Materials Chemistry and Physics 139 (2013) 1–7

Contents lists available at SciVerse ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Materials science communication

Optical, thermal and microhardness studies on dichloridobis(1-ethyl-2, 6-dimethylpyridinium-4-olate-κO) zinc(II)

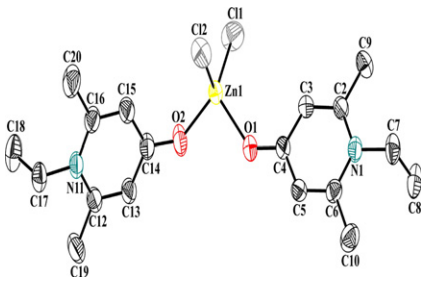
A. Philominal [a], S. Dhanuskodi [a,*], J. Philip [b]

[a] School of Physics, Bharathidasan University, Tiruchirappalli 620 024, India
[b] Sophisticated Test and Instrumentation Centre, Cochin University of Science and Technology, Cochin 682 022, India

HIGHLIGHTS

- A metal–organic coordination compound was designed and synthesized.
- The introduction of a metal improves the optical and thermal stability of the crystal.
- EDMPZC is a potential candidate for the fabrication of selected opto-electronic devices.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 7 April 2011
Received in revised form
11 October 2012
Accepted 1 November 2012

Keywords:
A. Optical materials
B. Crystal growth
C. DSC
Differential thermal analysis (DTA)
D. Crystal structure
D. Optical properties

PACS:
42.70 Mp
61.66 Hq
78.20. −e
78.30.-j

ABSTRACT

A newly engineered host–guest hydrogen bonded metal–organic coordination compound, dichloridobis(1-ethyl-2,6-dimethylpyridinium-4-olate-κO)zinc(II) (EDMPZC), $[C_{18}H_{26}Cl_2N_2O_2Zn]$ has been designed and synthesized. Single crystals of dimensions ($5 \times 5 \times 2$ mm^3) have been grown by slow evaporation technique. The unit cell dimensions and morphology are identified from single crystal XRD analysis. Further, it has been characterized by FT-IR absorption, FT-NMR spectroscopy, elemental analyses (CHN and XRF) and their thermal stability investigated following TG/DTA and DSC techniques. The thermal transport properties, thermal effusivity (e), thermal diffusivity (α), thermal conductivity (K) and heat capacity (C_p) have been measured by the photopyroelectric technique at room temperature. The laser damage threshold of the grown crystal was measured using Q-switched Nd:YAG laser (1064 nm, 10 ns, 10 Hz). The mechanical stability of the crystal has been studied from the Vicker's microhardness measurement. The UV absorption edge is 262 nm with a wide optical transmittance window covering the UV–Vis–NIR region and the optical band gap of the compound is found to be 3.5 eV.

1. Introduction

Extensive research in the field of nonlinear optics has revealed that metal–organic coordination compounds possess a higher degree of optical nonlinearity than their inorganic counterparts. From the technological point of view, inherent high nonlinearity, synthetic flexibility and scope to alter their properties by functional substitutions make these materials highly attractive [1–3]. Recent success in the design and synthesis of novel materials based on metal–organic coordination networks has prompted researchers to examine solids by exploiting the strong and highly directional metal–ligand coordination bonds. The coordination bonds can be

* Corresponding author. Tel.: +91 431 2407057; fax: +91 431 2407045.
E-mail address: dhanus2k3@yahoo.com (S. Dhanuskodi).

0254-0584/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.matchemphys.2012.11.003

utilized to counteract unfavourable centrosymmetric intermolecular interactions in the solid state [4,5]. One such molecule is 1-ethyl-2, 6-dimethyl-4(1H) pyridinone trihydrate (EDMP), which exhibits quadratic nonlinear optical (NLO) properties, in particular second harmonic generation (SHG) down to the UV region [6,7]. In the case of metal–organic coordination complexes, particularly group IIB metals in the periodic table are extensively chosen as their compounds usually have high transparency in the UV region because of their closed d^{10} shell [8]. In general, crystals of the type $M[tu]_2X_2$, where M = Cd, Co, Hg, Pb, Ti and Zn, tu is thiourea and X is a halogen have been found to exhibit good NLO properties. Thiourea crystallizes in centrosymmetric Pbnm space group and SHG inactive. The first reported complex type NLO crystal BTCC (bisthiourea cadmium chloride) with the space group of $Pmn2_1$ is optically negative, transparent from 300 to 1450 nm and has the SHG efficiency almost the same as that of urea. Also thiourea forms a number of other coordination compounds, tristhiourea zinc sulphate (ZTS) [9] and bisthiourea zinc chloride (BTZC) [10] are some of the potentially useful materials for frequency doubling of the NIR laser radiation and single crystals of these materials have very high laser damage threshold. Phthalocyanines (Pcs) are widely investigated organic compounds for many high-technology applications, such as nonlinear optics, photoconductivity, electrochromic and electroluminescent displays, photovoltaic cells, low-dimensional conductors, chemical sensors, optical data storage, recordable compact discs (CDs) and digital versatile discs (DVDs), Langmuir–Blodgett films, liquid crystals, photodynamic cancer therapy, rectifying devices, and others. Among these applications, third-order optical nonlinearities are of main interest due to their highly delocalized π-electron systems giving rise to strong nonlinearities, ultrafast response times, and tremendous structural flexibility. The optical limiting behaviour of organometallic phthalocyanine in solution has been observed using a laser with the pulse duration ranging from picoseconds to nanoseconds. The strong reverse saturation absorption (RSA) (optical limiting) which has been observed with high-peak-power, short-pulse lasers in Pt-phthalocyanine solutions can also be observed at low intensity with continuous-wave lasers. Optical switching based on the RSA is demonstrated. The RSA can be applied in designing photonic devices, for example optical limiting, optical modulations, optical bistable devices and other logic gates [11]. In the present work a metal–organic coordination compound dichloridobis(1-ethyl-2,6-dimethylpyridinium-4-olate-κO) zinc(II) (EDMPZC) has been synthesized and its structural, thermal, mechanical and optical properties have been investigated and the results are discussed.

2. Experimental

2.1. Material synthesis

1-Ethyl-2, 6-dimethyl-4(1H)-pyridinone trihydrate (EDMP) was synthesized from dehydroacetic acid (E-Merck: synthesis grade > 90%) by allowing the reaction with 70% aqueous ethylamine as reported elsewhere [6,12]. EDMPZC was synthesized by reacting EDMP and $ZnCl_2$ in the molar ratio 2:1 in an aqueous solution at 30 °C and it was further purified by the repeated recrystallization process [13].

2.2. Solubility and crystal growth

Solubility test is a key to select a suitable solvent and temperature to grow good quality single crystals. The EDMPZC solution was prepared with double distilled water at 30 °C, with continuous stirring to ensure homogeneity in temperature and concentration over the entire volume of the solution. On reaching saturation the contents of the solution were analyzed gravimetrically and this process was repeated for every 5 °C for water and water–ethanol (1:1) mixture in the temperature range 30–55 °C. It was found that it exhibited a positive temperature gradient in water. Saturated solution of EDMPZC in double distilled water was prepared at 30 °C and good quality single crystals of dimensions 5 × 5 × 2 mm^3 were harvested after a period of three weeks following slow evaporation technique (Fig. 2a).

3. Results and discussion

3.1. CHN analysis

The percentage composition of the elements, C, H, N present in the compounds EDMP [7] and EDMPZC was determined by CHN elemental analysis in an Elementar Systeme Model Vario EL III instrument and Zn by X-ray fluorescence technique. The observed (computed) values for the percentage composition of the elements C, H, N in EDMP were C = 52.23 (52.67), H = 10.61 (9.33), N = 6.59 (6.82), and in EDMPZC were C = 38.39 (35.38), H = 4.96 (4.95), N = 5.03 (4.60), Zn = 22.41 (21.40). It is evident that there is a good agreement between the measured and the computed values confirming the formation of the new compound.

3.2. FT-IR spectral studies

FT-IR spectroscopy was used to identify the functional groups of the synthesized compound and hence to elucidate its molecular structure [14]. FT-IR spectrum was recorded in the range 400–4000 cm^{-1} using a JASCO 460 PLUS FT-IR spectrometer following the KBr pellet technique (Table 1).

Due to the introduction of metal ($ZnCl_2$) into the EDMP entity, an overall shift can be observed in their characteristic vibrational frequencies. In EDMPZC the H-bonded, O–H stretching frequency shows a broad band at 3429 cm^{-1} at a molecular level. The fundamental vibrational mode at frequency 2976 cm^{-1} is due to the C–H stretching of the aromatic ring and the first overtone is identified at 1558 cm^{-1}, whereas EDMP shows these at 3000 cm^{-1} and 1549 cm^{-1} respectively. The C–H bending deformations in in-plane and out of plane are observed at 1479 cm^{-1} and 729 cm^{-1} respectively. The C–H of CH_3 bending is observed at 1373 cm^{-1} and 1336 cm^{-1} for EDMPZC. The Zn–O bond is observed at 452 cm^{-1}. The values of the other functional group frequencies for EDMPZC and EDMP are also listed in Table 1.

Table 1
Comparison of FT-IR vibrational frequencies of EDMPZC with EDMP.

Wave number (cm^{-1})		Assignment
EDMP [7]	EDMPZC	
3390–3185	3429	υ (O–H) H-bonded
3000	2976	υ (C–H)
1631	1624	υ (C=O)
1549	1558	υ (C–H), overtone
1525	1508	υ (C=C)
1455	1479	δ (C–H)
1375, 1338	1373, 1336	δ (C–H of CH_3)
1198, 1183	1195, 1181	υ (C–N) or ρ(C–H)
1034	1032	υ (C–N)
881, 848	869, 842	π (C–H)
697	729	π (C–H)
494	502	π (C=O)
–	452	υ (Zn–O)

υ – Stretching, δ – bending deformation in plane.
ρ – Rocking in plane, π – bending out of plane.