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Letter

# Novel Chiral $CsPbBr_3$ Metal Halide Perovskite Magic-Sized Clusters and Metal Halide Molecular Clusters with Achiral Ligands

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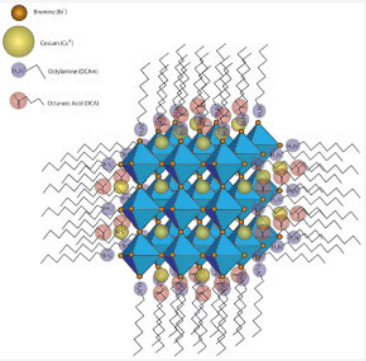
**ABSTRACT:** We have synthesized inherently chiral cesium lead halide perovskite magic-sized clusters (PMSCs) and ligand-assisted metal halide molecular clusters (MHMCs) using the achiral ligands octanoic acid (OCA) and octylamine (OCAm). UV−vis electronic absorption was used to confirm characteristic absorption bands while circular dichroism (CD) spectroscopy was utilized to determine their chiroptical activity in the 412−419 and 395−405 nm regions, respectively. In contrast, the larger sized counterpart of PMSCs, namely, perovskite quantum dots (PQDs), do not show chirality. The inherent chirality of the clusters is tentatively attributed to a twisted chiral layered structure, defect-induced chiral structure, or twisted Pb−Br octahedra.





Chiral nanostructures have been of interest for various applications including spin-filtering for spin selectivity and spin light-emitting diodes.[4,5,8] For instance, chiral organic molecules on the surface of nanoclusters have been shown to act as electron spin filters at room temperature, resulting in chirality-induced spin selectivity (CISS).[5] Perovskite magic-sized clusters (PMSCs) are ultrasmall crystallites of semiconductors that are stabilized with appropriate ligands.[1,6] They are smaller than typical quantum dots (QDs) and thus exhibit a stronger quantum size confinement effect and larger surface-to-volume (S/V) ratio. Fluorescent chiral nanoparticles have been employed as chiral optical probes for determining enantiomeric excess and identifying chiral molecules, attracting increasing research interest.[2,9] Most of the work done to date has focused on bulk crystals with chiral building blocks[4,7,20,21] or QDs with chirality induced by using chiral ligands.[2,3,5,9−11] Similar to QDs,[2] PMSCs and MHMCs could potentially acquire chirality through passivation using chiral ligands. However, it would be more interesting and desired if the clusters could possess intrinsic chirality[19] without the need to use chiral ligands to induce extrinsic chirality.

In this work, we report, for the first time, inherently chiral $CsPbBr_3$ perovskite PMSCs and MHMCs using a pair of achiral ligands: octanoic acid (OCA) and octylamine (OCAm). The ligands serve to passivate the clusters for stability and possess no chirality. Circular dichroism (CD) spectroscopy was employed to confirm the chirality of both the PMSCs and MHMCs with strong CD bands peaked at 413 nm for the PMSCs and 395 nm for the MHMCs. These CD minima match well the electronic absorption bands of the clusters measured using UV−Vis electronic absorption spectroscopy and established in our previous studies.[1,12,22]

In a typical synthesis of PMSCs using a modified ligand-assisted reprecipitation method, 5.00 mL of toluene was added to a 7.00 mL borosilicate vial with a small stir bar and secured to a mixer set to the maximum setting of 1150 rpm. In a second vial, the precursor was prepared using 8.51 mg of CsBr (0.040 mmol) and 14.68 mg of $PbBr_2$ (0.040 mmol), in 400 $\mu$L of DMF. The resulting solution was then shaken/stirred/sonicated at room temperature until everything was mostly dissolved. Next, 1.00 mmol of acid (158 $\mu$L of OCA) and 1.00 mmol of amine (162 $\mu$L of OCAm) was added to the vial. This solution was gently swirled (not sonicated) at room temperature until everything was dissolved to create the final precursor solution. Next, 50−100 $\mu$L of precursor solution was rapidly injected into 5.00 mL of toluene under vigorous stirring. The resulting formation was slow, forming some particles a minute or so after injection, but needing 5 min to finish reacting. The particles fluoresced a deep blue under ultraviolet light, and this can be used to track the progress of the reaction. If pure MHMCs were desired, CsBr was removed from the synthesis. Further stabilization of MHMCs can be achieved using an alternative ligand pair, valeric acid/butylamine, in a similar ratio. Following their synthesis,

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samples were immediately moved to storage in a fridge at ~2–4 °C to preserve the short-lived luminescent particles. Once clear samples are obtained, UV–vis and CD data can be collected. These finalized OCA/OCAm passivated $CsPbBr_3$ nanocluster samples will be termed OC-NCs from now onward.

Figure 1 shows a representative UV–vis electronic absorption spectrum for the OCA/OCAm passivated nano-

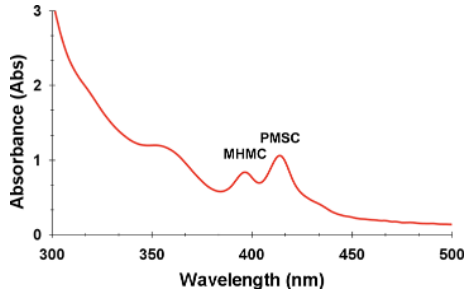


**Figure 1.** UV–vis electronic absorption of $CsPbBr_3$ with key bands at 413 nm (PMSCs) and 395 nm (MHMCs).

clusters, OC-NCs, taken at 2 °C. Here, the PMSCs and MHMCs showed key absorption bands at 413 and 395 nm, respectively. Based on our previous studies,[1,12,22] the 413 nm band is attributed to PMSCs while the 395 band is attributed to MHMCs. The 355 nm band could be due to formation of smaller clusters, and its origin will require further study in the future.

Figure 2 shows the average CD spectrum for OC-NC at 2 °C that shows bands peaked at 415 and 395 nm with an mdeg of approximately −4.0 and −3.3, respectively.

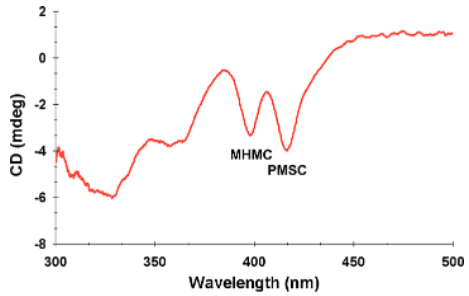


**Figure 2.** Average CD spectra of $CsPbBr_3$, compiled using OC-PMSC data from 12 baseline subtracted scans collected sequentially. Toluene was used for background subtraction. Key absorbance wavelengths are located at 412 nm for PMSCs and 395 nm for MHMCs. Smaller, broad bands are visible at 324 and 356 nm.

Two blue-shifted bands at 355 and 324 nm were also observed, indicating that either smaller particles also have chirality or higher-energy electronic transitions associated with the PMSCs or MHMCs also have the chiral property. A reduced temperature of 2 °C was utilized to help stabilize the particles for extended characterization. These data were taken simultaneously with the UV–vis data used as an independent measure of sample stability. The observed inherent negative CD signals indicate that the clusters favor absorption of right circularly polarized light.

The observation of the CD signal of the PMSCs and MHMCs was not based on any prior theoretical prediction but arose from a control experiment we were conducting to study chiral ligand induced chiral clusters. To explain the observed CD signal, we propose two possible explanations. The first is structural chirality[1,11–19,22] as a result of broken mirror symmetry, while the second is magnetism-induced chirality[23,24] via a weak magnetic field inherent to the clusters.

Figure 3 schematically shows three possible models we use to explain the observed intrinsic chirality of the PMSCs and MHMCs.

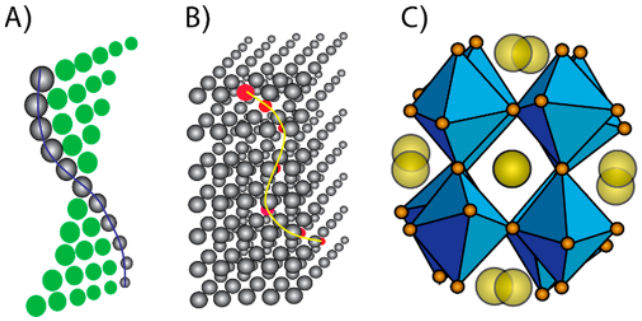


**Figure 3.** Proposed structures for the origin of chirality in the OCA/OCAm capped $CsPbBr_3$ PMSCs: (A) twisted chiral layered structure, (B) defect chiral structure (red balls with the yellow line for visualization), and (C) chirality induced by distorted octahedron. Similar mechanisms may apply to MCs. $Cs^+$ terminated $Pb–Br_2$ octahedra form the core structure, with alternating negative and positively charged OCA/OCAm ligands through $OCA^-$ to $Cs^+$ and $OCAm^+$ to $Br^-$ coordination, respectively.

One possible explanation, as shown in Figure 3a, is that the clusters are intrinsically chiral due to the twisting of layered structures. Layered structure of the clusters has been suggested in our previous work[1,12,22] and by others.[13,17,19] As the clusters are very small, they may be distorted or strained, resulting in a twisted structure that happens to be chiral. Another possible explanation is defect-induced chirality, as illustrated in Figure 3b and found in previous studies of QDs. Previous studies have found optical anisotropy within nanoplatelets and nanorods resulting from inherent defects during formation.[11,16,19] $CsPbBr_3$ perovskite nanoparticles were found to aggregate along a helical scaffold formed from either silica or polymers.[11,15]

The third possibility is chirality resulting from distortion of building block octahedra of the clusters due to ligand-related strain from the small size and large S/V ratio and thereby significant contribution of the ligands to the structure.[18] Size differences between the B-site $Pb^{2+}$ and $Cs^+$ A-site cations may result in broken mirror symmetry within nanoparticles, leading to inherent chirality.[14] While this effect has been found in QDs, it may be stronger within smaller sized particles like PMSCs and MHMCs due to higher surface tension or strain as well as involvement of more ligands used for passivation.[18] A similar effect has been previously observed and noted in the literature as a commonality within perovskites with large A-site cations.[13,14] The increased strain could result in structures that turned out to be chiral. Further experimental and theoretical studies are needed to determine the structural origin of the CD signal or the chirality observed in this work. These studies would most likely involve both HAADF-STEM and small-/wide-angle X-ray scattering, similar to the work of Zhang et al., where these measurements were used to determine a more exact structure for similar nanoparticles.[13] Using these


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methods, we would be able to determine which of the above structures is present or a combination of the three.

If the nanoclusters are chiral, then the interesting question is why only one chiral enantiomer was produced. A possible explanation is that the magnetic field from the magnetic stirring system during the synthesis induced the handedness of the nanoclusters. Previous literature has shown that magnetic fields used during synthesis can impact the structure of produced nanoparticles and impart chiroptical activity upon the clusters.[23,24] For example, magnetic alignment was utilized to create cobalt nanoparticle templates for gold nanoclusters to adhere to, which formed necklace structures due to the external field from magnetic stirring.[23] More recent work demonstrated that applying an external magnetic field to dispersed magnetic nanoparticles results in chiral structures that retain the chirality of the field.[24] This was done via a chiral quadrupole field generated via permanent magnets that reversibly assembled achiral $Fe_3O_4$/Au nanorods into diverse chiral superstructures. Using CD, chirality was confirmed following the application of the external field during growth phases, where parallel alignment of the magnets resulted in chiral superstructures and antiparallel alignment yielded a disappearance of CD signal. These results confirm that magnet polarity and alignment (repelling vs attracting) can be used to tune chirality, where reduced field gradients also reduce CD signal strength.

In our synthesis of MHMCs and PMSCs, a magnetic stir bar was used to disperse the antisolvent prior to and during nanoparticle formation. Thus, the entire reaction was conducted in the presence of a magnetic field from the stir plate. Previous work has demonstrated that stirring can compete with chiral selection within nanoscale aggregates, where molecules are locally tilted parallel to the domain boundary either clockwise or counterclockwise depending on the chiral handedness of the particles.[25] Therefore, it may be possible that the CD observed in our nanoclusters is due to chirality induced by the applied external field. Preliminary data comparing the CD signals of new samples made with magnetic or mechanical stirring in Figure S2 of the Supporting Information seem to support this hypothesis. However, further work is needed to clarify the true mechanism behind these observations in the future.

To summarize, OCA/OCAm passivated $CsPbBr_3$ PMSCs and MHMCs have been synthesized at room temperature using a modified ligand-assisted reprecipitation synthesis. Their optical properties were measured using UV−vis electronic absorption spectroscopy, and the PMSCs and MHMCs absorb around 412−419 and 395−405 nm, respectively. Both the $CsPbBr_3$ PMSCs and $PbBr_2$ MHMCs exhibit chirality based on CD measurement. This is important, especially considering that the ligands used for passivation are achiral. It is also interesting that the corresponding QDs are not chiral. This is a good demonstration that size matters fundamentally to the properties of nanostructures. The chiral nature of these clusters may find important applications in areas involving chiral induced spin activities and chiral catalysis, such as for spin-light-emitting-diodes and spin filtering.[4,5,8]

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.3c02581.

Alternative procedure for easier isolation of MHMCs similar to previous work[12] alongside materials sources and spectroscopic details; supportive PL data for the characterization of as-synthesized PMSCs (PDF)

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### Author Contributions

Celia Todd: Data curation, formal analysis, investigation, visualization, validation, and writing−original draft. Jin Zhang: Conceptualization, funding acquisition, methodology, project administration, supervision, resources, visualization, and writing−review and editing.

### Notes

The authors declare no competing financial interest.

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