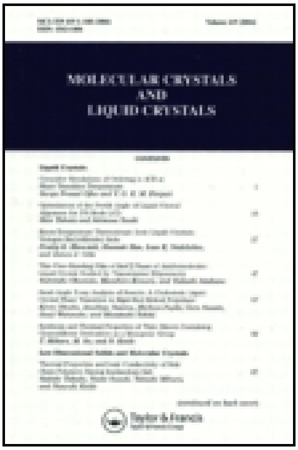

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Incorporation of Bulky Chromophore into PbBr-Based Layered Perovskite Organic/Inorganic Superlattice by Mixing of Chromophore-Linked Ammonium and Alkyl Ammonium Molecules

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Incorporation of Bulky Chromophore into PbBr-Based Layered Perovskite Organic/Inorganic Superlattice by Mixing of Chromophore-Linked Ammonium and Alkyl Ammonium Molecules

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PbBr-based layered perovskite organic-inorganic superlattice material where bulky carbazole chromophore is incorporated into organic layer was successfully prepared through the molecular mixing of carbazole-linked ammonium molecule and alkyl ammonium molecule in the organic layer.

Keywords: layered perovskite; superlattice; molecular mixing; chromophore; organic-inorganic composite

INTRODUCTION

A family of lead halide-based layered perovskites, $(RNH_3)_2PbX_4$, self-organizes a superlattice structure where organic ammonium layer(RNH_3) and a semiconductor layer of two-dimensional net work of corner-sharing octahedral PbX_6 are alternately piled up (Fig.1.a). Their low-dimensional semiconductor structure gives attractive optical properties due to formation of stable exciton: efficient exciton emission, electroluminescence and optical nonlinearity.[1)]

In the conventional layered perovskites, only alkyl ammonium molecules have been employed as organic layer. From the standpoint on material design of superlattice, employment of functionalized ammonium molecules such as chromophore-linked ones as organic layer is attractive; one can use organic layer not only as barrier layer but as functional layer to modulate electronic properties of semiconductor layer and to interact with the semiconductor layer.[2)]

Previously, we reported the preparation of PbBr-based layered perovskites with chromophore-linked ammonium molecules as an organic layer.[3)] In the work, only small or rod-like chromophores such as naphthalene and azobenzene were able to be incorporated in the layered perovskite structure, because of limited space of the organic layer. In this work, we found that bulky chromophore such as carbazole is incorporated into the layered perovskite through molecular mixing of chromophore-linked ammonium and alkyl ammonium molecules in organic layer.

EXPERIMENTAL

Bulky carbazole-linked ammonium bromide (1) was employed as organic layer material. Propyl ammonium bromide (C3) whose alkyl chain length is almost same with methylene chain length of 1 bromide was employed as second component of organic layer. Film samples were prepared on fused quartz substrates by spin-coating from DMF solutions of stoichiometric amounts of $PbBr_2$ and ammonium bromides ($PbBr_2$:ammonium bromides=1:2, where molar ratio of ammonium bromides 1:C3 = 1:0, 2:1, 1:1, 1:2, and 0:1).

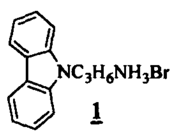

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FIGURE 1 Molecular structure of carbazole-linked ammonium bromides

RESULT AND DISCUSSIONS

Figure 2 shows absorption spectra of the film samples using carbazole-linked ammonium bromide. When only carbazole-linked

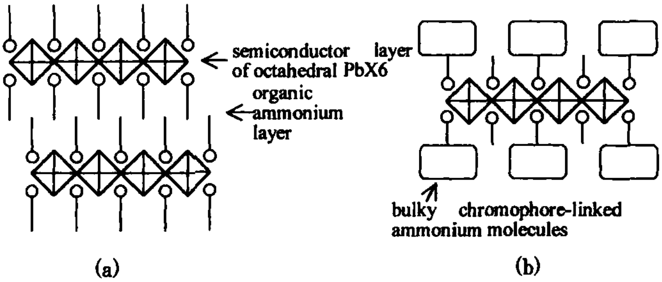

Figure 1 (a) Schematic structure of conventional lead halide-based layered perovskite and (b) lead halide-based perovskite with bulky chromophore-linked ammonium molecules incorporated into organic layer through molecular mixing.

ammonium bromide was employed, exciton absorption around 400 nm, which is characteristic of PbBr-based layered perovskite, was not observed, whereas the strong exciton absorption was observed when propyl ammonium bromides was used. Disappearce of the exciton absorption demonstrates that layered perovskite structure and electronic states due to the structure are not perfectly formed in the spin-coated film. However, when carbazole-linked ammonium bromide and propyl ammonium bromide were mixed, the film samples exhibit the strong exciton absorption, demonstrating the formation of PbBr-based layered perovskite structure.

Figure 3 shows X-ray diffraction profile of the film samples. The film samples of 1:C3=2:1 and 1:1 exhibit diffraction peaks corresponding to the same layer spacing (d=2.2 nm) with that of the film sample when only 1 was used. In addition, diffraction peaks corresponding to the layer spacing (d=1.3nm) of the layered perovskite with C3 as organic layer are not observed. These results suggest that ammonium molecules of 1 and C3 did not form mixture of each domain but mixed molecularly as shown in Fig.1.b). The molecular mixing is thought to give enough space to incorporate bulky carbazole chromophore in organic layer of the layered perovskites. As a result, PbBr-based layered perovskite with bulky carbazole chromophore was successfully prepared.

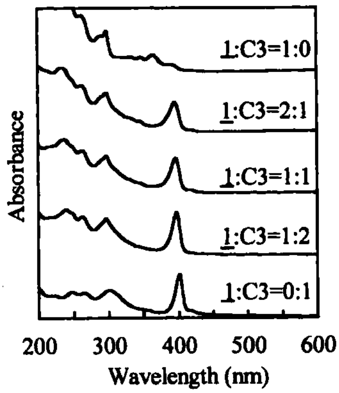

FIGURE 2 Absorption spectra of film samples.

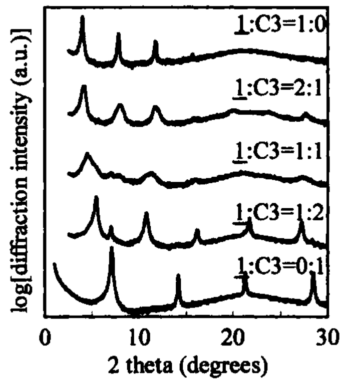

FIGURE 3 X-ray diffraction profiles of film samples.

CONCLUSION

PbBr-based layered perovskite with bulky carbazole chromophore was successfully prepared through molecular mixing of carbazole-linked ammonium and alkylammonium molecules in organic layer.

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