

# Influence of Processes of Photobleaching on Spectral Characteristics of Organic Nonlinear Optical Co-crystal 26DAP4N

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**Abstract:** In this paper, we used organic nonlinear optical materials based on 4-nitrophenol and 2,6-diaminopyridine co-crystals. The goal was to study the influence of photobleaching processes on spectral characteristics of mentioned co-crystals. We presented spectral characteristics of transmittance coefficients of material before photobleaching and after its exposure to light for 4 weeks. We also noted the breakdown of hydrogen bonds in a molecular complex of co-crystal under the influence of photobleaching. However, this breakdown does not lead to disruption of the integrity of the molecules that are a part of an aminopyridine-nitrophenol.

## 1 INTRODUCTION

Studies in the field of nonlinear optics are accompanied by constant search and implementation of new nonlinear optical materials with high values of nonlinear optical coefficients. In recent years in particular interest are molecular and polymeric nonlinear optical materials with high values of the nonlinear optical coefficients caused by high polarizability of molecules (Debrus, et al., 2002).

An example of such materials is prospective organic nonlinear optical co-crystals based on the aminopyridine series and optical chromophore 4-nitrophenol (Srinivasan, et al., 2007). These co-crystals possess noncentrosymmetric crystalline grid which leads to origin of nonlinear optical effects. This makes them interesting, first of all, for their potential uses as radiation transformers – generation of optical harmonics and generation of THz radiation. Early studies co-crystals of aminopyridine series showed that high enough values of nonlinear optical coefficients exist and that degradation of material under action of both an intensive laser radiation, and humidity (Pavlovetc, et al., 2016) (Krishnakumara, et al., 2012) (Draguta, et al., 2013) is absent. Results provided in operation (Zhevaikin, et al., 2018), show existence of considerable anisotropy of refraction indexes between crystallographic axes. That, in turn, brings to studies, provided in operations (Tu, et al 2016 (Esaulkov, et al., 2018) which show prospects

of use of these materials in terahertz area of radiation.

However, despite having promising nonlinear optical properties, these organic co-crystals have a flaw. They are brittle and require high complexity of machining. This therefore makes it necessary to search for another method of their processing in order to create elements on these co-crystals, as it is equally important. One of prospective methods is the use of degradation optical (and nonlinear optical) properties of crystals under the influence of active radiation. Structural changes created by directional radiation in certain sections of a crystal are nondestructive to the general integrity and allow to create miniature optical elements with high conversion factors of radiation (Mutter, et al., 2003). In this study we have researched stability of spectral characteristics of co-crystals of the aminopyridine series under the influence of optical radiation. Research of how radiation wavelength depends on intensity and time of illumination for degraded co-crystals will show a possibility of practical application of co-crystals. That will undoubtedly allow to expand a range of applied materials, and, therefore, an element basis of photonics in general.

## 2 MATERIALS AND METHODS

In this paper we have studied organic nonlinear optical co-crystals based on optical chromophores 4-nitrophen-

nol and 2,6-diaminopyridine. These co-crystals were synthesized and grown using a crystallization method of slow evaporation of solvent (Srinivasan, et al., 2007).

The co-crystals are named in the following way: 2,6-diaminopyridine-4-nitrophenol (2,6DAP4N). The structural formula of co-crystal is shown on Fig. 1.

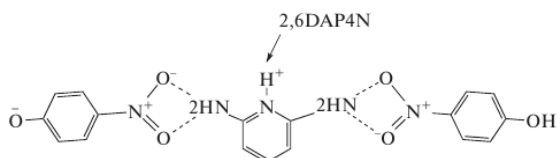


Figure 1: A structural formula of co-crystal 26DAP4N.

Studied LEDs have the following characteristics:

- 1) A red LED with wavelength of 625 nm, emissive power of 5 W and luminous flux of 400 lm;
- 2) A green LED with wavelength of 525 nm, emissive power of 5 W and luminous flux is 400 lm;
- 3) A UV-LED with wavelength of 405 nm, emissive power of 1 W and luminous intensity is 150 mcd.

We have used spectrophotometer Shimadzu UV-1800 to produce transmittance spectrums of studied co-crystals. To conduct a spectroscopic study in the IR area we have used an IR spectrometer Tensor 37 Bruker. The spectrometer was set to the range of 4000-600  $\text{cm}^{-1}$  with resolution of 2  $\text{cm}^{-1}$  and with averaging on 32 ranges using frustrated total internal reflection (FTIR).

In this study, we aimed to find out how photobleaching processes affect spectral characteristics of co-crystals transmittance coefficients. To do so we carried out experiences in the following fashion: we exposed 26DAP4N co-crystals to light of three LEDs that radiated different wavelengths. These wavelengths were red (625 nm), green (525 nm) and ultraviolet (405 nm). The way we have ensured the results of this study were consistent was by measuring transmittance spectrums of co-crystals before photobleaching and after, during the span of 4 weeks.

### 3 RESULTS AND DISCUSSIONS

The following is the summary of findings of this research. During the study, we have discovered that under the influence of light exposure all studied co-crystals had their transmittance spectrums lowered.

#### 3.1 UV-Spectroscopy of Co-crystals 26DAP4N

Photobleaching process for 26DAP4N co-crystals was done in a span of 4 weeks. We have used the following wavelength – 525 nm, 625 nm and 405 nm. Produced transmission spectrums are shown on Fig. 2 – Fig. 4.

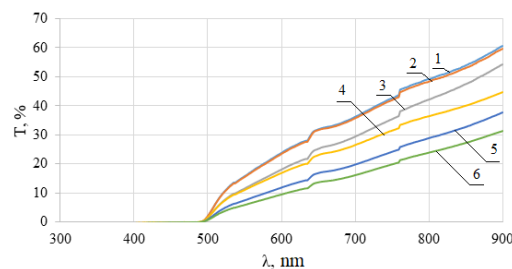


Figure 2: Transmittance spectrums of 26DAP4N co-crystals under exposure to light with wavelength of 525 nm. 1 – before photobleaching; 2 – photobleaching for 1 day; 3 – photobleaching for 1 week; 4 – photobleaching for 2 weeks; 5 – photobleaching for 3 weeks; 6 – photobleaching for 4 weeks.

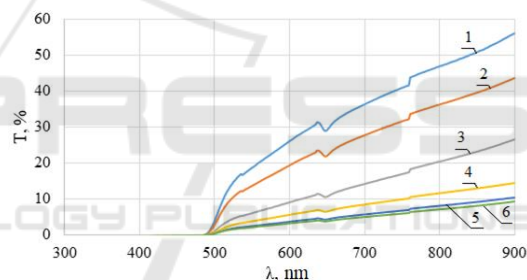


Figure 3: Transmission spectrums of 26DAP4N co-crystals under exposure to light with wavelength of 625 nm, where: 1 – before photobleaching; 2 – photobleaching for 1 day; 3 – photobleaching for 1 week; 4 – photobleaching for 2 weeks; 5 – photobleaching for 3 weeks; 6 – photobleaching for 4 weeks.

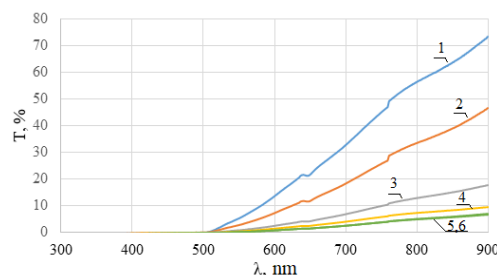


Figure 4: Transmission spectrums of 26DAP4N co-crystals under exposure to light with wavelength of 405 nm, where: 1 – before photobleaching; 2 – photobleaching for 1 day; 3 – photobleaching for 1 week; 4 – photobleaching for 2 weeks; 5 – photobleaching for 3 weeks; 6 – photobleaching for 4 weeks.

Spectral characteristics of transmittance coefficient demonstrate reduction of transmittance spectrums after photobleaching on all influencing wavelengths. On 625 nm (a red range) it decreased sharply from 56% to 9% on lengths of waves of 485-900 nm. On 525 nm (a green range) it fell from 60% to 31% on lengths of waves of 490-900 nm. On 405 nm (UV-range) it dropped from 73% to 7% on lengths of waves of 500-900 nm. Subsequently to long light exposure spectral characteristics reach the threshold values of photobleaching for this material, which is clearly visible for relations 5 and 6 (Fig. 4).

### 3.2 IR Spectroscopy of Co-crystals 26DAP4N

We have researched structural changes in 26DAP4N co-crystals under the influence of photobleaching using the IR method of spectroscopy. During IR-spectrometry we used nonphotobleached co-crystal 26DAP4N and photobleached co-crystal 26DAP4N exposed to wavelength 405 nm (UV-LED). Produced IR spectrums are shown on Fig. 5.

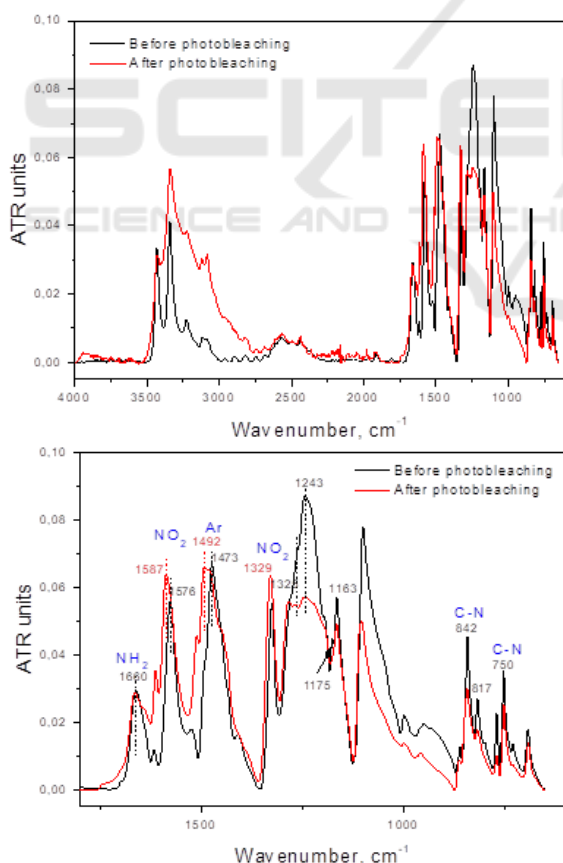


Figure 5: IR absorption spectrum of co-crystals 26DAP4N when illumination on wavelength of 405 nm.

During photobleaching of co-crystals the change in ranges is generally linked to the absorption bands connected to nitrogroup 4-nitrobenzole and an aminogroup 2,6-diaminopyridine. Bending vibrations of N-H in the  $C_{Ar}-NH_2$  group 2,6-diaminopyridine do not change the state after being exposed to light. Absorption bands of C-N bonds in the  $C_{Ar}-NO_2$  group also do not change their state. However, in symmetric and asymmetric stretching of N-O bonds in the  $C_{Ar}-NO_2$  group absorption bands shift as a result of light exposure. This means that bonds containing nitrogroup are involved in co-crystal formation and that these bonds break after being exposed to light. The most significant changes happen in composite band of  $1243\text{ cm}^{-1}$ , which includes bending of C-N bands in an aromatic ring, bending vibrations of C-N bands in  $C_{Ar}-NH_2$  and C-O-H phenolic group. It suggests that C-N bands in  $C_{Ar}-NH_2$  participate in formation of co-crystal, forming a band between  $NH_2$  and  $NO_2$  groups, which breaks as a result of light exposure. Therefore, during the process of light exposure molecular complex of aminopyridine-nitrophenol breaks down.

In addition, the contrast between exposed and not exposed areas (Fig. 6) is seen. This demonstrates structural changes in volume of co-crystal.

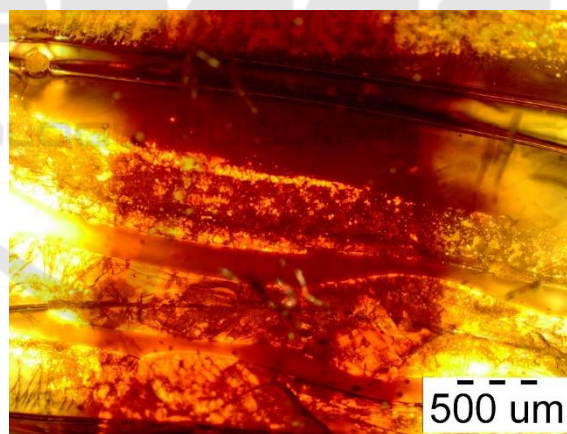


Figure 6: Micrograph of co-crystal 26DAP4N after photobleaching.

### 3.3 Spectral Characteristics of Solutions of Co-crystals 26DAP4N

We studied molecular integrity of aminopyridine-nitrophenol complex. In order to carry out this analysis we used photobleached and on nonphotobleached co-crystals 26DAP4N. We took exposed and not exposed to light co-crystals and dissolved them in isopropanol. Then we used spectrophotometer to study the spectrums of acquired

solutions. Characteristics of transmittance coefficients of solutions are shown on Fig. 7. Also, on Fig. 8 shown spectral characteristics of the components that are a part of a molecular complex aminopyridine-nitrophenol: 2,6 – aminopyridine (26DAP); 4 nitrophenol (4N - optical chromophore).

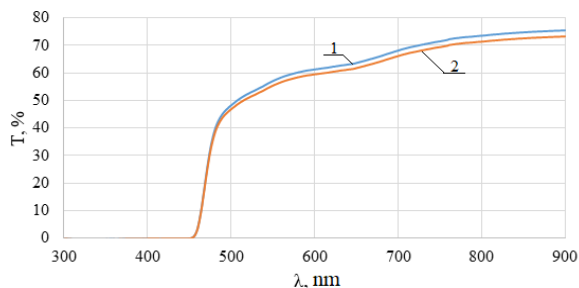


Figure 7: Transmission spectrums of solutions of co-crystals 26DAP4N: 1 – solution not lit co-crystal; 2 – solution lit co-crystal.

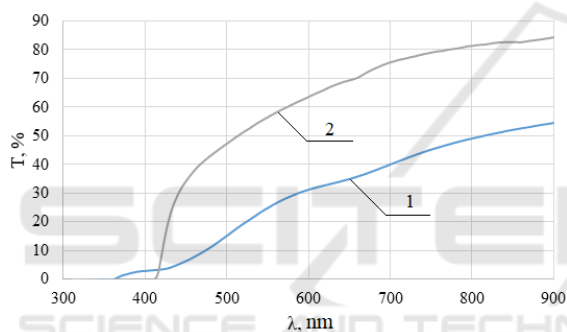


Figure 8: Transmission spectrums of the solutions forming a complex aminopyridine-nitrophenol: 1 – component 26DAP solution; 2 – component 4N solution (optical chromophore).

Transmittance spectrums of exposed and not exposed to light co-crystals demonstrate that during photobleaching of a molecule 2,6-diaminopyridine and 4-nitrophenol internal complex did not fail (the difference in spectral characteristics of components of co-crystals before and after exposure was minimal).

## 4 CONCLUSIONS

We studied the influence of photobleaching processes on spectral characteristics of organic nonlinear optical co-crystals of an aminopyridine series (2,6-diaminopyridine-4-nitrophenol). The main focus of the study was to investigate the influence of active light emission on mentioned co-crystals on the following wavelengths: 625 nm (red range); 525 nm

(green range); 405 nm (UV range). We have noted significant decrease in values of transmittance coefficients for co-crystals 26DAP4N with spectral characteristics reaching the threshold values of photobleaching for this material.

During IR-spectroscopy we discovered that hydrogen bonds in co-crystals breakdown under the influence of photobleaching, which leads to structural changes and violation of integrity of an aminopyridine-nitrophenol molecular complex.

Additionally we analysed the integrity of the molecules that are composing aminopyridine-nitrophenol molecule complex and confirmed that during light exposure the initial molecules do not break.

The results of this research aim to study stability of nonlinear properties of co-crystals that is necessary for practical application of these co-crystals in devices of nonlinear optics and photonics.

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