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Growth and characterization of L-histidinium – 4-nitrobenzoate (1:1) multi-component molecular complex

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ABSTRACT

A novel phase by reaction of L-histidine with 4-nitrobenzoic acid (4NBA) was obtained by solvent assisted grinding (SAG). The complex was crystallized from aqueous solution and characterized by X-ray powder diffraction (XRPD), single-crystal X-ray diffraction (SCXRD), infrared spectroscopy (FTIR) and thermal analysis (DSC/TGA). Additionally, the non-linear optical (NLO) properties were assessed for second harmonic generation (SHG). XRPD confirmed that a new phase was obtained, and this can be obtained pure from solution. However, when the complex appeared in SAG experiments, it was always in equilibrium with the precursors. The crystal structure of the complex revealed that a proton transfer took place from the carboxylic acid group of 4NBA to the unprotonated nitrogen atom in the imidazole ring of L-histidine to yield L-histidinium – 4-nitrobenzoate (LH4NBE) molecular complex. The FTIR spectroscopy depicted accurately the molecular characteristics of LH4NBE and the thermal analysis showed that it is stable up to 190 °C. Unfortunately, the complex displayed poor NLO properties and the sample suffered damage upon laser excitation.

1. Introduction

Nowadays there is considerable interest in designing molecular complexes, which can display large NLO susceptibilities. Organic compounds are the target to develop these NLO materials, considering that some of these compounds display characteristics such as highly polarizable electronic clouds and an asymmetric electronic distribution [1]. Furthermore, there is an inherent impact on the NLO properties of these molecules induced by changes in their molecular structure [2–4]. Among the wide range of available materials for this purpose, the amino acids have proved to be good candidates to develop NLO molecular complexes by combination with inorganic salts [5–10].

For example, glycine and L-alanine have produced hybrid semi-organic materials by combination with sodium nitrate [11,12]. Specially, glycine-sodium nitrate (GSN) has been widely studied because of its relatively good NLO [13–16] and ferroelectric properties [17]. In terms of its NLO properties, it was reported that GSN displayed SHG efficiency two times larger than the observed in the standard KDP [13]. L-histidine has also formed hybrid NLO materials by combination with HBF_4 [18], HCl, HBr, HF, H_2CO_4 [19], HNO_3 [20] and H_2SO_4 [21] to give some examples. Among the amino acid based materials, recent investigations showed evidence of formation of new molecular complexes by combination with nitrobenzene derivatives [22,23]. What is more, these materials showed good NLO performance, for example, L-histidinium 2-nitrobenzoate displayed SHG efficiency two times than KDP values [22] and L-arginine 4-nitrobenzoate monohydrate showed SHG efficiency four times than that of KDP [23].

In the search for potential NLO compounds, we decided to

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perform solvent assisted grinding (SAG) experiments of the amino acid L-histidine with 4-nitrobenzoic acid in (1:1) molar ratio. The IR spectrum of the sample L-histidine – 4-nitrobenzoic acid 1:1 M suggested that a new phase was produced. LH4NBE was then characterized by XRPD, SCXRD, infrared (FTIR) spectroscopy, TGA/DSC thermal analysis and SHG experiment. Although, the material displayed relatively good thermal stability, its SHG efficiency was poor and displayed damage upon laser exposure.

2. Materials and methods

2.1. Synthesis

L-histidine (≥99% pure) and 4-nitrobenzoic acid (≥98% pure) were purchased from Sigma–Aldrich and used without further recrystallization. The initial samples were prepared by the SAG technique using double distilled water and commercial solvents (chloroform, DMSO, ethanol and acetone). The procedure to prepare the samples was as follows: L-histidine (0.1552 g, 1 mmol) with 4-nitrobenzoic acid (0.1672 g, 1 mmol) in a 1:1 M ratio were placed in a mortar adding 50 μL of double-distilled water or the solvent to assist the mechanical grinding. The samples were grinded manually for 10 min.

The samples were initially characterized by FTIR to look for changes in the IR spectra (see Figs. S1–S5 in the supplementary material). Apparently, the IR spectra of the sample L-histidine – 4-nitrobenzoic acid 1:1 M from water and ethanol suggested that a new phase was obtained. The samples were then characterized by XRPD to confirm the presence of the new crystalline form. To obtain suitable samples for SCXRD, we decided to set up a crystallization experiment in solution. A mixture of L-histidine (1.552 g, 10 mmol) and 4-nitrobenzoic acid (1.672 g, 10 mmol) in a 1:1 M ratio was grinded in a mortar. Then, the mixture was placed in a vessel and double distilled water was added until the sample was completely dissolved. The solution was left to evaporate at room temperature. Suitable single crystals for SCXRD experiments were obtained after a week.

2.2. Characterization

The IR spectra were recorded using a PerkinElmer UATR Spectrum Two in the range of 3500 to 500 cm^{-1}. The spectra were recorded in the solid-state.

The XRPD experiments were carried out on a Bruker D8 Advance diffractometer equipped with a LYNXEYE Super speed detector, using Ni-filtered CuK$_\alpha$ radiation. The equipment was operated at 40 kV and 30 mA and, generally, the XRPD patterns were acquired from 5° to 50° 2θ with a step size of 0.033° during 3 s.

SCXRD experiment was performed on a Bruker D8 QUEST diffractometer system equipped with a Multiyaler mirrors monochromator and a Cu K$_\alpha$ Microfocus sealed tube $\lambda = 1.54178$ Å). Frames were collected at $T = 300$ K via ω/ϕ-scans. The measured intensities were reduced to F^2 and corrected for absorption with SADABS (SAINT-NT) [24]. Structure solution was carried out using SHELXT V2014/4 [25] and refinement on F^2 and data output were carried out with the SHELXL-2014/7 [25] within the WinGX program package [26]. Non-hydrogen atoms were refined anisotropically. C–H, C–H$_2$ and N–H$_3$ hydrogen atoms were placed in geometrically calculated positions using the riding model. N–H hydrogen atoms have been located from iterative examination of difference Fourier maps following least squares refinements $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{N})$. The crystal structure analysis was performed using Platon [27] and Mercury 3.1 software [28]. Crystallographic data for the crystal structure was deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-1409158.

Thermal analysis was carried out on a TA Instruments STD Q600 using simultaneous differential thermal and thermo-gravimetric analysis (DTA-TGA) mode. Approximately 8.775 mg of sample was used and analysed in the temperature range of 30–550 °C at a heating rate of 15 °C/min using argon flow rate of 50 mL/min.

The SHG experiment was performed by the Kurtz-Perry technique [29]. The sample was packed between two transparent glass slides. The SHG signal was obtained by irradiating the sample with a Quanta ray INDI series pulsed laser beam of Nd:YAG (1064 nm). The length of the pulses was 8 ns at 56 mJ/pulse and 10 Hz. The SHG output signal was analysed with a Jobin-Yvon monochromator Triax320 and detected with a HORIBA-Jobin Yvon i-Spectrum Two ICCD.

3. Results and discussion

From the SAG experiments, it was noticed that when LH4NBE was formed, it was always in equilibrium with the precursors. At the moment, it is not possible to obtain pure LH4NBE from SAG experiments in our laboratory. However, crystallization from solutions allowed us to obtain good quality crystals for a full characterization of the complex.

3.1. FTIR spectroscopy

Fig. 1 displays the infrared spectra of the phase LH4NBE obtained from solution and the precursors 4NBA and L-histidine.

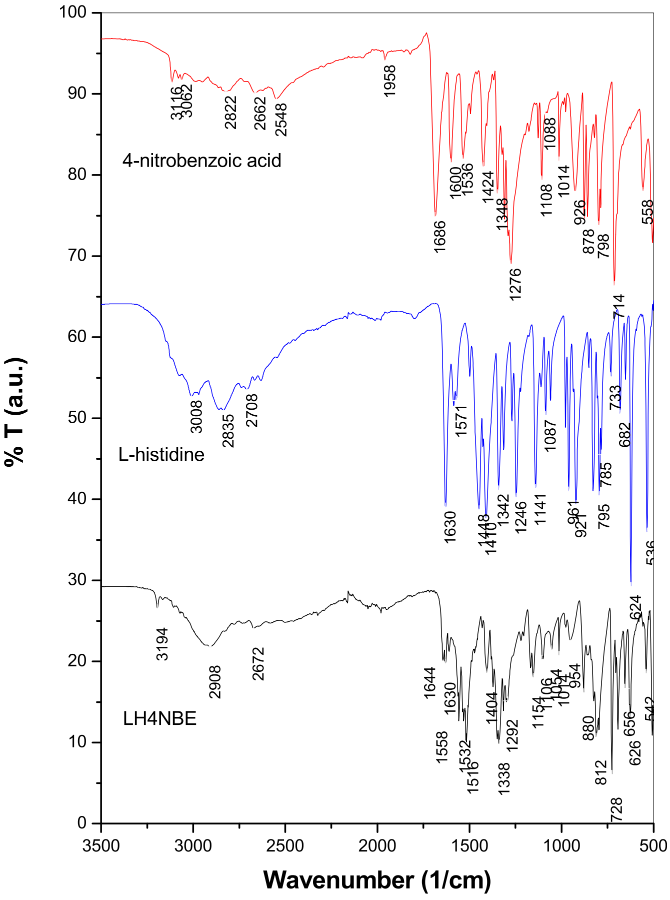

Fig. 1. IR spectra of 4-nitrobenzoic acid (red), L-histidine (blue) and LH4NBE (black). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)