Journal of Molecular Structure 1035 (2013) 483–492

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Structure

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

Spectral, crystal structure, thermal and antimicrobial characterisation of an organic charge transfer complex-3,5-dimethylpyrrazolinium picrate

T. Dhanabal [a], G. Amirthaganesan [a,*], M. Dhandapani [a], Samar K. Das [b]

[a] Department of Chemistry, Sri Ramakrishna Mission Vidyalaya College of Arts and Science, Coimbatore 641 020, Tamil Nadu, India
[b] School of Chemistry, University of Hyderabad, Hyderabad 500 046, Andhra Pradesh, India

HIGHLIGHTS

- The complex, 3,5-dimethylpyrrazolinium picrate was grown by slow evaporation method.
- The thermal stability of the complex indicates that it was stable up to 140 °C.
- The complex exhibited good antibacterial and antifungal activities.
- The nonlinear optical property of the complex was studied.

ARTICLE INFO

Article history:
Received 2 October 2012
Received in revised form 4 November 2012
Accepted 4 November 2012
Available online 23 November 2012

Keywords:
Crystal growth
Growth from solution
Infrared spectroscopy
Thermogravimetric analysis
Crystal structure
Optical materials

ABSTRACT

A novel organic charge transfer complex, 3,5-dimethylpyrrazolinium picrate was grown and crystallized by slow evaporation solution growth method at room temperature. The absorption of the grown crystal was studied using UV–visible spectral analysis and observed that the crystal possesses minimum absorption between 250 and 900 nm. The lower cut-off wavelength and the optical transmittance window were identified by optical transmittance study. The emission spectrum of the complex shows peaks at 505 and 758 nm are due to the green and red fluorescence emissions respectively. The thermogravimetry–differential thermal analyses (TG–DTA) were used to investigate the thermal stability of the complex. The single crystal X-ray diffraction method indicates that the complex crystallizes in monoclinic system with space group $P2_{(1)}/c$. The FTIR and polarised Raman spectra were used to confirm the presence of various functional groups. The different kinds of protons and carbons were assigned through NMR (^{1}H and ^{13}C) spectroscopic techniques. The nonlinear optical property (NLO) of the material was studied by modified Kurtz–Perry powder technique. The complex exhibits good antibacterial and antifungal activities against various bacteria and fungi species.

1. Introduction

Charge transfer complexes play a central role in bioelectrical and biological systems such as bactericides, fungicides, insecticides and various light-driven physical and chemical processes [1–4]. The charge transfer interaction of organic complexes were used in different pharmaceuticals [5,6], micro-emulsion [7] and also as organic semiconductors [8]. Organic nonlinear optical materials (NLO) have attracted attention in the recent years due to their high nonlinear efficiencies equivalent to those of inorganic materials [9,10]. Picric acid derivatives are used in human therapy such as treatment of burns, antiseptic and astringent agent [11]. Generally, SHG requires that a material should have noncentrosymmetric structure that give rise to large second order NLO susceptibility. The packing arrangements of materials must also be noncentrosymmetric unless a magnetic dipole [12–14] or an electric quadrapole [15] contributes to the bulk susceptibility. Nonlinear optical properties in dipolar molecular complexes arise from intramolecular charge transfer [16,17]. It has also been established that hydrogen bonds play a vital role in governing NLO property [18–21]. Various addition complexes were prepared using different heterocyclic nitrogen complexes with picric acid that exhibit NLO properties due to hydrogen bonding and π–π interactions [22,23]. Picric acid derivatives are interesting candidates, because of the presence of phenolic OH favours the formation of salts with various organic bases. Due to the formation of conjugated base, picrate, the value of molecular hyperpolarisability increased because of the proton transfer [24]. On the basis of these facts, in this present work, we describe the synthesis and characterisation of 3,5-dimethylpyrrazolinium picrate crystal (hereafter abbreviated as DMPP). Characterisation of the grown crystals were made by UV–visible absorption,

* Corresponding author. Tel.: +91 9442002233; fax: +91 422 2693812.
E-mail address: profga@yahoo.co.in (G. Amirthaganesan).

0022-2860/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.molstruc.2012.11.004

optical transmittance, band gap energy, emission analysis, TG–DTA, single crystal X-ray diffraction, FTIR, polarised Raman and NMR spectroscopic techniques. The NLO property and antimicrobial activity of the complex were also studied.

2. Experimental details

2.1. Materials

Analytical grades of 3,5-dimethylpyrrazole and picric acid were obtained from Sigma Aldrich and used without further purification. The solvent, methanol used is HPLC grade.

2.2. Synthesis of DMPP crystals

Single crystals of DMPP were grown by slow evaporation solution growth method at room temperature. One mole of 3,5-dimethylpyrrazole and one mole of picric acid reacted to form DMPP crystals. Methanolic solutions containing analytical grades of one mole of each of the substance were prepared separately. The two solutions were mixed together and stirred well for about 6 h to get a homogeneous solution using a mechanical stirrer and the resulting solution was filtered into a clean dry beaker through a Whatman 40 filter paper. The beaker was covered by an ordinary filter paper. The filtrate was kept in dust-free environment for crystallization. Care was taken to minimise the temperature gradient and mechanical shack.

Under the experimental conditions bright, transparent and yellow coloured DMPP crystals were obtained within 10–15 days with average dimension of $0.6 \times 0.3 \times 0.2$ cm^3. The grown crystals were collected from the mother liquid by using well cleaned forceps. The formation of DMPP crystal is shown in Scheme 1.

2.3. Physical measurements

The electronic absorption and optical transmittance spectra of the complex was recorded using Lambda 35 UV–visible spectrophotometer in the range from 250 to 900 nm. The band gap energy was calculated from the transmittance data of the complex. The emission spectrum of the complex was recorded using JASCO FP 6600 spectrofluorometer in the wavelength range between 400 and 850 nm. TG–DTA analysis was carried out using a STA 409 PC thermal analyser under nitrogen atmosphere. The FTIR spectrum of the complex was recorded on a JASCO-5300 FTIR spectrophotometer model instrument using KBr pellet technique at room temperature. The polarised Raman spectrum of the complex was analysed by using Confocal Raman Microscope (CRM-Alpha 300S). The NMR spectrum of the complex was carried out using Bruker DRX 50–400 MHz spectrometer using tetramethyl silane [TMS] as the internal standard and d_6-DMSO used as the solvent. The second harmonic generation (SHG) property of the material was carried out by modified Kurtz–Perry powder technique using Q-switched Nd:YAG laser.

2.4. X-ray crystal structure determination

The crystallographic data of the complex has been collected at 298 K on a Bruker SMART APEX CCD, area detector system [λ (Mo Kα) = 0.7103 Å]. A graphite monochromator, 2400 frames were recorded with an ω scan width of 0.3°, each for 10 s, crystal-detector distance 60 mm, collimator 0.5 mm. Data reduction was carried out by SAINTPLUS [25] and absorption correction was made using an empirical method SADABS [26]. The structure solution was studied using SHELXS-97 [27] and refined using SHELXL-97 [28]. All non-hydrogen atoms were refined anisotropically. Cambridge Crystallographic Data Centre (CCDC No. 838802) contains the supplementary crystallographic data for the complex. This can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

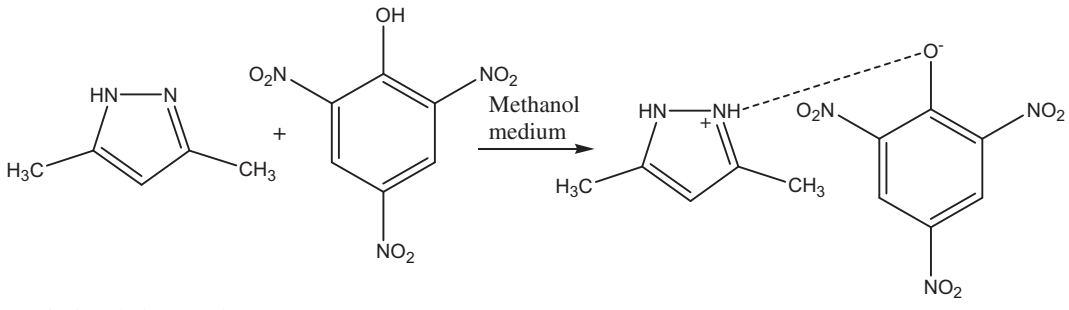
2.5. Antimicrobial studies

2.5.1. Preparation of chemical extract

Hundred microgram of the chemical compound was weighed. Then it was mixed with 1 ml of the DMSO solvent. The filtrate was obtained by filtration with Whatman No. 1 filter paper and the filtrate disc was kept in test tube containing chemical compound. The disc was allowed to dry in laminar airflow chamber. Control was maintained by adding solvent on the disc.

2.5.2. Antibacterial activity

The antibacterial activity of newly synthesized complex was tested against four Gram-positive bacteria *Staphylococcus epidermidis*, *Staphylococcus aureus* (Lab isolate), *Enterococcus faecalis* and *S. aureus* (Clinical isolate) and five Gram-negative bacteria *Proteus* sp., *Escherichia coli*, *Pseudomonas aeruginosa*, *Pseudomonas* sp. and *Klebsiella pneumoniae* [29,30]. Media with DMSO solvent was setup as control. The discs measuring 5 mm in diameter were prepared from Whatman No. 1 filter paper sterilized by dry heat at 140 °C for 1 h. The sterile discs previously soaked in a concentration of the test compounds were placed in a nutrient agar medium. The petri plates were invested and kept in an incubator for 24 h at 37 °C and growth was monitored both visually. The screening was performed at 100 μg/ml concentration of test complexes and antibiotic disc. Tetracycline (30 mg/disc, Hi-Media) was used as control. Logarithmic serially two fold diluted amount of test complexes and controls was inoculated within the range 10^{-4}–10^{-5} cfu/ml. To obtain the diameter of zone, 0.1 ml volume of culture was taken from each organism and spread on agar plates.



Scheme 1. Synthetic reaction of DMPP crystal.