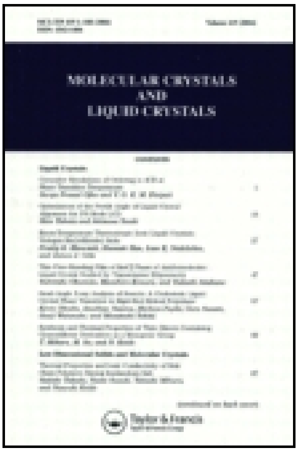

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Novel Organic-Inorganic Hybrid Compounds Containing Alkyldiammonium Salts

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Novel Organic-Inorganic Hybrid Compounds Containing Alkyldiammonium Salts

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Novel organic-inorganic hybrid compounds, $C_nN_2PbBr_4$ (n=4,6,8 and 10) and $C_2N_2PbBr_4 \cdot$ DMSO, were prepared by the self-organization of lead bromide and a variety of alkyldiammonium cations. The powder X-ray diffraction patterns of $C_nN_2PbBr_4$ demonstrated that the compounds form layered perovskite structures and the interlayer spacing are dependent on the length of alkyl chain. The absorption and fluorescence spectra of $C_nN_2PbBr_4$ and $C_2N_2PbBr_4 \cdot$ DMSO crystalline powder showed an excitonic absorption peak at around 390 nm, which suggests that the formation of two-dimensional inorganic sheets and quantum confinement structure.

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

INTRODUCTION

Organic-inorganic hybrid compounds have recently attracted much attention due to their interesting optical properties. In particular, layered perovskite compounds, $(C_nH_{2n+1}NH_3)_2PbX_4$ (X=halogen) naturally form a quantum-well structure in which two-dimensional semiconductor layers of corner-sharing PbX_6 octahedra are sandwiched between organic insulator layers.[1-3] Due to the low-dimensionality of the inorganic semiconductor region, the exciton has large binding energies (>300 meV) and oscillator strength resulting from the quantum confinement effect, which enables strong excitonic absorption and emission even at room temperature.[4-9] It has been reported that the dimensions of inorganic semiconductor region are controllable by changing organic cation species, but alkylmonoammonium salts are mostly used as organic cation species to prepare these compounds. In this paper, we report the synthesis and characterization of novel organic-inorganic hybrid compounds containing alkyldiammonium salts, and the crystal structure and optical properties were characterized by X-ray diffraction and optical measurements.

EXPERIMENTAL

Alkyldiammonium dibromide was prepared by treating the alkyldiamine with a HBr aqueous solution. $C_nN_2PbBr_4$ crystals were obtained by the recrystallization from a mixed solution of dimethylformamide and methanol containing lead bromide and alkyldiammonium dibromide. $C_2N_2PbBr_4$ • DMSO crystals were obtained by the solvent-diffusion recrystallization from a dimethylsulfoxide solution with methanol as a poor solvent. The chemical formula of the compounds was determined by elemental analysis and ICP emission spectroscopy. Absorption spectra of the crystalline powder were measured by using a SHIMAZU UV3100. Fluorescence spectra of the crystalline powder were taken on a HITACHI F-4500 spectrometer. X-ray diffraction measurements of the crystalline powder were performed on a Rigaku Rint 2000.

RESULTS AND DISCCUSSION

Figure 1 shows X-ray diffraction pattern of crystalline powder of $C_{10}N_2PbBr_4$ and $C_2N_2PbBr_4$ • DMSO. A series of

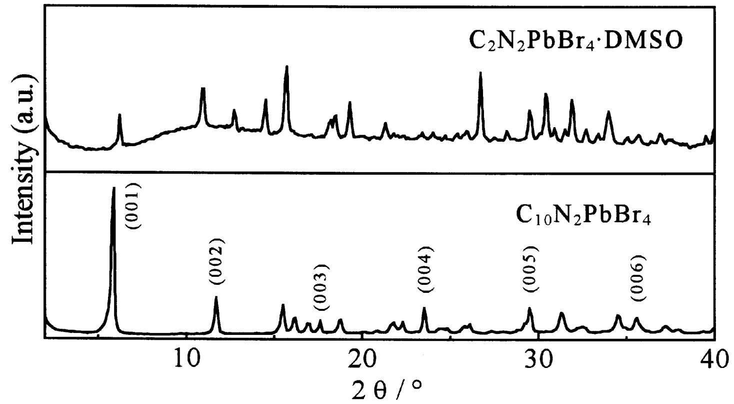

FIGURE 1 X-ray diffraction patterns of crystalline powder of $C_{10}N_2PbBr_4$ and $C_2N_2PbBr_4$·DMSO.

(001) diffractions attributed to the interlayer spacing were observed in the low angle region of $C_{10}N_2PbBr_4$. The observation of these characteristic diffractions supports that the layered perovskite structure was successfully formed by the self-organization of lead bromide and alkyldiammonium dications. In $C_nN_2PbBr_4$, the layer spacings increased with the increase in the length of alkyl chains. This result indicates that the distance between the inorganic layers can be controlled by changing the length of alkyl chain in the layered perovskite. In contrast, $C_2N_2PbBr_4 \cdot$ DMSO did not show such (001) bragg reflections.

Figure 2 shows the absorption and photoluminescence spectra of $C_{10}N_2PbBr_4$ crystalline powder. This compound exhibited sharp excitonic absorption and fluorescence peaks, which implies that quantum confinement structure was constructed. All of the $C_nN_2PbBr_4$ crystalline powder showed an exciton peak at around 390 nm due to the exciton states of two-dimensional inorganic structure. [10-12]

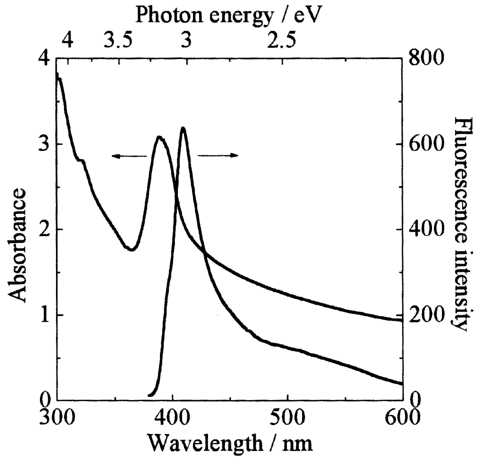

FIGURE 2 Absorption and fluorescence spectra of $C_{10}N_2PbBr_4$. (Ex : 350 nm)

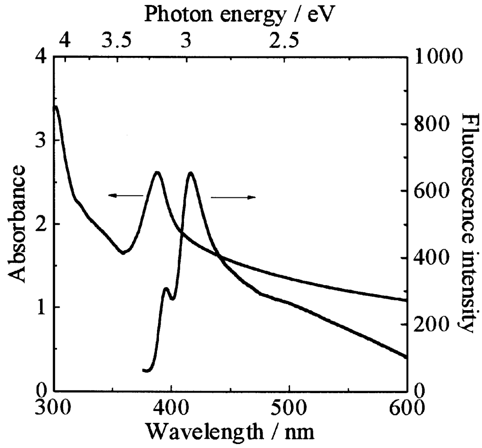

FIGURE 3 Absorption and fluorescence spectra of $C_2N_2PbBr_4$ • DMSO. (Ex : 350 nm)

Although the distance between the inorganic layers changes from 15.0 Å for (n=10) to 10.2 Å for (n=4), the similar absorption spectra are observed in these compounds. This result indicates that the distance between the inorganic layers is long enough to cause the quantum confinement effect.

Figure 3 shows the absorption and fluorescence spectra of $C_2N_2PbBr_4$ • DMSO crystalline powder. The compound showed an absorption peak at 388 nm as well as $C_nN_2PbBr_4$ crystals, whereas the fluorescence peaks were split into 395 nm and 413 nm. This results suggests that the electronic band structure of $C_2N_2PbBr_4$•DMSO is different from that of $C_nN_2PbBr_4$ due to the coordination of DMSO molecules.

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