

LETTER

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Photobleaching of nonlinear organic co-crystals 2,6-diaminopyridine-4nitrophenol-4-nitrophenolate

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Abstract

The processes occurring during photobleaching of a new nonlinear optical co-crystal 2,6-diaminopyridine-4-nitrophenol-4 nitrophenolate are investigated. Using infrared spectroscopy of co-crystals, destruction of an aminopyridine-nitrophenol molecular complex by photoactinic radiation without breakage of aminopyridine and nitrophenol molecules integrity is shown. Differential scanning calorimetry and thermogravimetric analysis of the co-crystals showed a decrease in temperature of transitions of exposed co-crystals due to structural changes. Intensities of the second harmonic of the co-crystals under study were measured before and after photoactinic exposure; the results showed the decrease in the intensities of the second harmonic during prolonged illumination due to the structural changes in volume of the co-crystals confirming the breakage of the aminopyridine-nitrophenol molecular complex with preservance of the integrity of the molecules forming the molecular complex. Methods of terahertz absorption spectroscopy showed changes in absorption and a refractive index of a co-crystal in the range of 0.3-2.5 THz after the exposure to the photoactinic radiation, which can be interpreted as a result of destruction of the crystal structure. All the results obtained clearly showed that a co-crystal structure is disordered and the aminopyridine-nitrophenol bond is broken on the exposure to the photoactinic radiation, while the molecules of both components do not collapse, which leads mainly to disappearance of nonlinear optical properties. The investigated process is suitable for creating nonlinear optical lattices in the co-crystals using the photolithography method.

Keywords: molecular co-crystals, aminopyridine, photodegradation, IR spectroscopy, thermochemical analysis, second-harmonic generation

(Some figures may appear in colour only in the online journal)

1. Introduction

The rapid development of photonics, optoelectronics and related fields of science and technology require constant search for nonlinear-optical materials with high non-linear-optical parameters and resistance to influence of external aggressive environment.

Inorganic nonlinear optical materials (KTiOPO₄, KD₂PO₄, LiNbO₃, etc) has become widespread today due to their resistance to high-intensity laser radiation, but polymer and organic

nonlinear optical materials are also becoming increasingly popular to investigate because of having a number of advantages: high values of nonlinear optical coefficients and low dielectric constant values due to high polarizability of molecules [1]. So, co-crystals based on organic salt of 4-nitrophenol and compounds of aminopyridine series are of great interest [2, 3].

This study is a continuation of a cycle of works [4] dedicated to influence of photodegradation processes on spectral and nonlinear optical characteristics of organic nonlinear optical co-crystals based on aminopyridine-nitrophenol. Early studies have shown the resistance of these materials to high-intensity laser radiation [5], as well as relevance of their use in a terahertz (THz) technique [6, 7]. However, despite promising nonlinear optical properties, the investigated organic co-crystals have a serious drawback: high complexity of machining due to fragility of these materials; therefore, it is practically important to search for a method of their processing to create elements on these cocrystals. One of the promising methods is the use of degradation of the optical (and nonlinear-optical) properties of the co-crystals when exposed to active radiation. Structural changes being made in certain parts of the co-crystal by directional radiation and being non-destructive to overall integrity allow us to create miniature optical elements with high conversion factors [8, 9].

The purpose of this work is to conduct a comprehensive study on the effect of the photodegradation processes on organic nonlinear optical co-crystals 26DAP4N which includes the following: IR and THz—spectrometry; thermal analyzes (thermogravimetric analysis (TG) and differential scanning calorimetry (DSC)); measurement of the second-harmonic generation intensities. The results obtained during the work will show the prospects of using the photodegradation method to create optical structures, in particular, creation of periodic arrays and waveguide structures based on co-crystal data. The results of the THz spectroscopy of 26DAP4N crystals will demonstrate a perspective for their use in THz photonics applications.

2. Used materials and research methods

2,6-diaminopyridine-4-nitrophenol-4 nitrophenolate co-crystals were synthesized and grown by crystallization with slow evaporation of the solvent. The method and conditions for growth of the co-crystals are described in our previous articles [5]. Initial components for crystals are 2,6-diaminopyridine (Aldrich, 141-86-6) and 4-nitrophenol (Aldrich, 100-02-7).

Photobleaching was carried out using UV LED with the following exposure parameters: a distance from the LED to the sample was 16mm; a radiation wavelength of 405 nm; radiation power was 1 W; illumination—617 lx.

Microphotographs of the co-crystals were performed on an Olympus STM6 instrument microscope.

Spectroscopic studies in infrared region were carried out on a Bruker Tensor 37 IR spectrometer in the range of $4000-600 \,\mathrm{cm^{-1}}$ with resolution of $2 \,\mathrm{cm^{-1}}$ with averaging over 32 spectra using an impaired internal reflection attachment (ATR).

The research of thermal stability of the organic co-crystals during the prolonged illumination was done with the use of the following:

- a thermogravimetric (TG) analyzer TG 209 F1 Libra NETZSCH in the temperature range from 25 °C to 900 °C with a heating rate of 10 °C min⁻¹ in an inert gas 40 ml min⁻¹;
- a universal differential scanning calorimeter DSC 204 F1 Phoenix from NETZSCH in the temperature range from 60 °C to 180 °C with a heating rate of 10 °C min⁻¹ in a nitrogenous medium with a flow rate of 40 ml min⁻¹.

To study the changes in the intensities of the second optical harmonic (SHG) in the process of the prolonged illumination, a solid-state pulsed (Nd: YAG) laser LF117 (a radiation wavelength of 1064 nm; pulse duration of 15 ns; pulse repetition frequency of 10 Hz) was used, the radiation of which was focused on the co-crystal fixed in a rotary movement. An installation diagram and detailed description are given in the article published earlier [5]; the measurements were carried out with rotation of a movable stand with the sample with a rotation step of 15° .

To investigate the absorption spectra in the THz range, a time-domain THz spectrometer was used. The circuit and its detailed description are presented in the previous work [10]. An important advantage of such a spectrometer is possibility of registering an amplitude and a phase spectrum of a THz field passed simultaneously. Amplitudes of incident and transmitted fields were determined from the measured time profiles of the incident THz pulse and the THz pulse transmitted through the sample. Subsequent Fourier transform was used for the calculation of dielectric characteristics of the crystal under study.

To generate THz pulses in the spectrometer, the surface of a low temperature GaAs semiconductor was chosen; for electro-optical detection a $\langle 1\,1\,0\rangle$ ZnTe crystal with thickness of 0.3 mm was used. The complex spectrum was calculated using the Fourier transform of the time profile of the THz pulse. Such spectrum contains information about a refractive index and an absorption coefficient of the medium. Taking the thickness of the crystal under study into consideration, its optical density and the refractive index were determined in the THz range. The selected combination of a source and a receiver for the THz radiation provided registration of the spectra in the range from 0.3 to 2.5 THz.

3. Experimental results and discussion

In this paper, we consider the effect of the photodegradation processes on molecular nonlinear optical co-crystals of the aminopyridine series (26DAP4N). As shown in our work [4], the optical characteristics of the crystal change under the action of photoactinic radiation with conservation of integrity of the crystal. At the same time, for the crystals with the thickness of up to 2 mm, a decrease in optical transmittance occurs within 2–3 weeks, followed by stabilization of the properties.



Figure 1. Micrograph of the 26DAP4N co-crystals after 28 d of the exposure to light in a polarized reflection mode.



Figure 2. The intensity of generation of the second harmonic at the angle of rotation; in the inset is the co-crystal 26DAP4N.

Micrographs of the 26DAP4N co-crystals after the prolonged illumination (28 d) are shown in figure 1.

3.1. Second harmonic generation of the 26DAP4N co-crystals

Due to the fact that the observed aminopyridine-nitrophenol copolymers have high nonlinear susceptibility coefficients, a study of the degradation of the nonlinear optical properties (the second harmonic generation intensity) with the exposure to the photoactinic radiation was conducted. For the study we used the LF117Nd: YAG laser (the wavelength of 1064 nm), the radiation of which was focused on the 26DAP4N cocrystal fixed in a rotary slide. The second-harmonic radiation at a wavelength of 532 nm was detected by a photodetector when the co-crystal was rotated 360 in increments of 15°. The co-crystal was exposed to photoactinic radiation with the wavelength of 405 nm; the measurements were taken before the exposure, after 1 d, after 1 week, after 1 month (figure 2). The results obtained showed the decrease in the intensity of generation of the second harmonic under the action of the photoactinic radiation, and the results obtained after 7 d and 28 d also confirm stabilization of the changes in the properties of the co-crystal.

Thus, under the influence of the photoactinic radiation on the co-crystals of the aminopyridine series, the nonlinear-optical characteristics of the co-crystals degrade.



Figure 3. IR absorption spectra of the 26DAP4N co-crystals with light at 405 nm [4].

Previously, to quantify the NLO response the comparison of the samples of aminopyridine co-crystals with KTP crystal was made. Taking into account the thickness of the crystals, the relative SHG efficiency of co-crystal 26DAP4N is found to be greater than that of KTP ($d(26DAP4N) = 21 \text{ pm V}^{-1}$; $d(\text{KTP}) = 13.7 \text{ pm V}^{-1})$ [5].

3.2. IR spectroscopy of the 26DAP4N co-crystals

To study the structural changes in the co-crystals of 26DAP4N under the action of photobleaching, these materials were examined by IR spectroscopy. An uncooled co-crystal of 26DAP4N and the co-crystal of 26DAP4N illuminated at the wavelength of 405 nm (UV-LED) for 28 d were used in conducting the IR spectroscopy. The most significant changes in the spectra are presented in figure 3 (Reproduced with permission from Proceedings of PHOTOPTICS 2019. Copyright 2019, SciTePress Digital Library). Corresponding structural areas are described in table 1.

In the process of photobleaching of the co-crystals, the changes in the spectra mainly concern absorption bands associated with a nitro group of 4-nitrophenol and an amino group of 2,6-diaminopyridine (table 1).

This suggests that the C–N bonds in C_{Ar} –NH₂ involved in co-crystal formation, forming a bond between the –NH₂ and –NO₂ groups, are destroyed during the exposure. In the process of the exposure to light, the molecular complex aminopyridine-nitrophenol is destroyed. However, the results of the work [4] showed that during the exposure to light, the molecules that form the molecular complex retain their integrity, which means that during the photodegradation the molecular complex is destroyed with preservation of the integrity of the molecules that form it.

3.3. TG analysis of the co-crystals 26DAP4N

Initially, thermal stability of the organic co-crystals was studied on a TG 209 F1 Libra NETZSCH TG analyzer. TG curves

Wavenumber, cm ⁻¹	Assigment	Change
1660	νNH_2 of aminopiridine	Does not change
1576	ν N–O in C _{Ar} –NO ₂	Shifts to $1587 \mathrm{cm}^{-1}$ after exposure
1473	$C_{ m Ar}$	Shifts to 1492 cm ⁻¹ after exposure
1325	$\delta C-N$ in $C_{Ar}-NO_2$	Shifts to $1329 \mathrm{cm}^{-1}$ after exposure
1243	δ C–H in the aromatic ring, δ C–N in C _{Ar} –NH ₂ , C–OH in nitrophenol	Intensity decreases
1163	-C-N amino group aminopyridine	Shifts at 1175 cm ⁻¹ after exposure
1100	-C-O-H nitrophenol	Intensity decreases
850, 817	δC –N in C _{Ar} –NO ₂	Intensity decreases
750	δ C–N in aminopyridine	Intensity decreases

Table 1. The main changes in the spectrum of the crystal 26DAP4N in the process of the light exposure.



Figure 4. TG curves of the co-crystal 26DAP4N in the process of photobleaching.

obtained before and after the prolonged exposure to light are presented in figure 4.

The research has shown that the thermal stability of these co-crystals varies in the temperature range from 175.8 °C to 191.6 °C, and the most stable (the beginning of the degradation temperature is 191.6 °C) is the unilluminated co-crystal. The thermal stability of the co-crystal illuminated within 1 d drops sharply to 187.8 °C and reaches a stable level, but then, after 2 weeks, continues to decrease to the level of the co-crystal exposed to light during 1 month. The decrease in evaporation temperature of the material during the exposure to light confirms the presence of structural changes in the volume of the co-crystal, which are most likely to be the destruction of hydrogen bonds, resulting into the destruction of the aminopyridine-nitrophenol molecular complex. For a more detailed study of the structural changes in the volume of the co-crystal during the exposure process, the thermal stability analysis was performed using the method of differential scanning calorimetry (DSC).

3.4. DSC of the 26DAP4N co-crystals

Further, to study the structural changes in the co-crystal volume as a result of the photodegradation, phase transitions were considered during heating. The thermal stability of the organic co-crystals was studied on a DSC 204 F1 Phoenix universal differential scanning calorimeter. DSC curves obtained



Figure 5. DSC curves of the 26DAP4N co-crystal in the process of photobleaching.

before and after the prolonged exposure to light are presented in figure 5.

The study revealed that the melting point of these co-crystals varies in the temperature range from 154.5 °C to 152.2 °C, and the most stable (the beginning of the melting point is 154.5 °C) is the unilluminated co-crystal. The photodegradation introduces the special effect in the first 2 weeks of the exposure to light reaching the stable level subsequently (the difference in the melting temperatures of the exposed cocrystals for 1 week and 1 month is 0.1 °C). According to the data presented previously [3, 7], the melting temperature of the 26DAP4N co-crystal is approximately 150 °C, while the decrease in the first-order phase transition temperature (the melting temperature) indicates the destruction of the aminopyridine-nitrophenol molecular complex. This observation also confirms the decrease in a peak area (heat of fusion) during the exposure to light which undoubtedly appears to be the destruction of the molecular bonds forming the aminopyridine-nitrophenol complex.

3.5. THz spectroscopy of the 26DAP4N co-crystals

To assess the prospects for using the studied co-crystals in THz photonics problems, we studied the absorption spectra of experimental samples in the frequency range from 0.3 to 2.5 THz. Spectral dependence of the optical density and the refractive index of the 26DAP4N co-crystal before and after



Figure 6. THz spectra of the optical density and the refractive index of the 26DAP4N co-crystal before and after the exposure to the photoactinic radiation.

the exposure to photoactinic radiation is shown in figure 6. The optical density of the co-crystal under study at the frequency of 1 THz is 20 cm^{-1} (in comparison with a DAST crystal $\alpha = 100 \text{ cm}^{-1}$ at the frequency of 1 THz using to generate the THz radiation [11]). After photobleaching, the THz absorption of the crystal increases, which can be caused by the destruction of the hydrogen bonds of the aminopyridine-nitrophenol molecular complex, which was already discussed when considering the thermal stability of the crystals.

The figure 6 depicts that the refractive index increases markedly after photobleaching. This suggests that the co-crystals of the 26DAP4N aminopyridine series can be used in the THz applications that require formation of periodic structures, for example, by the exposure to the photoactinic radiation.

4. Conclusion

As a result of the comprehensive study of the effects of the photoactinic radiation on the 2,6-diaminopyridine-4-nitrophenol-4 nitrophenolate co-crystal, which has the nonlinear optical properties, nature of this process has been determined. So, by infrared spectroscopy of the co-crystals, the destruction of the aminopyridine-nitrophenol molecular complex without integrity damage of the aminopyridine and nitrophenol molecules is shown. The DSC and the TG analysis of the cocrystals showed the decrease in the temperature of transitions of the exposed co-crystals due to the structural changes. The method of measuring the generation of the second harmonic shows the decrease in the second-order nonlinear-optical coefficient, confirming the destruction of the aminopyridine-nitrophenol molecular complex with preserving the integrity of the molecules forming the molecular complex. The methods of the terahertz absorption spectroscopy showed the change in the absorption and the refractive index of the co-crystal in the range of 0.5-2.5 THz, which can be interpreted as a result of the destruction of the crystal structure and the appearance of free molecules in the crystal.

Based on the analysis of the obtained changes in the cocrystal with retaining its external integrity and transparency, we assumed the following nature of the observed effect: under the action of photoactinic radiation on the co-crystal, the aminopyridine-nitrophenol bond is broken and the crystal structure is disordered, while the molecules of both components are not destroyed. The observed effect mainly leads to disappearance of the nonlinear-optical properties with a slight change in other parameters. The investigated process is suitable for creating nonlinear optical lattices in the co-crystal by photolithography with the exposure of the photoactinic radiation through a mask. As a result, a lattice is formed with a periodic modulation of the nonlinear second-order coefficient and the absence of the modulation of other parameters. Such lattices are suitable for laser wavelength conversion in the quasi-phase matching mode and are of great practical importance.

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