This article was downloaded by: [University of California, San Diego]

On: 15 August 2012, At: 23:23 Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH,

UK



Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/gmcl19

Incorporation of Bulky
Chromophore into PbBrBased Layered Perovskite
Organic/Inorganic Superlattice
by Mixing of ChromophoreLinked Ammonium and Alkyl
Ammonium Molecules

Masanao Era ^a & Akihiro Shimizu ^a

^a Department of Chemistry and Applied Chemistry, Faculty of Science and Engineering, Saga University, Honjo 1, Saga, 840-8502, Japan

Version of record first published: 24 Sep 2006

To cite this article: Masanao Era & Akihiro Shimizu (2001): Incorporation of Bulky Chromophore into PbBr-Based Layered Perovskite Organic/Inorganic Superlattice by Mixing of Chromophore-Linked Ammonium and Alkyl Ammonium Molecules, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 371:1, 199-202

To link to this article: http://dx.doi.org/10.1080/10587250108024721

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

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

MASANAO ERA and AKIHIRO SHIMIZU

Department of Chemistry and Applied Chemistry, Faculty of Science and Engineering, Saga University, Honjo 1, Saga 840-8502, Japan

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.

<u>Keywords</u>: layered perovskite; superlattice; molecular mixing; chromophore; organic-inorganic composite

INTRODUCTION

A family of lead halide-based layered perovskites, (RNH₃)₂PbX₄, self-organizes a superlattice structure where organic ammonium layer(RNH₃) and a semiconductor layer of two-dimensional net work of corner-sharing octahedral PbX₆ 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

FIGURE 1 Molecular structure of carbazole-linked ammonium bromides

quartz substrates by spin-coating from DMF solutions of stoichiometric amounts of PbBr₂ and ammonium bromides (PbBr₂:ammonium bromides=1:2, where molar ratio of ammonium bromides 1:C3 = 1:0, 2:1, 1:1, 1:2, and 0:1).

RESULT AND DISCUSSIONS

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

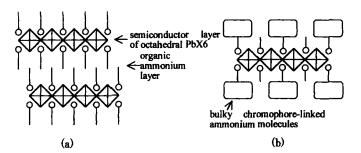
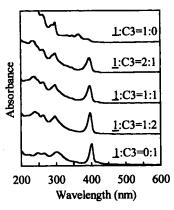


Figure 1 (a) Schematic structure of conventional lead halide-based layered perovskite and (b) lead halide-based perovskite with bulky chromophore-linked ammonium molecules incorporated into organic layer through molecular mixing.

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.



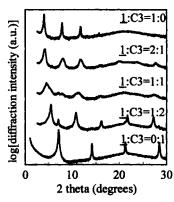


FIGURE 2 Absorption spectra of film samples.

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.

This work is supported by the Core Research for Evolutional Science and Technology Program from Japan Science and Technology Corporation (CREST/JST).

References

- 1) D.B.Mitzi, Prog. Inorg. Chem., 48, 1 (1999).
- 2) M.Era et al., Thin Solid Films, 331, 285 (1998).
- 3) M.Era et al., Chem. Lett., 1235(1997)