Synthesis, crystal structure and optical properties of quasi-one-dimensional lead (II) iodide: C$_{14}$H$_{18}$N$_{2}$Pb$_{2}$I$_{6}$

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**Article info**

*Article history:* Received 17 June 2009
Received in revised form 25 September 2009
Accepted 14 October 2009
Available online 28 October 2009

*Keywords:* Natural crystal growth
Inorganic–organic hybrid
Optical properties

**Abstract**

Quasi-one-dimensional lead (II) iodide compound, C$_{14}$H$_{18}$N$_{2}$Pb$_{2}$I$_{6}$, with unique crystal structure was synthesized and solved for the crystal structure. These novel inorganic–organic hybrids have high thermal stability of up to 300°C and show excitonic and charge-transfer features in their optical properties. An attempt has been made to understand the structural and optical mechanisms between inorganic one-dimensional polymeric PbI nano ribbons and the guest organic moiety for future applications in nanoscaled electronic devices.

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**1. Introduction**

Self-assembly techniques take advantage of weak intermolecular interactions to create more complex crystal structures and preserve the unique characteristics of individual components. Current research is focused on synthesis of low-dimensional crystalline inorganic–organic metal halides with a possibility of incorporating properties associated with functional inorganic and organic moieties. Low-dimensional lead (II) iodide based hybrid crystals are of particular interest due to their unique structural, magnetic, optical nonlinear and optoelectronic functionality [1–9]. Due to the low-dimensionality, they show strong room-temperature excitonic optical features with large exciton binding energy and oscillator strengths. Apart from low-dimensionality, the large dielectric mismatch between the organic and inorganic moieties, greatly influences the physical and optical properties [10–12]. Low dimensional complexes include zero dimensional (0D), one dimensional (1D) and two dimensional (2D) lead iodide networks with organic moieties as spacers [8,10–15]. Among them, one-dimensional hybrids [16–21] are much attractive in nanoscaled electronic devices. Here the nature of organic moiety would modify overall inorganic–organic heterostructure arrangement and thereby the electronic interactions between inorganic ‘nanowires’ and organic moieties [22–24]. Here we report the synthesis, crystal structure, physical and optical features of quasi-one-dimensional compound, C$_{14}$H$_{18}$N$_{2}$Pb$_{2}$I$_{6}$. In this inorganic–organic hybrid the non-covalent interaction between organic and inorganic network unusually alter the normal coordination around Pb(II) and as a consequence the hybrid show unique optical and structural properties. These systems could also be visualized as inorganic polymeric ‘nanoribbons’ enclosed by organic spacers, in which the charge-transfer transition between the inorganic and organic moieties are of particular interest.

**2. Experimental**

Single crystals of Ethyl Viologen Lead Iodide (C$_{14}$H$_{18}$N$_{2}$Pb$_{2}$I$_{6}$) (hereafter EVPI), were grown by the slow evaporation technique. 0.1 mmol (23.05 mg) of lead (II) iodide was dissolved in 5 ml DMSO solution. Similarly 0.1 mmol (23.41 mg) of Ethyl Viologen diiodide (C$_{14}$H$_{18}$N$_{2}$I$_{2}$) (EVI) was dissolved in 5 ml of DMSO solution separately. The prepared solutions were mixed together at room temperature with constant stirring. The solution was allowed to evaporate slowly under controlled atmosphere. Within few weeks dark red single crystals of dimensions nearly 1 × 0.2 × 0.2 mm$^3$ were grown. The crystals were filtered and dried for the single crystal X-ray diffraction studies. Single crystal diffraction studies were carried out by Bruker APEX CCD diffractometer with a Mo K$_{α}$
(0.71073 Å) sealed tube at 273 K. The program SMART [25] was used for collecting frames of data, indexing reflection and determination of lattice parameters, SAINT [25] for integration of the intensity of reflections and scaling. SADABS [26] was used for absorption correction and SHELXTL [27] for space group and structure determination and least-squares refinements on F². The lead atoms were located first and then remaining atoms were deducted from subsequent difference Fourier syntheses. The hydrogen atoms were located using geometrical constraints. All the non-hydrogen atoms were refined anisotropically. The least-squares refinement cycles on F² were performed until the model converged. Molecular graphics were presented by softwares, Mercury v2.2 and Diamond v2.1c.

Thermo-Gravimetry (TG) and Differential Thermo Gravimetry (DTG) were carried out between 30 and 800 °C at a scan rate of 5 °C/min under N₂ atmosphere. The crystals were dissolved in polar solvent, DMSO, and drop-coated onto a glass substrate and was heated to about 65 °C. Once the solvent started evaporating, the substrate containing the solution has been quickly transferred to a spin-coater and spun at 1500 rpm for 30 s. The uniform dark red thin film thus obtained has been used for Glancing Angle X-ray Diffraction (GLAXRD) using CuKα radiation, UV–visible absorption and Photoluminescence (PL) experiments. PL was attributed at room temperature. PL spectrum was acquired on Fluorolog-3 (FL 3–11) modular spectrofluorometer. PL imaging was carried out on modified Fluoview (FV1000) laser scanning confocal microscope which was equipped with 447 nm excitation laser, rocking mirrors arrangement and a PMT.

3. Results and discussion

The compound crystallizes as monoclinic in the space group P2₁/c. The asymmetric unit consists of three (PbI₃)₂⁺ units and one and a half mole of ethyl viologen (EV²⁺) units. The complete details of the crystallographic data are given in Table 1. The crystal structure features one-dimensional polymeric column of edge-shared PbI₆ octahedra. There are three types of iodide atoms defined by their location within the unit cell. (a) Terminal atoms I(1), I(2) and I(11), (b) double bridging atoms I(3), I(4), I(5), I(6) and I(9) and (c) triple bridging iodide atom I(7). Similarly there are two types of lead atoms defined by their location within the column. (a) Outer lead atom Pb(1) bonded to terminal iodide and (b) inner lead atoms Pb(2) and Pb(3) bonded to triple bridging iodides.

Pb(1), Pb(2) and Pb(3) are collinear and are bonded to iodide atoms as shown in Fig. 1A. With the point of inversion C, at the middle of Pb(2), Pb(2)'(2), I(4) and F(4), all the atoms are repeated and are named with the primed ones. It is further to note that iodide atom I(10) is same as that of I(9) and I(8) is same as I(7). The centre of inversion symmetry, it forms a single unit and the column is extended by the edge sharing of iodide atoms I(5), I(7) and I(9) (Fig. 1C), extended along (0 1 0) direction. The shortest Pb–I bond distance (2.987(2) Å) is between Pb(1) to I(1) and Pb(1) to I(2) and the longest (3.394(2) Å) is between Pb(3) and I(11). The cis Pb–I bonding angles vary between 81.93(4)° and 95.44(7)°, while for trans Pb–I bonding angle varies between 179.61(5)° and 166.08(5)°. suggesting distorted PbI octahedra from its perfect structure. This could be due to the differences in the strengths of the covalent bonding between Pb atoms to the terminal, double bridging and triple bridging iodides. In one of the previously reported quasi-one-dimensional crystal [16], where the organic moiety is methyl-viologen (MV²⁻), the PbI₆ octahedral structure is face-shared and MV²⁻ ions are accommodated in closely packed [PbI₆]ₙ infinitely extended chains. However, in the titled compound three (PbI₆)₂⁺ are edge-shared and repeated to form polymeric column, which is surrounded by organic moiety EV²⁺ di-cations in such a way to maximize the number of nearest neighboring iodine atoms around the cations (Fig. 1B). This is mainly due to the non-covalent interactions between inorganic and organic cation, for example, the nearest contact distance between N and I in the present case is 4.889 Å which is higher (3.629 Å) than that of the reported compound [16].

In organic cations, the values of individual C–C and C–N bond lengths range from 1.320(3) Å to 1.560(4) Å and 1.541(3) Å respectively. Within the hexagonal ring, the bond lengths of C–C and C–N varies from 1.270(3) Å to 1.280(3) Å and 1.432(3) Å to 1.560(4) Å respectively. The central ring is the imine part and the bond angles are in the range of bond angles 110.42(2)° and 126.38(2)°. Further, the inorganic–organic heterostructure is dominated by two kinds of hydrogen bonding between EV²⁺ di-cations to the PbI network: (1) terminal iodides and (2) nearby double bridging iodides with respective bond lengths 2.907 Å and 3.024 Å (Fig. 1).

Table 1

| Crystallographic data of ethyl viologen lead iodide (C₁₄H₁₈N₂Pb₂I₆). |
|-------------------------|---------------|
| Crystal data            | Details       |
| Empirical formula       | C₁₄H₁₈N₂Pb₂I₆ |
| Formula weight          | 2085.16 g/mol |
| a, Å                    | 12.089(5)     |
| b, Å                    | 14.044(5)     |
| c, Å                    | 24.827(9)     |
| Temperature             | 273(2) K      |
| Radiation               | MoKα          |
| Diffractometer          | Bruker Smart Apex CCD |
| Crystal system          | Monoclinic    |
| Space group             | P2₁/c         |
| Volume                  | 4215(3) Å³    |
| Z                       | 4             |
| dcalc, gc               | 3.286         |
| Crystal                  | Rod, dark red |
| Crystal size, mm         | 0.15 × 0.13 × 0.12 |

3.942/1.956

The optical absorption spectra of thin film shows a strong peak at 3.19 eV, associated with a broad shoulder at red end at ~2.8 eV (Fig. 3A). According to Ishihara et al. [12,22], the absorption peak at 3.19 eV could be attributed to the lowest excitons of PbI chains. The associated shoulder in the region of 2.4–2.8 eV is attributed to charge transfer (CT) transition between non-bonding state of the negatively charged PbI nanoribbons to the lowest unoccupied molecular orbital (LUMO) of the positively charged EV²⁺ di-cations.
On the other hand, the photoluminescence spectra of EVPI thin film show two distinct emission peaks: one at 2.35 eV associated with a shoulder at 2.19 eV and another intense peak at \( \sim 3 \) eV (Fig. 3A). The PL at 3 eV could be related to excitonic related transition. Other PL peak at 2.35 eV and the shoulder at 2.19 eV could be due to charge-transfer related transitions. However, it is to be noted that, unlike other 1D and 2D PbI based hybrids [15], EVPI is comparatively a poor emitter. For comparison, in those 1D and 2D Lead-based hybrids, optical bandgap of organic moiety (\( \sim 6 \) eV) is much higher than inorganic (\( \sim 3 \) eV), therefore the origin of PL is solely from low-lying inorganic exciton energy levels [28]. Whereas, in the present type of quasi-1D crystals, such as methylviologen lead iodide [12,29], organic (\( \sim 4 \) eV) and inorganic (\( \sim 3.4 \) eV) optical bandgaps are very close to each other. We have verified by performing extended Hückel tight-binding band structure calculation and found that the bandgap for the present molecule is 3.75 eV. Therefore, in these systems, charge-transfer transitions play a vital role rather than excitonic transitions. Apart from thin film emission, we have also recorded single crystal imaging using confocal high-resolution microscope, to confirm the morphology and emission characteristics. Fig. 3B reproduces the confocal (i) transmission (ii) laser scattering and (iii) Photoluminescence images. For laser scattering and PL imaging, crystals were excited with 447 nm (2.77 eV), 40 mW laser. A bandpass filter (BA465–495) has been used for PL measurements. In general, the absorption and emission transitions of EVPI thinfilms are distinctly red-shifted, compared to single crystal absorption and emission features of previously reported Methyl viologen lead iodide [12].
In general, these compounds are of much importance, specially understanding the behavior of charge carriers in these quasi-one-dimensional systems for many electronic and optoelectronic applications. Experiments such as photo and electronic conductivity experiments are needed to understand electronic interactions between inorganic and organic molecules. Those experiments are currently under progress in our labs.

4. Conclusions

Here we have synthesized unique one-dimensional lead iodide polymeric nanoribbons: Ethyl viologen lead iodide (EVPI). Detailed crystal structure of EVPI was solved and analysed. The unusual crystal structure features one-dimensional column of edge-shared PbI$_6$ octahedra, where the non-covalent interaction between organic and inorganic moieties modifies the layered PbI$_2$ network into complex 1D polymeric column. The thermal stability of these one-dimensional crystals is as high as 300°C. In thin film form, they are ordered in (011) direction and show distinct excitonic as well as strong charge-transfer related absorption and emission characteristics. These one-dimensional hybrids are of considerable attention in nanoscaled electronic devices; therefore, for future applications, more experiments are needed to understand the mechanism between inorganic polymeric column and the guest organic moiety.

Acknowledgements

Authors are thankful to Prof. A Ramanan, Department of Chemistry, IIT Delhi, and Prof. J.J. Baumberg, Cavendish Laboratory, University of Cambridge, UK, for their helpful discussions. One of the authors (GVP) acknowledges the financial support from DST, India. This work is part of UK-India Education and Research Initiative (UKIERI) programme.

Supplementary data

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-720062. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

References