# **Electronic Supplementary Information**

# A New Class of Chiral Semiconductors: Chiral-Organic-Molecule-Incorporating Organic-Inorganic Hybrid Perovskites

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# **Experimental Section**

#### **Reagents and Materials Used**

(R)-(+)- $\alpha$ -methylbenzylamine (R-MBA, 98%, optical purity > 97%), (S)-(-)- $\alpha$ -methylbenzylamine (S-MBA, 98%, optical purity > 97%), (±)- $\alpha$ -methylbenzylamine (rac-MBA (99%), *N*,*N*-anhydrous dimethylformamide (DMF), anhydrous dimethyl sulfoxide (DMSO), lead oxide (PbO, 99.999%), and 57% aqueous hydriodic acid (HI) solution (99.95%, stabilized by H<sub>3</sub>PO<sub>2</sub>) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Ethanol (99.9%) was purchased from Daejung Chemical (Korea). (R)-(-)-sec-butylamine (R-BA, 98%) and (S)-(+)-sec-butylamine (S-BA, 98%) were purchased from TCI Chemicals (Nihonbashi-honcho, Chuo-ku, Japan).

## Synthesis of (R-MBA)<sub>2</sub>PbI<sub>4</sub>, (S-MBA)<sub>2</sub>PbI<sub>4</sub>, and (rac-MBA)<sub>2</sub>PbI<sub>4</sub> Powders

First, 200 mg (0.896 mmol) of PbO was fully dissolved in 6 ml of a 57% HI solution. Then, 200  $\mu$ l (1.57 mmol) of R-, S-, or rac-MBA was added to the solution. This resulted in the immediate formation of a precipitate. The solution containing the precipitate was heated to 100 °C using an oil bath to re-dissolve the precipitate. The reaction stock solution was then cooled to room temperature under ambient conditions, resulting in the crystallization of orange needles. These crystals were vacuum filtrated, and the filtrate was rinsed with toluene several times. Finally, the product was dried in a vacuum desiccator for at least two days.

### Fabrication of (R-MBA)<sub>2</sub>PbI<sub>4</sub>, (S-MBA)<sub>2</sub>PbI<sub>4</sub>, and (rac-MBA)<sub>2</sub>PbI<sub>4</sub> Thin Films

Soda lime glass was used as the substrate material for the fabricated films. Substrates with the desired dimensions were washed using ethanol in a sonicator for 10 min. Next, the substrate surface was cleaned by an ultraviolet-ozone cleaner for 15 min. The precursor solutions for the chiral perovskites were prepared by dissolving the perovskite powders in DMF in the desired concentration (20, 40, 50, and 66 wt%). In some cases, DMSO was also

added to the coating solution in a DMSO/Pb mole ratio of 1:1. To form the films, 20  $\mu$ l of the precursor solution was spread on the cleaned surface of the substrate, and spin-coating was performed. Unless specified, the spin-rate was 2000 rpm and the coating time was 30 s. Finally, the as-spin-coated film was annealed at 65 °C or 100 °C for 8 min on a hot-plate to induce crystallization.

#### Synthesis of (R-BA)<sub>2</sub>PbI<sub>4</sub> and (S-BA)<sub>2</sub>PbI<sub>4</sub> Powders and Films

First, 200 mg (0.896 mmol) of PbO was fully dissolved in 6 ml of a 57% HI solution. Then, 200  $\mu$ l of R- or S-BA was added to the solution. A precipitate formed immediately formed. The solution containing the precipitate was heated to 100 °C using an oil bath to re-dissolve the precipitate. The reaction stock solution was then cooled to the room temperature under ambient conditions, resulting in the crystallization of pale-yellow needles. The crystals were vacuum filtrated, and the filtrate was rinsed with toluene several times. Finally, the product was dried in a vacuum desiccator for at least two days. Films were then spin-coated on soda lime glass substrates cleaned by sonication in ethanol for 10 min and using an ultraviolet-ozone cleaner for 15 min. To form the films, 20  $\mu$ l of a 20 wt% perovskite solution in DMF was spread on the soda lime glass substrate, and spin-coating was performed at 2000 rpm for 30 s. The as-spin-coated film was annealed at 100 °C for 8 min on a hot-plate to induce crystallization.

#### Characterization

The phases of the chiral perovskite powders and films were analyzed using an X-ray diffraction (XRD) system (SmartLab, Rigaku, USA) with a Cu-K $\alpha$  radiation source (0.15406 nm). The crystalline structures of (R-, S-, and rac-MBA)<sub>2</sub>PbI<sub>4</sub> were visualized with the software VESTA using the respective crystallographic information files of the perovskite crystals.<sup>S1, S2</sup> The diffuse transmittance circular dichroism (DTCD) data, transmission CD data, and extinction data were collected using a CD spectrometer (J-815, JASCO, Easton, MD, USA). An integrating sphere was used to collect the DTCD data, while the transmission CD data were collected without the sphere. The background was air, and the spectra were obtained at a scan rate of 100 nm/min, with the data pitch being 1 nm. The anisotropy factor (g-factor) was calculated using following equation: g=CD/(32980 × extinction). The microscopy (SEM) system (JSM-7800F, JEOL, Tokyo, Japan). The absorption spectra were obtained using an ultraviolet-visible spectrophotometer (V-670, Jasco, Easton, MD, USA) equipped with an integrating sphere. In order to obtain the pure absorption spectra (see **Figure S7**). the total reflectance of the films was subtracted from their total transmittance.

(S1) Billing, D. G. Acta Cryst. 2002, E58, m669-m671.

(S2) Billing, D. G.; Lemmerer, A. CrystEngComm 2006, 8, 686-695.



Fig. S1 Crystalline structure of (rac-MBA)<sub>2</sub>PbI<sub>4</sub>.



**Fig. S2** (a) Photograph of KBr pellet with perovskite powder and (b) CD spectra of (R-MBA)<sub>2</sub>PbI<sub>4</sub>, (S-MBA)<sub>2</sub>PbI<sub>4</sub>, and (rac-MBA)<sub>2</sub>PbI<sub>4</sub>.



Fig. S3 CD and extinction spectra of R-MBA and S-MBA organic molecules in ethanol.



**Fig. S4** (a) Molecular structures of (S)-(+)-sec-butylamine (S-BA) and (R)-(-)-secbutylamine (R-BA) and (b) XRD patterns, (c) transmission CD spectra, and (d) extinction spectra of lead iodide perovskite films containing S-BA and R-BA as organic cations.



**Fig. S5** XRD patterns of  $(R-MBA)_2PbI_4$  films formed using 50 wt% precursor solution: (a) heated at 65 °C for 8 min and (b) heated at 100 °C for 8 min, with DMSO added to precursor solution.



**Fig. S6** Extinction spectra of  $(R-MBA)_2PbI_4$  films formed by spin-coating of 20, 40, 50, and 66 wt% precursor solutions at 2000 rpm for 30 s and subsequent annealing at 100 °C for 8 min.



**Fig. S7** (a) XRD patterns, (b) extinction spectra, (c) CD spectra, (d) normalized extinction spectra, and (e-f) cross-sectional SEM images of  $(R-MBA)_2PbI_4$  films formed by spin-coating of 66 wt% precursor solution at 2000, 5000, and 9000 rpm for 30 s and subsequent annealing at 100 °C for 8 min.



**Fig. S8** Absorption spectra of  $(R-MBA)_2PbI_4$  films formed by spin-coating of 20, 40, 50, and 66 wt% precursor solutions at 2000 rpm for 30 s and subsequent annealing at 100 °C for 8 min in absence of DMSO (note that the reflectance was eliminated).



**Fig. S9** Absorption spectra of  $(R-MBA)_2PbI_4$  films formed by spin-coating of 20, 40, 50, and 66 wt% precursor solutions at 2000 rpm for 30 s and subsequent annealing at 100 °C for 8 min in absence of DMSO (note that the reflectance was eliminated).



Fig. S10 XRD patterns of as-made, 3-, 5-, 7-days-aged (R-MBA)<sub>2</sub>PbI<sub>4</sub> films.