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Template-Synthesis of Dimension-Diminished Lead Halide Clusters at the Interlayer of Multibilayer Cast Films[1)]

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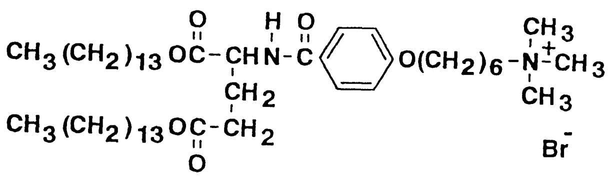
Anionic lead halide clusters of $PbBr_4^{2-}$ were synthesized at the interlayer space of cationic multibilayer cast films either by the co-casting method or by the ion-exchange method. Marked blue shifts in exciton absorption spectra indicated the formation of dimension-diminished clusters and their two dimensional assembly.

Spatially controlled synthesis of inorganic clusters in diminishing dimensions is of paramount importance for the development of microscopic to mesoscopic materials which possess desired electronic and optical properties.[2-4)] Many approaches have been explored for the preparation of small inorganic clusters, including the use of colloids, micelles, vesicles, and solid matrices.[2-4)] However, there is still no general method to prepare an organized assembly of structure-controlled clusters, except for the metal calcogenide clusters synthesized in zeolite supercages.[2,5)]

We have reported that cast films of synthetic bilayer membranes provide matrices for the preparation of two-dimensional polymer networks (acrylate polymers[6)] and polysiloxanes[7)]) and oriented iron oxide particles.[8)] In addition, quantum-sized CdS particles have been synthesized with preorganized cast films of Cd^{2+} and amphiphilic cyclams.[9)] In order to produce specific clusters, it is desirable to maintain coordination and/or electrostatic interactions between the membrane surface and growing clusters throughout the cluster formation process. As a typical example, we describe herein the preparation and characterization of anionic lead halide clusters formed in the interlayer of cationic multibilayer cast films of **1**.



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Multibilayer cast films were prepared by casting aqueous bilayer dispersions of **1** onto quartz plates or fluorocarbon membrane filters. Lead halides were chosen as cluster-forming compounds, since perovskite type layered lead halides are known to be exciton-exhibiting materials and enable spectral investigation with respect to the cluster structure.[10] Synthesis of lead bromide clusters was conducted by dipping cast films **1** into aqueous $PbBr_2$(20 mM)/KBr(4 M) mixtures or by casting aqueous dispersions or DMF solutions of $[\mathbf{1}]_2{}^{2+}PbBr_4{}^{2-}$. Potassium bromide was employed in the dipping method to solubilize $PbBr_2$ in water. Dodecylammonium bromide (DA) was used as a reference matrix since $(C_nH_{2n+1}NH_3)_2PbX_4$ (X = Cl, Br, I) is known to form two-dimensional layered perovskite compounds (Fig. 1).[10,11]

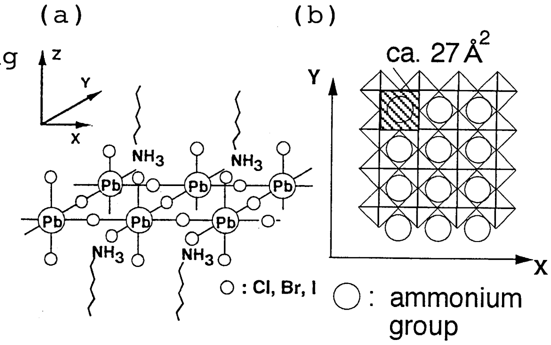

Fig. 1. Schematic representation of (a) perovskite-type layered lead halides[10] and (b) its in-plane view.

Figure 2a shows absorption spectra of $[\mathbf{1}\text{ or DA}]_2{}^{2+}PbBr_4{}^{2-}$ that are cast from DMF solutions. The $[DA]_2{}^{2+}PbBr_4{}^{2-}$ film gives λ_{max} at 386 nm, which is consistent with the reported exciton transition for the two-dimensional perovskite structure.[11] On the other hand, $[\mathbf{1}]_2{}^{2+}PbBr_4{}^{2-}$(from DMF) shows λ_{max} at a much shorter wavelength of 355 nm. Interestingly, a cast film of $[\mathbf{1}]_2{}^{2+}PbBr_4{}^{2-}$ from water shows a λ_{max} shift further to 324 nm (Fig. 2b). Since the UV absorption is absent in the region above 300 nm in the aqueous dispersion (Fig. 2b), the electronic absorption observed in these cast films must be unique to the solid state, consistent with the excitonic character. The observation of two λ_{max}'s for the cast films of $[\mathbf{1}]_2{}^{2+}PbBr_4{}^{2-}$(solvent, either DMF or H_2O) is indicative of the formation of two distinct quantized clusters.[10)]

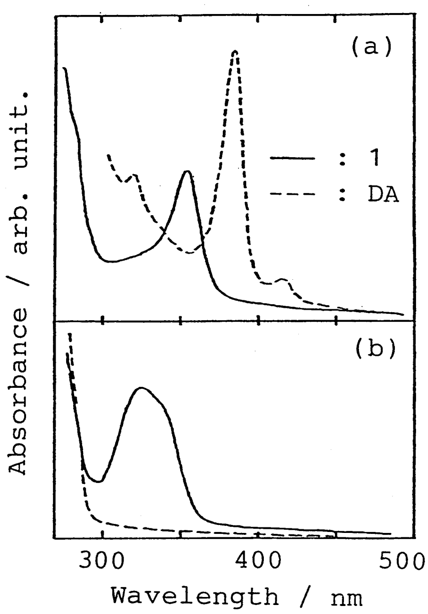

Fig. 2. Absorption spectra of (a) cast films of $[\mathbf{1}\text{ or DA}]_2{}^{2+}PbBr_4{}^{2-}$ from DMF solutions. (b) $[\mathbf{1}]_2{}^{2+}PbBr_4{}^{2-}$. solid line, cast film from water; dotted line, aqueous dispersion. $[\mathbf{1}] = 2 \times 10^{-4}$ M, 20 °C.

Dipping of cast film **1** in aqueous $PbBr_2$/KBr gives rise to a composite film with elemental composition of **1** : Pb^{2+} = 2 : 1, as determined by ICP emission spectrometry and spectrometric titration using Sulfarsazene.[12,13] Therefore, the $PbBr_4{}^{2-}$ species must have undergone complete ion exchange with Br^-. The λ_{max} value (320 nm) of the ion-exchanged film is close to

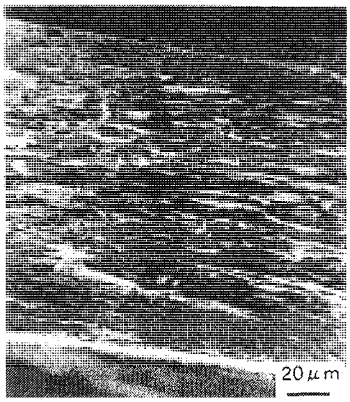

Fig. 3. Scanning electron micrograph of the cross section of a $[\mathbf{1}]_2{}^{2+}PbBr_4{}^{2-}$ cast film. (SEM ; Hitachi S-900)

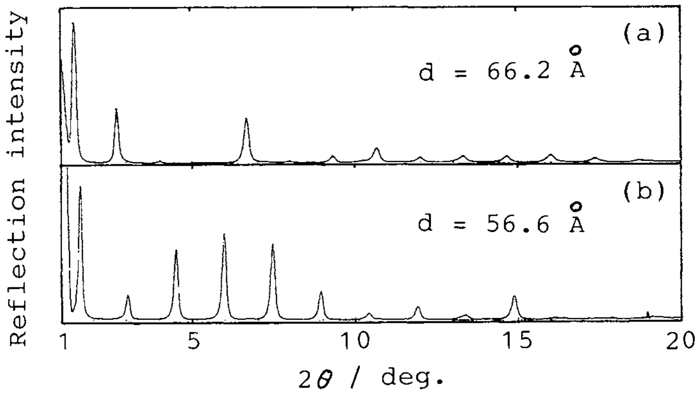

Fig. 4. XRD patterns of cast multibilayer films of (a) **1** and (b) $[\mathbf{1}]_2{}^{2+}PbBr_4{}^{2-}$.
(X-ray diffractometer ; Rigaku Denki RAD-R-32)

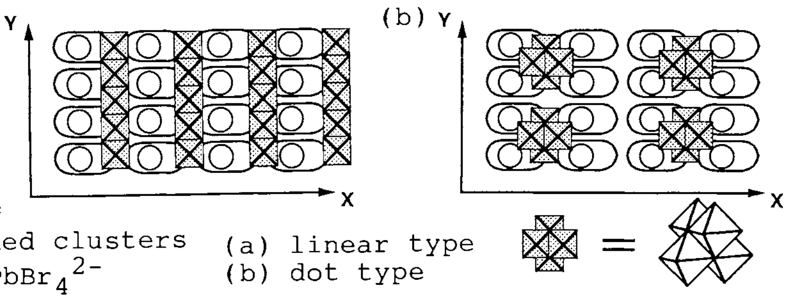

Fig. 5. Schematic in-plane view of dimension-diminished clusters of the composition $[\mathbf{1}]_2{}^{2+}PbBr_4{}^{2-}$

that (324 nm) of the above-mentioned film.

Figure 3 shows a scanning electron micrograph of the cross-section of a $[\mathbf{1}]_2{}^{2+}PbBr_4{}^{2-}$ composite film obtained by the ion exchange method. A layered structure parallel to the film plane can be seen clearly. Figure 4a and 4b compares reflection X-ray diffraction patterns of a single-component cast film of **1** and the ion-exchanged composite cast film. The single-component film gives a series of reflections that correspond to a long spacing of 66.2 Å up to 13th order (Fig. 4a). The ion-exchanged film of $[\mathbf{1}]_2{}^{2+}PbBr_4{}^{2-}$ shows altered diffraction patterns, in which a long spacing of 56.6 Å is the only component (Fig. 4b). This pattern was identical with that obtained for the co-cast film, which was aged under saturated humidity at 48 °C for 6 hrs.[13] These results clearly indicate the maintenance of ordered multibilayer structures during the cluster formation process.

The exciton absorption and X-ray diffraction patterns of the composite cast film were temperature-dependent. The initial λ_{max} at 324 nm at 20 °C irreversibly shifted to 347 nm by heating the film above ca. 57 °C, and this spectral change was accompanied by disappearance of higher order X-ray diffraction patterns.[13] Obviously, the cluster displaying λ_{max} of 324 nm is stable only in the presence of the regular multibilayer.

The observed blue shifts are explained as follows, in comparison with that reported for two-dimensional perovskite compounds $(C_nH_{2n+1}NH_3)_2PbBr_4$.

Two-dimensionally extended perovskite structures can be generated only when its unit area surrounded by four Pb^{2+} ions (ca. 27 $Å^2$)[14] shows satisfactory fitting to the cross-section of the ammonium molecule (Fig. 1). However, the unit area is too small for **1** that possesses the molecular cross section of ca. 50 $Å^2$.[15] As a result, $PbBr_4^{2-}$ cannot assume extended 2D cluster structures on the regular membrane surface of **1**. Instead, a still lower dimensional cluster (linear- or dot-shaped) will be formed (Fig. 5). The observed unusual exciton confinement effect must be derived from these specific structures, which could be constructed from some finite groups of octahedra that share vertices, edges, and/or faces.[16] The electrostatic interaction operating between the clusters and regulary packed ammonium head groups will require some specific cluster structures with uniform interlayer distribution.

In conclusion, cast films of synthetic bilayer membranes act as superior templates for the synthesis and organization of novel dimension-diminished lead bromide clusters. Construction of two-dimensional cluster assemblies cannot be achieved by manipulation of bulk materials. The present methodology would be applied widely to organization of quantized clusters of interest.

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