Tuning the Structures and Optical Properties of Perovskites by Varying the Alkylamine Type and Chain Length

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ABSTRACT: Organic–inorganic perovskites, (RNH3)2PbX4, have attracted much attention as one of the most promising light-harvesting and light-emitting materials. The present work investigated the steric effects of the organic parts on the perovskites by varying the alkylamine type and chain length. Primary, secondary, and tertiary amines with various chain lengths were introduced into organic–inorganic perovskites. Extending the chain length raised the phase transition point and shortened the absorption wavelength. In addition, the introduction of secondary and tertiary amines resulted in red- and blue-shifting of the absorption peaks, respectively.

INTRODUCTION

Organic–inorganic metal halide-based perovskite compounds have attracted significant attention since the report of their application to photovoltaic devices by Miyasaka et al. in 2009.1 As the study of perovskite solar cells (PSCs) has progressed over the last several years and new methods of fabricating perovskite materials and devices have been developed, the power conversion efficiency of PSCs has increased from 3.8% to more than 20%.2−9 The main advantage of perovskite compounds is the tunability of their chemical and physical properties, which in turn is derived from the wide range of possible structures. Typically, three-dimensional (3D) perovskites having the general formula AMX3 (A = CH3NH3+, Cs+, CH(NH2)3+, M = Pb2+, Sn2+, X = Cl−, Br−, I−) naturally form layered structures consisting of 2D sheets of [PbX6]12− octahedra and organic alkylammonium (RNH3+) layers. Owing to the presence of these hydrophobic organic layers, such materials exhibit significant stability in the presence of water. These compounds also show exceptional optical properties due to the formation of quantum wells. The organic alkylammonium layers have wide band gaps, whereas the band gaps of the inorganic [PbX6]12− layers are considerably smaller. Consequently, excitons are confined in the inorganic layers such that these perovskites behave as ideal 2D materials. This results in unique optical properties and significant potential for applications in optical devices such as light-emitting diodes, photodetectors, and lasers. These 2D compounds are often synthesized using simple primary alkylamines, such as butylamine, pentylamine and hexylamine.10−14 Single X-ray crystallographic analysis of these compounds revealed that crystal structure of 2D perovskite with short alkylamines was orthorhombic (Pbca) or monoclinic (P21/a) at room temperature (r.t.).15 Secondary and tertiary amines have been rarely applied in iodoplumbate systems, and so the effects of the type of amine remain unclear. It would be helpful to investigate such materials, because the influence of additional methyl groups around the amine sites would be expected to produce a steric effect at the organic–inorganic interface and so could affect the optical properties. In the present study, we introduced primary, secondary, and tertiary alkylamines with chain lengths of 6 or 18 into a 2D perovskite compound to assess the effects of the type of amine. Furthermore, to examine the effect of chain length, a series of perovskites was synthesized using primary amines with varying chain lengths (n = 6, 12, 14, 16, or 18) (Figure 1).

RESULTS AND DISCUSSION

Hydroiodides based on primary, secondary, or tertiary amines, CnH2n+1NH3I (n = 6, 12, 14, 16, or 18), CnH2n+1NH(CH3)I (n = 6 or 18), and CnH2n+1N(CH3)2I (n = 6 or 18), were obtained by reacting equivalent amounts of the corresponding amines, CnH2n+1NH2 (n = 6, 12, 14, 16, or 18), CnH2n+1NH(CH3) (n = 6 or 18), or CnH2n+1N(CH3)2 (n = 6 or 18), with hydroiodic acid, respectively. Perovskite solutions were prepared by reacting stoichiometric amounts of these hydroiodides with PbI2 in N,N-dimethylformamide (DMF). Films of the resulting (CnH2n+1NH3)2PbI4 (abbreviated as CnPbI3), (CnH2n+1N(CH3)2H)2PbI4 (NCnPbI), and (CnH2n+1N-
(CH$_3$)$_2$H)$_2$PbI$_4$ (NNC$_n$PbI) were fabricated on preheated glass substrates at 100 °C by spin-coating at 2000 rpm. Figure 2a shows the out-of-plane X-ray diffraction (XRD) profiles of C$_n$PbI films having n values of 6, 12, 14, 16, and 18. A series of diffractions corresponding to the interlayer d-spacing between the inorganic layers was clearly observed for each film. The d-spacing values for C$_6$PbI were 16.3 Å ($n = 6$), 24.4 Å ($n = 12$), 26.9 Å ($n = 14$), 29.4 Å ($n = 16$), and 31.9 Å ($n = 18$), respectively. The d-spacing values along the c-axis increased in a linear manner with increases in n. Figure 2b presents the UV−vis absorption spectra of the C$_n$PbI spin-coated films. All C$_n$PbI spin-coated films generated an exciton absorption band around 500 nm, suggesting the formation of stable excitons. However, although C$_6$PbI produced an exciton absorption peak at 514 nm, the peaks of those films having longer alkyl chain lengths ($n \geq 12$) appeared in the vicinity of 490 nm.

The structural transitions of the perovskite compounds were investigated by differential scanning calorimetry (DSC). Figure 3a shows the DSC curves acquired from C$_n$PbI microcrystals fabricated by a precipitation process using DMF as a good solvent and dichloromethane as a poor solvent. All compounds exhibit two phase transition points above r.t., which shift toward higher temperatures with increasing chain length. These phase transitions are denoted as I and II. The associated enthalpies increased along with chain length. These results indicate that phase transitions I and II are associated with structural changes in the inorganic and organic layers, respectively. At r.t., C$_6$PbI was in a different phase from the other compounds. As the quantum confinement structures in each perovskite were affected by the inorganic phase transition, the optical properties of C$_n$PbI were different, as shown in Figure 2b. Each C$_n$PbI film showed color change at its phase transition point, with the exception of the C$_6$PbI. As shown in Figure 3b, the C$_{12}$PbI film was yellow at r.t. and turned to orange above 50 °C because of the phase change at 42 °C. On the other hand, C$_6$PbI was orange at both r.t. and 50 °C, as shown in Figure 3b.

Figure 4a,b shows the out-of-plane XRD patterns of C$_n$PbI, NC$_n$PbI, and NNC$_n$PbI spin-coated films having n values of 6 or 18. A series of diffractions are observed for each sample,
indicating that the compounds formed layered structures. The d-spacing values calculated from the diffraction peaks are summarized in Table 1. The interlayer spacing of the NC18PbI was greater than that of the C18PbI and NC6PbI. Similarly, the NC18PbI had the largest interlayer spacing among the three n = 6 samples. The tertiary amine was larger than primary amine owing to having the two additional methyl groups around the N atom, and the resulting steric effects evidently increased the d-spacing. As for the secondary amines, the effect of an additional methyl group on the d-spacing value is larger for NC18PbI compared to that for NC6PbI. Although the d-spacing of NC6PbI and NC18PbI is almost similar, the value of NC6PbI is about 3 Å larger than that of NCNC6PbI. This may be due to the difference of relaxation properties and packing of alkyl chain.

Figure 5 shows the in-plane XRD profiles of C6PbI, NNC6PbI, and NNC6PbI spin-coated films. C6PbI showed a diffraction peak at 14.2° (6.4 Å). The distance between the Pb and I in this material was 3.2 Å, whereas the distance to the nearest neighboring Pb ion was 6.4 Å. Thus, the octahedra in this compound shared corners with one another to form an inorganic sheet parallel to the substrate. In contrast, the NNC6PbI generated a diffraction peak at 11.3° (7.8 Å), which is larger than that of corner-sharing octahedra (6.4 Å). This implies the distortion of octahedra networks in NNC6PbI. As previously reported,19–21 various modes of octahedral tilting of perovskite compounds exist. Also, some perovskites with larger amines formed hybrid structure in which corner-sharing and face-sharing network of octahedral networks coexisted.22 The face-sharing octahedra have larger Pb–Pb distance than that in corner-sharing ones. Therefore, NNC6PbI might have a face-sharing structure. NC6PbI and NNC6PbI gave diffraction peaks at 3.1 and 4.3°, which attributed to the interlayer spacing values between inorganic layers, respectively. This suggests that the crystalline growth of NC6PbI and NNC6PbI spin-coated films was partially perpendicular to the substrate.

Figure 6 presents the UV–vis absorption spectra of C6PbI, NNC6PbI, and NNC6PbI spin-coated films. Exciton absorption peaks attributed to quantum confinement structures were observed for each of the compounds. This result suggests the formation of stable excitons in the perovskites. As noted, the C6PbI produced an absorption peak around 500 nm. However, when the secondary amines were introduced into the perovskite, the NC6PbI and NC18PbI peaks were shifted toward longer wavelengths by approximately 7 and 33 nm, respectively. Conversely, including tertiary amines, as in NNC6PbI and NNC18PbI, shifted the absorption toward shorter wavelengths by about 89 and 54 nm, respectively. Presumably, these shifts in optical properties were caused by rearrangements of the iodoplumbate frameworks and affected the band gaps on perovskite. It has been reported that perovskite with face-sharing octahedra shows blue-shifted peaks than a standard layered structure.22 By taking into consideration that NNC6PbI series have face-sharing octahedra as shown in XRD, the blueshift of absorption bands is reasonable. We believe that the steric effect of the additional methyl group modified the quantum confinement structures.

### CONCLUSIONS

Several 2D perovskites were fabricated, having primary, secondary, or tertiary amines with various chain lengths. Our results demonstrate that the phase transition points increased and the absorption peaks appeared at shorter wavelengths with increases in the chain length. Introducing secondary or tertiary amines into the perovskite red-shifted or blue-shifted the absorption peaks, respectively. These shifts are attributed to tilting of the inorganic framework due to the steric effects of the additional methyl groups. These results indicate that the optical properties of such materials can be modified while retaining the quantum confinement structure, by changing the type of amine. Our research could be one of the clues to reveal the influence of the structure of A-site cation on 2D-layered perovskite for further applications.

| Table 1. Major XRD Diffraction Peaks (Less Than 15°) and d-Spacing Values for C6PbI, NNC6PbI, and NNC6PbI (n = 6 or 18) |
|-------------------------------|----------------------|----------------------|
| C6PbI | NNC6PbI | NNC6PbI |
| Out-of-plane | In-plane | Out-of-plane | In-plane |
| n | 6 | 6 | 6 | 6 |
| Peak /° | 5.4 | 2.8 | 4.5 | 2.8 | 4.4 | 2.6 | 14.2 | 5.2 | 14.4 | 3.1 | 12.6 | 2.0 | 5.5 | 13.9 | 4.3 | 11.6 | 11.1 |
| d value / Å | 16.3 | 31.9 | 19.5 | 31.1 | 20.0 | 34.1 | 6.2 | 16.9 | 6.2 | 28.3 | 7.0 | 44.2 | 16.6 | 6.4 | 20.8 | 7.6 | 7.9 |

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**EXPERIMENTAL SECTION**

**Materials.** Hydroiodic acid (HI, 57 wt % aqueous solution) and DMF (super dehydrated) were purchased from Wako Pure Chemical Industries, Ltd. and used as received. Dichloromethane was purchased from Tokyo Chemical Industry Co., Ltd. Amine hydroiodides, C$_{2n+1}$NH$_3$I (n = 6, 12, 14, 16, or 18), C$_{2n+1}$NH(CH$_3$)$_2$I (n = 6 or 18), and C$_{2n+1}$N(CH$_3$)$_2$HI (n = 6 or 18) were synthesized by neutralizing C$_{2n+1}$NH$_3$H (n = 6, 12, 14, 16, or 18), C$_{2n+1}$NH(CH$_3$)$_2$H (n = 6 or 18), and C$_{2n+1}$N(CH$_3$)$_2$H (n = 6 or 18) with stoichiometric amounts of hydroiodic acid, respectively.

**Sample Preparation.** C$_{2n+1}$NH$_3$I and PbI$_2$ were dissolved in DMF at 50 °C for 1 h to obtain the precursor solutions for the preparation of [CH$_3$(CH$_2$)$_n$-NH$_3$I]$_2$PbI$_4$. The concentrations of these solutions were 40 wt % (for X-ray diffraction measurements) and 10 wt % (for UV−vis absorption spectroscopy measurements). Similarly, precursor solutions of (C$_{2n+1}$-N(CH$_3$)$_2$H)$_2$PbI$_4$ and (C$_{2n+1}$-N(CH$_3$)$_2$H)$_2$PbI$_4$ were synthesized using a Mikasa 1H-D7 spin coater. The substrates were heated at ca. 100 °C during the spin-coating process to obtain high-quality films.

Microcrystalline powders were obtained by pouring the precursor solutions into dichloromethane. After vacuum-drying, orange powders (n = 6) and yellow powders (n = 12, 14, 16, or 18) of [CH$_3$(CH$_2$)$_n$-NH$_3$I]$_2$PbI$_4$ were obtained.

Elemental analysis data for [CH$_3$(CH$_2$)$_n$-NH$_3$I]$_2$PbI$_4$ (n = 6), C$_{12}$H$_{24}$PbI$_4$: Calcd C, 15.6%; H, 3.38%; N, 3.13%; I, 45.4%. Exp. C, 15.6%; H, 3.18%; N, 3.31%; I, 45.3%.

Elemental analysis data for [CH$_3$(CH$_2$)$_n$-NH$_3$I]$_2$PbI$_4$ (n = 12), C$_{4n}$H$_{12n}$PbI$_4$: Calcd C, 26.5%; H, 5.06%; N, 2.58%; I, 44.7%. Exp. C, 26.4%; H, 4.30%; N, 2.58%; I, 44.6%.

Elemental analysis data for [CH$_3$(CH$_2$)$_n$-NH$_3$I]$_2$PbI$_4$ (n = 14), C$_{4n}$H$_{14n}$PbI$_4$: Calcd C, 29.4%; H, 5.64%; N, 2.45%; I, 44.1%. Exp. C, 29.4%; H, 5.42%; N, 2.42%; I, 44.3%.

Elemental analysis data for [CH$_3$(CH$_2$)$_n$-NH$_3$I]$_2$PbI$_4$ (n = 16), C$_{4n}$H$_{16n}$PbI$_4$: Calcd C, 32.0%; H, 6.05%; N, 2.33%; I, 42.3%. Exp. C, 32.1%; H, 5.82%; N, 2.33%; I, 42.2%.

Elemental analysis data for [CH$_3$(CH$_2$)$_n$-NH$_3$I]$_2$PbI$_4$ (n = 18), C$_{4n}$H$_{18n}$PbI$_4$: Calcd C, 34.4%; H, 6.42%; N, 2.23%; I, 40.4%. Exp. C, 34.6%; H, 6.45%; N, 2.25%; I, 40.4%.

**Characterization.** The optical absorption spectra of the spin-coated films were obtained with a Shimadzu UV-3100PC UV−vis−NIR spectrophotometer at room temperature. The XRD profiles were obtained over the 2θ range of 1.5−35° with a Rigaku SmartLab X-ray diffractometer operating at 45 kV and 200 mA using a Ni-filtered Cu Kα target. Thermal analysis was performed using a Hitachi DSC 7200 differential scanning calorimeter under a nitrogen flow of 40 mL min$^{-1}$.

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