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Synthesis, crystal growth, thermal and spectroscopic studies of acentric materials constructed from aminopyridines and 4-nitrophenol

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ABSTRACT

A series of single co-crystals of non-centrosymmetric complexes of different mono- and diaminopyridines, namely 4-aminopyridine, 3,4-diaminopyridine, 2-amino-6-methylpyridine, 2,6-diaminopyridine, 2-aminopyridine, with 4-nitrophenol were grown by slow evaporation technique from solution at constant temperature. Optical transparency in the region of 300–1100 nm was found to be suitable for nonlinear optical applications with cut off wavelengths at 420–474 nm for these co-crystals. Single crystal X-ray analysis confirms the non-centrosymmetric packing. Thermogravimetric and differential thermal analysis shows good thermal stability of the studied compounds with melting point at range 99–172 °C for different co-crystals. The second harmonic generation efficiency has been measured on single crystals by comparative SHG technique relative to KTP crystal. The nonlinear optical coefficient of the compounds was found to be up to 39 pm/V.

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1. Introduction

During last years, organic nonlinear optical materials with high second-order nonlinear susceptibilities has found some applications in electro-optical devices such as optical waveguides or frequency modulators [1]. Three classes of electro-optical (EO) materials are used today: inorganic crystals (e.g., LiNbO₃), polymers or dendrimers doped with electro-optical dye molecules, and organic crystals with large EO coefficients [2,3]. Among organic crystals mostly well known is 4-N,N-dimethylamino-4'-N'-methylstilbazolium tosylate (DAST), especially interesting material for nonlinear optical (NLO) device applications due to its large EO coefficient and a low dielectric constant ($\epsilon=5.2$), giving rise to a high modulator figure of merit and thermal stability up to 250 °C [4]. According to data in [5], DAST exhibits the second-order NLO susceptibility $X^2=2020 \pm 220$ pm/V at $\lambda=1318$ nm and the electro-optical figure of merit $n^3 r_{11}=(530 \pm 60)$ pm/V at $\lambda=1313$ nm.

Large disadvantage of DAST NLO crystals is their low stability under laser action and moisture. Absorption edge in 560 nm and high absorbance at 532 nm [6] do not allow to use DAST for second harmonic generation of Nd:YAG laser.

New class of organic non-linear materials-aminopyridine-nitrophenol based co-crystals- does not have some disadvantages of DAST. In case of second order nonlinear optical applications creation of crystalline materials requires to orient donor-acceptor chromophores in non-centrosymmetric lattice [7]. To obtain non-centrosymmetric packing, heterocyclic molecules of different aminopyridines were co-crystallized with NLO chromophore 4-nitrophenol (4N). Aminopyridine complexes are well-known series of compounds [8–12] with good optical properties, thermal stability [10–12], and suitability for optoelectronic devices. 4-Nitrophenol is a classic dipolar NLO chromophore, and the possibility of proton transfer of the phenolic OH of 4-nitrophenol to various organic bases results in increasing of its molecular hyperpolarizability [8,13].

In comparison to well know NLO crystals MNA, DAST, COANP, new aminopyridine-nitrophenol complexes have advantage of absence of hygroscopicity and good optical threshold for laser power. First publication of crystal structures of some of this co-crystals was presented by Prakash et al. [8].

In the presented communication, we continue our previous studies in field of NLO crystals including DAST [14] and different NLO molecular co-crystals [13,15,16].

We report here single crystal growth process, X-ray studies, optical, thermal and SHG properties including first time non-linear

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second order coefficient measurements of a series of co-crystals of non-centrosymmetric complexes: 4-aminopyridine-4-nitrophenol-4-nitrophenolate, 3,4-diaminopyridine-4-nitrophenol-4-nitrophenolate, 2-amino-6-methylpyridine-4-nitrophenol-4-nitrophenolate, 2,6-diaminopyridine-4-nitrophenol-4-nitrophenolate and 2-aminopyridine-4-nitrophenol-4-nitrophenolate.

2. Experimental

2.1. Synthesis and crystal growth

All initial reagents (Fig. 1) were obtained commercially and used without further purification. Crystals were grown by slow evaporation technique at a fixed temperature. This technique is widely used by several groups of scientists [8–12,17–19]. We followed the synthetic procedure of co-crystals production with 4-nitrophenol that was published by Prakash et al. [8]. A ethanol solution of 4-nitrophenol was added to a ethanol solution of each N-base (4-aminopyridine; 3,4-diaminopyridine; 2-amino-6-methylpyridine; 2,6-diaminopyridine; 2-aminopyridine). Reagents has been taken in molar ratio 2:1.

2.2. Preparation of 4-aminopyridine-4-nitrophenol-4-nitrophenolate (4AP4N)

4-nitrophenol (0.926 g, 6.66 mmol) was dissolved in 100 ml of ethanol; 4-aminopyridine (0.313 g, 3.33 mmol) was dissolved in 33 ml of ethanol and then mixed. The mixture of solutions has yellowish color.

2.3. Preparation of 3,4-diaminopyridine-4-nitrophenol-4-nitrophenolate (34DAP4N)

4-nitrophenol (0.926 g, 6.66 mmol) was dissolved in 100 ml of ethanol; 3,4-diaminopyridine (0.363 g, 3.33 mmol) was dissolved in 36 ml of ethanol and then mixed. The mixture of solutions has yellow/brown color.

2.4. Preparation of 2-amino-6-methylpyridine-4-nitrophenol-4-nitrophenolate (26MAP4N)

4-nitrophenol (0.926 g, 6.66 mmol) was dissolved in 100 ml of ethanol; 2-amino-6-methylpyridine (0.360 g, 3.33 mmol) was dissolved in 36 ml of ethanol and then mixed. The mixture of solutions has yellowish color.

2.5. Preparation of 2,6-diaminopyridine-4-nitrophenol-4-

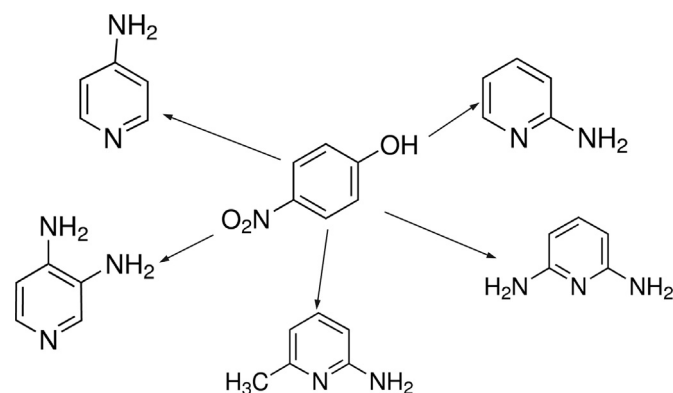


Fig. 1. Structural formulas of initial reagents.

nitrophenolate (26DAP4N)

4-nitrophenol (0.926 g, 6.66 mmol) was dissolved in 100 ml of ethanol; 2,6-diaminopyridine (0.363 g, 3.33 mmol) was dissolved in 36 ml of ethanol and then mixed. The mixture of solutions has yellow/brown color.

2.6. Preparation of 2-aminopyridine-4-nitrophenol-4-nitrophenolate (2AP4N)

4-nitrophenol (0.926 g, 6.66 mmol) was dissolved in 100 ml of ethanol; 2-aminopyridine (0.313 g, 3.33 mmol) was dissolved in 34 ml of ethanol and then mixed. The mixture of solutions has yellow color.

The mixture of solutions was stirred at room temperature for 1 h using magnetic stirrer. Continuous stirring ensured that obtained mixture of solutions is homogeneous. High purification level of synthesized compound was achieved by successive recrystallization of obtained crystals in the same solvent. The solution was filtered by funnel with quartz cells of micron size. A glass vessel with synthesized clear solution was covered with pores filter paper and placed into the thermostat at 25 °C for slow evaporation of the ethanol. After 15–30 days, the solutions were evaporated and the crystals were grown (Fig. 2). Five co-crystals of 4-nitrophenol with different aminopyridines were grown successfully with dimensional sizes up to centimeters, namely 4AP4N, 34DAP4N, 26MAP4N, 26DAP4N, and 2AP4N.

2.7. X-ray diffraction

Data collection for single crystal X-ray diffraction analysis of this complex was collected by Bruker-AXS SMART APEX II CCD diffractometer with monochromatized Mo K α radiation ($\lambda=0.71073$ Å) and obtained results completely corresponds to published earlier [13]. The CCDC numbers for the deposit CIF files are 886323, 886324 and 886327.

2.8. UV-Vis

The UV-vis-NIR spectra of these crystals were recorded with Shimadzu UV-1800 spectrophotometer in the range 190–1100 nm and the recorded spectra are shown in Fig.3.

2.9. Thermal characteristics studies

The thermogravimetric and differential thermal analysis of the crystal samples was carried out using Thermo Gravimetry/Differential Thermal Analyzer(TG/DTA) HITACHI STA7200. Samples were weighted in an Al₂O₃ pans with a microprocessor driven temperature controller. TGA and DTA curves of the crystals were recorded in nitrogen atmosphere between ambient temperatures and 350 °C.

3. Results and discussion

3.1. Single crystal X-ray diffraction analysis

Single crystal X-ray diffraction study confirms the unit cell parameters of the grown aminopyridines-4-nitrophenol co-crystals as it was published earlier [13]. The acentricity is the most characteristic feature of the five reported pyridine compounds. Two of them (4AP4N; 34DAP4N) crystallize in the polar P2₁ space group, which allows a maximum contribution to the molecular optical nonlinearity and three compounds (26MAP4N; 2AP4N and 26DAP4N) crystallizes in acentric orthorhombic Pna2₁ space

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