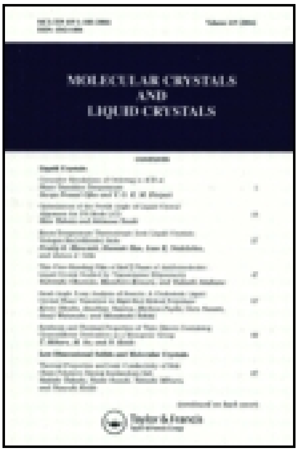

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Crystal Structure and Optical Properties of $C_{10}H_{10}N_2PbBr_4$ and $C_{10}H_{22}N_2PbBr_4$

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Crystal Structure and Optical Properties of $C_{10}H_{10}N_2PbBr_4$ and $C_{10}H_{22}N_2PbBr_4$

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Novel organic-inorganic hybrid compounds, $C_{10}H_{10}N_2PbBr_4$ and $C_{10}H_{22}N_2PbBr_4$ were prepared and characterized by X-ray and optical measurements. The result of single crystal X-ray analysis showed that the inorganic region of $C_{10}H_{10}N_2PbBr_4$ consisted of one-dimensional chains of line-sharing $PbBr_6$ octahedra, whereas that of $C_{10}H_{22}N_2PbBr_4$ consisted of two-dimensional sheets of corner-sharing $PbBr_6$ octahedra. Each crystal exhibited an excitonic band at 307 nm for $C_{10}H_{10}N_2PbBr_4$ and 383 nm for $C_{10}H_{22}N_2PbBr_4$, which is attributed to the excitonic states of low-dimensional inorganic structures. These results indicate that the dimensional structure of these compounds can be systematically controlled by changing the chemical structure of organic ligands.

Keywords Organic-inorganic hybrid compounds; Perovskite; Excitons; Quantum confinement effect; bipyridine; bipiperidine

INTRODUCTION

Lead halide and its low-dimensional compounds have attracted much attention due to the interesting optical properties. Layered perovskite compounds, $(RNH_3)_2PbX_4$ (X = halogen), naturally form a quantum-well structure where a two-dimensional semiconductor layer of PbX_6 octahedra is sandwiched between organic insulator layers. [1-6] As a result of a quantum confinement effect due to the low-dimensionality of the inorganic semiconductor structure, they form a stable exciton with large binding energy and oscillator strength, which makes possible strong photoluminescence, third-harmonic generation, and polariton absorption.[7-11] Although there is a significant interest in the optical properties of low-dimensional lead halide compounds, chemical structure on the fabrication of low-dimensional lead halide compounds are limited by the paucity of organic ligands. In this paper, we focused on the synthesis of novel organic-inorganic hybrid compounds incorporating 4,4'-bipyridinium and 4,4'-bipiperidinium cations. Crystal structures and optical properties of the organic-inorganic hybrid compounds, $C_{10}H_{10}N_2PbBr_4$ and $C_{10}H_{22}N_2PbBr_4$, were characterized by single crystal X-ray structural analysis and optical measurements.

EXPERIMENTAL

$PbBr_2$ and 4,4'-bipyridinium dibromide were dissolved in dimethylsulfoxide (DMSO), and the hybrid compound $C_{10}H_{10}N_2PbBr_4$ was obtained by the solvent-diffusion recrystallization from the DMSO solution with methanol as poor solvent. $C_{10}H_{22}N_2PbBr_4$ was prepared by reacting $PbBr_2$ and 4,4'-bipiperidinium dichloride in a HBr solution. The HBr solution was heated to 100 °C, and then slowly cooled to room temperature at a rate of 2 °C/h. X-ray crystal structure data collections of the compounds were performed on an imaging plate diffractometer (Rigaku RAXIS-RAPID Imaging Plate) using a monochromated MoK α radiation. The structure solution and refinement were carried out with Direct Methods (SIR 92). Reflection spectra of the crystalline powder were measured with a HITACHI U3500 spectrometer at room temperature. Fluorescence spectrum measurements were carried out by using a HITACHI F-4500 spectrometer with a monochromated Xe lamp as an exciton source.

RESULTS AND DISCCUSSION

The crystal structure of $C_{10}H_{10}N_2PbBr_4$ is shown in Figure 1. $C_{10}H_{10}N_2PbBr_4$ belongs to a monoclinic space group with a= 16.512 Å, b=13.513 Å, c=7.638Å, and β =116.072°. The monoclinic crystal structure consists of one-dimensional inorganic chains of line-sharing $PbBr_6$ octahedra extending to the (001) direction. The 4,4'-bipyridinium cations are parallel to the ab-plane and attach to halogens of $PbBr_6$ octahedra with the hydrogen-bond interaction.

The bipiperidinium analogue, $C_{10}H_{22}N_2PbBr_4$, was also characterized by single crystal X-ray structural analysis. $C_{10}H_{22}N_2PbBr_4$ belongs to a monoclinic space group with a= 11.853Å, b=5.989 Å, c=12.065Å, and β =91.244°. As shown in Figure 2, the monoclinic crystal structure consists of two-dimensional inorganic sheets of corner-sharing $PbBr_6$ octahedra. The 4,4'-bipiperidinium cations form perpendicular array to the ab plane of the structure as barrier layers. The piperidinium heads fit within the layered perovskite framework and form the hydrogen-bond interaction with the halogens in the inorganic sheets. These results suggest that the hydrogen-bond interaction between organic and inorganic components have an important role to form low-dimensional inorganic structures.

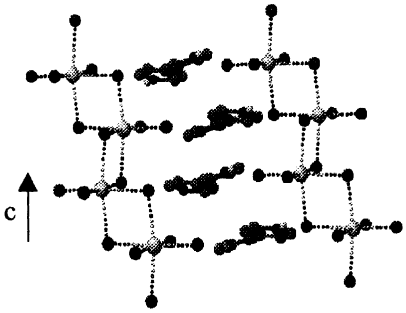

FIGURE 1 Crystal structure of $C_{10}H_{10}N_2PbBr_4$.

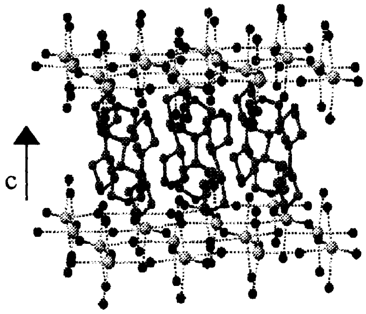

FIGURE 2 Crystal structure of $C_{10}H_{22}N_2PbBr_4$.

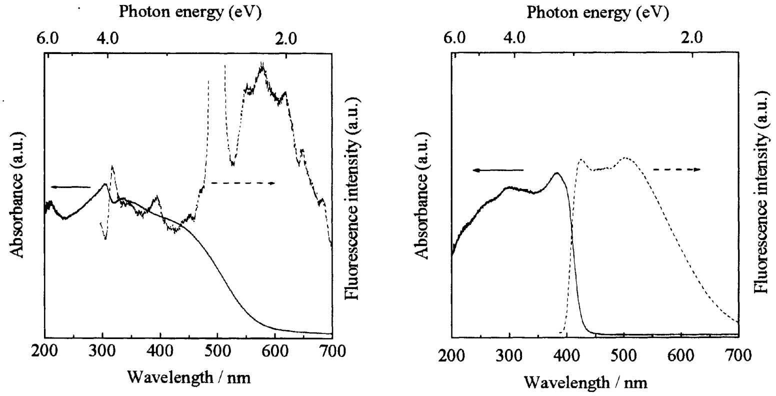

FIGURE 3 Reflection and fluorescence spectra of $C_{10}H_{10}N_2PbBr_4$ (left) and $C_{10}H_{22}N_2PbBr_4$(right).

The optical properties of these compounds are dominated by an excitonic transition associated with the band gap of the inorganic region. Figure 3 shows the reflection and fluorescence spectra of $C_{10}H_{10}N_2PbBr_4$ and $C_{10}H_{22}N_2PbBr_4$ crystalline powder. The excitonic peaks of $C_{10}H_{10}N_2PbBr_4$ and $C_{10}H_{22}N_2PbBr_4$ were observed at 307 and 382 nm, while their photoluminescence peaks at 330 and 423 nm, respectively. As the dimension of inorganic region decreases, the excitonic peaks shifted to high photon energy due to the increase in the bandgap.

Conclusion

These results demonstrated that the low-dimensional inorganic structure could be controlled by changing the chemical structure of organic ligands. These structural and optical data suggested that novel quantum confinement structures were constructed from the self-organization between lead bromide and novel organic cations.

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