

# Spontaneous and stimulated emission of thin-film polymer structures in the presence of nitrotoluene vapour

Sh.T. Berdybaeva, E.N. Tel'minov, T.A. Solodova, E.N. Nikonova,  
L.G. Samsonova, T.N. Kopylova

**Abstract.** The features of spontaneous and stimulated emission of polyfluorenes, polyvinylcarbazole, and low-molecular-weight electron-donor compounds incorporated into various materials are studied in the presence of nitrotoluene vapour. Lasing in planar thin-film waveguides is achieved. The dynamics of the lasing spectra of a thin-film optical chemical sensor is presented. It is shown that the response time of the sensor in the lasing regime is 30 s before the lasing intensity decreases by 50% from the initial level.

**Keywords:** luminescence, luminescence quenching, lasing, molecular sensor, analyte, nitro compounds.

## 1. Introduction

Interest of researchers in the development of simple and reliable chemosensors is caused by a high demand for warning devices, which are used in safety systems, for controlling technological processes, for environment monitoring, and in some other cases.

There exist a large number of types of chemosensors, but most of them require direct electric contact with the sensor layer or heating of the sensitive material in the presence of analyte. These drawbacks can be overcome using integrated optical molecular chemosensors, which operate in the luminescence regime and provide high sensitivity [1]. They have a number of advantages over the other sensor types, but also have some drawbacks, for example, cross-influence of analytes on indicator molecules and the necessity of using several sensors for one and the same analyte to ensure a large dynamic detection range. The main advantages of these devices are their simplicity, low production cost, wide choice of sensor materials for different analytes and application conditions, and the possibility of operation without heating and direct electric contact with the sensor layer, which allows their use in explosive atmospheres.

Among numerous chemical compounds contaminating the environment, a prominent place is occupied by nitroaromatic compounds, many of which enter the composition of explosive materials. The latter are detected using various physical methods [2]. A sensitive and comparatively inexpensive method is based on quenching of the luminescence of

organic molecules upon their interaction with molecules of nitrotoluenes, which have strong electron-acceptor properties. The interaction of nitrotoluene molecules with excited organic molecules, which have electron-donor properties, leads to the formation of short-lived (several nanoseconds) complexes with a strong electron density transfer to the nitro compound. As a result of this interaction, the organic molecule nonradiatively decays to the ground electronic state. Thus, the luminescence intensity is observed to decrease. In some works [1, 3, 4], this principle was used as a basis for developing sensors of nitrotoluene vapours.

Recently, to broaden the dynamic range and increase the sensitivity of optical chemical sensors, enhanced attention has been paid to the use of thin-film organic laser-active media. For example, the passage from the luminescence mode to the threshold stimulated emission mode increases the device sensitivity on average by two orders of magnitude [3–5]. The thin-film element radiation intensity in the threshold laser regime depends on the chemical composition of the surrounding medium, and the presence of a small amount of a material quenching the luminescence can lead to complete oscillation suppression.

The aim of the present work is to demonstrate the possibility of fabricating an inexpensive and effective chemical sensor based on organic compounds for detecting vapours of nitroaromatic compounds, which operates in the low-threshold lasing regime on the basis of luminescence quenching of organic compounds.

## 2. Objects and methods of investigation

It is known that polyfluorene is a sensitive fluorophore used in sensor structures for detecting nitro compounds [5–9]. In the present work, we use ADS129 and ADS229 polyfluorenes (American Dye Source, Inc.), which emit in the blue spectral region [10] and have different fixed terminal groups. To excite these fluorophores, it is convenient to use the third harmonic of a Nd<sup>3+</sup>:YAG laser because the absorption bands of these compounds lie near the wavelength of this harmonic ( $\lambda = 355$  nm). Note that detection of nitroaromatic compounds was also performed using the PIM-1 polymer [11]. However, its absorption band lies at 425 nm, i.e., it is necessary to use for its excitation a parametric oscillator pumped by a Nd<sup>3+</sup>:YAG laser. This complicates the practical use of this polymer.

To compare the specific features of luminescence quenching of polyfluorenes on different substrates in the presence of nitrotoluene vapour, we additionally studied compounds widely used in organic electronics, namely, PVK (polyvinylcarbazole), which has a good sensitivity to nitrotoluene, and low-molecular electron-donor compounds TPD [N,N'-bis

Sh.T. Berdybaeva, E.N. Tel'minov, T.A. Solodova, E.N. Nikonova,  
L.G. Samsonova, T.N. Kopylova Tomsk State University, prosp.  
Lenina 36, 634050 Tomsk, Russia; e-mail: sheirn@mail.ru,  
telminov@ngs.ru

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(3-methylphenyl)-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine] and NPD [N,N-bis(naphthalene-1-yl)-N,N-bis(phenyl)benzidine]. The structures of the fluorophores are presented in Fig. 1. As an analyte, we used para-nitrotoluene (NT).

The spectral properties of compounds (electronic absorption and luminescence spectra) and the luminescence decay kinetics were studied using a CM2203 spectrophotometer (SOLAR).

As substrates for fluorophores, we used Sorbfil (Sf) plates for thin-film chromatography, methylcellulose (in the form of pellets), and polypropylene and viscose microfibrils knitted in the form of cloth. The two latter materials were used in [12] for developing sensor devices. To fabricate the samples, the compounds were dissolved in chloroform (concentration  $3 \times 10^{-3}$  M), after which 50  $\mu$ L of the solution were deposited onto prepared substrates and dried for 24 h at room temperature.

Luminescence quenching was studied by the following method: a small amount of analyte (NT) was placed on the bottom of a quartz cell  $1 \times 1$  mm in size, and the cell was covered by a lid and kept until the free space was saturated by analyte vapour. Then, the prepared sample with the sensor compound was promptly placed in the cell, and we immediately began to record the luminescence kinetics at the wavelength of the luminescence peak. The luminescence kinetics was recorded for 5 min.

To achieve sensor operation in the laser regime, it is necessary to provide distributed feedback (DFB) [11] or to use the waveguide regime [13]. The making of DFB in thin-film structures requires advanced technologies with the use of electron-beam lithography. The fabrication of planar waveguides is

less expensive, technologically simpler, and requires only two conditions, namely, the refractive index of the active layer ( $n_{al}$ ) should be higher than the substrate refractive index ( $n_{sub}$ ) and the air refractive index ( $n_{air}$ ), i.e.,

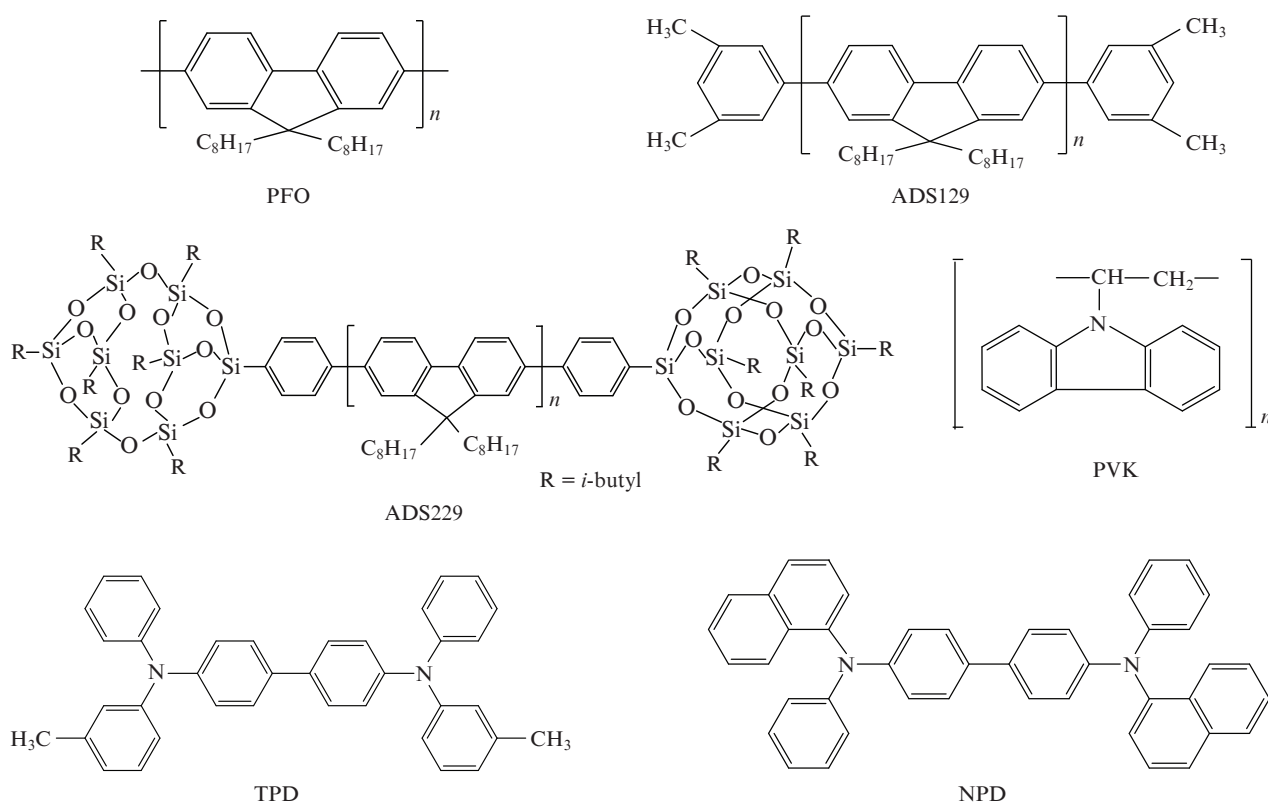
$$n_{al} > n_{sub}, \quad (1)$$

$$n_{al} > n_{air}. \quad (2)$$

In this case, the travelling wave regime is easily realised due to total internal reflection. It was previously demonstrated [14] that the deposition of an additional layer of hydrolysed tetraethoxysilane with the refractive index  $n = 1.44$  [15] has a positive effect (decreases lasing threshold and increases efficiency). In the present work, to improve the waveguiding properties of thin-film structures with ADS129 and ADS229 ( $n \approx 1.78$  [16]), we deposited a similar layer on the glass substrate ( $n = 1.5$ ), which additionally smoothed its surface.

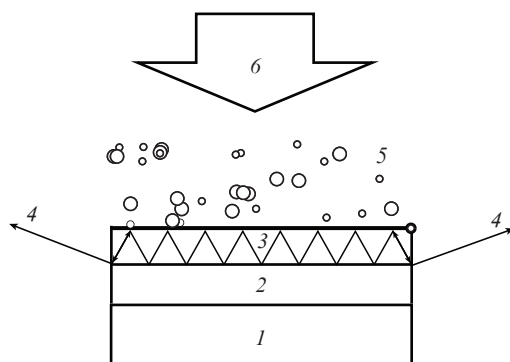
The simplest method of the formation of such thin-film structures is spin coating. To fabricate thin-film samples, the chosen fluorophores were dissolved in chloroform or toluene with a concentration of  $10^{-3}$  M, and the obtained solutions were deposited on microscope glasses, which were preliminarily coated with hydrolysed tetraethoxysilane by spin coating [14]. Thus, the studied thin-film samples had a three-layer structure consisting of a glass substrate, an additional layer improving the optical waveguiding properties, and a sensor polymer layer (Fig. 2).

To study the lasing characteristics, the sensor film was placed into a cell and blown with argon for 3 min. Next, we



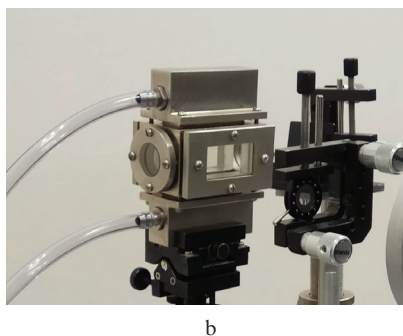
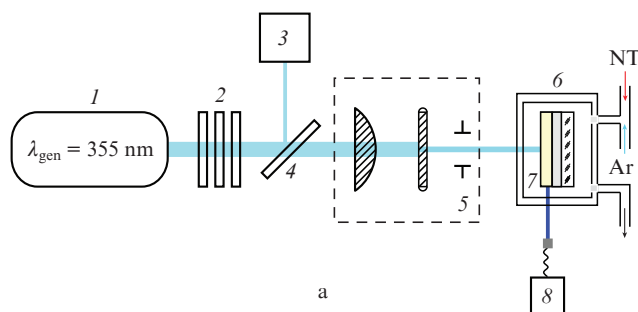
**Figure 1.** Molecular structures of fluorophores PFO, ADS129 and ADS229 polyfluorenes, PVK (polyvinylcarbazole), TPD [N,N'-bis(3-methylphenyl)-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine], and NPD [N,N-bis(naphthalene-1-yl)-N,N-bis(phenyl)benzidine].

measured the lasing spectrum of the sample and then added analyte vapour into the cell. The lasing intensity was measured for 30 s after adding NT vapours. The saturated nitrotoluene vapours were obtained by keeping NT powder in a closed vessel for 24 h at room temperature (295 K). The saturated vapour concentration was  $\sim 100$  ppbv [17].



**Figure 2.** Schematic of a laser integrated optical sensor: (1) transparent substrate; (2) adhesive layer; (3) laser-active medium; (4) output laser radiation; (5) air + analyte; (6) pump radiation.

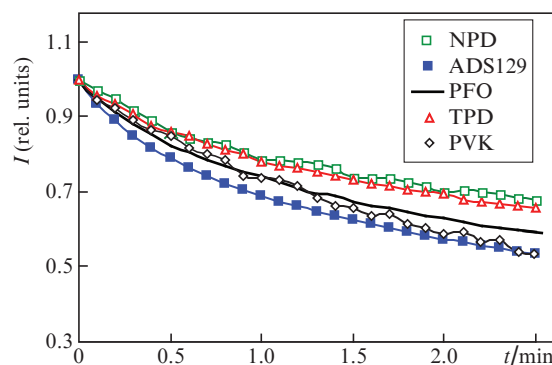
Figure 3 shows the scheme of the experimental setup used to measure the spectral-luminescent and lasing characteristics. The samples were pumped by the third harmonic of a  $\text{Nd}^{3+}$ :YAG laser, and the lasing spectra were measured using an AvaSpec-2048 spectrometer.



**Figure 3.** (a) Scheme of the setup for measuring the spectra-luminescent and lasing characteristics and (b) gas cell photograph: (1)  $\text{Nd}^{3+}$ :YAG laser ( $\lambda = 355$  nm); (2) system of non-selective light filters; (3) Gentec EO ED-100A-UV energy meter; (4) beam splitter; (5) pump beam-forming optical system; (6) gas cell; (7) thin-film sample under study; (8) AvaSpec-2048 spectrometer.

### 3. Results and discussion

The changes in the luminescence intensity of fluorophores deposited on Sf substrates under the action of NT vapours are shown in Fig. 4. Similar curves were obtained for substrates of other materials. The luminescence quenching efficiency determined as  $(1 - I/I_0) \times 100\%$ , where  $I$  and  $I_0$  are the luminescence intensities after the action of a quencher and at the initial instant, respectively, depend on the sensor nature. A sharp decrease in the luminescence intensity in NT vapours was observed for all studied fluorophores.



**Figure 4.** Luminescence kinetics of the studied fluorophores on Sf substrates under action of NT vapours.

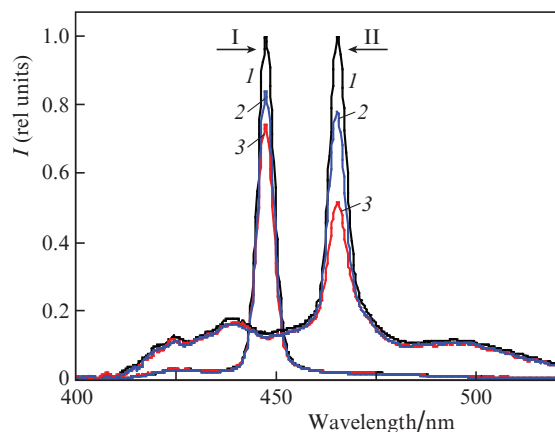
The experimental results are listed in Table 1. All fluorophores used in this work demonstrate a pronounced response to NT vapours. Concerning the substrate materials, the strongest effect among the four proposed types was observed in the case of Sf substrates.

**Table 1.** Luminescence quenching (%) of the studied samples on different substrates upon interaction with NT vapour for 2 min.

Fluoro-phore	Sf substrate	Polypropylene microfibres	Viscose microfibres	Methyl-cellulose
ADS129	43	14	25	31
PVK	41	9	19	19
PFO	37	19	17	19
NPD	30	15	30	7
TPD	30	9	21	14

The maximum (43%) efficiency of luminescence quenching by NT vapours for 2 min is demonstrated by ADS129 on the Sf substrate. The luminescence quenching efficiencies for the other fluorophores on the same substrate were also high and exceeded 30%.

Thus, the sensitivity to NT vapours is demonstrated by all studied organic fluorophores, in particular, with efficiencies of 30%–40% on Sf substrates, 20%–30% on the surface of viscose microfibres, 10%–20% on the surface of polypropylene microfibres, and 10%–30% on the surface of methylcellulose. The lasing spectra of ADS129 films in NT vapours are presented in Fig. 5. One can see that the lasing wavelength of the film formed in toluene solution is shifted to shorter wavelengths ( $\lambda_{\text{las}} = 447$  nm) with respect to the lasing wavelength of the film synthesised in chloroform solution ( $\lambda_{\text{las}} = 466$  nm), and the threshold pump radiation intensities in these cases are 200 and 80  $\text{kW cm}^{-2}$ , respectively.



**Figure 5.** Lasing spectra of ADS129 films on a glass substrate (I and II denote the films formed in toluene and chloroform solutions, respectively) (1) after blowing with argon, (2) after adding NT, and (3) after the second blowing with argon.

The sensitivity of the sensors was different. In the case of the ADS129 film formed in toluene solution, the lasing intensity under the action of analyte decreased by 25% with subsequent recovery to 84% (Fig. 5). The lasing intensity of the ADS129 sample synthesised in chloroform solution after the action of NT vapours was 50% of the initial value, while the recovered lasing intensity was 80% of the initial one. This decrease in the lasing intensity of the sample with ADS129 obtained in chloroform solution was recorded after 30-s action of NT, which is considerably shorter than 2 min used to study the luminescence of organic fluorophores deposited on different substrates, when the maximum luminescence quenching by NT vapours was 43%.

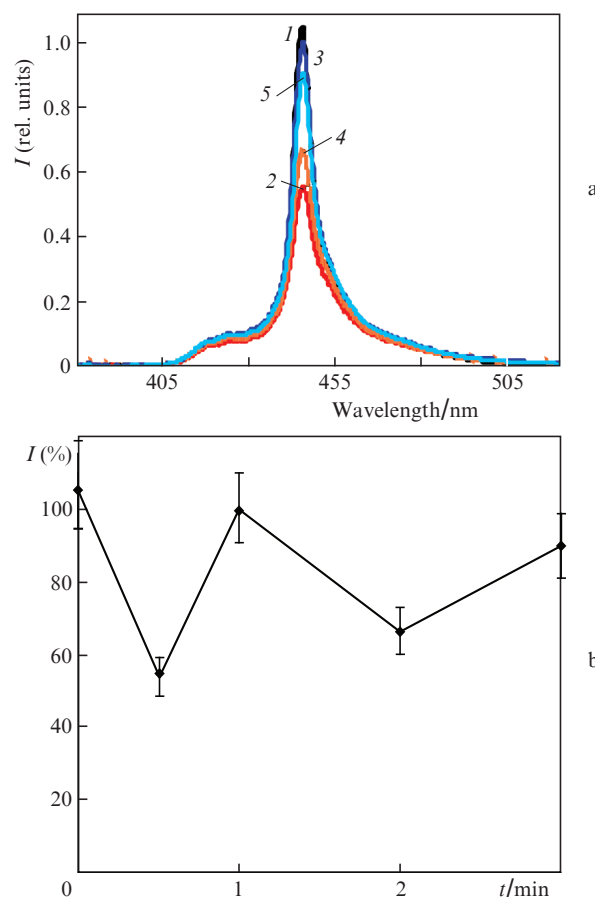
The wavelength of the maximum laser radiation intensity of the ADS229 polymer in the film obtained in toluene solution was 447 nm at a pump radiation intensity of  $140 \text{ kW cm}^{-2}$ . Figure 6 shows the relative recovery of the lasing intensity of the ADS229 film after its interaction with NT.

To study the recovery of films after the action of NT vapours, the cell was blown with argon for 1 min, after which the sensitivity of the samples was recovered. The lasing intensity decreased by 43% after the first addition of analyte in the cell with the film, and then was recovered to the initial value. After the second action of analyte vapours, the lasing intensity decreased to 66% and then was recovered to 90% of the initial level.

#### 4. Conclusions

We have studied the sensitivity of three polymers (ADS129, ADS229, and PVK) and two compounds of the phenylamine family to the presence of NT vapour. The sensitive materials were deposited on different substrates. In the spontaneous emission regime, all compounds demonstrated an intense sensor response to the presence of NT in the surrounding atmosphere. The strongest response was demonstrated by ADS129 on an Sf substrate (the fluorescence intensity decreased by 43% for 2 min).

A thin-film planar waveguide structure is formed and lasing is obtained in ADS129 and ADS229 polymer compounds under excitation by the third harmonic of a  $\text{Nd}^{3+}$ : YAG laser ( $\lambda = 335 \text{ nm}$ ). The ADS229 film sensitivity to NT vapours is studied in the lasing regime in the case of the repeated action



**Figure 6.** (a) Lasing spectra of ADS229 films formed in toluene solution after repeated blowing of the cell with argon and action of NT vapours: (1) ADS229 + Ar (first blow, 1 min), (2) ADS229 + NT (first action, 30 s), (3) ADS229 + Ar (second blow, 1 min), (4) ADS229 + NT (second action, 30 s), and (5) ADS229 + Ar (third blow, 1 min); (b) lasing intensity dynamics.

of NT vapour. The response time of the sensor in this regime (30 s) is considerably shorter than in the luminescence regime (2 min), while the decrease in the intensity of the spectra was 50 and 43%, respectively.

In this work, it is shown that a waveguide laser in a simple planar geometry with the use of an additional layer, which improves the optical waveguide properties, has a low lasing threshold and a fast response to the presence of NT. The active compounds are commercially available polyfluorenes and well absorb the third harmonic of  $\text{Nd}^{3+}$ : YAG lasers. In addition, the use of microscope glasses as substrates and the deposition of films by spin coating considerably reduce the cost of devices.

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