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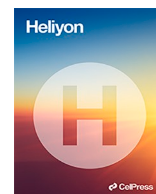


# Influence of continuous wave laser light at 532 nm on transmittance and on photoluminescence of DNA-CTMA-RhB solutions

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ABSTRACT

Recent results obtained in our experimental investigation on the influence of the illumination with continuous wave (c.w.) laser light at 532 nm on the transmittance at this wavelength and on the photoluminescence of the DNA-CTMA-RhB in butanol compound are reported. The temporal dependence of absorption changes induced by c. w. light at 532 nm in DNA-CTMA-RhB in butanol solution, and, for comparison, in RhB in butanol solution, is investigated experimentally and analyzed in order to assess the effect of DNA-CTMA on this light-induced process. The evolution in time of the peak's amplitude and wavelength of the photoluminescence spectra in solutions of DNA-CTMA-RhB in butanol, during their excitation with laser light at 532 nm wavelength has been also investigated and discussed.

## 1. Introduction

The deoxyribonucleic acid (DNA) biopolymer is an environmentally friendly optical material intensively studied in recent years due to its promising applications in photonics [1–6]. The complex formed by the DNA and the surfactant CTMA (cetyl-trimethyl-ammonium chloride) can be dissolved in many organic solvents as e.g., different alcohols. It can be used as matrix that can be doped with different chromophores, ensuring in this way an appropriate photosensitivity for the desired photonic functionalities [7,8].

One important photonic functionality recently experimentally demonstrated in a dye–doped DNA compound, namely in DNA-CTMA-RhB (RhB – Rhodamine B) in butanol solution, is the laser emission [4,9–11]. In Ref. [4] the lasing of DNA-CTMA matrix doped with RhB in butanol, optically pumped by a pulsed frequency-doubled Nd:YAG laser at 532 nm wavelength, are investigated and compared to those of RhB-butanol solution. The impact of the biopolymer matrix on the properties of the laser emission process has been assessed.

We present recent results obtained in our experimental investigation on the influence of the illumination with c. w. laser light at 532 nm (second harmonic of the Nd:YAG laser) on the transmittance at the illumination wavelength and on the fluorescence of the DNA-CTMA-RhB in butanol. The light with $\lambda = 532$ nm wavelength, highly absorbed by RhB, is usually used as optical pump, for optical excitation of the light emission in Rhodamine B embedded in different matrices. The evolution in time of the changes of the

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light absorption magnitude at the pump wavelength and of the photoluminescence emission spectra (magnitude and wavelength of the peak) excited by the considered c. w. green light in the aforementioned compound, during its illumination, have been monitored. Both of these two factors, light-induced changes of absorption and photoluminescence, directly affect the light emission in the studied compound.

The efficiency of the optical pumping process in DNA-CTMA-RhB solution in butanol depends on the photochemical stability of the dye molecules. The pump light induces a loss of light emitting dye molecules along the optical path through the cuvette in which the solution is placed (the photobleaching process, accompanied by a decrease of the pump light absorption), and also an accumulation of new photoproducts, as result of the photobleaching process, which can induce supplementary losses of the optical pumping light. Thus, the efficiency of the optical pumping is dependent on time and on the illumination conditions. On the other hand, the light-induced loss of the dye molecules (photobleaching) diminishes the light emission due to the decrease of the number of photoluminescent molecules in the illuminated volume of the solution. The temporal dependence of the changes induced by green light in the absorption properties of the solution can also affect the light emitted by photoluminescence as an effect of the change of the optical pumping intensity along the light path through the solution. Thus, the photo-chemical changes induced in DNA-CTMA-RhB in butanol solution by light at the wavelength of 532 nm have a complex influence on the light emission process in this compound.

In this paper, the temporal dependence of absorption changes induced by c. w. light at 532 nm in solutions in butanol of DNA-CTMA-RhB, and, for comparison, of RhB, is for the first time experimentally investigated, to our knowledge, at high RhB concentrations (units of g/L), in order to evaluate the effect of DNA-CTMA on this light-induced process. The light at $\lambda = 532$ nm wavelength, which is highly absorbed by RhB, is frequently used to optically pump the light emission in RhB embedded in different matrices. The evolution in time of the peak's amplitude and wavelength of the photoluminescence spectra in the DNA-CTMA-RhB in butanol solutions during their illumination with an excitation laser beam (c.w.) at $\lambda = 532$ nm wavelength has been also investigated. The use of highly concentrated RhB solutions in lasing experiments allows a tuning range of the laser wavelengths. This range is larger in solutions of DNA-CTMA-RhB in butanol (~15 nm), than that in solutions of RhB in butanol (~10 nm), with the same RhB concentration. The DNA-CTMA matrix shifts also the lasing lines toward shorter wavelengths [4].

## 2. Materials and methods

The schematic of the experimental setup utilized in the investigation of the influence of laser light (c.w.) at $\lambda = 532$ nm on absorbance at this wavelength and on the photoluminescence of DNA-CTMA-RhB in butanol is shown in Fig. 1.

The light source of the green light ($\lambda = 532$ nm, c. w.) utilized in our experiments is a frequency doubled Nd:YAG laser (Apel Laser SRL, Romania). This wavelength is near the peak wavelength of the absorption spectra of the investigated solutions in butanol (DNA-CTMA-RhB compound and RhB alone, respectively). The residual infrared (IR) light of the pump laser diode used in the Nd:YAG laser is blocked at the output of the laser with the filter FIR, thus only the green light beam ($\lambda = 532$ nm) is passing through the rest of the setup. The green laser beam has a transversal intensity distribution near to a Gaussian, with the factor $M^2 = 1.01$. The diameter of the unfocused laser beam spot, at the sample plane, is $d = 862$ μm. In order to monitor the temporal stability of the Nd:YAG laser power during the experiments and to consider the eventual power fluctuations in the processing of the experimental data, a thick glass plate (beam splitter – BS) is introduced in the laser beam in order to extract a small fraction (~4%) of the laser power, which is monitored with a detector model OP-2-Vis (Det., in the setup) coupled to a powermeter. The A1 and A2 apertures are used for the spatial filtering of the laser beam incident on the sample, and of the laser beam extracted with the beam-splitter BS, respectively. The investigated sample is fixed on a micrometric vertical translation stage, which ensures the adjustment of its vertical position relative to the incident laser beam. After carefully aligning the input end of the spectrometer's optical fiber, which collects the emitted light, in order to maximize the measured photoluminescence signal, the sample is translated vertically over a distance greater than the size of the excitation laser beam. In this way, the measured photoluminescence signal is generated in a fresh zone of the sample, not previously exposed to the excitation laser light, and the position of the input end of the optical fiber relative to the sample is kept at the optimum one, which was fixed during the previous optical alignment. The power of the laser beam incident on the sample is modified using neutral density filters ($F_{ND}$), calibrated at the laser wavelength $\lambda = 532$ nm. The powers of all laser beams involved in our experiment (incident beam, transmitted beam, and monitoring beam extracted with the BS, respectively) are measured with computer controlled Fieldmax powermeters (Coherent) with power sensors OP-2-Vis (Det, in the setup) for the spectral range 400 nm–1100 nm.

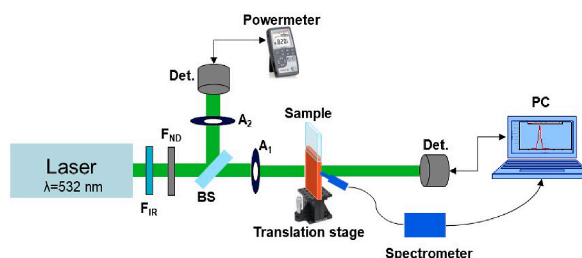


**Fig. 1.** The schematic of the experimental setup utilized in the investigation of the influence of laser light (c.w.) at $\lambda = 532$ nm on absorbance at this wavelength and on the photoluminescence of DNA-CTMA-RhB in butanol.

The evolution in time of the transmission of the green laser beam (λ = 532 nm, c. w.) through the cell with the thickness of 0.1 mm has been monitored for the incident power ~ 7 mW. The corresponding incident intensity was ~1200 $mW/cm^2$.

The photoluminescence process and the temporal evolution of the photoluminescence spectra of the samples during their irradiation with the beam at λ = 532 nm were investigated and recorded with a spectrometer (Ocean Optics HR4000 CG-UV-NIR) with optical fiber, coupled to a computer. The solutions have been introduced in cuvettes of 0.1 mm thickness, the same as in the transmission experiments. The photoluminescence spectra have been acquired at 10-min time intervals, during 1 h of green light illumination (λ = 532 nm, c. w.). The photoluminescence light has been collected with a spectrometer. The input end of its optical fiber is arranged almost perpendicular to the incident excitation beam direction.

The investigated studied samples are solutions of DNA-CTMA-RhB in butanol. The DNA is produced by Ogata Research Laboratory, Ltd, Chitose, Japan. The DNA functionalization with CTMA was performed following the procedure described by Grote et al. [12] and consists in adding dropwise the DNA solution to the CTMA solution. The obtained DNA – CTMA precipitate is then filtered and dried in oven at 40 °C. The obtained white compound is grinded until the particle size is sufficiently small for its use in DNA-CTMA-Rhodamine B solutions.

The Rhodamine B luminophore (Exciton company, Dayton, USA) was used as supplied. As organic solvent was used butanol that has a low vapor pressure (6.7 hPa(20 °C), compared to other alcohols as, for example, ethanol (59 hPa(20 °C) [13]. It ensures a relatively slow evaporation and also has a moderate viscosity [14]. The DNA-CTMA concentration in butanol was 30 g/L. Solutions with several concentrations of RhB (5.03%, 7.34%, 9.11%, 11.08%, and 12.82%) have been investigated. These concentrations represent the percentages of the RhB dye mass with respect to the DNA-CTMA matrix dry mass.

The investigated DNA-CTMA-RhB solutions in butanol, with different dye concentrations, and the solutions of RhB in butanol, with similar dye concentrations, are summarized in Table 1.

Special Quartz cuvettes (0.1 mm thickness, optical quality, transparent in the range 200 nm–2500 nm) purchased from Hellma, Germany have been used to investigate the prepared solutions. The cuvettes consist of two sliding parts fixed in a metallic holder, as it is shown in Fig. 2. In thicker cuvettes (0.5 mm thickness) at λ = 532 nm the incident laser beam is totally absorbed inside the cuvette by the investigated solutions. This kind of cuvettes made from two detachable parts ensures their facile filling and also the facile cleaning of their interior.

The Fresnel reflections on external (air - Quartz) and internal (Quartz - solution) cuvette interfaces have been considered when the powers of the incident and transmitted beams have been measured. The refractive index of investigated solutions was considered to be that of the butanol solvent, n = 1.4022 [15].

## 3. Results

### 3.1. *Temporal evolution of transmission*

In [4], it was shown the blue shift of the absorption spectrum of DNA-CTMA-RhB solution in butanol, compared to that of RhB in butanol with the same concentration. This means that at λ = 532 nm the solution containing DNA-CTMA absorbs more than the one without DNA-CTMA, a fact revealed also by the transmittance curves for the five sets of the investigated samples, with and without DNA, shown in this paper.

In Fig. 3 the absorption spectra of solutions in butanol of DNA30-RhB3 and of RhB3, respectively, are shown. These samples have the RhB concentration in the middle of the considered concentration range. The wavelength of the laser used in experiments is marked with green color.

Green line - the wavelength of the laser used in experiments.

The temporal dependence of the transmittance for a c. w. incident intensity of ~1200 $mW/cm^2$, for the two sets of five samples from Table 1, DNA30-RhB1-5 and RhB1-5, with different RhB concentrations, is shown in Fig. 4(a–e), 5(a-d).

In Fig. 6 a photo of DNA30-RhB1 sample after 6000s of local illumination with a green c. w. laser beam at 532 nm is shown. In the photo it is possible to see the irradiated area (non-coloured spot on a white background), a consequence of the photoinduced bleaching process.

From Figs. 6 and 4a, it is possible to see that even if the illuminated area looks visually discolored, there is significant loss for the light with the wavelength of 532 nm.

The analysis of the transmittance curves at λ = 532 nm shown in Fig. 4(a–e) and 5(a-d), for both types of samples, with and without DNA-CTMA, reveals that their temporal evolutions start with an initial increase of the transmittances, followed by their asymptotic

**Table 1**
The investigated solutions, DNA-CTMA-RhB in butanol, and RhB in butanol, respectively.

| Name of the sample | Rhodamine B concentration in DNA-CTMA samples | | Rhodamine B concentration inRhB samples g/L |
|---|---|---|---|
| | With respect to DNA-CTMA, % | In solution g/L | |
| DNA30-RhB1/RhB1 | 5.03 | 1.62 | 1.62 |
| DNA30-RhB2/RhB2 | 7.34 | 2.42 | 2.42 |
| DNA30-RhB3/RhB3 | 9.11 | 3.02 | 3.02 |
| DNA30-RhB4/RhB4 | 11.08 | 3.84 | 3.84 |
| DNA30-RhB5/RhB5 | 12.82 | 4.43 | 4.43 |

**Fig. 2.** The demountable cuvette used in our experiments.

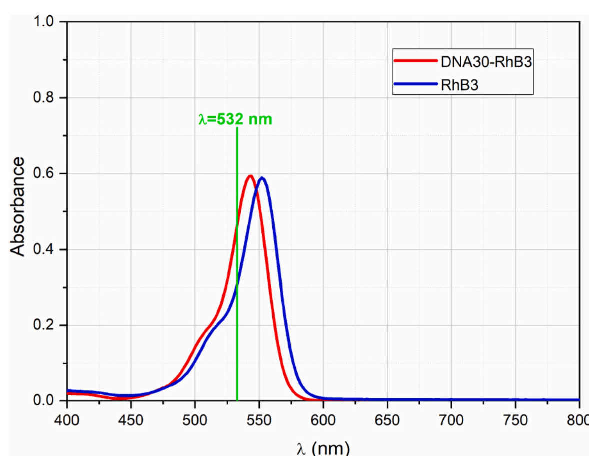


**Fig. 3.** The absorption spectra of DNA30-RhB3 and of RhB3 solutions in butanol.

decrease to constant values. The temporal evolution of the transmittance can be attributed to the process of photobleaching experienced by RhB molecules during their illumination with c. w. green light at a wavelength of 532 nm, which is highly absorbed by the solutions in butanol of RhB and of DNA-CTMA-RhB, respectively, as it is possible to see in Fig. 3.

Photobleaching is a process in which the molecules of a photoluminescent dye are degraded by the photochemical reactions that occur when the dye is illuminated with light within its absorption band. It affects the light absorption in two ways, one of them consisting in the diminishing of the number of dye molecules that can absorb light and another one in the formation of reaction products as the result of the photochemical processes undergone by the dye molecules [16–18]. The absorption properties of these reaction products can be very different compared to those of dye molecules. The photoluminescence can be also strongly affected by the photobleaching process. The decrease in the number of absorbing dye molecules means the corresponding decrease in the number of molecules that are able to emit the photoluminescence light. The photogenerated reaction products can also affect the light emission and the propagation of the emitted light through the solution by introducing supplementary optical losses at the wavelengths of the excitation and of the emitted light, respectively.

As a result of the photobleaching process the concentration of RhB molecules is locally decreased in the illuminated volume, along the green light path through the sample, starting from the input face. Thus, the exponential decay of the green light intensity along its path in the sample, which in the absence of photobleaching occurs according to Lambert-Beer law (valid for a constant absorption), is modified during the illumination as the photobleaching changes in time and space the light absorption, starting from the input face of the sample.

Other fact that makes even more complicated the temporal dynamics of the transmittance is the transversal spatial profile of the laser beam intensity, near to a Gaussian, followed by a similar transversal profile of the photobleaching rate. The photobleaching is faster in the centre of the illuminated area, where the local light intensity is higher, and becomes gradually slower toward the regions illuminated by the tails of the Gaussian beam.

The transversal profile of intensity of the incident Gaussian laser beam results in non-uniform local heating of the solution. The

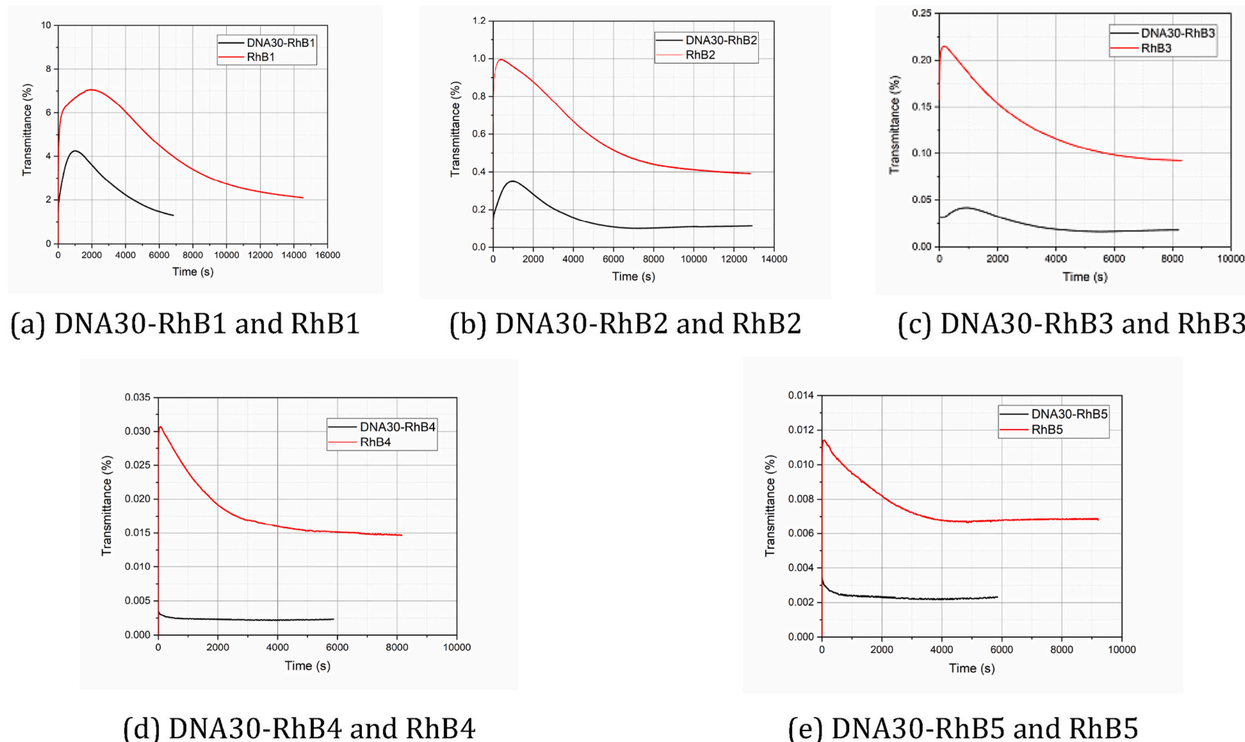


**Fig. 4.** The time dependence of the transmittance at 532 nm wavelength, for a c. w. incident intensity of ~1200 mW/cm$^2$, for the couples of samples (Table 1) with the same concentrations of RhB (a–e), respectively.

heating follows the spatial distribution of the light intensity in the sample, being maximal at the center of the incident laser beam. The temperature gradient in the illuminated volume is followed by a local movement inside the liquid due to the convective heat transfer.

On the other hand, as a result of the light-induced photochemical decomposition of RhB molecules, new photoreaction products are generated and accumulated in the illuminated volume of the solution [16–18]. These photo-products can induce even greater losses in transmittance at 532 nm than the RhB molecules themselves [16,17], a fact that is also suggested by the temporal evolution of the experimental transmittance curves shown in Fig. 4(a–e), 5(a-d).

The aforementioned light-induced processes have a complex spatio-temporal evolution that is difficult to model for an accurate quantitative explanation. Qualitatively, they are responsible for the complicated temporal dynamics of the transmission curves for the investigated solutions, with and without DNA-CTMA.

The comparative analysis of the transmittance curves for the investigated solutions, with and without DNA-CTMA, with the same RhB concentration, reveals that the initial increase of their transmittance, a direct contribution of RhB molecules photobleaching, is slower in RhB solutions containing DNA than in those without DNA. This behaviour can be an indicative of the fact that DNA-CTMA has a favourable effect on photochemical stability of RhB molecules, protecting in a way against their photobleaching induced by the green light. Previous work by You et al. [14] and Perianu et al. [19] have shown that small molecules can bind to DNA through intercalation or grooves, while large molecules such as Rhodamine will intercalate between CTMA surfactant chains. The DNA double-stranded helix represents the template of the interaction of RhB dye molecules with the CTMA chains. This possible interaction could explain the observed differences between the results obtained for the investigated solutions, with and without DNA-CTMA. Regarding the transmittances, they asymptotically evolve to constant values, which are lower in the samples without DNA (samples RhB1-5) than in the samples with DNA (samples DNA30-RhB1-5), with respect to the corresponding initial values of their transmittances. This tendency becomes stronger with increasing RhB concentration. The lower asymptotic relative decrease of the transmittance in the samples with DNA could also be an indicative of the fact that the DNA environment somehow protects the RhB molecules against the photochemical processes experienced by RhB molecules when they are illuminated with c. w. laser beam at 532 nm wavelength and provides a better photochemical stability of the dye molecules.

### *3.2. Temporal evolution of photoluminescence*

The experimental results obtained in the investigation of the temporal evolution of photoluminescence in DNA30-RhB1-5 samples during 1 h of their excitation with c. w. laser light at $\lambda = 532$ nm are shown in Fig. 7. Fig. 7a1, 7b1, 7c1, 7d1, 7e1 present the photoluminescence spectra of the samples DNA30-RhB1-5. The acquired spectra, for each sample, have been normalized to the peak amplitude of the corresponding initial spectrum, acquired at the moment when the c. w. green excitation light has been switched ON.

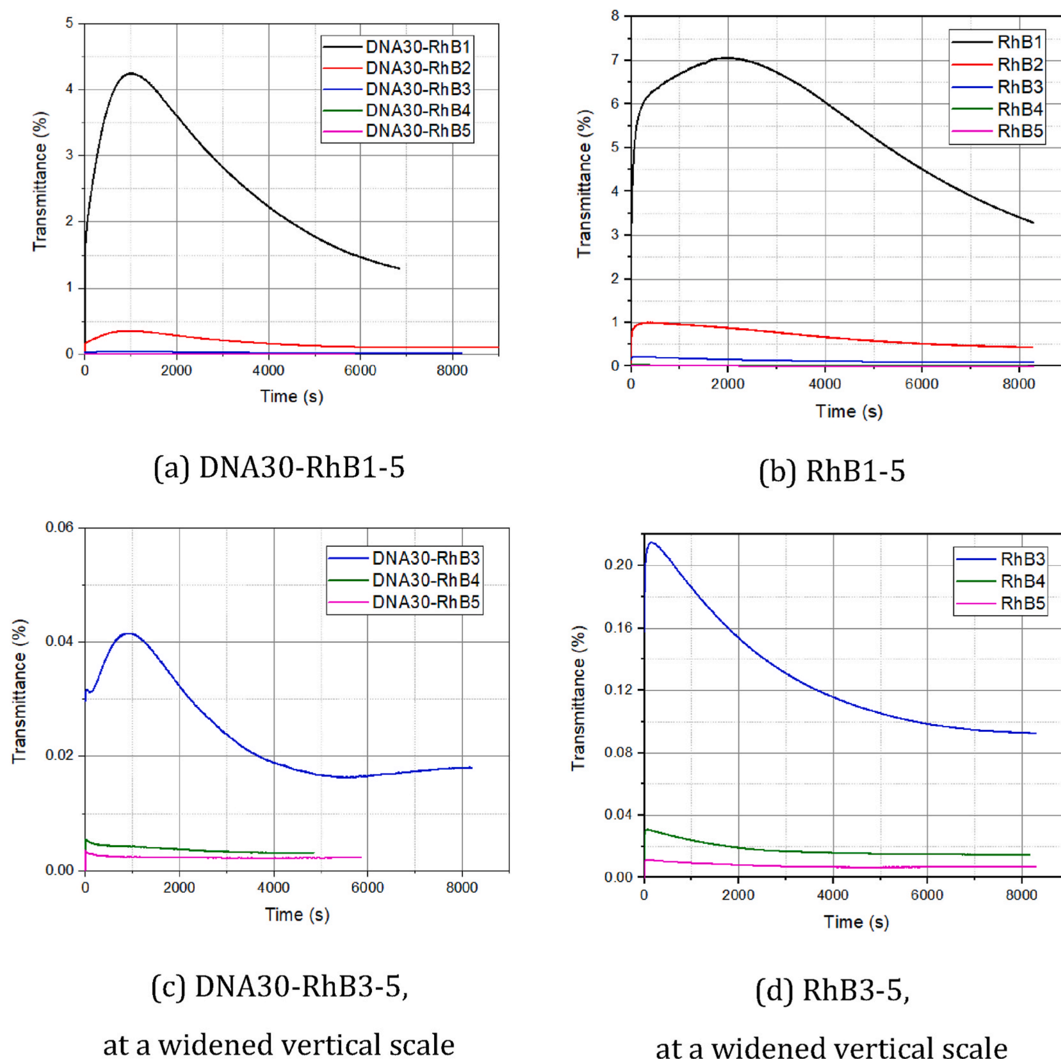


**Fig. 5.** The grouped transmission curves for the five samples DNA30-RhB1-5 with different RhB concentrations (a) and for the five samples RhB1-5 without DNA-CTMA with different RhB concentrations (b). The transmission curves, at a magnified vertical scale of the transmittance, for the samples DNA30-RhB3-5 (c) and RhB3-5 (d).

The temporal evolution of the photoluminescence spectra peak amplitudes and of the wavelengths corresponding to the spectra peaks are shown in Fig. 7a2-e2 and in Fig. 7a3-e3 for each sample, respectively.

The temporal evolutions of the photoluminescence spectra peak amplitudes and of their wavelengths, for the entire group of DNA30-RhB1-5 samples during 1 h of excitation with c. w. laser light at $\lambda = 532$ nm are shown in Fig. 8a and b, respectively, for a better comparison between the values of the two mentioned parameters.

The difference $\Delta\lambda$ between the wavelengths corresponding to the peaks of the photoluminescence spectra at the moments $t = 0$ and $t = 60$ min, respectively, for the samples DNA30-RhB1-5 is shown in Fig. 9.

The normalized photoluminescence spectra of DNA30-RhB1-5 samples, acquired immediately after the start of the excitation ($t = 0$), have been compared with the spectra of corresponding RhB1-5 samples with the same RhB concentration, acquired at the same moment.

The spectra for the couples of samples with the lowest RhB concentration (DNA30-RhB1; RhB1) and for the samples with the highest RhB concentration (DNA30-RhB5; RhB5) are shown in Fig. 10a and b, respectively.

The normalized photoluminescence spectra, acquired immediately after the start of the excitation ($t = 0$), for the entire group of samples with DNA, DNA30-RhB1-5, and for the entire group of samples without DNA, RhB1-5, are shown in Fig. 11a and b, respectively. The wavelengths corresponding to the peaks of the photoluminescence spectra, at $t = 0$, for the samples DNA30-RhB1-5 and for the samples RhB1-5 are shown in Fig. 11c and d, respectively. For an easier comparison, the wavelengths corresponding to the peaks of the photoluminescence spectra, for both sets of samples are shown in Fig. 11e.

The wavelength separation between the peaks of the photoluminescence spectra in samples with DNA-CTMA, DNA30-RhB1-5, is

**Fig. 6.** Photo of DNA30-RhB1 sample after 6000 s of local illumination with a green c. w. laser beam at $\lambda = 532$ nm. The discolored spot is the illuminated area.

higher than those in the samples without DNA-CTMA, RhB1-5, with the same concentrations of RhB.

The results of the experimental study of photoluminescence in the samples with DNA, DNA30-RhB1-5, and in the samples without DNA, RhB1-5, excited by the illumination of the samples with c. w. laser light at 532 nm, revealed several important aspects related to their photoluminescence spectra, discussed below.

The photoluminescence spectra of DNA30-RhB1-5 and RhB1-5 samples are shifted towards higher wavelengths (red-shift) when the Rhodamine B concentration is increased in the investigated samples, as it is shown in Fig. 11 and as it was also reported in Refs. [4,9]. The origin of this shift is the aggregation of the RhB molecules. As the aggregation increases with the RhB concentration, the magnitude of the shift increases also with the dye concentration [20].

In highly diluted ($1{\cdot}10^{-4}$ g/L $\div$ $1{\cdot}10^{-2}$ g/L) RhB solution in butanol there is a significant overlapping of the emission and absorption spectra. The left side of the emission spectrum is significantly superimposed on the right side of the absorption spectrum, which leads to a partial re-absorption of the photoluminescence signal [13].

This overlapping decreases with the increase in the RhB concentration, due to the red shift of the photoluminescence spectrum, as it is possible to see in Fig. 12a and b. On the other hand, the decrease in RhB concentration in the illuminated area has the effect of blue-shifting the photoluminescence signal during laser excitation at $\lambda = 532$ nm, as an effect of the photobleaching process. In turn, this increases the superposition of the photoluminescence and absorption spectra and, consequently, increases the re-absorption of the photoluminescence signal.

During the illumination with the c. w. excitation laser beam at $\lambda = 532$ nm the photoluminescence of the investigated DNA-CTMA-RhB solutions in butanol decreases over time (Fig. 7) with an asymptotic tendency of the photoluminescence peaks to decrease to constant values (Fig. 8). In these figures it can be seen also that the photoluminescence peaks move towards shorter wavelengths (blue shift) and their amplitudes decrease due to the decrease in RhB concentration in the illuminated area as effect of the photobleaching process, as mentioned above. The shift of the photoluminescence peak decreases with the RhB concentration in the samples DNA30-RhB1-5. Thus, after 60 min from the start of excitation with c. w. laser light at $\lambda = 532$ nm, the shift of the luminescence peaks for the investigated samples is $\Delta\lambda_1 \cong$ 4 nm (DNA30-RhB1), $\Delta\lambda_2 \cong$ 3.5 nm (DNA30-RhB2), $\Delta\lambda_3 \cong$ 3 nm (DNA30-RhB3), $\Delta\lambda_4 \cong$ 2.7 nm (DNA30-RhB4), $\Delta\lambda_5 \cong$ 2.3 nm (DNA30-RhB5).

Concerning the evolution in time of the photoluminescence spectra in RhB solutions, in Fig. 13 is shown, as an example, the evolution in time of the photoluminescence spectra, emitted by RhB3 solution with the RhB concentration in the middle of the considered concentration range, normalized to the peak amplitude of the corresponding initial spectrum. The spectra are recorded during 1 h of excitation of RhB3 sample with c. w. laser light at $\lambda = 532$ nm.

The analysis of Fig. 13 reveals the fact that the decrease of the peak amplitudes of the acquired photoluminescence signals, relative to the initial moment of the excitation, is lower than that in the sample DNA30-RhB3, with the same concentration of RhB. A similar

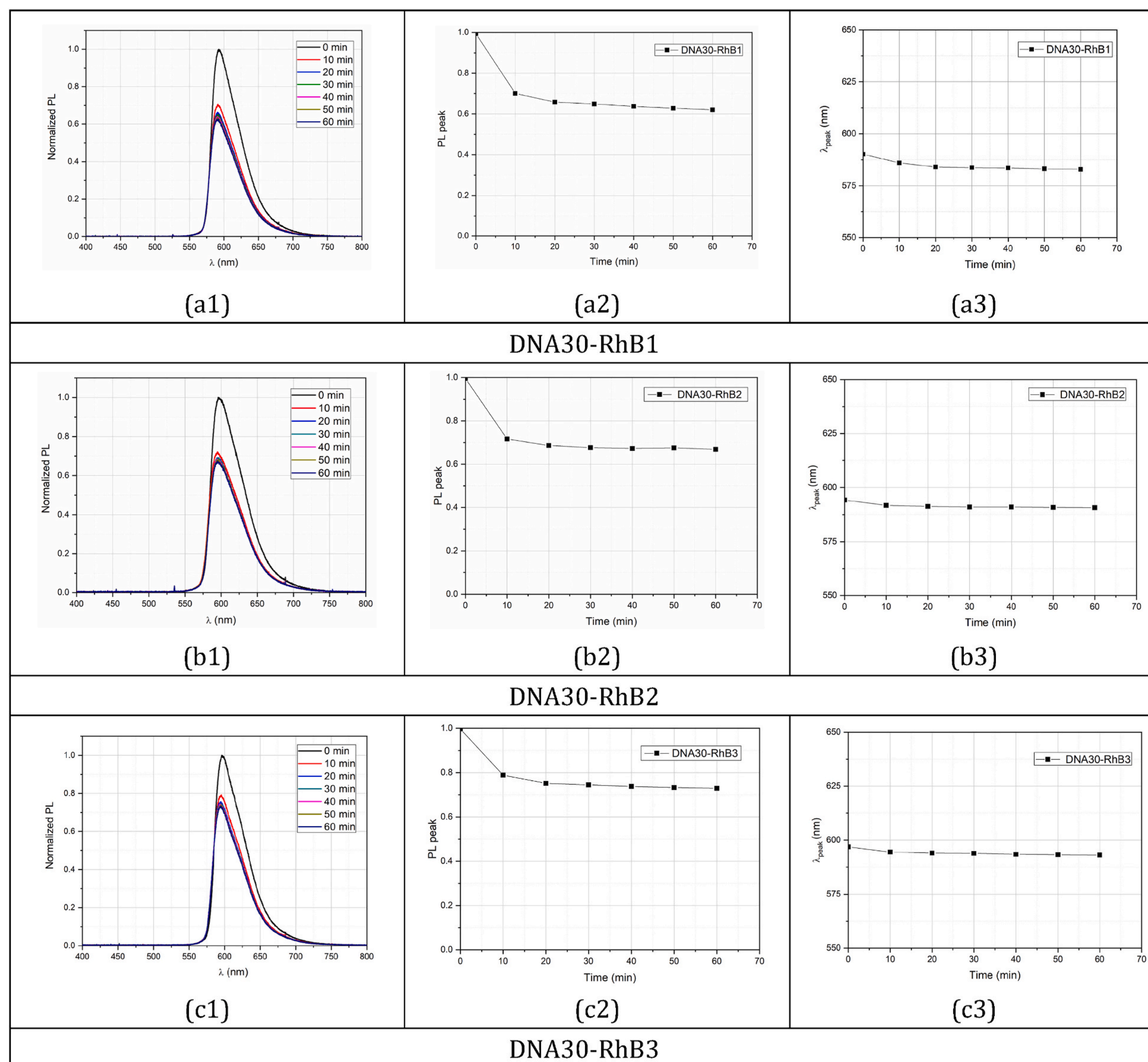


**Fig. 7.** The evolution in time of the photoluminescence emission spectra of DNA30-RhB1-5 samples during 1 h of their excitation with c. w. laser light at $\lambda = 532$ nm. The acquired spectra, normalized to the peak amplitude of the corresponding spectrum acquired at the moment when the c. w. green excitation light has been switched ON (a1-e1); the evolution in time of the luminescence spectra peak amplitudes, for each sample (a2-e2); the evolution in time of the wavelengths corresponding to the spectra peaks, for each sample (a3-e3).

behavior is for all spectra from RhB1-5 samples in comparison with the spectra from DNA30-RhB1-5 samples, with the same concentrations of RhB.

The recorded photoluminescence signal is influenced by several factors that affect the emission process itself, as the temporal evolution of the number of molecules able to emit light and how they are excited, and also factors that affect the propagation of the emitted light between the point where it is generated and the point where it is collected by the optical fiber of the spectrophotometer.

Thus, the number of RhB molecules able to fluoresce is directly influenced by the photobleaching process. Also, the fluorescent molecules are excited non-uniformly in time, due to the temporal evolution of the absorption of excitation light, and in space, due to the time-dependent longitudinal and transversal gradients in the light intensity inside the illuminated area of the sample. A brief qualitative discussion of these factors was presented above, in section 3.1. Temporal evolution of the transmission. The laser-induced local heating in the illuminated area generates a convection movement in the liquid, which directly influences the refreshment of the solution in the illuminated area, bringing there from surrounding zones new RhB molecules able to fluoresce. This movement process is also dependent on the solution viscosity. The local heating of the light-excited area generates also a non-uniform local change of the refractive index, due to the thermo-optic effect, influencing the propagation of the excitation light in its path throught the solution.

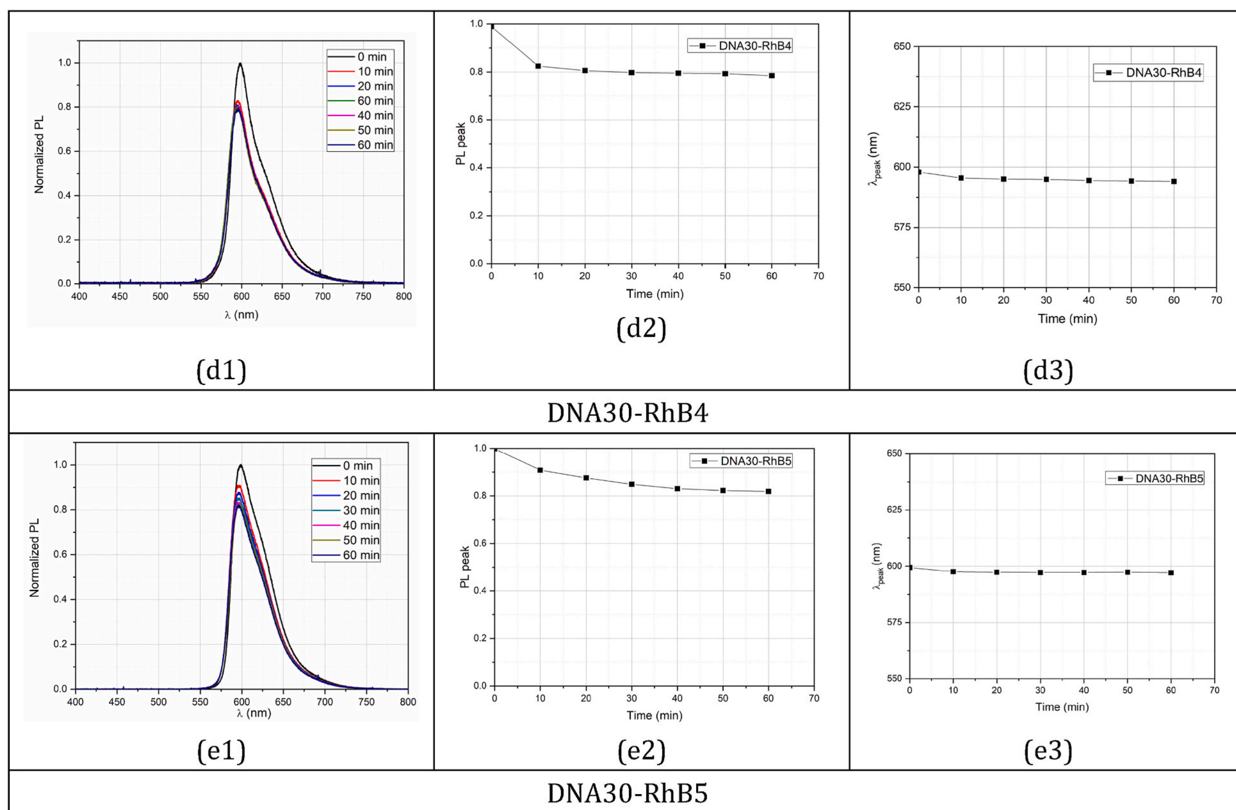


**Fig. 7.** (*continued*).

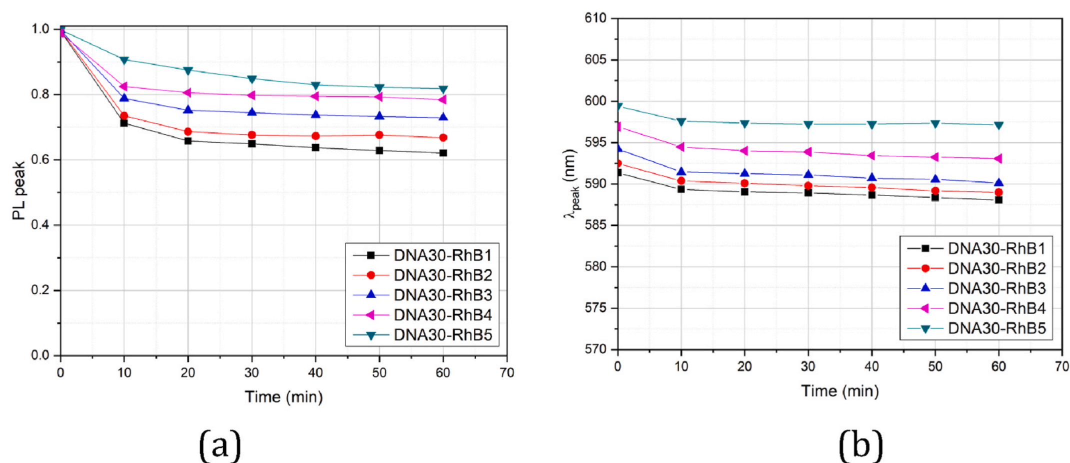


**Fig. 8.** The evolution in time of the photoluminescence spectra peak amplitudes (a) and of their wavelengths (b), for DNA30-RhB1-5 samples excited with c. w. laser light at $\lambda = 532$ nm.

Some of the aforementioned processes also affect the propagation of the emitted light to the collection system of the spectrophotometer. Thus, the light emitted in different points of the laser-excited area, along its path to the collection point, in a direction orthogonal to that of the excitation light, experiences the propagation through zones with different, material dependent, absorptive and refractive optical properties.

The differences in physical properties as e.g. light absorption, refractive and thermo-optic properties, viscosity, and in their temporal evolutions during the laser excitation, between the solutions in butanol of DNA-CTMA-RhB and of RhB, respectively, have different influences on both the light-emission process itself and on the collection of the emitted fluorescence signal in the two kinds of samples. A detailed quantitative analysis and modeling of the processes influencing the emission and the collection of the

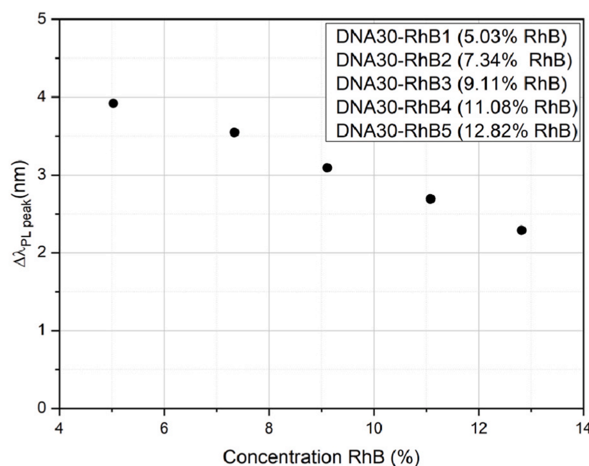


**Fig. 9.** The difference Δλ between the wavelengths corresponding to the peaks of the photoluminescence spectra at the moments t = 0 and t = 60 min, respectively, for the solutions with DNA, DNA30-RhB1-5.

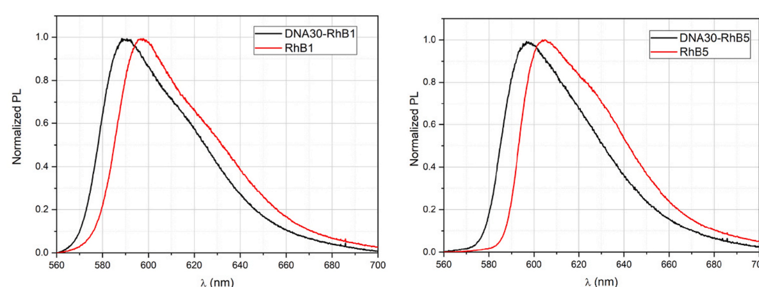


**Fig. 10.** The normalized photoluminescence spectra, acquired immediately after the start of the excitation (t = 0), for the couple of samples (DNA30-RhB1; RhB1) with the lowest RhB concentration (a) and for the couple of samples (DNA30-RhB5; RhB5) with the highest RhB concentration (b), respectively.

photoluminescence light in the RhB solutions in butanol, with and without DNA-CTMA, is beyond the scope of this paper.

Regarding the comparative analysis of the influence of c. w. laser light at 532 nm on the investigated samples, with and without DNA-CTMA, a more straitforward comparison can be done for the temporal evolution of absorbance than for that of the photoluminescence. In absorption experiments the entire transmitted light is collected and measured, while in the photoluminescence experiments just a tiny part of the emitted light is collected by the optical fiber of the spectrophotometer, in a direction orthogonal to that of the excitation light. In this last case, the factors affecting the propagation of the light rays between the emission point and the collection point affect much more the measured photoluminescence signal.

## 4. Conclusions

The specific influence of the illumination with continuous wave (c.w.) laser light at 532 nm on the transmittance at this wavelength and on the photoluminescence of the DNA-CTMA-RhB in butanol has been experimentally revealed.

The study performed on the Rhodamine B solutions (with and without DNA CTMA) showed that the photobleaching process of the dye is faster (higher rate) in the case of RhB-butanol solutions compared to that of DNA-CTMA-RhB butanol solutions, which suggests an important consequence, namely that DNA-CTMA provides protection to Rhodamine molecules against photochemical processes of photodegradation.

The relative asymptotic decrease of transmission compared to the initial one, lower in DNA-CTMA-RhB in butanol than in RhB solution, also suggests that DNA-CTMA provides protection to RhB molecules against photodegradation.

At the same time this study revealed that it can be possible to tune the emission wavelength by using DNA-CTMA as matrix and modifying the Rhodamine concentration, the maxima of the fluorescence spectra of the DNA-CTMA-RhB samples in butanol being more separated in wavelength than those of the RhB samples in butanol.

The results obtained in this study are important for the use of DNA-CTMA-RhB solutions in butanol in lasing applications and in nonlinear photonics.

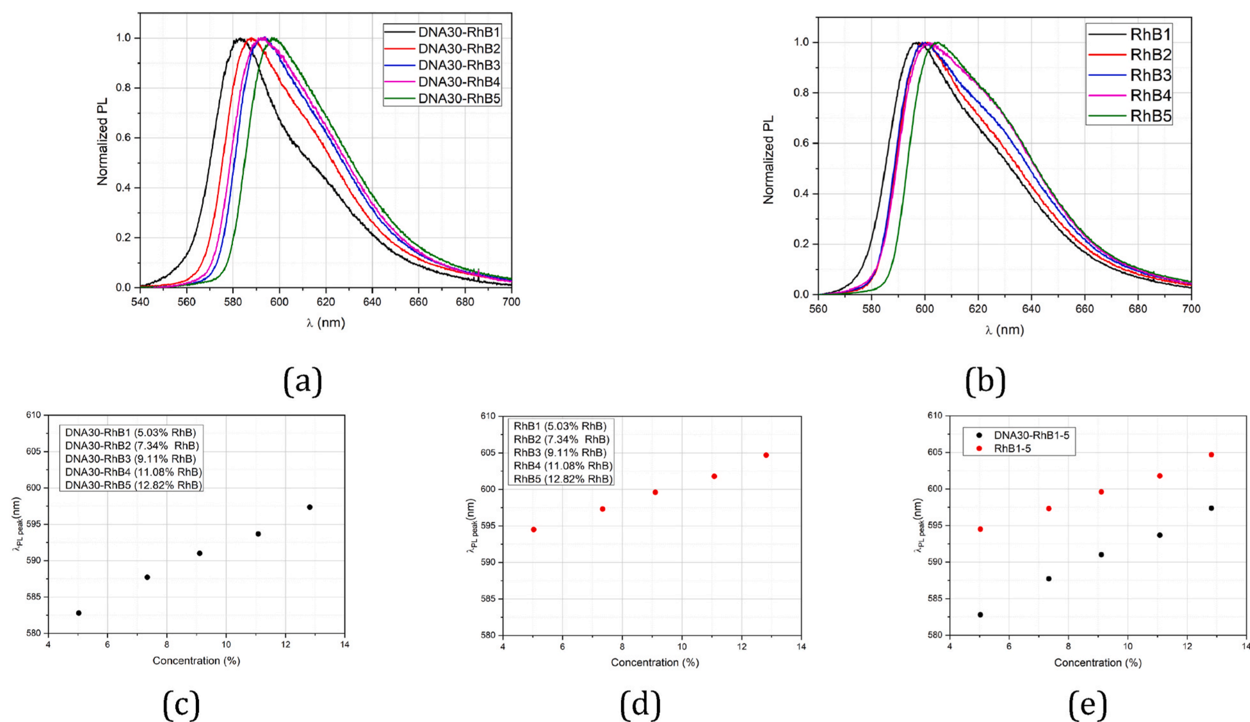


**Fig. 11.** The normalized photoluminescence spectra acquired at t = 0, for the samples DNA30-RhB1-5 (a) and for the samples RhB1-5 (b); the wavelengths corresponding to the peaks of the photoluminescence spectra for the samples DNA30-RhB1-5 (c) and for the samples RhB1-5 (d); the wavelengths corresponding to the peaks of the photoluminescence spectra, for both sets of samples (e).

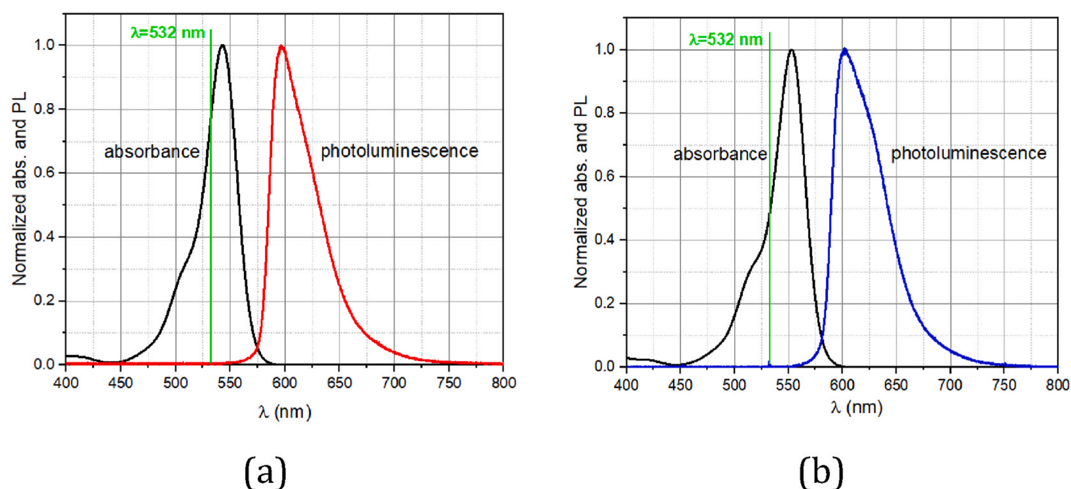


**Fig. 12.** The normalized absorption and photoluminescence spectra, acquired immediately after the start of the excitation (t = 0), for the samples DNA30-RhB3 (a) and RhB3 (b), respectively. Green line - the wavelength of the laser used in experiments.

## Author contribution statement

Adrian Petris: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper. Petronela Gheorghe: Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper. Ileana Rau: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

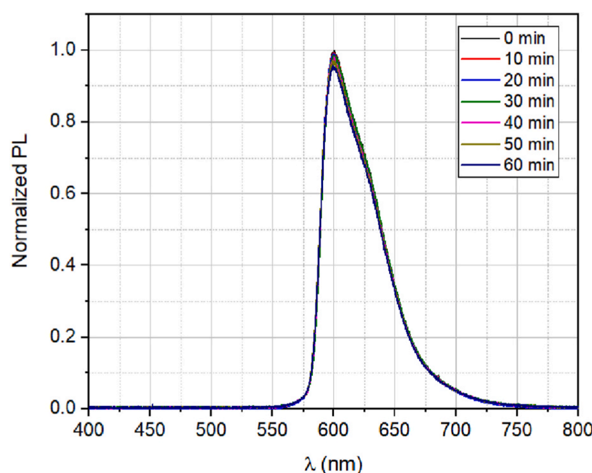


**Fig. 13.** The evolution in time of the photoluminescence spectra of RhB3 sample during 1 h of its excitation with c. w. laser light at $\lambda = 532$ nm. The acquired spectra are normalized to the peak amplitude of the corresponding spectrum acquired at the moment when the green excitation light has been switched ON.

## Data availability statement

Data included in article/supp. material/referenced in article.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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