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Synthesis, crystal structure, vibrational spectra, optical properties and theoretical investigation of a two-dimensional self-assembled organic-inorganic hybrid material

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ABSTRACT

Organic–inorganic hybrid material of formula $(C_4H_3SC_2H_4NH_3)_2[PbI_4]$ was synthesized and studied by X-ray diffraction, Infrared absorption, Raman scattering, UV–Visible absorption and photoluminescence measurements. The molecule crystallizes as an organic–inorganic two-dimensional (2D) structure built up from infinite PbI_6 octahedra surrounded by organic cations. Such a structure may be regarded as quantum wells system in which the inorganic layers act as semiconductor wells and the organic cations act as insulator barriers. Room temperature IR and Raman spectra were recorded in the 520–3500 and 10–3500 cm^{-1} frequency range, respectively. Optical absorption measurements performed on thin films of $(C_4H_3SC_2H_4NH_3)_2[PbI_4]$ revealed three distinct bands at 2.4, 2.66 and 3.25 eV. We also report DFT calculations of the electric dipole moments (μ), polarizability (α), the static first hyperpolarizability (β) and HOMO–LUMO analysis of the title compound investigated by GAUSSIAN 09 package. The calculated static first Hyperpolarizability is equal to 11.46×10^{-31} esu.

1. Introduction

Nonlinear optical (NLO) materials have recently attracted a lot of attention due to their potential applications in optoelectronic technologies [1–5]. The development of photonic and optoelectronic technologies rely heavily on the growth of NLO materials with high non-linear optical responses and the development of novel and more efficient materials [6]. To date, some inorganic NLO materials such as KDP and KTP have been exclusively used in electro optic devices [7–9]. In past two decades, organic NLO materials have been an intense research because their chemical flexibility and variety of synthetic strategies. Recently, the search for new NLO materials has included hybrid organic-inorganic compounds due to their advantages over traditional organic and inorganic compounds [10–12]. These NLO hybrid materials are of special interest for their capability in offering important opportunities to combine the useful properties of inorganic materials (good electrical mobility, mechanical and thermal stability, band gap tunability and magnetic or dielectric transitions) and organic materials (structural diversity, ease of processing, high NLO coefficients and efficient luminescence) and within a single molecular scale composite [11,13]. With the guidance of this theory, many hybrid organic–inorganic materials with good NLO effect have been designed and synthesized [14,15]. (2-thiophene) ethyl ammonium tetraiodoplumbate (TEPI) belongs to this large organic inorganic NLO family.

Our last published paper has been devoted to optical studies of TEPI [16]. As an extension of our searches for exploring new properties concerning organic inorganic materials, we report in this paper, the growth, structural characterization, vibrational spectra investigation, optical properties (UV–visible and photoluminescence) as well as the theoretical study of the nonlinear optical properties of the TEPI by Density Functional Theory (DFT) calculations.

2. Experimental

2.1. Preparation

The single crystals of $(C_4H_3SC_2H_4NH_3)_2[PbI_4]$, abbreviated as TEPI, were grown by the slow evaporation of a solution containing lead iodide and $(C_6H_{10}NS)I$ salts, at room temperature. An aqueous solution of HI and (2-thiophene) ethylamine was prepared to

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synthesize $(C_6H_{10}NS)I$ precursor. Under ambient conditions, stoichiometric amounts of $(C_4H_3SC_2H_4NH_3)I$ and PbI_2 with excess of HI were mixed in DMF solvent. The mixture was stirred till becoming clear then kept to evaporate. After 4 weeks of evaporation, plate crystals are formed. The purity of the solution is improved by a second re-crystallization.

2.2. X-ray data collection

A single crystal of about 0.4 mm × 0.2 mm × 0.02 mm was selected for the diffraction experiments. The X-ray data collection was carried out on an Enraf-Nonius C4DDA four circles diffractometer using Mo Kα radiation (λ = 0.71073 Å) at 293 K. The crystal structure was solved by the direct method and refined by the full matrix least-square technique using the SHELXL-2013 crystallographic software package [17]. The basic crystallographic data and the details of the measurements and refinements are summarized in Table 1. Supplementary crystallographic data for this article in CIF format are available as Electronic Supplementary Publication from Cambridge Crystallographic Data Centre (CCDC 1043214). This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (international): +44 1223/336 033; e-mail: deposit@ccdc.cam.ac.uk).

2.3. Spectroscopic measurements

The Fourier transform infrared (FT-IR) spectrum of TEPI is recorded in the range 520–3500 cm^{-1} using PERKIN–ELMER FT-IR spectrometer. The resolution of the spectrum is ±2 cm^{-1}.

The Raman spectrum is recorded using Horiba Jobin-Yvon Lab-RAM HR 800 Dual Spec-trophotometer. The excitation line was the 632.8 nm from a Helium–Neon laser. Thin films of $(C_4H_3SC_2H_4NH_3)_2[PbI_4]$ were grown on a quartz substrate by spin coating at 2000 rpm and for 20 s duration. The crystals were first dissolved in DMF solution. Then optical absorption spectra of the films were measured at room temperature using a conventional UV–vis absorption spectrometer (Hitachi, U-3300).

The room temperature photoluminescence spectrum was recorded using a JOBIN YVON HR 320 spectrometer and exciting with 350 nm radiation.

2.4. Computational details

The molecular geometry optimization and vibrational wavenumbers calculations of TEPI was performed by DFT method using the Gaussian 09 package [18]. The Becke three-parameter hybrid exchange functional and the Lee–Yang–Parr correlation functional (B3LYP) were utilized in the calculation with the LANL2DZ basis set. The Los Alamos National Laboratory basis sets, known as LANL2DZ and developed by Hay and Wadt, [19] have been widely used in quantum chemistry, particularly in the study of clusters containing heavy elements [20]. In order to take into account the effect of intermolecular interactions on geometrical parameters and vibrational spectroscopy, we have considered the cluster built up from one anion (Pb_2I_{11}) and two cations $(C_6H_{10}SN)$ linked by N–H···I hydrogen bonds. All the parameters were allowed to relax and all the calculations converged to an optimized geometry which corresponds to a true energy minimum revealed by the lack of imaginary values in the wavenumbers calculations.

It is well known that the nonlinear optical response of an isolated molecule in an electric field $E_i(\omega)$ can be presented as a Taylor series expansion of the total dipole moment, μ, induced by the field:

$$\mu = \mu_0 + \alpha_{ij}E_j + \beta_{ijk}E_jE_k + \cdots$$

where α is the linear polarizability, μ_0 is the permanent dipole moment and β_{ijk} are the first hyperpolarizability tensor components. The isotropic linear polarizability is defined as:

$$\alpha = \frac{1}{3}\left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right)$$

The first hyperpolarizability β was calculated using B3LYP/LanL2DZ basis set. The components of the first hyperpolarizability can be calculated using the following equation

$$\beta_i = \beta_{iii} + \frac{1}{3}\sum\left(\beta_{ijj} + \beta_{jij} + \beta_{jji}\right), \quad (i \neq j)$$

Using the x, y and z components, the magnitude of the first hyperpolarizability tensor can be calculated by

$$\beta = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2}$$

The complete equation for calculating the magnitude of the first hyperpolarizability from Gaussian 03 output is given as follows

$$\beta_{tot} = \left(\beta_{xxx} + \beta_{xyy} + \beta_{xzz}\right)^2 + \left(\beta_{yyy} + \beta_{yzz} + \beta_{yxx}\right)^2 + \left(\beta_{zzz} + \beta_{zxx} + \beta_{zyy}\right)^2$$

Since these β values of GAUSSIAN09 are reported in atomic units (a.u.), the calculated β_{tot} values were converted into electrostatic units (esu) (1 a.u. = 8.6393 × 10^{-33} esu).

Table 1
Crystal data and structural refinement for $(C_6H_{10}NS)_2[PbI_4]$.

Crystal data	Details
Empirical formula	$(C_6H_{10}NS)_2PbI_4$
Formula weight	1942.44
Crystal system	Monoclinic
Space group	Cc
a	12.2840 (8) Å
b	12.3250 (9) Å
c	31.381 (3) Å
α	90°
β	90.972 (5)°
γ	90°
Volume	4750.4 (6) $Å^3$
Z	4
$Density_{calc}$	2.82 g cm^{-1}
Crystal color	Yellow
R_{int}	0.0541
R_1	0.0443

3. Results and discussion

3.1. Crystallographic study

From the single crystal X-ray diffraction analysis, the title compound, $(C_4H_3SC_2H_4NH_3)_2[PbI_4]$ crystallizes as monoclinic system in Cc space group, with a unit cell of dimensions: a = 12.2840(8) Å, b = 12.3250(9) Å, c = 31.381(3) Å, β = 90.972 (5) and Z = 4.

The results are in good agreement with those found by Pradeesh [21]. The ORTEP plot (30% probability ellipsoids) with atoms being labeled and thermal ellipsoid for $(C_4H_3SC_2H_4NH_3)_2[PbI_4]$ is shown in Fig. 1a. The optimized geometry of the title compound is given in Fig. 1b. The computed structural parameters combined with experimental data are listed in Table 2. The selected bond angles are