$[C_6H_5CH_2NH_3]_3BiCl_6{\cdot}0.5H_2O$: Photoluminescence Properties of a Red-emitting One-dimensional Organic Bismuth Halide

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Abstract

A novel red-emitting one-dimensional organic-inorganic hybrid, $[C_6H_5CH_2NH_3]_3BiCl_6{\cdot}0.5H_2O$, has been synthesized by the slow evaporation method and characterized by single crystal X-ray diffraction using synchrotron at 100K. It crystallizes in the monoclinic space group, $P2_1/c$, in which the unit cell parameters are a = 17.044(3) Å, b = 7.6090(15) Å, c = 22.478(5) Å, and β = 102.31(3)°. The crystal consists of a corner sharing octahedral bismuth chloride chains $[BiCl_6^{3-}]_\infty$ along the b-axis, which are surrounded by the benzyl ammonium $C_7H_{10}N^+$, chloride, and lattice water between the chains. The chains are linked via hydrogen bonds and ionic interaction between Cl···H(OW) and N-H···Cl, respectively. This unique one-dimensional structure makes it possible to emit strong photoluminescence properties in red-light region at room temperature. The detailed characterization of its optical properties, such as photoluminescence(PL) spectra, Infrared spectra, and UV-vis reflectance spectra, are also investigated.

Introduction

- Organic-inorganic hybrid metal halides are important class of crystalline materials for following reasons:
  - Facile synthetic methods – low temperature, solution processability.
  - Band structure tunability – optoelectronic devices (photovoltaic cells, LED, lasers).
- Structural diversity – Zero to three dimensional organic metal halide perovskites.
- White-light emitting perovskites:

$(C_6H_{13}N_3)PbBr_4$, (N-MEDA)[a]$PbBr_4$, (EDBE)[b]PbX4 (X = Cl and Br), $(FC_2H_4NH_3)_2PbCl_4$, (DMAPA)[c]$PbBr_4$, (DMEN)[d]$PbBr_4$, (DMABA)[e]$PbBr_4$

[a]N1-methylethane-1,2-diammonium, [b]2,2`-(ethylenedioxy)bis(ethylammonium), [c]3-(Dimethylamino)-1-propylammonium, [d]2-(Dimethylamino)ethylammonium, [e]4-dimethylaminobutylammonium.

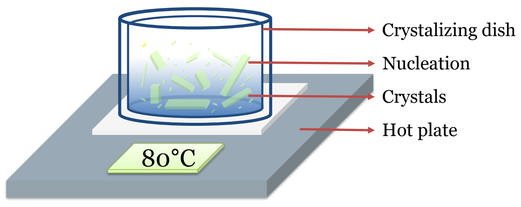
Synthesis

❖ Slow evaporation

$$C_6H_5CH_2NH_2 + conc.HCl + Acetone \rightarrow C_6H_5CH_2NH_3^+Cl^-$$

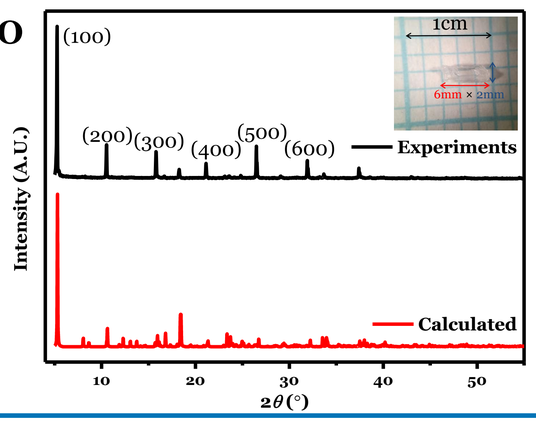
$$BiCl_3 + 3\,C_6H_5CH_2NH_3Cl^a + conc.HCl \rightarrow [C_6H_5CH_2NH_3]_3BiCl_6{\cdot}0.5H_2O$$

[a]Benzylammonium Chloride



❖ Results

A single crystal and powder X-ray diffraction patterns for $[C_6H_5CH_2NH_3]_3BiCl_6{\cdot}0.5H_2O$ with experimental pattern (black) and calculated pattern (red). The experimental pattern reveals preferred orientation for the (n00) plane.



Structural details

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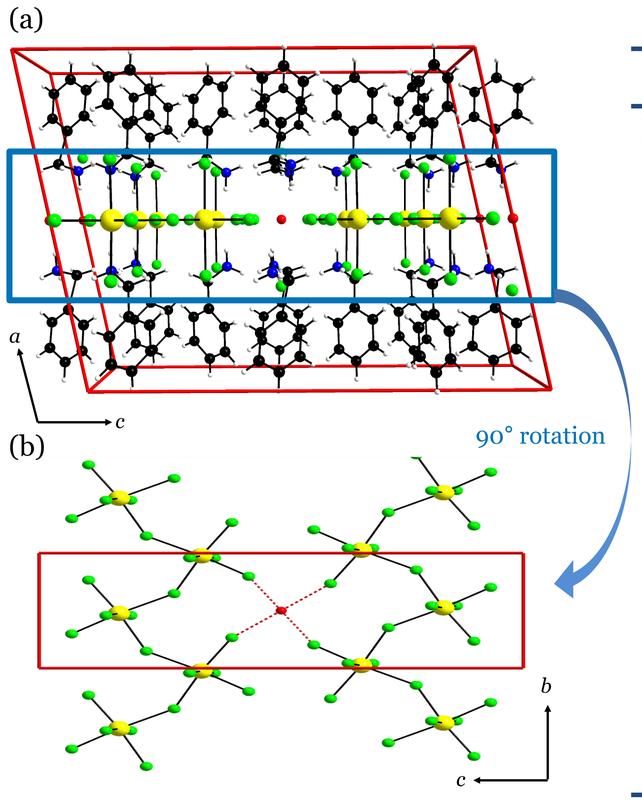


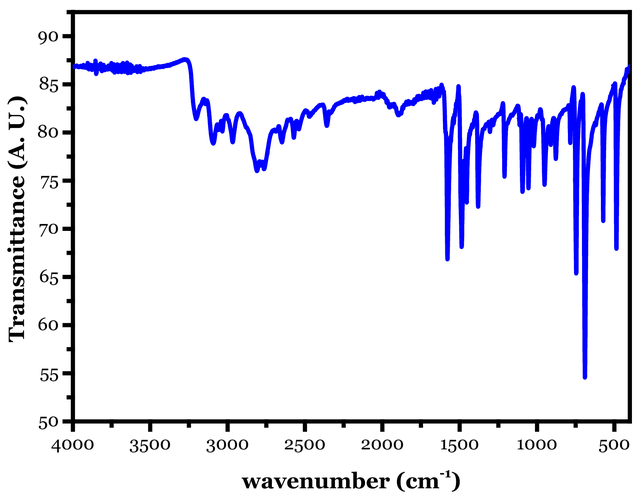
Formula	$[C_6H_5CH_2NH_3]BiCl_6{\cdot}0.5H_2O$
FW (g mol^{-1})	719.155
Space group	$P2_1/c$ (No. 14)
a (Å)	17.044(3)
b (Å)	7.6090(15)
c (Å)	22.478(5)
β (°)	102.31(3)
V (Å^3)	2848.1(10)
Z	4
T (K)	298(2)
λ (Å)	0.6100
$R(F)^a$	0.0444
$R_w(F_o^2)^b$	0.1246

$^aR(F) = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $^bR_w(F_o^2) = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

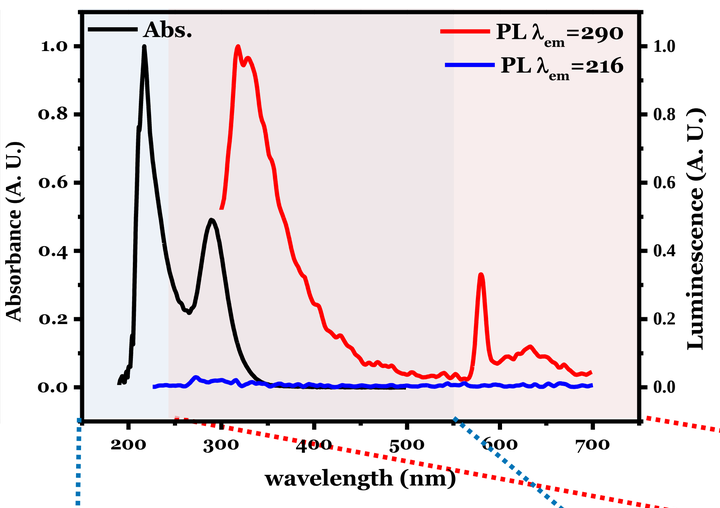
- Ball-and-stick representation of (a) $[C_6H_5CH_2NH_3]_3BiCl_6{\cdot}0.5H_2O$ (yellow, Bi; black, C; blue, N; green, Cl; red, O; white, H) and (b) one-dimensional chain of $[BiCl_6]^{3-}$ octahedra connected by corner sharing. The each chains reveal zig-zag pattern of $BiCl_6$ polyhedra and are linked by hydrogen bonding of Cl···H(OW) in lattice water.
- Table of structural details of $[C_6H_5CH_2NH_3]_3BiCl_6{\cdot}0.5H_2O$.

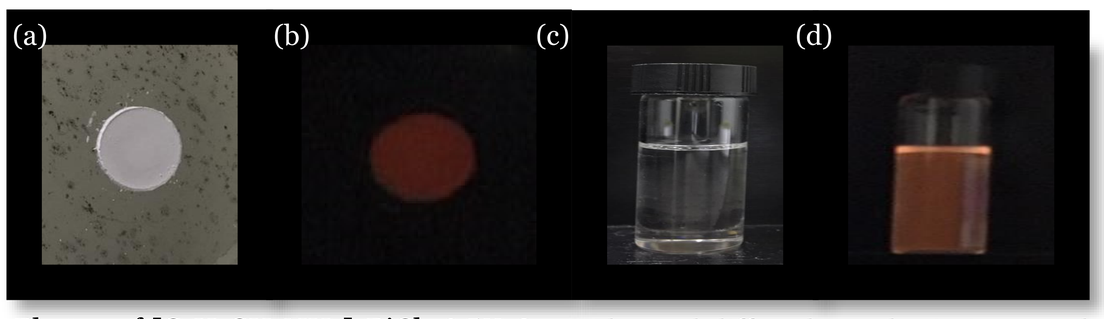
Photophysical properties

❖ Infrared Spectrum



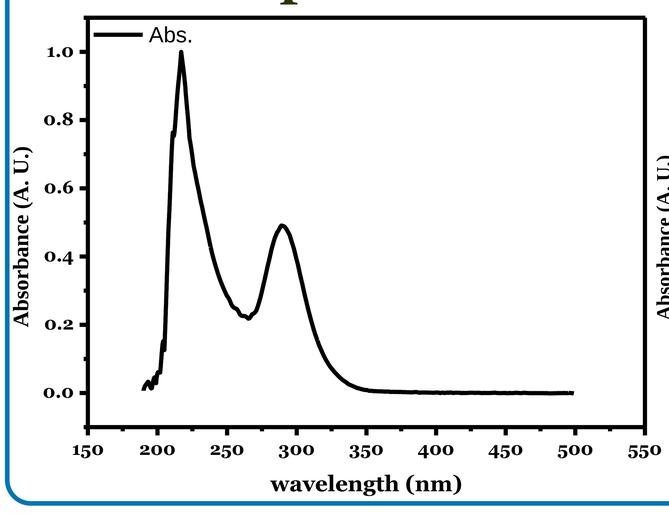
❖ Photo-Luminescence

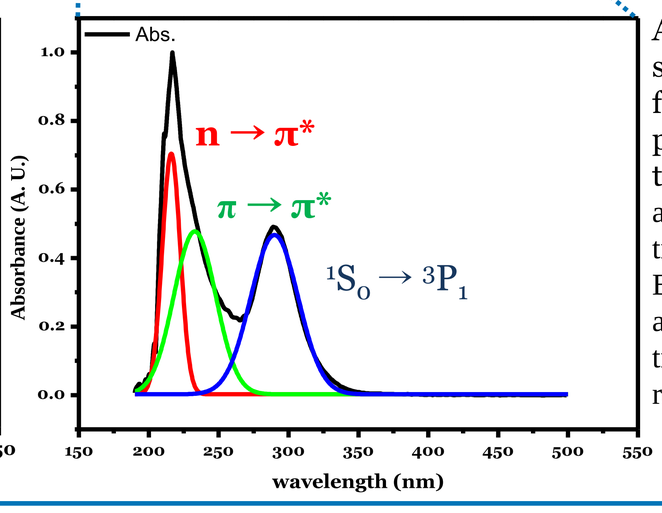




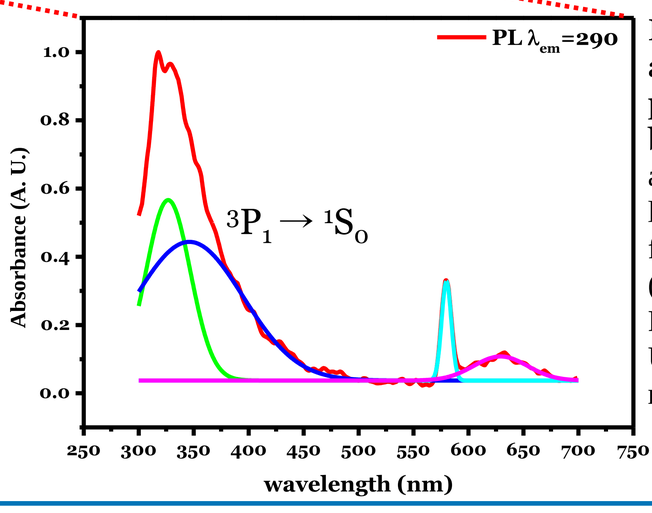
Photos of $[C_6H_5CH_2NH_3]_3BiCl_6{\cdot}0.5H_2O$ powder and diffused powder in isopropyl alcohol under (a), (c) ambient light and (b), (d) UV light (365nm, Hg lamp), respectively.

❖ UV-vis Spectrum





Absorption spectrum are fitted by three peaks denoted as to be n → π* (Red) and π → π* (Green) transition on Benzylammonium and $^1S_0 \rightarrow {}^3P_1$ (Blue) transition on Bi^{3+}, respectively.



Emission spectrum are fitted by four peaks assigned as to be $^3P_1 \rightarrow {}^1S_0$ (Green and blue) transition, light source originated from 290nm excitation (Cyan), and decay of Pb` centers created by UV irradiation (pink), respectively.

Conclusion

We have synthesized a novel hydrated benzylammonium bismuth chloride, $[C_6H_5CH_2NH_3]_3BiCl_6{\cdot}0.5H_2O$, by slow evaporation. The crystal structure and optical properties of IR-spectrum, UV-vis spectrum, and photoluminescence spectrum are also reported. The compound represent one-dimensional chain structure which is composed of corner shared BiCl6 octahedra with the zig-zag moiety. Each chains are divided by benzylammonium and reveal hydrogen interaction with lattice water between the chains. The compounds shows PL properties on UV-region as an result of absorption and emission for Bi^{3+} $^3P_1 \rightarrow {}^1S_0$ and *vice versa*. Of particular interest is the emission in the region of yellow to red, which is originated by imperfection of crystals created by UV irradiation. The excitation of red luminescence occurs due to diffusion of excitons from Pb` centers.

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