Circular dichroism and chirality in hybrid lead halide perovskites

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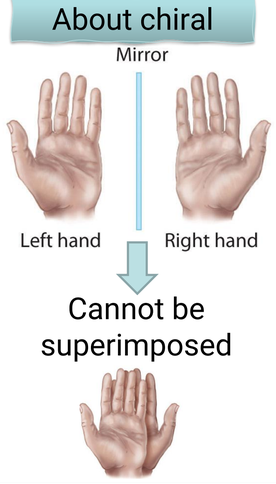
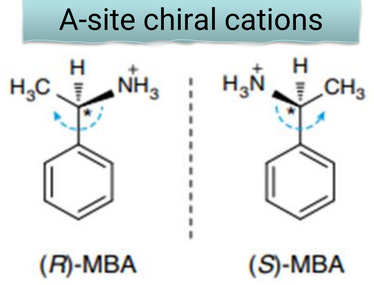
Introduction

About chiral

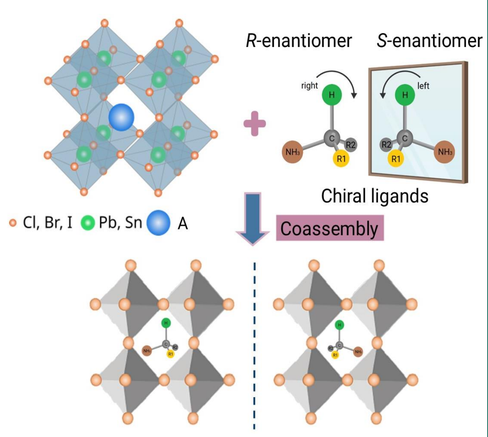


A-site chiral cations

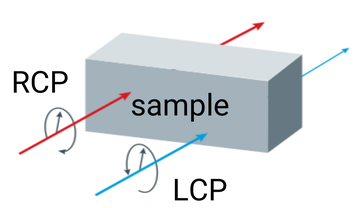


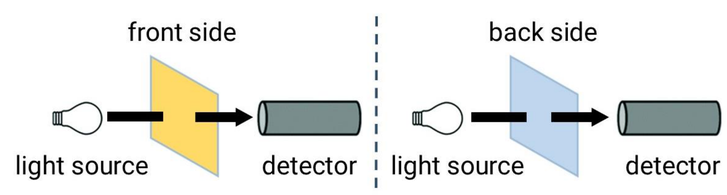
Chiral organic ligands of MBA and FMBA serve as the A-site cation. These ligands have two stereoisomers, R- and S-, which denote the chiral center's configuration.

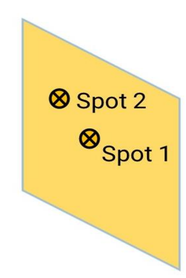
Co-assembly



Experimental approach



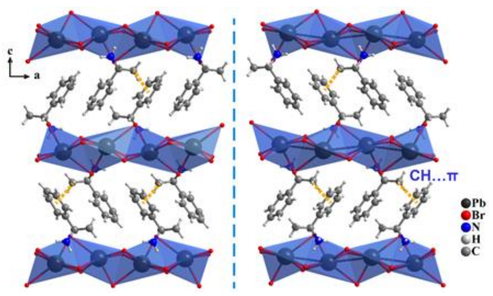


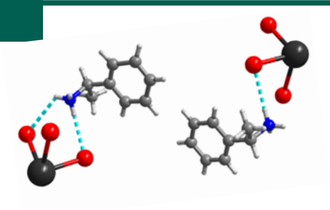


- Circular dichroism (CD) is the differential absorption of left-handed and right-handed circularly polarized light.
- Here, CD was measured from both the front and back side of different parts of the films.

1D and 2D Chiral Perovskites

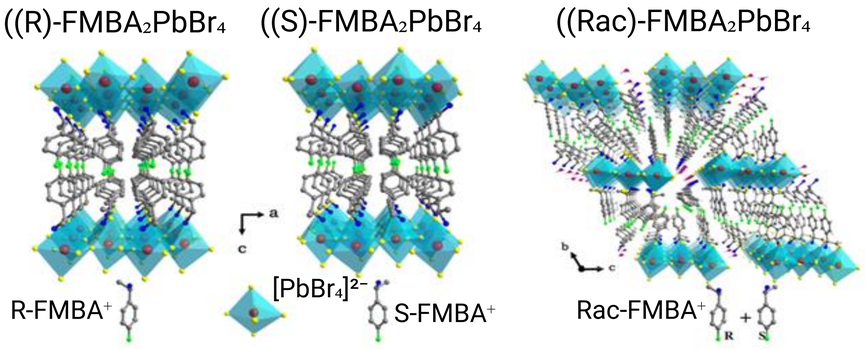
((R)-MBAPbBr$_3$) ((S)-MBAPbBr$_3$)





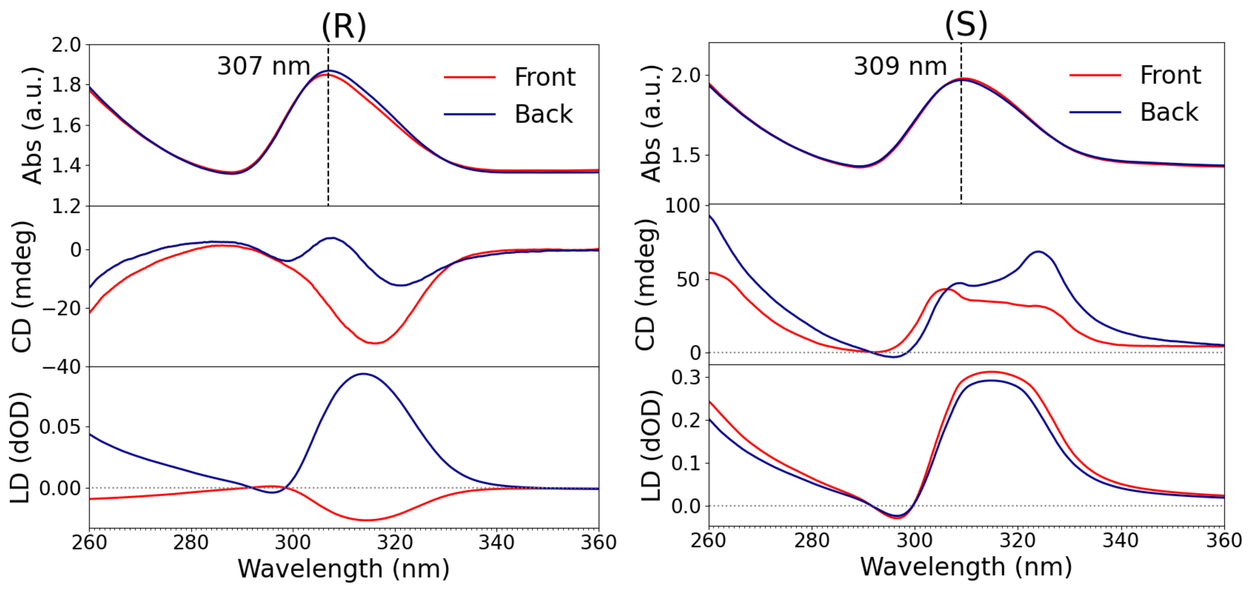
Inorganic chain interacts with organic amine cations via electrostatic forces and N-H···Br hydrogen bonding.

((R)-FMBA$_2$PbBr$_4$) ((S)-FMBA$_2$PbBr$_4$) ((Rac)-FMBA$_2$PbBr$_4$)

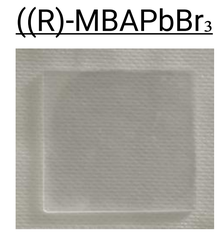


Crystal structure of the chiral perovskites: Top-left represent the 1D (R- and S-MBA)PbBr$_3$, bottom-left show the 2D ((R- and S-FMBA)$_2$PbBr$_4$ and bottom-right 1D (Rac)-FMBA$_2$PbBr$_4$.

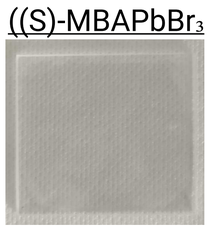
Circular Dichroism of MBA-system



((R)-MBAPbBr$_3$)



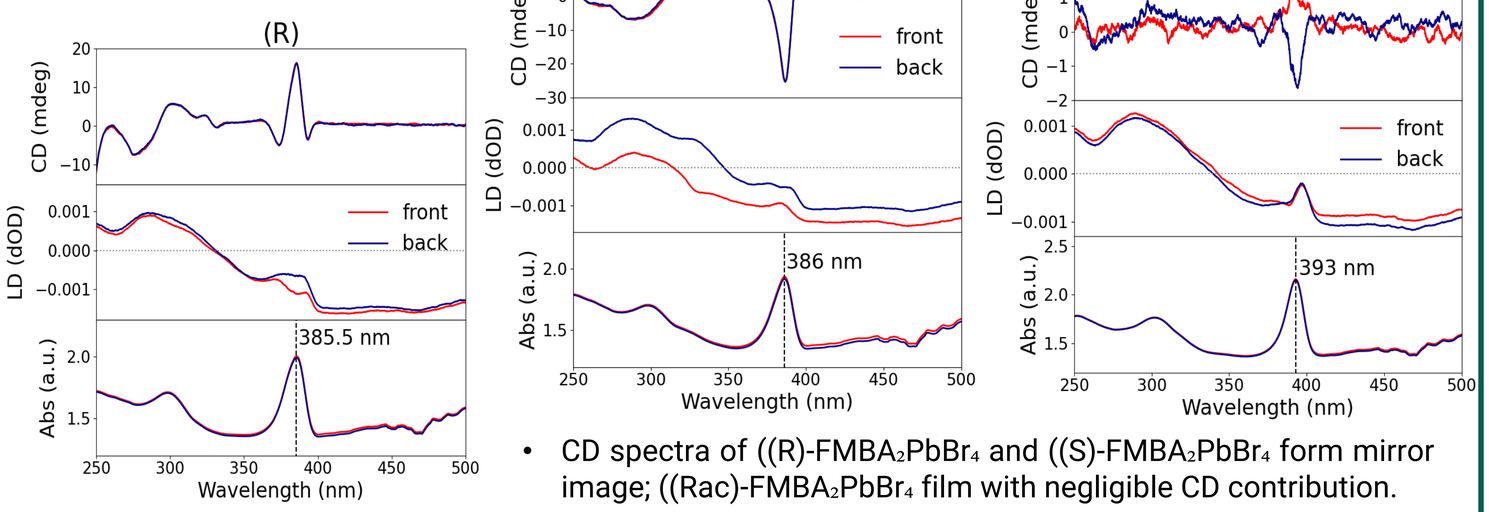
((S)-MBAPbBr$_3$)



The figures show the UV-visible absorption spectrum, CD spectra, and linear dichroism contribution of ((R)-MBAPbBr$_3$ and ((S)-MBAPbBr$_3$ at different spots on the front and back sides of the films.

- The CD spectra from front and back sides of the films do not resemble each other.
- CD signal differs significantly, sign changes.
- Large linear dichroism observed for both ((R)-MBAPbBr$_3$ and ((S)-MBAPbBr$_3$ films.

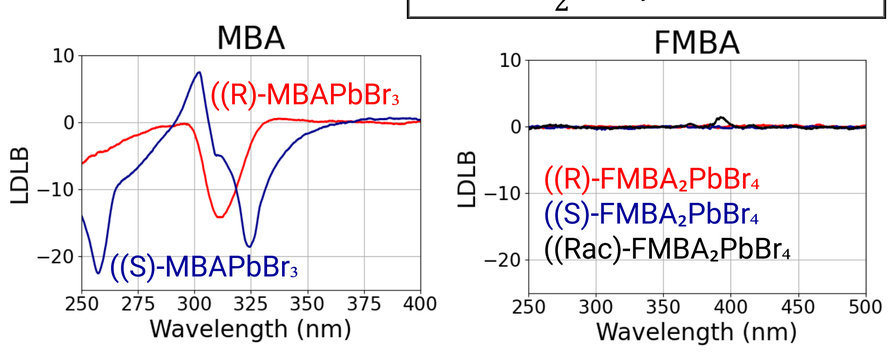
CD of FMBA-system



- CD spectra of ((R)-FMBA$_2$PbBr$_4$ and ((S)-FMBA$_2$PbBr$_4$ form mirror image; ((Rac)-FMBA$_2$PbBr$_4$ film with negligible CD contribution.

Linear contributions

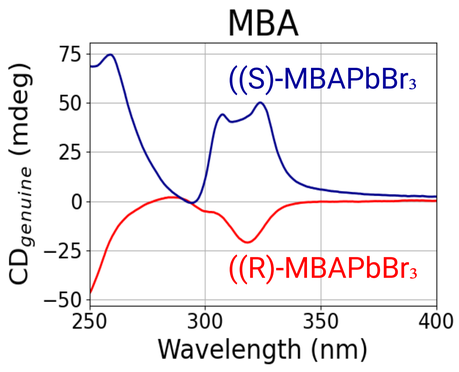
$$LDLB = \frac{1}{2} \cdot (CD_{front} - CD_{back})$$

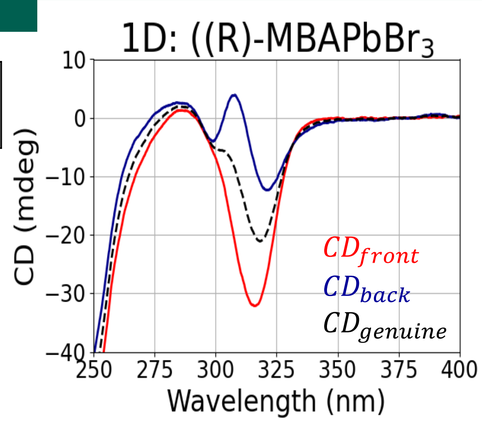


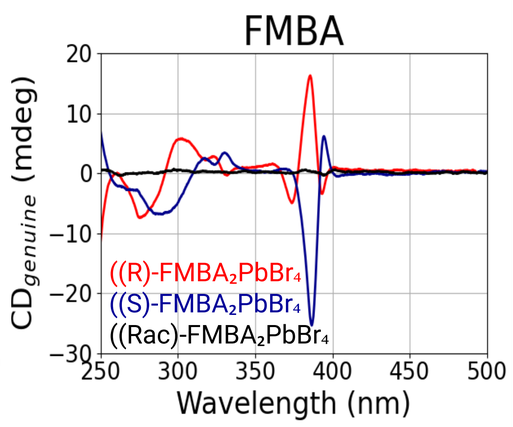
- Large (linear dichroism linear birefringence) LDLB contribution is observed for the 1D MBA system – which can be attributed to a textured film.
- In contrast, 2D FMBA films have small LDLB, which indicate the measured CD is very close to isotropic $CD_{genuine}$.

Extraction of genuine CD

$$CD_{genuine} = \frac{1}{2} \cdot (CD_{front} + CD_{back})$$







- From the CD data of MBA and FMBA chiral perovskites, it is possible to determine the values for the $CD_{genuine}$ and g_{CD}.

Anisotropy factor, g_{CD}

$$g_{CD} = \frac{CD\ [mdeg]}{32\,980\ x\ Absorption}$$

- Figure of merit for chiroptical activity number between -2 and 2
- $CD_{genuine}$ can be extracted from $CD_{genuine}$ maximum.

1D Perovskites :

	CD$_{genuine}$	g_{CD}
((R)-MBAPbBr$_3$	-21	-0.0003
((S)-MBAPbBr$_3$	324	0.0050

Summary

- Textured films can give artifacts in CD measurements due to strong linear effects.

References:

[1] Makhija, Urmila et al. (2024) "Effect of film morphology on circular dichroism of low-dimensional chiral hybrid perovskites." *The Journal of chemical physics*, 160(2), 021102.
[2] Zhao et al. (2023) "Circularly polarized luminescence enlargement from crystals to oriented films of Enantiopure 2d Hybrid perovskites." *Chemical Communications*, 59(45), 6881–6884.

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