures of: a) Phloxine B, disodium salt [18472-87-2] (other names: Acid Red 92, Magdala Red Technical, Cyanosine) b) Poly[1-(2-oxo-1-pyrrolidinyl)ethylene] [9003-39-8] (other names: poly(*N*-vinylpyrrolidone), poly(1-vinyl-2-pyrrolidone), povidone, PVP).

Slab waveguides made of polymers can be readily prepared by spin coating of polymer solutions on various substrates (glass or silica plates, silicon wafers with buffer SiO_2 layers, *etc.*). In some studies we found it convenient to use a host polymer with good optical properties and incorporate guest molecules in it. A good host polymer for such studies [5] is poly(*N*-vinylpyrrolidone), PVP (its molecular structure is shown in Figure 1b). Among many features of this polymer, it is well soluble in many solvents, including water and alcohols, it has a refractive index of appr. 1.53 (632.8 nm), and is therefore capable of forming waveguides on the surface of common glass microscope slides (refractive index typically 1.51 at 632.8 nm) and, when not doped, shows remarkably low waveguide propagation losses (typically a few tenths of a dB/cm at 632.8 nm). PVP is highly transparent above 220 nm in the UV-visible spectral range. It is capable to accommodate up to about 30 wt% of dopant dyes, due to its complexing ability. A disadvantage of PVP is, however, a sensitivity of its refractive index to the external humidity and a tendency to develop cracks during long term (a few years) storage.

The films were prepared by spin coating filtered solutions of 30 wt% PVP (molecular weight 40000, Sigma) in 1-methyl-2-pyrrolidone (*N*-methylpyrrolidone) containing various amounts of commercial dyes. The spinning was in the range 1000–3000 rpm for about 1 min and that resulted in uniformly thick films in the range of 2–6 μm. The substrates were either fused silica or glass slides. The films were dried under dynamic vacuum in the oven, at 100–120°C, for up to 24 hours. A Metricon 2010 prism coupler was used for both the determination of the thickness and refractive indices of the polymer films and to monitor propagation of light in the waveguides, visually and using a CCD camera coupled to a frame grabber equipped computer running an image processing program. A Shimadzu Model 3101 PC spectrophotometer was used to record the absorption spectra of the films. Figure 2 shows an absorption spectrum of Phloxine B in PVP film. The decadic absorption coefficient α_{10} was derived from optical density measurements (absorbance) normalized to the film thickness and the dye content. A sharp absorption maximum appears at 560 nm ($\alpha_{10} = 1.4\times10^5$ cm^{-1}, molar absorption coefficient $\varepsilon = 9.7\times10^4$ cm^{-1}mol^{-1}dm^3). Due to the polymer environment, it is shifted to longer wavelength as compared to the literature data: $\lambda_{max} = 538.5$ nm for the dye in water solution, and $\lambda_{max} = 547.5$ nm in ethanol [6]. The fluorescence spectra were recorded with an Alton Instruments Lamda Series LS-2000 spectrograph with a CCD detector.

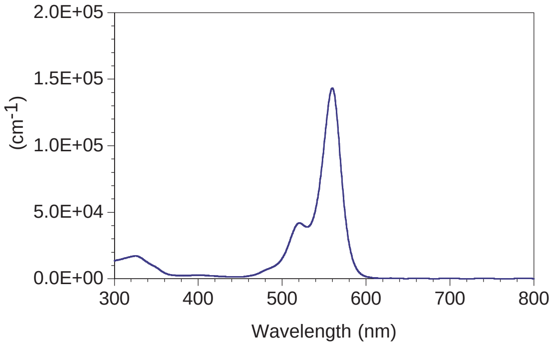


Figure 2. Absorption spectrum of Phloxine B in poly(*N*-vinylpyrrolidone) film. The decadic absorption coefficient α_{10} (cm^{-1}) was extrapolated to 100 wt% of the dye. The main features are: λ_{max} = 560 nm, ($\alpha_{10} = 1.4\times10^5$ cm^{-1}, $\varepsilon = 9.7\times10^4$ cm^{-1}mol^{-1}dm^3), the shorter wavelength maximum at 520.5 nm ($\alpha_{10} = 4\times10^4$ cm^{-1}, $\varepsilon = 2.8\times10^4$ cm^{-1}mol^{-1}dm^3) and 325 nm (α_{10} = 1.5×10^4 cm^{-1}, $\varepsilon = 1.0\times10^4$ cm^{-1}mol^{-1}dm^3).

RESULTS AND DISCUSSION

Upconversion of 632.8 nm light in PVP films doped with Phloxine B. The PVP films doped with the xanthene dye have been found to exhibit emission of yellow light when a red 632.8 nm beam was coupled into them. The wavelength of 632.8 nm lies well below the first absorption band of the dye (560 nm), therefore, due to low attenuation, the propagation of a He-Ne beam can be readily observed even for reasonably high concentrations of the dye in PVP films. The emission is so strong that it is readily seen with a naked eye and its yellow colour dominates over the red light scattered from the waveguide. Figure 3 shows an example of the spectrally resolved emission from a Phloxine B/PVP waveguide. A broadband character of the upconverted emission is consistent with an assumption that the emission is due to fluorescence of Phloxine molecules. Figure 3 shows a comparison of the emission from a waveguide with the propagating He-Ne beam with the emission obtained by side irradiation with a defocused Ar ion laser beam. The spectra are very similar. The luminescence maximum is at 577 nm.

One should note that the emission of fluorescence can also be excited in Phloxine B/PVP waveguides by propagation of blue or green beams from an Argon ion laser inside the waveguide. The major difference is, however, the absorption of Phloxine which is orders of magnitude stronger at the green (514.5 nm) or blue (488 nm) wavelengths of an Ar laser than at the wavelength of a He-Ne laser. Therefore, fluorescence due to propagation of an Ar beam could only be studied at very low concentrations of the dye in the host polymer (typically 10^{-4} M or less). At such low concentrations the dye is rather rapidly bleached by the strongly absorbed light (*cf.* [3]). Alternatively, fluorescence of Phloxine B in a PVP waveguide can also be excited by a process of two-photon absorption of short laser pulses. We used a mode-locked train of 800 nm 100 fs pulses from a Coherent Mira Ti-sapphire laser and observed very intense streaks of yellow fluorescence along the propagation path of the beam.

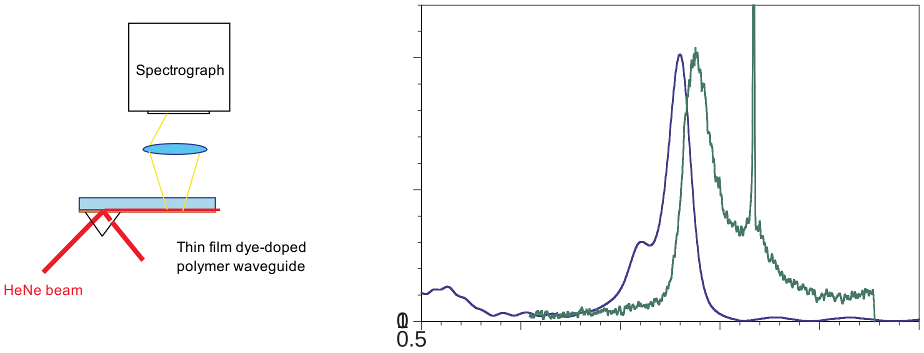


Figure 3. a) Scheme of the experiment of measuring the spectrum of upconverted emission from a polymer waveguide. He-Ne laser beam was coupled to the waveguide with a prism. The emission was collected with the lens positioned at nearly 2f-2f distances, the focal length f = 55mm.
b) Comparison of the emission spectra normalized to maximum intensity measured in Phloxine B in polyvinylpyrrolidone films – curve 1: the upconverted emission excited by propagation of a 632.8 nm He-Ne laser beam in 2.5 μm thick film containing 0.25 wt% dye; curve 2: 2 μm thick film, 2.47 wt% dye, was exposed to 488 nm light beam of the cw Ar ion laser; curve 3: absorption spectrum of the 2 μm thick film, 2.47 wt% dye, was normalized to the value at the maximum. The sharp peaks at 488 nm and 632.8 nm are due to excitation sources.

Fluorescence of a dye in a polymer waveguide, whether excited by one-photon absorption or by two-photon absorption of short pulses is a common occurrence and we observed it in numerous cases. However, the case of Phloxine B in PVP is unusual in the ability of the dye to fluoresce with upconversion when excited by a low power cw beam. Apparently, a two-photon absorption mechanism is highly improbable since the light intensities involved are relatively low. Typically, we couple in about 20–40 % of a 1 mW beam with a diameter of approximately 1 mm into a slab waveguide of 3 μm thickness (the cross section of the beam in the waveguide is thus appr. 3×10^{-5} cm^2). This results in the light intensity I of about 10 W/cm^2 of He-Ne laser light in the waveguide, and the photon flux $\Phi = I/(h\nu) = 3\times10^{19}$ cm^{-2}s^{-1}, taking $h = 6.626\times10^{-34}$ Js, $\nu = 4.74\times10^{14}$ s^{-1}. Thus, efficient two-photon absorption (corresponding to, for example, the effective absorption coefficient of $\alpha_{\text{eff}} = 0.1–10$ cm^{-1}) would require the effective two-photon absorption coefficients $\beta = \alpha_{\text{eff}}/I$ of the order of 0.01–1 cm/W. A typical β value for a two-photon absorber is of the order of cm/GW. It would give α_{eff} of the order 10^{-8} cm^{-1} for the intensity level applied in our experiment. It is obvious that an intermediate long-lived state must be involved. We postulate that the mechanism of upconversion involves the first triplet state and generation of delayed fluorescence by these states.

The mechanism of upconversion. We consider possible mechanisms of upconversion involving triplet states of the dyes as schematically shown in Figure 4. As seen, we consider the generation of the triplet states of a dye to take place either by the route of absorption to a singlet S_1 state and intersystem crossing or by direct

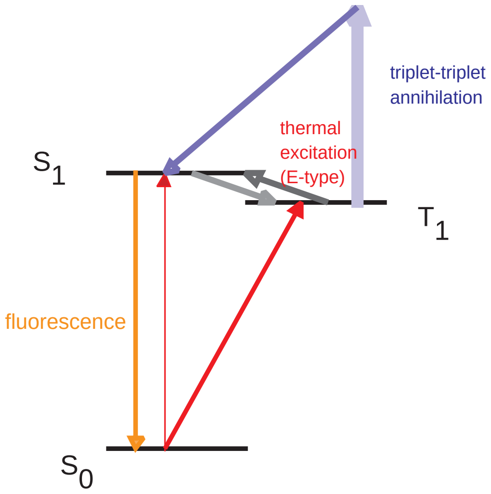


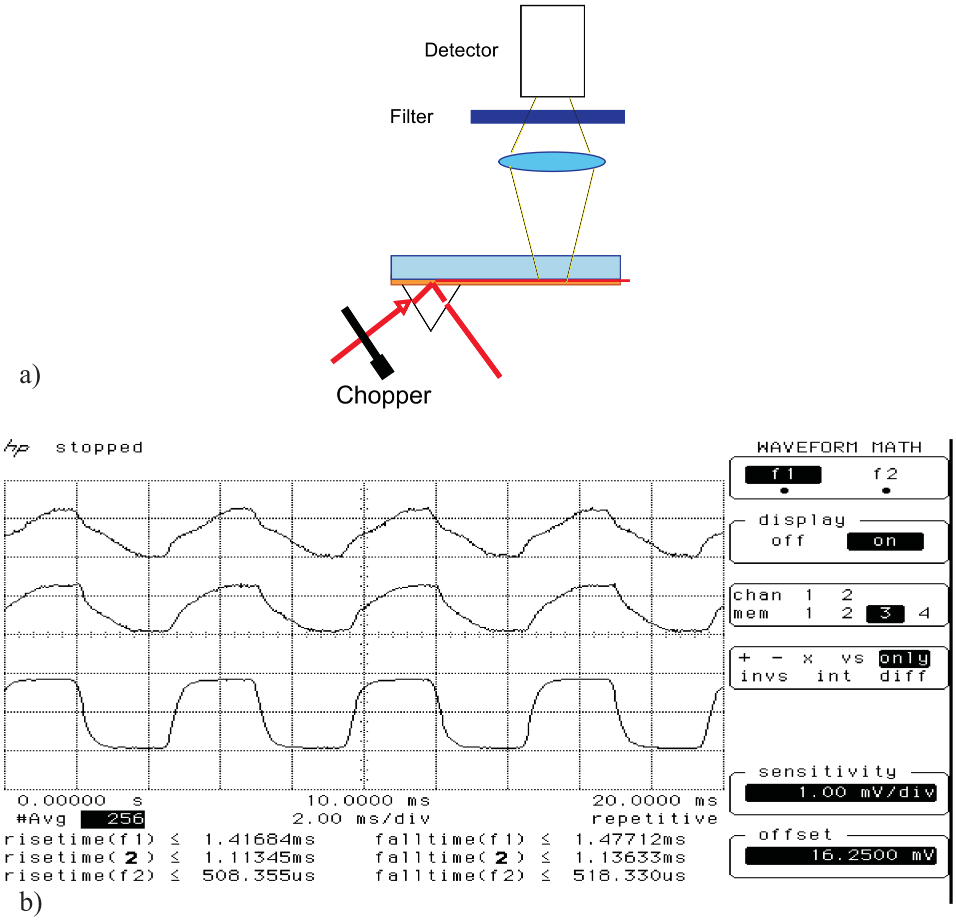
Figure 4. A simplified scheme of processes involved in the generation of delayed fluorescence in xanthene dyes. Shown in the scheme is both the direct absorption leading to the triplet states and singlet absorption followed by intersystem crossing, annihilation type delayed fluorescence and E-type delayed fluorescence.

(forbidden) absorption to the T_1 state. Delayed fluorescence can be generated by several routes: i) a bimolecular triplet-triplet annihilation process; ii) a thermal excitation of a triplet to the singlet state (E-type delayed fluorescence); iii) absorption of a photon by a triplet leading to a higher triplet state and its conversion to a singlet. All three above processes should be characterized by a relatively slow relaxation time because of the involvement of long-lived triplet states. To prove that the upconverted fluorescence observed by us has a character of the delayed fluorescence, we performed an experiment depicted in Figure 5, where the response of the waveguide fluorescence to chopping of the excitation beam is shown. It is evident that the lifetime of the fluorescence is of the order of a millisecond in both cases: that of Phloxine B and that of Ethyl Eosine. Thus, the involvement of triplet states is very likely.

To discuss the mechanism further we consider the following kinetic equations: the decay of the light flux Φ along the propagation path z can be described as

$$\frac{d\Phi}{dz} = -\alpha\Phi - \sigma_{T_1-T_2}[T_1]\Phi \tag{1}$$

where the first term on the right hand side of the equation is the ordinary one-photon absorption and the second term is the absorption of photons by excited triplet states. The triplet states themselves may be generated in two ways: by the forbidden ground singlet – first triplet absorption or by absorption to the first singlet and intersystem crossing to the triplet state. The triplet can then decay either by monomolecular or by bimolecular decay channels. Therefore, one can write the following kinetic equation:



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0.00000   s          10.0000 ms            20.0000 ms
#Avg  256            2.00 ms/div           repetitive
risetime(f1) ≤  1.41684ms    falltime(f1) ≤  1.47712ms
risetime( 2 ) ≤  1.11345ms    falltime( 2 ) ≤  1.13633ms
risetime(f2) ≤  508.355us    falltime(f2) ≤  518.330us
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Figure 5. Measurements of the speed of response of the upconverted fluorescence to chopping of the excitation (He-Ne) light. a) Scheme of the experiment. b) Oscilloscope picture showing the exciting light (bottom trace, the risetime and the falltime ≈ 0.5 ms), the response from a Phloxine B waveguide (top trace, the risetime and the falltime ≈ 1.4 ms) and an Ethyl Eosine waveguide (middle trace, the risetime and the falltime ≈ 1.1 ms). The film contained 0.25 wt% Phloxine B, it was 2.5 μm thick, the other film contained 0.60 wt% Ethyl Eosin, it was 3.3 μm thick.

$$\frac{d[T_1]}{dt} = \sigma_{S_0 - T_1}[S_0]\Phi + k_{ic}[S_1] - \frac{[T_1]}{\tau_{T_1}} - \sigma_{T_1 - T_2}[T_1]\Phi - \gamma[T_1]^2 \tag{2}$$

where S_0 is the ground state, T_1 is the lowest triplet state, Φ is the photon flux, σ is the absorption cross section and τ is the excited state lifetime. The bimolecular rate constant for the triplet-triplet annihilation is γ and the intersystem crossing rate constant is k_{ic}. Although the kinetics may in general be quite complicated, considerations of the steady state case ($d[T_1]/dt = 0$) can bring some useful conclusions. One expects that, depending on the values of the rate constants and the flux, the triplet population can be either controlled by the monomolecular decay or by the bimolecular annihilation. Assuming for simplicity that the rate of production of the triplets given

by the first two terms on the right hand side of Eq. (2) is proportional to Φ, one finds that the dominance of the bimolecular decay mechanism (likely to occur at high light intensities) gives $[T_1] \propto \Phi^{1/2}$ (in the derivation the sum of the first two terms and the fifth term in Eq. (2) is equated to zero), whereas the dominance of monomolecular decay (which is likely at low intensities) leads to $[T_1] \propto \Phi$ (in this case the sum of the first two terms and the third term in Eq. (2) is equated to zero). Therefore, for the three mentioned above possible mechanisms of the generation of the upconverted fluorescence, one can expect the following input power dependencies:
i) For the annihilation of triplets the delayed fluorescence rate will be proportional to $[T_1]^2$, thus the delayed fluorescence will be proportional to Φ^2 at low intensities and to Φ at high intensities. It should be noted that, under our experimental conditions, the steady state concentrations of triplets are quite likely to be high enough to correspond to the "high intensity" regime and thus to the linear dependence of the delayed fluorescence on Φ. The steady state concentration of triplets estimated from the first and third term of Eq. (2) is $[T_1] = \tau_{eff}\,\sigma_{eff}\,[S_0]\Phi \approx 3\times10^{16}$ cm^{-3}, taking τ_{eff} about 1 ms, $\sigma_{eff}[S_0] \approx 1$ cm^{-1} (σ_{eff} is the one-photon cross section, $\sigma_{eff}[S_0]$ is the effective absorption coefficient), and $\Phi \approx 3\times10^{19}$ s^{-1}cm^{-2}. This concentration is several orders of magnitude above the range expected for the dominance of monomolecular decay (in antracene crystals [7] bimolecular annihilation is dominant for $[T_1] > 10^{12}$ cm^{-3}). We may conclude that bimolecular annihilation is probable in our experiment and that it leads to the linear dependence of the intensity of delayed fluorescence on the incident light.
ii) For E-type delayed fluorescence the fluorescence intensity is proportional to $[T_1]$, thus, a linear dependence on Φ is expected.
ii) Photoexcitation of triplets is a process dependent on $[T_1]\Phi$, thus, the delayed fluorescence dominated by this process should be proportional to Φ^2.

Figure 6 shows the power dependence of the delayed fluorescence intensity measured in a Phloxine B film with the He-Ne beam being progressively attenuated. The linearity of the plot indicates that either of the two processes: annihilation of triplets or E-type delayed fluorescence may be taking place and these results alone do not allow one to distinguish between these two cases.

We note here that the considered xanthene dyes contain halogen atom substituents increasing the spin-orbit coupling and, therefore, are likely to exhibit enhanced probabilities of various transitions between singlet and triplet states. Literature data indicate that the delayed fluorescence in the xanthene dyes is a commonly observed phenomenon and that both the annihilation and thermal promotion mechanisms are operational [8–26]. It is difficult to ascertain the agreement of our present data with those of various authors, who investigated mechanisms of the delayed fluorescence in xanthene dyes. It is known that the kinetic parameters, decisive for the dominance of appropriate terms in the kinetic equations, do depend on the type of the dye, the number of heavy halogen atoms in it, the environment of the dye (*e.g.* the T_g of a polymer in which the dye is embedded), temperature *etc*. An important factor contributing to the triplet exciton kinetics is the presence of oxygen [8,12,13,17,23,27–33].

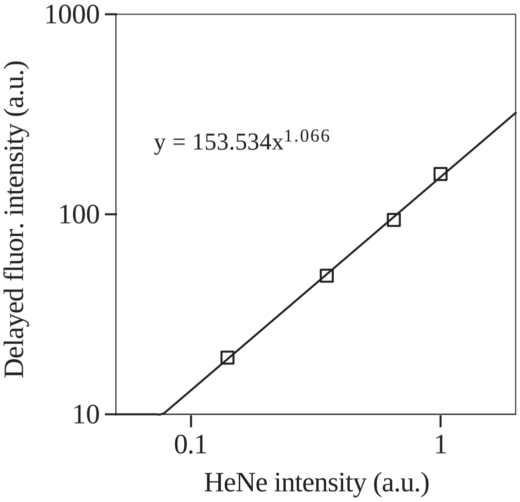

Figure 6. Excitation intensity dependence of the delayed fluorescence emission from a 2.47 wt% Phloxine B/PVP waveguide (double logarithmic plot).

Xanthene dyes are well known as promoters of singlet oxygen and the role of oxygen in the generation of delayed fluorescence has been described in several papers. Our experiments were mostly performed under normal oxygen containing atmosphere, thus, the involvement of oxygen in the kinetics of triplet interactions cannot be excluded. An experiment, in which the prism coupler chamber has been flushed with nitrogen did not reveal any changes in the brightness of the delayed fluorescence streak in our films, however, this does not provide a conclusive evidence that oxygen was not important in our case.

Determination of waveguide losses using upconversion. The upconverted fluorescence is a convenient indicator of waveguide losses. We have found that a Phloxine B/PVP layer can be conveniently applied to study *e.g.* losses induced by scattering on an imperfect substrate [4]. Indeed, among methods of determination of planar waveguide losses, perhaps the simplest consists in monitoring the light scattered out of the waveguide with a CCD camera. The scattered light is, however, often dominated by a small number of bright spots, due to point defects in the waveguide or the substrate layer. The existence of a uniform emission, originating in the waveguide core or its cladding, may be therefore helpful in imaging the intensity profile of the waveguide along its length.

Figure 7 shows the comparison of two images obtained from the same slab waveguide made of a PhloxineB/PVP film. In the first image the total light has been collected resulting in the measured streak of light being dominated by scattering of the He-Ne light from material inhomogeneities. The second image was obtained by only letting the fluorescence light through to the camera. This picture shows clearly the decay of the light intensity, due to waveguide losses.

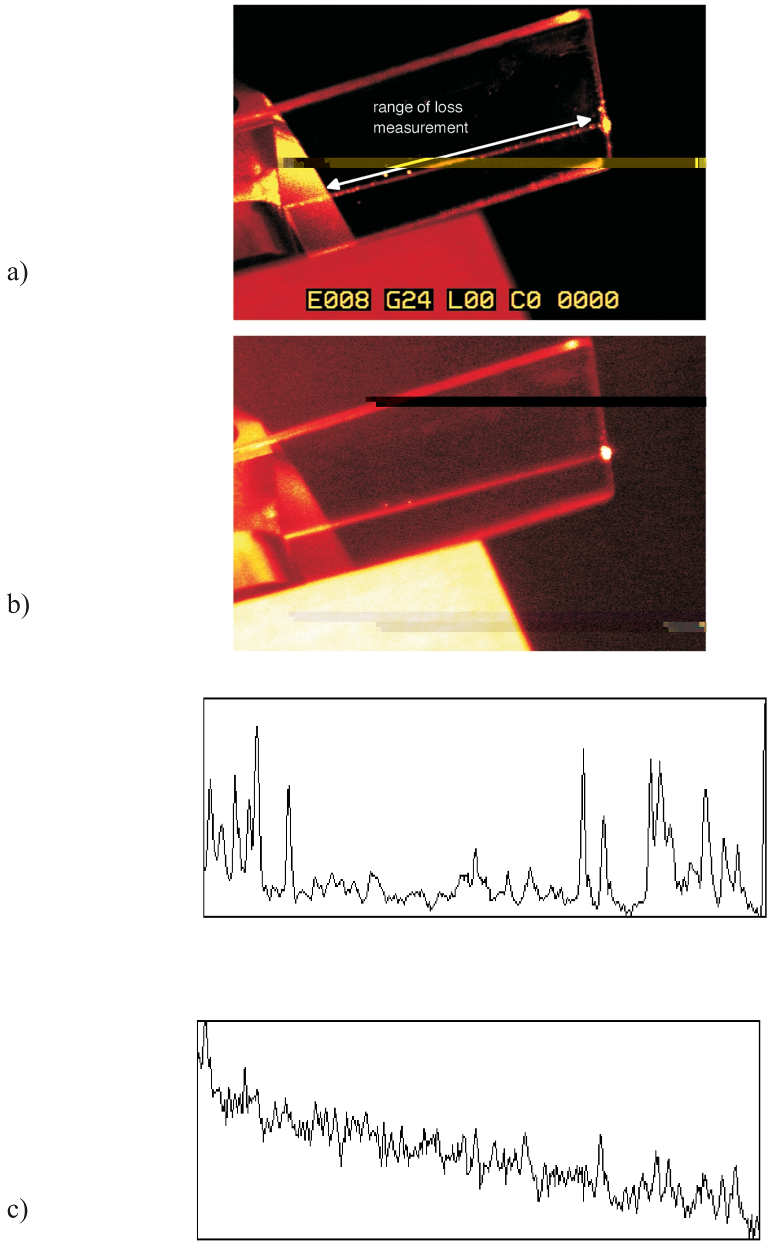

Figure 7. Images of propagation of a He-Ne beam in a Phloxine B doped PVP film (3.1×10^{-2} wt%, 3.9 µm thick) deposited on silica and the light intensity distributions along the propagation streak read from the corresponding CCD photographs. The top image (a) shows He-Ne laser light scattered on imperfections and a streak of luminescence, the bottom image (b) shows a streak of luminescence observed through yellow filter. The profiles of the light intensity read from the digitized image *vs*. distance (approximately 3 cm) are shown in c). We find that logarithm of intensity decays linearly with propagation, the slope giving the total loss factor about 1.1 dB/cm.

Figure 8 shows the comparison of the decay curves obtained similar like in Figure 7 for a Phloxine B doped film at several He-Ne laser intensities. It is apparent that the linear dependence of the upconverted emission on the propagating He-Ne intensity is preserved over a range of intensities. The decay of the intensity with distance along a waveguide fulfills the Bouguer-Lambert's law. The attenuation coefficient is the rate of diminution of average optical power with respect to distance along a waveguide. It is defined by the equation [34]:

$$P(z) = P(0)10^{-(\alpha'_{10}z/10)} \tag{3}$$

where P(z) is the power at distance z along the guide and P(0) is the power at z = 0; α'_{10} is the attenuation coefficient (the waveguide loss factor) in decibels (dB) per unit length, dB/cm if z is in centimeters. Using Eq. (3) we find for the light intensity (the power per unit area) denoted I_0 at z = 0 and I at the distance z along the guide

$$\log_{10} I = \log_{10} I_0 - \alpha_{10} z \tag{4}$$

where α_{10} is the optical loss factor (the decadic absorption coefficient) expressed in cm^{-1}. Eq. (4) represents the Beer-Lambert law for the absorbance $A = \log_{10}(I_0/I)$, (the optical density) of the sample. The relationship between the coefficients is α'_{10} (dB/cm) = 10 α_{10} (cm^{-1}). The natural absorption coefficient α (cm^{-1}) in Eq. (1) is related to the decadic absorption coefficient *via* the 2.303 factor, *i.e.*, α (cm^{-1}) = 2.303 α_{10} (cm^{-1}), due to the use of logarithms to the base 10, $\log_{10}(I_0/I)$, and $\ln(I_0/I)$ in the Beer-Lambert law alternative forms [35,36] frequently utilized in practical applications.

The fact that α_{10} is found independent of the He-Ne intensity confirms that processes such as excited state absorption (*cf.* Eq. (1)) are not important.

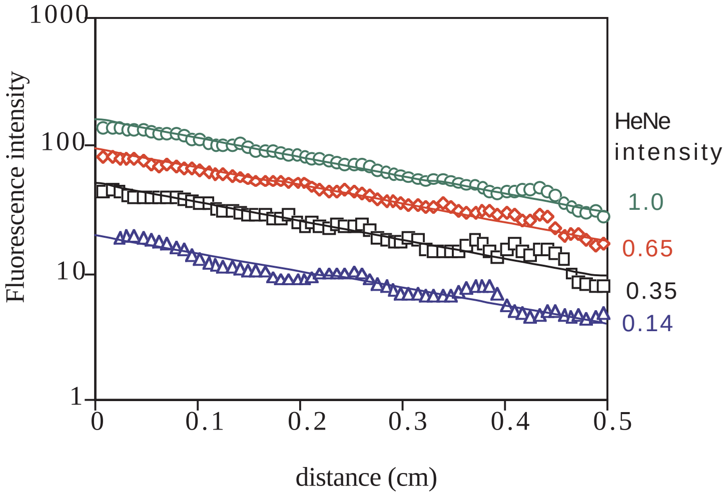

Figure 8. Semilogarithmic plot of the decay of upconverted light intensity at a moderately high concentration (2.47 wt%) of Phloxine in PVP. Relative intensities of the He-Ne beam used in the four measurements are marked in the Figure.

Figure 9 shows a collection of optical loss data obtained on films of PVP containing different concentrations of Phloxine B. It might be noted that the concentration of the dye in PVP of the order 10^{-3}–10^{-2} wt% was sufficient to see the fluorescence induced with a 1 mW He-Ne laser. The plot is linear indicating that Beer's law holds and the slope of the plot allowed us to determine that the extrapolated (decadic) absorption coefficient of Phloxine B at 632.8 nm is $\alpha_{10} = 54$ cm^{-1} ($\alpha'_{10} = 540$ dB/cm). The intercept of the line corresponds to the optical loss of neat PVP film: approximately 0.6 dB/cm, which is close to the total attenuation factor of 0.4–0.5 dB/cm at 632.8 nm, induced by scattering and absorption, measured in neat PVP slab waveguides. We have also found that the propagation characteristics could be conveniently studied when a Phloxine B/PVP overlayer is excited with the distribution of evanescent field emitted from a graded index silicon waveguide [37,38].

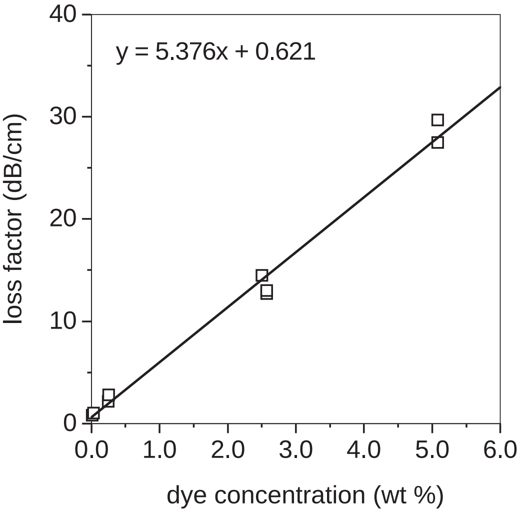

Figure 9. The loss factor (in dB/cm) determined by observation of the decay of upconverted fluorescence *vs*. propagation distance in waveguides doped with various concentration of Phloxine B in PVP. The slope of the dependence shows the extrapolated decadic absorption coefficient of Phloxine B being close to 54 cm^{-1} at 632.8 nm. The intercept shows that the loss of the host polymer was about 0.6 dB/cm for the results shown in the Figure.

CONCLUSIONS

We investigated the phenomenon of efficient upconversion of low intensity He-Ne light in Phloxine-doped polymer waveguides. The upconversion mechanism is identified as delayed fluorescence with the lifetime in millisecond range. Literature data indicate that there is a possibility of contributions from triplet-triplet annihilation as well as that of E-type delayed fluorescence and sensitized delayed fluorescence (possibly involving oxygen).

We find that monitoring delayed fluorescence, emitted from a waveguide, is a convenient way of investigating waveguide losses and evanescent field distribution. Other applications of the upconversion process are also possible, *e.g.* in microscopy. An important observation is that the xanthene dyes appear to be quite photochemically stable, when a 632.8 nm beam is causing the generation of the delayed fluorescence. Contrary to that, excitation of the same dyes in PVP matrix with strongly absorbed light (*e.g.* from an Argon laser at 488 or 514.5 nm) leads to irreversible bleaching. Recent papers by Sarkisov [39,41] also reported observation of upconverted luminescence from a DCM dye doped polymer waveguide, however, those papers indicated that efficient bleaching was present in that case.

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