# Peer Review File

**Manuscript Title:** Room temperature spin injection across a chiral-perovskite/III-V interface

## Reviewer Comments & Author Rebuttals

### Reviewer Reports on the Initial Version:

Referees' comments:

Referee #1 (Remarks to the Author):

This is a transformative work of spin-light-emitting diodes (spin-LEDs) consisting of both chiral hybrid perovskite (c-HP) and standard semiconductor III-V $(Al_xGa_{1-x})_{0.5}In_{0.5}P$ multiple quantum well (MQW) light emitting diode (LED). Following their pioneering work of spin-LEDs using fully hybrid perovskite materials (Ref. 13), this work, for the first time, demonstrated successful compatibility of chirality-induced spin selectivity (CISS) effect for spin-injection into the traditional semiconductors. This concept is exceptionally novel, providing a 'game-changing' strategy to achieve high-performance spin-LEDs at room temperature which was the bottleneck problem for opt-spintronics for the class of III-V materials. The manuscript is well-organized from the motivation to device fabrication, and device performance, which is suitable for general audiences who may be not familiar with the CISS effect and spin-LED configurations. The obtained room temperature circularly polarized electroluminescence, or the defined 'degree of circular polarization (DOCP)' up to ~15% is remarkably large. This value is a five-fold increase over the previous CISS demonstration in the hybrid perovskite-based LED, showing the great potential of the CISS effect in the III-V structures. Overall, I would recommend the publication of this work in Nature after my concerns are addressed.

[1] Whereas the observed circularly polarized emission is decisive and proves the successful spin injection from c-HP into MQW, the high thickness (up to 200nm, as confirmed by SEM) of the p-type cladding layer between the c-HP and MOW layer makes me worried that there is inadequate spin current being injected. The short spin diffusion length of III-V materials at room temperature would make this statement even more vulnerable. Do the authors measure the spin diffusion length of the p-type cladding layer (i.e., > 200nm)? Is there any thickness dependence of the p-type cladding layer that shows an exponential decay of DOCP at higher thicknesses? Alternatively, could the authors provide a list of examples of similar trilayer structures (p-type cladding/MQW/n-type cladding) that have been applied to traditional III-V-based spin-LEDs?

[2] Have the authors confirmed that the measured DOCP is not coming from the linear/circular birefringence of the c-HP layer? It would be better to show the circularly polarized photoluminescence of the c-HP layer (which wavelength?) in the S.I. to separate from the obtained DOCP at the wavelength of 590nm.

[3] One of the main motivations of this spin-LED configuration is to mitigate the conductivity mismatch problems between conventional ferromagnetic metals and semiconductors. Could authors provide the out-of-plane conductivity measurements in the c-HP, p-type cladding layer, and the MQW respectively to validate this statement?

[4] The spin injection from the c-HP is convincingly proven by the optical Hanle effect measurement (Fig. S5) which could be further developed as a standard tool for validating the spin injection via the CISS effect. From the shown Hanle curve, it is still difficult to determine the HWHM that is directly related to the spin relaxation time crossing the entire device configuration. Could authors estimate the spin relaxation time from it? Is the measured spin relaxation time consistent with the reported one in the III-V materials at room temperature? Usually, the spin relaxation time in the GaAs system is around several ten picoseconds at T=300K. Please see Nature Communications 7, 10296 (2016).

It is not clear in the figure caption about the direction of the magnetic field. Is the magnetic field applied along the out-of-plane direction of the device or perpendicular to the chiral axis of the c-HP?

[5] Is this optical Hanle effect separate from the classical magnetic field effect of the c-HP or III-V layer? In the hole-transport layer, there might be bipolaron formation at higher current densities and bipolaron-induced magnetic field effect in the c-HP layer showing a similar Lorentz-shape response.

Some minor issues:

[6] For the best performance of spin-LEDs, the external quantum efficiency (EQE) needs to be shown.

[7] In the main text, the circular polarization is defined as ‘DOCP’, while in Fig. 2 and Fig. S5, it shows ‘CPEL’. Please make them consistent throughout the entire manuscript.

[8] Please add labels for each layer in Fig. S1F.

[9] The caption of Fig. S3 is incorrect. There are many mistakes in this caption probably due to the multiple iterations of revisions. Please fix it.

[10] There are many technical details about the device fabrication description in the main text which could be considered moving to the S.I. while focusing the discussion on the device performance and mechanism in the main text.

[11] Please consider adding descriptions about why the maximum polarization degree in III-V is 50%, which would be helpful for the general audience. For instance, the majority spin-polarized carriers vs. minority in the GaAs is 3:1, etc.

[12] Please change the label of “PVK” to “c-HP” in Fig. 3a.

[13] On page 7, first paragraph, the authors stated that "Most systems that exhibit CISS, on the other hand, are also not suitable and have not been used for spin injection into conventional SCs (e.g. III-Vs, Si) because most CISS systems are insulating and consists of molecular layers. " This may be incorrect. Many chiral metals can exhibit the CISS effect.

Referee #2 (Remarks to the Author):

The manuscript investigates the integration of 2D chiral perovskite into a conventional III-V multiple quantum well (MQW) LED, aiming to demonstrate a spin-polarized LED operating at room temperature. Previous research by Kim et al. (Science 371, 1129, 2021) has utilized the chirality-induced spin selectivity (CISS) in 2D chiral perovskites to generate spin-polarized charge transport and achieve room-temperature spin-polarized LEDs without the need for magnetic fields or ferromagnetic contacts. Additionally, several other publications have also reported the use of chiral perovskites for achieving room-temperature spin LEDs (eg, Ye et al, J. Am. Chem. Soc. 2022, 144, 22, 9707; Wang et al, Adv. Mater.2023, 2305604; Jang et al, Adv. Mater, doi.org/10.1002/adma.202309335 and others). As a result, the novelty of using chiral-induced selectivity to demonstrate a spin LED over chiral halide perovskite may be limited, and there seem to be minimal technical advancements presented in this paper. Furthermore, the manuscript contains multiple errors and lacks refinement, rendering it unsuitable for publication in its current state. Therefore, substantial revisions are necessary to address the mentioned concerns and improve the overall quality of the manuscript before it can be considered for publication.

1. While perovskite has been utilized as an LED emissive layer with a high external quantum efficiency (EQE), chiral perovskite has also been used in spin LEDs, achieving circular polarization over 12% at room temperature (Jang et al, Adv. Mater, doi.org/10.1002/adma.202309335). It should be important to clarify the advantages of incorporating conventional MQWs for spin LED. Is the use of a cladding layer and MQWs necessary to achieve efficient spin LEDs?

2. Why not add another chiral perovskite layer to improve spin polarization by injecting spin-polarized electrons?

3. The manuscript lacks solid experimental evidence demonstrating spin injection across chiral halide perovskite/cladding layer interfaces. It is essential to provide information on the spin polarization and spin lifetime in chiral perovskites within the LED context.

4. Could the authors elaborate on the consequences of injecting polarized spin into the p-type cladding layer? Are there any losses observed? Moreover, what are the dynamics and efficiency of spin injection from the chiral perovskite to the cladding layer and subsequently to the MQWs?

5. Figures S6 and S7 lack descriptions and explanations in the main text, making it difficult for readers to understand their significance. Figure captions of A1-B2 are also missing in Fig. S6 and S7.

6. Could the author explain why the circular polarization of devices (PVK/MQWs) in Fig. S6 and S7 is lower compared to the device with the cladding layer?

7. Please provide the external quantum efficiency (EQE) of the device.

8. It would be helpful to identify the literature source used to obtain the band alignment information for the device.

9. Figure G is missing from Figure S3.

Referee #3 (Remarks to the Author):

The authors have succeeded in integrating chiral perovskite semiconductors with standard III-V LED structures and demonstrated efficient spin injection across the clean interface. The new type of spin LED shows a circularly polarized light emission with a maximum polarization degree of ~15% at room temperature and without magnetic field, which significantly exceeds a previous device performance. The perovskite/III-V semiconductor interface is well characterized by some analysis approach. The proposed methods to directly contact the halide perovskite with the traditional III-V semiconductors and the resulting demonstration of the high-performance spin LEDs are quite new and attractive to the relevant researchers. However, I cannot recommend publication in its current form. The following concerns should be clarified before publication in Nature.

1) Chiral induced spin selectivity (CISS), which is the basis of the results of this study, should be carefully explained in the supplementary for the reader.

2) What are the main factors that contributed to the significant increase in DOCP compared to a previous study [Science 2021, 371 (6534), 1129]?

3) Although the authors claim from the cross-sectional TEM images that a HOIS/III-V interface is formed with no oxide barrier, detailed elemental analysis should be performed by STEM-EDX. The results should provide strong evidence for the formation of oxide-free interface.

4) The Hanle effect result shown in Fig. S5 seems poor evidence because the result of only one device is described. The decrease in DOCP due to the application of external magnetic field is small.

The results of a number of devices should be shown as with the current dependence of DOCP. In addition, the DOCP at stronger magnetic fields should also be shown.

5) In Fig. 2(e), the number of devices measured above 5 mA is decreasing. What could be the reason for this? Also, the authors claim that it was not possible to measure devices above 15 mA, explain why.

6) On a related note, the P_CP-EL varies widely from device to device. What is the main reason for this? I am concerned that it may be differences in the quality of the c-HP/SC spin injection interface, which is the main issue of this study. This concern should be carefully investigated and clarified.

Some minor comments are as follows.

7) The following statement exists in the main text, but “Fig. S4” corresponding to this statement is not shown in the supplemental.

“In addition, we performed a pseudo in situ experiment, where the LED is continuously operated and the quarter waveplate was rotated selecting for RH and LH circular polarization (Fig. S4) over multiple cycles with continuous collection. While the overall EL intensity decreases with time due to joule-heating, the difference in intensity between RH and LH CP-EL remains > 10%.”

8) For the caption in Fig. S3, "(A) Images....device." should be deleted.

9) For Figs. S6 and S7, units of “Polarization” should be described.

10) For the results of B2 in Fig. S7, the vertical and horizontal axes are “Polarization (%)” and “Current (mA)”, respectively.

**Author Rebuttals to Initial Comments:**

Code:

Blue: Comment discussing the reviewer's question

Orange: Changes made to the main text

Referee #1 (Remarks to the Author):

This is a transformative work of spin-light-emitting diodes (spin-LEDs) consisting of both chiral hybrid perovskite (c-HP) and standard semiconductor III-V (AlxGa1-x)0.5In0.5P multiple quantum well (MQW) light emitting diode (LED). Following their pioneering work of spin-LEDs using fully hybrid perovskite materials (Ref. 13), this work, for the first time, demonstrated successful compatibility of chirality-induced spin selectivity (CISS) effect for spin-injection into the traditional semiconductors. This concept is exceptionally novel, providing a 'game-changing' strategy to achieve high-performance spin-LEDs at room temperature which was the bottleneck problem for opt-spintronics for the class of III-V materials. The manuscript is well-organized from the motivation to device fabrication, and device performance, which is suitable for general audiences who may be not familiar with the CISS effect and spin-LED configurations. The obtained room temperature circularly polarized electroluminescence, or the defined 'degree of circular polarization (DOCP)' up to ~15% is remarkably large. This value is a five-fold increase over the previous CISS demonstration in the hybrid perovskite-based LED, showing the great potential of the CISS effect in the III-V structures. Overall, I would recommend the publication of this work in Nature after my concerns are addressed.

Response: We appreciate the comments from the reviewer and the time spent to read and make helpful comments which we address below.

[1] Whereas the observed circularly polarized emission is decisive and proves the successful spin injection from c-HP into MQW, the high thickness (up to 200nm, as confirmed by SEM) of the p-type cladding layer between the c-HP and MOW layer makes me worried that there is inadequate spin current being injected. The short spin diffusion length of III-V materials at room temperature would make this statement even more vulnerable. Do the authors measure the spin diffusion length of the p-type cladding layer (i.e., > 200nm)? Is there any thickness dependence of the p-type cladding layer that shows an exponential decay of DOCP at higher thicknesses? Alternatively, could the authors provide a list of examples of similar trilayer structures (p-type cladding/MQW/n-type cladding) that have been applied to traditional III-V-based spin-LEDs?

Response: This is an excellent point. We had concern over this exact issue. First, based on previous literature of spin LEDs, it is well within reason for the carriers to traverse our 200 nm p-type cladding layer. While most devices that are targeted for III-V spin LEDs are gown with a thinner cladding layer (100 nm in this example https://journals.aps.org/prapplied/pdf/10.1103/PhysRevApplied.16.014034 ), examples such as https://www.pnas.org/doi/10.1073/pnas.1609839114 and https://pubs.acs.org/doi/full/10.1021/nl5003312 use a cladding layer thickness of 500 nm and still maintain spin polarization at room temperature during the long traverse.

We do think that the injection through the cladding layer likely does cause some spin scattering that is partially responsible for lowering the DOCP and inducing the voltage-dependent behavior. To investigate this we have calculated the traverse time (<1.9 ps) of carriers across the 200 nm AlGaInP p-clad and relate it to hole spin lifetimes (ps time scale) and included the following discussion in the main text:

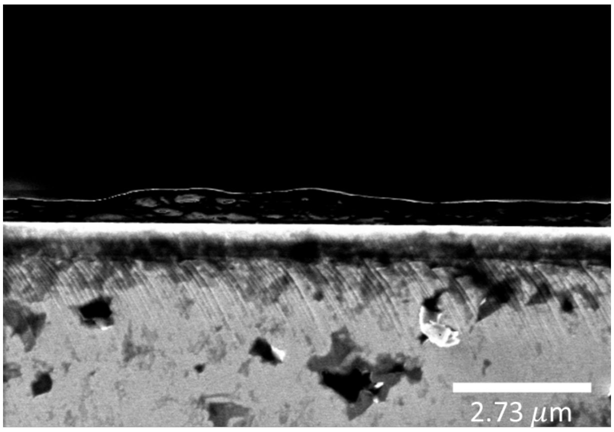
To determine the velocity (Vel) of carriers in our device and determine the carrier traverse time ($\Delta t$) across the AlGaInP p-clad, we rely on the equations: $Vel = E \cdot \mu_{hole}$ where E is the electric field strength and $\mu_{hole}$ is the hole mobility (injected spin polarized carrier) and $\Delta t = \frac{\Delta x}{Vel}$ where $\Delta x$ is the distance of the p-clad. (200 nm).

To determine the velocity (Vel) of carriers in our LED and determine the carrier traverse time (Δt) across the AlGaInP p-clad, we rely on the equations: Vel=E·μ_hole where E is the electric field strength and μ_hole is the hole mobility (injected spin polarized carrier) and Δt=Δx/Vel where Δx is the distance of the cladding layer. We collected Hall measurements on the p-type cladding layer and determined the hall mobility (holes in p-clad) to be μ_hole = 713 cm2/V ·s. The field strength across the p-type cladding layer is difficult to accurately determine but can be estimated by our results of the simulated band diagram (fig 3) where there is a 0.3 V potential across the 200 nm under an applied simulation voltage of 3 V across the entire LED resulting in a field of 1.5×10^6 V/m in the cladding layer. Using the simulated band diagram voltage drop of Vel = 1.07×10^5 m/s equates to Δt = 1.9 ps. Furthermore, it is important to note that the potential drop is likely much larger under operating conditions than the simulated band diagram (applied bias across the LED is 3V), where the voltage applied in emission experiments for the DOCP determination is ~6.5 V. To better frame our estimation, a larger voltage drop of 1 V (field = 5×10^6 V/m) across the p-type cladding layer would result in a carrier traverse time of 0.56 ps, a significantly shorter spin lifetime.

As mentioned this carrier traverse time being close to hole spin lifetimes found in literature, thus we suspect that the increase in bias on the device leads to more spins crossing the p-clad. layer, increasing the DOCP. We have included the following discussion in the main text:

We considered two possible sources of the current/bias dependence of the DOCP. (1) It arises due to the barriers from poorly aligned type-II bands (Fig 3a) at the c-HP/AlGaInP interface. When the carriers equilibrate (at 0 V bias, Fig. 3b), there is a large depletion region into the c-HP with low carrier concentration, which allows for the formation of a 2D hole gas within the c-HP at the interface. A large depletion region with intermittent carriers provides opportunities for spin scattering during spin-injection.[31] However, a higher bias (3V is shown in Fig. 3b) collapses the depletion region and gives injected carriers more energy that reduces interactions at the interface. Similar mechanisms of spin scattering due to depletion region and interface barrier heights have been suggested previously.[30,32] (2) It arises due to spin scattering/relaxation as holes traverse the 200 nm p-type cladding layer residing between the c-HP and MQW. We estimate the traverse time of carriers across this p-cladding layer to be <1.9 ps, which shortens with increased applied bias (see Methods for calculation details). Measuring the spin hole relaxation time in our current LED architecture is challenging (where isolating the p-type cladding layer is not feasible). Low temperature measurements in related III-V and room temperature measurements group IV semiconductors suggest hole spin relaxation is on the ps time scale at room temperature, close to the carrier traverse time.[33,34] As traverse time shortens with the increase applied bias of our LED during operation, there is less time during transport for spin relaxation and more carreirs maintain their spin polarization causing the increase in the DOCP at higher bias. Further tailoring of the III-V device architecture to have a thinner p-type cladding layer could enhance the DOCP in our devices.

Furthermore, we have attempted to etch the p-clad layer to a smaller thickness in operating devices. The cladding layer etching was successfully achieved with an Ar-ion etcher. However, these experiments yielded devices that would not operate for unknown reasons. This top-down approach for making a thinner cladding layer was not ideal in that the chemical etch likely caused unexpected surface chemistry issues and ruined the contact of the perovskite/AlGaInP or introduced an insulating surface materials (such as $Al_2O_x$) that ruined the device operation. Furthermore, SEM images (5 minute etch shown below) produced low quality materials (pitting, extra features compared to pristine. In the future we hope to use a bottom-up growth of materials with designed and variable cladding layers.



[2] Have the authors confirmed that the measured DOCP is not coming from the linear/circular birefringence of the c-HP layer? It would be better to show the circularly polarized photoluminescence of the c-HP layer (which wavelength?) in the S.I. to separate from the obtained DOCP at the wavelength of 590nm.

Response: Thank you for the suggestion. The issue of birefringence from the c-HP layer must be ruled out as a possibility. First, we have collected absorbance, photoluminescence (PL) and circular dichroism (CD) of the $(R/S\text{-}MBA)_2PbI_4$ and included it in extended data Fig. 8. We included the following discussion in the ruling out the contribution of optical phenomena to the DOCP in our devices.

While the emitted light does pass through the c-HP this cannot account for the large DOCP because (1) the circular dichroism is very small (extended Fig. 7) and (2) the c-HP absorbs at wavelength much shorter than the EL (590 nm).

Description in methods:

To further rule out the possibilities of birefringence or related phenomena in the (R/S-MBA)$_2$PbI$_4$ contributing to the DOCP we have collected absorbance, photoluminescence (PL), and circular dichroism of the individual (R/S-MBA)$_2$PbI$_4$ (extended data Fig. 7). The absorbance onset begins at 525 nm and the PL is centered at 511 nm, all well below the 590 nm EL of the AlGaInP device. Furthermore, we collected circular dichroism of (R/S-MBA)$_2$PbI$_4$ which shows features beginning below 550 nm and peaks at 508 nm and 498 nm (corresponding to the exciton resonance). We do not observe any circular dichroism at 590 nm, the center of our EL emission. From these results we do not expect any optical contributions of the (R/S-MBA)$_2$PbI$_4$ to the DOCP as the absorbance, PL, and CD are outside the spectral range of the devices EL.

Furthermore, we have attempted to characterize the circularly polarized photoluminescence (CPL) of the (R/S-MBA)$_2$PbI$_4$. The results are shown in our reviewer only file (Fig 1) for (R/S-MBA)$_2$PbI$_4$. We do not observe any significant CPL in our measurement, which is convoluted by the decay of PL intensity with collection number (i.e. laser irradiation). We verify our CPL measurement setup with a control of Eu(facam)$_3$ which shows a high DOCP. Thus we conclude that the room temperature CPL of (R/S-MBA)$_2$PbI$_4$ is weak, which is in agreement for room temperature reports on (R/S-MBA)2PbI$_4$ microplates shown here: https://pubs.acs.org/doi/full/10.1021/acsnano.9b00302 (Figure 4 for RT data).

[3] One of the main motivations of this spin-LED configuration is to mitigate the conductivity mismatch problems between conventional ferromagnetic metals and semiconductors. Could authors provide the out-of-plane conductivity measurements in the c-HP, p-type cladding layer, and the MQW respectively to validate this statement?

Response: Thank you for the question. We can estimate the conductivity of (R/S-MBA)$_2$PbI$_4$ by comparison to an analogous compound (BA)$_2$PbI$_4$ (BA= butylammonium) with a reported dark out-of-plane conductivity ($\sigma$) of $\sigma_{pvk} = 8.72 \times 10^{-12}\ S/m$ [https://doi.org/10.1021/jacs.8b03659]. We determined the conductivity of the top p-clad layer as $\sigma_{p-clad} = 1.79 \times 10^{8} S/m$ by Hall measurements (which should be isotropic). Using the simple description of the conductivity mismatch as a requirement from Rashba et al. (10.1103/PhysRevB.62.R16267) of $\frac{\sigma_{FM}}{\sigma_{SC}} \ll 1$, where the device in our study should replace $\sigma_{FM}$ with $\sigma_{c-HP}$ and $\sigma_{SC}$ with $\sigma_{p-clad}$. This yields $\frac{\sigma_{c-HP}}{\sigma_{p-clad}} = 4.87 \times 10^{-20}$ , which is significantly below 1 as required for the conductivity mismatch. However, the expanded equation from Wees et al. (10.1103/PhysRevB.62.R4790) requires some formalisms that may not directly translate to our devices. For example, that equation applies to the FM/SC/FM geometry where here we have CISS/SC/SC geometry. Ultimately though, the ratio of $\sigma_{c-HP}$ and $\sigma_{p-clad}$ being below 1 and the experimental results of large DOCP demonstrate that spin injection from semiconductors in our device geometry does not appear to have a conductivity mismatch issue.

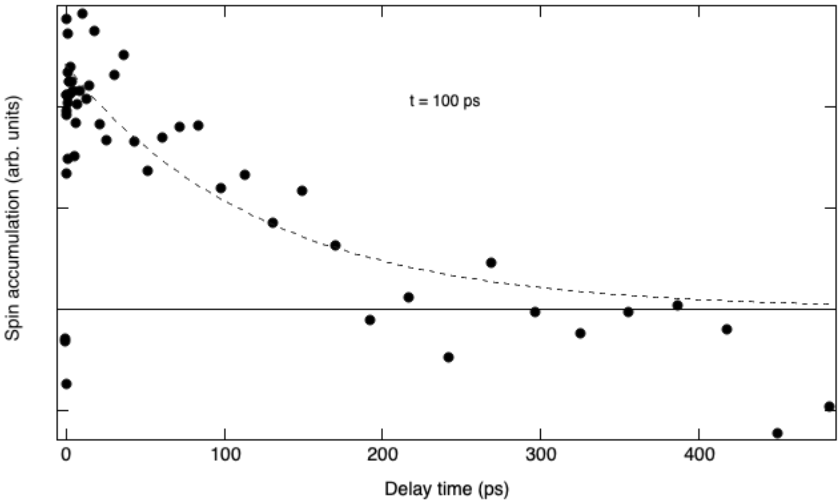
To address this and remain within the word limit, we have added the following discussion in the main text to focus on the comparison to DMS spin injection, which is a better analogue to our device, and not focusing on the conductivity mismatch only relevant with metallic systems:

A high spin-accumulation in conventional SCs at room temperature and no applied magnetic field has been difficult to achieve due to the required SC/spin injector interface and subsequent spin scattering at that interface.[38] A typical spin injector such as a FM in direct contact with a SC suffers from a conductivity mismatch that results in spin scattering and a tunnel oxide barrier is required to achieve efficient spin injection. Such interfacial architectures are hindered by undesired traits such as intrinsic-defects that decrease the spin injection efficiency.[28,32,39–41] For the c-HP/SC developed here the conductivity of the c-HP is lower than the p-cladding SC layer receiving the injection (opposite situation of a FM/SC interface) and do not require a tunnel oxide barrier as evidenced by the spin accumulation in our devices. This is similar to the situation of diluted magnetic semiconductor (DMS) spin injection systems, which have lower conductivities than metallic FM contacts.[38] In fact, the best spin injection analog to c-HP are DMS, which have the advantage of forming a SC/SC interface with no conductivity mismatch issue, allowing efficient spin injection. However, typical DMS have curie temperatures well below RT, which inhibits their utility.[42]

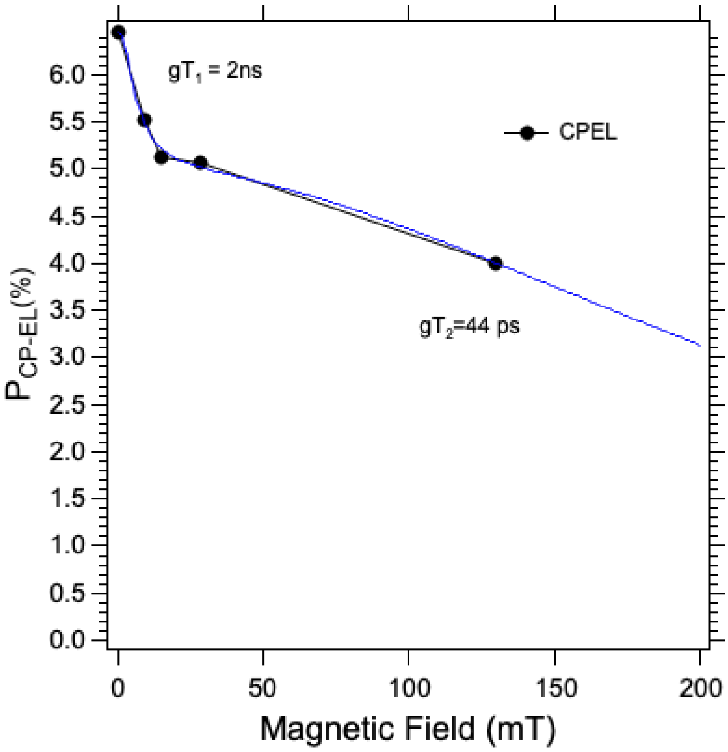
[4] The spin injection from the c-HP is convincingly proven by the optical Hanle effect measurement (Fig. S5) which could be further developed as a standard tool for validating the spin injection via the CISS effect. From the shown Hanle curve, it is still difficult to determine the HWHM that is directly related to the spin relaxation time crossing the entire device configuration. Could authors estimate the spin relaxation time from it? Is the measured spin relaxation time consistent with the reported one in the III-V materials at room temperature? Usually, the spin relaxation time in the GaAs system is around several ten picoseconds at T=300K. Please see Nature Communications 7, 10296 (2016).
It is not clear in the figure caption about the direction of the magnetic field. Is the magnetic field applied along the out-of-plane direction of the device or perpendicular to the chiral axis of the c-HP?

Response: We thank the referee for this important question. We agree that the Hanle effect should be further developed in the CISS community and is something that we are pursuing going forward. While these measurements are of the optical Hanle effect we also are pursuing more traditional electrical Hanle measurements of the CISS effect.

To address this issue, we measured the spin-lifetime at room temperature in the III-V quantum well samples. The lifetime we find is 100 ps (extended data Fig. 9). For this experiment we optically generated spin-polarized carriers in the multiple quantum well sample using circularly polarized light. We then measured the decay of the spin accumulation using a time-resolved circular dichroism spectroscopy.



The Hanle effect is parallel to the inorganic planes of the c-HP. We have included Hanle measurements which are orthogonal to the inorganic planes (transverse). Both orientations appear to decrease the DOCP with magnetic field albeit to different extents. This suggests that the spin orientation direction is non-trivial (i.e. neither along the a-b direction nor in the c direction of the c-HP). Furthermore, we found that there are two decays of the Hanle curve in both field directions. In the transverse direction the degree of polarization initially decreases and then slightly increases. The increase in polarization can occur either through the Zeeman splitting of the energy levels or through more complicated spin dynamics, e.g., contributions from nuclear spin orientation through the hyperfine interactions; namely dynamic nuclear spin polarization via the Overhauzer induced field). Such complicated spin-dynamics are a function of the III-V multiple quantum well sample and while could be interesting to study in more detail that is not the focus of our current manuscript. (see for example, PRB, 87, 235320, 2013 and for reference “Optical Orientation”, F. Meier, B.P. Zakharchenya, 1984). We can estimate the spin-lifetime from the longitudinal optical Hanle measurements, where we find two different spin relaxation processes. Note that in our multiple quantum well samples we do not know the Lande g-value of the electrons and holes, thus in the Hanle measurement we can only extract the product of the spin lifetime and g-value, i.e., (gT).



We find that the ($gT_1$) = 2 ns and $gT_2$ = 44 ps. Comparing to our spin-lifetime measurements we can estimate the g-value to be 0.44 for the faster component. This is in reasonable agreement for holes in III-V quantum well samples.

We have added the in plane Hanle measurement to the extended data Fig. 8 and adjusted the caption as follows:

Hanle effect measurement for (a) out-of-plane applied magnetic field (i.e. parallel to the inorganic planes of the (R/S-MBA)$_2$PbI$_4$ or long axis of the device) and (b) in-plane applied magnetic field (orthogonal to the inorganic planes of the (R/S-MBA)$_2$PbI$_4$; along the short axis of the device). Both orientations appear to decrease the DOCP with magnetic field albeit to different extents. This suggests that the spin orientation direction is non-trivial (i.e. neither along the a-b direction (parallel, out-of-plane) nor in the c direction (orthogonal, in-plane) of the (R/S-MBA)$_2$PbI$_4$ ).[53]

[5] Is this optical Hanle effect separate from the classical magnetic field effect of the c-HP or III-V layer? In the hole-transport layer, there might be bipolaron formation at higher current densities and bipolaron-induced magnetic field effect in the c-HP layer showing a similar Lorentz-shape response.

Response: Thank you for the question. The classical magnetic field effect we would expect the polarization to increase with magnetic field. While these measurements are not decoupled from the classical magnetic field effect, our conclusions remain the same that DOCP decreases with applied field, successfully showing the spin accumulation.

The bipolaron formation at higher current densities is a complex issue, in that it may lead to lower conductivity in the hole transport layer at higher magnetic fields. However, the hole transport layer comes before the CISS layer and thus the MC would only impact the total EL intensity *not the polarization*. We did not measure the EL intensity in a rigorous manor to compare point to point, and our setup is highly subject to positioning of the sample and confocal emission collection.

Second the MFE based on the bipolaron mechanism should show no dependence on field direction. While here we do see a striking difference depending on field direction. The different dependence on field direction is a direct consequence of the spin-dynamics in the III-V emitter layer due to the spin-accumulation in that layer and is also indicative that any MFE from the organic layer does not impact the spin-accumulation in the III-V layer.

Some minor issues:
[6] For the best performance of spin-LEDs, the external quantum efficiency (EQE) needs to be shown.

Response: We agree that EQE is a useful measurement to improve our understanding of the light-emitting performance of this LED. However, obtaining accurate values and meaningful insights from these measurements is quite challenging on III-V materials. We have included a measurement of EQE on the Au/n-type AlGaInP/AlGaInP MQWs/p-type AlGaInP/Au LED that serves as our platform (excludes c-HP, TFB, IZO layers). We have measured an EQE of <0.1% at 2A/cm$^2$ shown in reviewer only figure 6. The absolute values are quite low for several reasons related to nuances in the design and fabrication of III-V LEDs:

- The LED fabrication and design is not optimized for light emission in the same way a commercial packaged III-V LED is. The LED layers are left on the absorbing back substrate (GaAs in our case). A highly conductive current-spreading layer was not included, which leads to carrier injection and photon generation predominantly under the top metal contacts. Finally, antireflection coatings or other light extraction features were not included, which results in a very small fraction of light actually being emitted (the escape cone is rather small).
- The temperature of the LED was not rigorously controlled during the measurements. The rather long integration times lead to heating at high drive currents.

These aspects differ substantially from perovskite LEDs, and it is beyond our means to optimize every detail of the III-V LED fabrication in the same way industry has optimized over decades. Without this optimization, it will be difficult to separate the effects of the perovskite layer on electrical efficiency losses at the perovskite/III-V interface and any effects it has on the optical transmission of emitted light on the EQE values.

Given that the perovskite acts mainly as an injection layer, we do not expect it to impact the radiative recombination in the III-V MQW layers (which are separated from the perovskite by a cladding layer). We also do not believe the low EQE has a significant impact on the circularly polarized photoluminescence, where spin polarized carriers and unpolarized carriers should recombine (both non-radiatively and radiatively) at similar rates. The lack of EQE does not change our conclusions demonstrating the successful injection of spin-polarized carriers into a conventional semiconductor. In fact, previous III-V based spin LED reports did not report (or only roughly estimate) the EQE of their LEDs due to the challenges of measuring/optimizing EQE on a III-V emitter as well as the lack of relevance to the circular polarization physics (Citations 28,32,39-40 in main text).

[7] In the main text, the circular polarization is defined as 'DOCP', while in Fig. 2 and Fig. S5, it shows 'CPEL'. Please make them consistent throughout the entire manuscript.

Response: Thank you for catching this inconsistency in terminology. We have corrected the figures axis labels to be DOCP and edited the main text to consistently state it as "DOCP".

[8] Please add labels for each layer in Fig. S1F.

Response: Labels have now been added for the LED cross section.

[9] The caption of Fig. S3 is incorrect. There are many mistakes in this caption probably due to the multiple iterations of revisions. Please fix it.

Response: Thank you for catching this error. We have corrected the caption.

[10] There are many technical details about the device fabrication description in the main text which could be considered moving to the S.I. while focusing the discussion on the device performance and mechanism in the main text.

Response: Thank you for the suggestion. We have moved a section of the discussion on the detailed LED architecture to the methods section.

[11] Please consider adding descriptions about why the maximum polarization degree in III-V is 50%, which would be helpful for the general audience. For instance, the majority spin-polarized carriers vs. minority in the GaAs is 3:1, etc.

Response: Thank you for the suggestion. We have added a brief description of the 50% maximum polarization degree to the main text tailored for a general audience (orange text is new text added):

"A DOCP >15% implies a much higher spin accumulation since DOCP is a product of the spin accumulation multiplied by the circular polarization efficiency in the III-V MQWs, which based on the lack of confinement in our MQWs (as shown by the lack of blueshifted PL) is estimated to have a maximum of ~ 50%. This is due to the optical selection rules in the III-V semiconductor and transition probabilities favoring the heavy-hole over light-hole sub band in a 3:1 ratio, producing 3 right (left) handed to 1 left (right) handed circularly polarized photons when 100% spin polarized carriers are introduced.[23,24] Thus, the high DOCP implies that the spin-injection process is highly efficient.

[12] Please change the label of "PVK" to "c-HP" in Fig. 3a."

Response: We have corrected the labels to read c-HP.

[13] On page 7, first paragraph, the authors stated that “Most systems that exhibit CISS, on the other hand, are also not suitable and have not been used for spin injection into conventional SCs (e.g. III-Vs, Si) because most CISS systems are insulating and consists of molecular layers.” This may be incorrect. Many chiral metals can exhibit the CISS effect.

Response: Thank you for the comment. It is true that chiral metal systems could be integrated to manipulate spin, however, we believe they may not be suitable for this specific problem of spin polarized carrier injection into semiconductors, as they may have the same issues as metallic ferromagnetic contacts. That remains to be demonstrated though. To clarify in the main text, we have added the following:

There are some examples of chiral metallic systems[44] exhibiting CISS, but these may also suffer from the same conductivity mismatch as metallic FMs.

Referee #2 (Remarks to the Author):

The manuscript investigates the integration of 2D chiral perovskite into a conventional III-V multiple quantum well (MQW) LED, aiming to demonstrate a spin-polarized LED operating at room temperature. Previous research by Kim et al. (Science 371, 1129, 2021) has utilized the chirality-induced spin selectivity (CISS) in 2D chiral perovskites to generate spin-polarized charge transport and achieve room-temperature spin-polarized LEDs without the need for magnetic fields or ferromagnetic contacts. Additionally, several other publications have also reported the use of chiral perovskites for achieving room-temperature spin LEDs (e.g., Ye et al, J. Am. Chem. Soc. 2022, 144, 22, 9707; Wang et al, Adv. Mater.2023, 2305604; Jang et al, Adv. Mater, doi.org/10.1002/adma.202309335 and others). As a result, the novelty of using chiral-induced selectivity to demonstrate a spin LED over chiral halide perovskite may be limited, and there seem to be minimal technical advancements presented in this paper. Furthermore, the manuscript contains multiple errors and lacks refinement, rendering it unsuitable for publication in its current state. Therefore, substantial revisions are necessary to address the mentioned concerns and improve the overall quality of the manuscript before it can be considered for publication.

Response: We appreciate the helpful comments of Referee 2 and will address them point-by-point below.

1. While perovskite has been utilized as an LED emissive layer with a high external quantum efficiency (EQE), chiral perovskite has also been used in spin LEDs, achieving circular polarization over 12% at room temperature (Jang et al, Adv. Mater, doi.org/10.1002/adma.202309335). It should be important to clarify the advantages of incorporating conventional MQWs for spin LED. Is the use of a cladding layer and MQWs necessary to achieve efficient spin LEDs?

Response: Thank you for the comment and question.

First, the major advance of this work is the integration of a spin injector with traditional III-V optoelectronics. As we have noted in the paper, the FM injection layer on III-Vs will require overcoming significant engineering challenges to produce a large DOCP. Here we are utilizing CISS as a new method for overcoming this. III-Vs are a very important target for spin injection as they serve as the commercial basis of the LED industry. The incorporation of CISS with III-Vs is not a straightforward guarantee to be feasible, but our methods of utilizing c-HP and tailoring the III-V surface chemistry (the novel demonstration here) enable CISS to be integrated with III-Vs for the first time. Hopefully this work will inspire future work into integrating CISS with other III-V based Optospintronics that may not have been realized without our demonstration. The use of a cladding layer is essential in III-V LEDs for operation of the device to form a p-i-n junction for operation.

Second, there are multiple routes to electrically driven circularly polarized light emission. The first involves the injection of spin polarized carriers, which recombine radiatively to emit circularly polarized light via conservation of angular momentum. This can be considered somewhat agnostic to the emitter material in that the circularly polarized light is driven by the spin-polarized carrier injection into the emitter, not by asymmetry or chirality of the emitter material itself. This is what we have demonstrated in this work since AlGaInP in our case, is highly symmetric and achiral.

The second route is the emission of a *circularly polarized emitter* i.e. a material with asymmetry, such as chiral ligands present on a nanocrystal, which exhibit circularly polarized *photo*luminescence (CPL). This large CPL can be attributed to phenomena such as Rashba splitting, chiral ligand induced broken symmetry, or chiral space groups. For example, the study highlighted above https://pubs.acs.org/doi/full/10.1021/jacs.2c01214 has CPL of $g_{lum}$ = 4.0 e-3 and CP-EL of $g_{CP-EL}$ = 6.0e-3 which are very similar values and it is unclear if the electrically driven CP-EL is the result of spin polarized carrier injection via the shell or the broken symmetry induced by the chiral shell on the quantum dots (which is the source of the CPL experiments in that work). Other work such as https://onlinelibrary.wiley.com/doi/10.1002/adma.202309335 relies on similar core@shell chiral material@QD. In this work, they do demonstrate the CISS effect via magnetic conductive AFM, the mechanism of the CP-EL is again unclear since the study cannot discriminate between the contributions of spin polarized carriers or broken symmetry of the emitter material to the circularly polarized light emission.

The distinction between these two routes to electrically driven CP-EL is important. The first case represents a *spin* LED that emits CP-EL via spin injection whereas the second case represents a *circularly polarized* LED, which is driven by symmetry breaking in emitter materials (or in the referenced papers, it is unclear which mechanism). In the case of a spin LED, driven by spin polarized currents, there are major implications for a broad range of spintronic applications, which at bare minimum require spin generation, manipulation, and detection. In the case of spin injection (the spin generation step), our demonstration shows that the CISS effect can achieve high efficiency room temperature spin injection into a III-V with no applied magnetic field. The detection in our case is the circularly polarized luminescence, but other detection mechanisms would enable other impactful applications, such as utilizing another CISS layer or heavy metal/magnetic layer to realize a magnetic tunnel junction or a spin FET. In the case of circularly polarized emitters, there is not a broad opportunity for utilizing the effect in applications beyond a circularly polarized LED.

We have included extended data Table 1 in the manuscript to show a collection of all CISS – hybrid organic-inorganic systems used for circularly polarized electroluminescence. This should provide context for readers on the DOCP of our LED.

We have also revised our text to better reflect our perspectives (including the paragraph that follows for convenience):

Our spin-LED has several advantages over previous literature reports of similar spin-LEDs enabled by CISS (Extended Data Table 1). In a previous report, we coupled c-HP with a non-chiral HP emitter layer. Spin-polarized holes were injected into the HP emitter to achieve DOCP of ~ 3%.[15] Here, we achieve a five-fold increase and the improved performance likely results from the improved spin lifetimes within the III-V emitter. We directly determined the spin lifetime in the AlGaInP MQW via time resolved circularly polarized spectroscopy (details in Methods) to be ~100 ps (Extended Data Fig. 9), which is about a 5x time increase in the spin lifetime compared to the previously used perovskite emitter layer. In another approach, Jang et. al. reported a DOCP of ~ 12% at room temperature when they incorporated a core/shell HP nanocrystal emitter layer, where the shell consists of a 2D c-HP, into a LED. When carriers transverse through the NC shell into the core they become spin-polarized.[50] In contrast, the spin-LEDs developed here show a higher DOCP, but also demonstrate that c-HP can be integrated with traditional III-V or IV semiconductor platforms.

We have demonstrated direct contact of the HP with traditional semiconductors is possible and that the HP semiconductor behaves like another semiconductor within the device stack. Thus, integration of c-HP transforms an existing commercially relevant III-V LEDs from a conventional LED semiconductor structure that controls the interconversion of light and charge to one that now also controls light-to-spin. Our approach produces a functional spin-based semiconductor structure operating at room temperature with no external magnetic fields. The high spin injection efficiency is a result of the c-HP/III-V interface we have developed, where TEM, XPS, and KPFM indicate a direct SC-SC interface, which allows carrier equilibration and efficient spin injection. The c-HP SC/SC interface developed here forms the basis of a new class of spin injectors to achieve spin-accumulation for a variety of spin functionalities.”

Lastly, The use of cladding layer (p or n doped) at both sides of the MQW is important for supplying electron-hole pairs for the recombination in MQW to emit the light. The thickness of top cladding layer plays a critical role to adjust the band bending in the MQW. If the cladding layer is too thin, a large depletion layer will be created directly inside the MQW, resulting in a large increase of the carrier lifetime due to the quantum Stark effect. As a consequence, small Pc and low emitting light will occur. However, if the cladding layer is too thick, the carrier spin is completely depolarized before reaching the MQW for light emission.

2. Why not add another chiral perovskite layer to improve spin polarization by injecting spin-polarized electrons?

Response: Thank you for the question. This is an interesting hypothesis to test and would also develop a better understanding of the LED's operation in future work. However, our system is not suitable for such an attempt and our rationale behind this is the following: a limitation of our LED architecture is that the bottom contact i.e. GaAs substrate cannot be etched off to expose an n-type cladding layer for successful integration of another chiral perovskite layer to introduce spin -polarized electron injection. The mechanical reality of this would be extremely challenging to overcome.

3. The manuscript lacks solid experimental evidence demonstrating spin injection across chiral halide perovskite/cladding layer interfaces. It is essential to provide information on the spin polarization and spin lifetime in chiral perovskites within the LED context.

Response: Thank you for the comment, The PL is circularly polarized which is a direct measure of the spin accumulation in the III-V emitter layer. The Hanle effect measurements and now added absorbance, PL, and CD (extended Fig. 7) further demonstrate this is a result of spin polarized carriers. The only place spin accumulation can be achieved is thru the chiral perovskite layer, which is clearly previously demonstrated in (R/S-MBA)$_2$PbI$_4$ https://www.science.org/doi/full/10.1126/sciadv.aay0571. On the note about the spin lifetime in the chiral perovskite, in our situation the emission does not come from the c-HP, the c-HP serves as a spin injector and the AlGaInP MQW emits the CP-EL. Thus, the spin-lifetime of the c-HP here is not determined because the spins in the chiral perovskite are the majority spins and carriers don't remain in the chiral perovskite. We have measured the spin lifetime of the AlGaInP MQWs (shown in extended data Fig. 9) which is 100 ps and long enough to allow efficient CP-EL.

4. Could the authors elaborate on the consequences of injecting polarized spin into the p-type cladding layer? Are there any losses observed? Moreover, what are the dynamics and efficiency of spin injection from the chiral perovskite to the cladding layer and subsequently to the MQWs?

Response: To the best of our knowledge, this work is the first example of injecting polarized spins from a chiral perovskite into a III-V. The spin injection efficiency is demonstrated to remain high to achieve the high degree of polarized emission. It would require extensive modeling and better theory describing CISS (mechanism of spin polarization) to determine the exact spin injection efficiency from the perovskite into the III-V. There are of course losses of spin polarization throughout the process. The theoretical efficiency of this LED is 50% DOCP, yet at best we achieve 15%. The 35% loss comes from three possible sources 1. scattering at the perovskite/AlGaInP interface 2. during the p-clad traverse and 3. spin precession in the MQWs. Based on the traverse time discussed above (reviewer 1 Q1) we do not believe that the p-clad is a significant source of spin relaxation. The MQW spin lifetime of 100 ps is an improvement upon previous efforts (such as CsPb(Br$_{0.1}$I$_{0.9}$)$_3$) emitter, but is on the order of or faster than carrier recombination in LEDs, which would lead to losses in the DOCP. As mentioned, the spin injection from the perovskite to the AlGaInP is the most complex component to determine losses. Methods of modeling CISS based injection must be invented to properly determine losses. What is clear from our result is that relative to FM injection materials, specifically those with similar emitter III-V design, the CISS process is highly efficient as indicated by our large magnitude of DOCP which suggests the spin injection step does not produce significant losses.

5. Figures S6 and S7 lack descriptions and explanations in the main text, making it difficult for readers to understand their significance. Figure captions of A1-B2 are also missing in Fig. S6 and S7.

Response: Thank you for the suggestion. The labeling in S6 and S7 was too informal and incorrect at poitns. These are the same architecture of LEDs as shown in the main text. We have changed the figure caption to reflect this:

Extended data Fig. 4 Continued examples of independently fabricated LEDs CP-EL with (R-MBA)$_2$PbI$_4$

Circularly polarized emission data (a,c) from (R-MBA)$_2$PbI$_4$ spin injection into AlGaInP (same LED architecture as the main text; device 1 and device 2 labeled) and the corresponding polarization vs. current plots (b, d). Error bars are 1 standard deviation of 5 consecutive measurements (n=5).

Extended data Fig. 5 Continued examples of independently fabricated LEDs CP-EL with (S-MBA)$_2$PbI$_4$

Circularly polarized emission data (a,c) from (S-MBA)$_2$PbI$_4$ spin injection into AlGaInP (same LED architecture as the main text; device 3 and device 4 labeled) and the corresponding polarization vs. current plots (b, d). Error bars are 1 standard deviation of 5 consecutive measurements (n=5).

Furthermore, we have referenced these figures in the main text:

"…range (Fig. 2d). Replications of these LEDs are shown in Extended Data Fig. 4 & 5. In addition…"

6. Could the author explain why the circular polarization of devices (PVK/MQWs) in Fig. S6 and S7 is lower compared to the device with the cladding layer?

Response: Thank you for the question. The devices in Fig. S6 and Fig. S7 (now extended data figure 4 and 5) are the same architecture as the devices shown in the main text (i.e. no differences in cladding layer). We have clarified the figure caption to reflect this as discussed in the previous comment.

There are numerous possibilities for variations of the DOCP: First there are numerous layers impacting this device. The conformal coating of TFB, $Al_2O_x$, and Indium doped zinc oxide are not guaranteed and batch to batch variation may occur when depositing. The deposition of these materials is quite novel for our c-HP system and only have been optimized to a reasonable extent. An example of potential cause for variation, utilization of spiro-oMeTAD hole transport layers (an analog of TFB in our LEDs) in the perovskite solar cell field were hampered by difficult-to-control factors such as the degree of oxidation (and resulting doping) in the spiro-oMeTAD induced by exposure to ambient conditions and lead to significant variations in solar cell devices performance.

Similar (or perhaps unrelated) processes that we cannot control for at this time may be impacting our device performance.

In addition, the c-HP/AlGaInP cladding layer interface was controlled to the best of our ability, including laboriously utilizing fresh deposition inks, the base LEDs being etched immediately prior to use, and exact spin coating deposition conditions noted in the methods with no deviation. However, reproducibility in the spin coating process is a notorious issue in the halide perovskite field, specifically parameters such as pinholes in the film can be difficult to control. In the early research on halide perovskite solar cells, the community experienced notorious issues with film processing reproducibility of film processing. These impediments were overcome through intense investigations into the crystallization of 3D halide perovskite and optimization of controllable parameters. Unfortunately, the insights for 3D perovskite are not directly translatable to 2D perovskites, and specifically the 2D chiral halide perovskites we use here, which undergo significantly different growth dynamics (see for example the spherulitic growth shown in extended data figure S1). We have not found a method of producing compact films that avoid this spherulitic growth, but we expect that avoiding this structure would improve our batch to batch variance. However, in light of the fact that this perovskite/III-V interface is novel and not previously demonstrated in any capacity (where a halide perovskite is in direct contact with a III-V and no buffer layers), we believe that the variance in this work is completely acceptable and within the expectations of a new system.

7. Please provide the external quantum efficiency (EQE) of the device.

Response: We agree that EQE is a useful measurement to improve our understanding of the light-emitting performance of this LED. However, obtaining accurate values and meaningful insights from these measurements is quite challenging on III-V materials. We have included a measurement of EQE on the Au/n-type AlGaInP/AlGaInP MQWs/p-type AlGaInP/Au LED that serves as our platform (excludes c-HP, TFB, IZO layers). We have measured an EQE of <0.1% at 2A/cm$^2$ shown in reviewer only figure 6. The absolute values are quite low for several reasons related to nuances in the design and fabrication of III-V LEDs:

- The LED fabrication and design is not optimized for light emission in the same way a commercial packaged III-V LED is. The LED layers are left on the absorbing back substrate (GaAs in our case). A highly conductive current-spreading layer was not included, which leads to carrier injection and photon generation predominantly under the top metal contacts. Finally, antireflection coatings or other light extraction features were not included, which results in a very small fraction of light actually being emitted (the escape cone is rather small).
- The temperature of the LED was not rigorously controlled during the measurements. The rather long integration times lead to heating at high drive currents.

These aspects differ substantially from perovskite LEDs, and it is beyond our means to optimize every detail of the III-V LED fabrication in the same way industry has optimized over decades. Without this optimization, it will be difficult to separate the effects of the perovskite layer on electrical efficiency losses at the perovskite/III-V interface and any effects it has on the optical transmission of emitted light on the EQE values.

Given that the perovskite acts mainly as an injection layer, we do not expect it to impact the radiative recombination in the III-V MQW layers (which are separated from the perovskite by a cladding layer). We also do not believe the low EQE has a significant impact on the circularly polarized photoluminescence, where spin polarized carriers and unpolarized carriers should recombine (both non-radiatively and radiatively) at similar rates. The lack of EQE does not change our conclusions demonstrating the successful injection of spin-polarized carriers into a conventional semiconductor. In fact, previous III-V based spin LED reports did not report (or only roughly estimate) the EQE of their LEDs due to the challenges of measuring/optimizing EQE on a III-V emitter as well as the lack of relevance to the circular polarization physics (Citations 28,32,39-40 in main text).

8. It would be helpful to identify the literature source used to obtain the band alignment information for the device.

Response: Thank you for the suggestion. Citations were added to the Fig. 3 caption showing the UPS literature sources of the individual device layers. We have also included a citation for Band Diagram Program version 3.1.6 used for the device simulations.

"**Fig. 3. Further characterization of the CP-EL** (a) band alignments determined from literature UPS values.[22,34–36] (b) Band bending at 0V and 3V determined by semiconductor simulations. Dashed lines show the electron/hole quasi-fermi level splitting. (c) Cross-sectional Kelvin probe force microscopy and AFM of the spin LED. The electric field drop is seen across the $(R\text{-}MBA)_2PbI_4$ (labeled c-HP) in good agreement with our calculated energy band diagrams. Simulations were done with Band Diagram Program version 3.1.6.[37]"

9. Figure G is missing from Figure S3.

Response: Thank you for pointing that out. We have corrected this error.

Referee #3 (Remarks to the Author):

The authors have succeeded in integrating chiral perovskite semiconductors with standard III-V LED structures and demonstrated efficient spin injection across the clean interface. The new type of spin LED shows a circularly polarized light emission with a maximum polarization degree of ~15% at room temperature and without magnetic field, which significantly exceeds a previous device performance. The perovskite/III-V semiconductor interface is well characterized by some analysis approach. The proposed methods to directly contact the halide perovskite with the traditional III-V semiconductors and the resulting demonstration of the high-performance spin LEDs are quite new and attractive to the relevant researchers. However, I cannot recommend publication in its current form. The following concerns should be clarified before publication in Nature.

Response: We appreciate the comments for the reviewer and the time to read and make helpful comments.

1) Chiral induced spin selectivity (CISS), which is the basis of the results of this study, should be carefully explained in the supplementary for the reader.

Response: Thank you for the suggestion. We have now specifically mentioned recent reviews for those interested which provide thorough detail on the CISS effect:

"Chiral induced spin selectivity (CISS) describes the spin dependent transmission of charge carriers through an oriented chiral potential, where the resulting spin orientation is parallel to the chiral helicity, i.e., the chiral structure determines the spin-orientation (see recent reviews on CISS)."

(8) Yang, S.-H.; Naaman, R.; Paltiel, Y.; Parkin, S. S. P. Chiral Spintronics. *Nature Reviews Physics* **2021**, *3* (5), 328–343. https://doi.org/10.1038/s42254-021-00302-9.
(9) Naaman, R.; Paltiel, Y.; Waldeck, D. H. Chiral Molecules and the Electron Spin. *Nature Reviews Chemistry* **2019**, *3* (4), 250–260. https://doi.org/10.1038/s41570-019-0087-1.
(10) Lu, H.; Vardeny, Z. V.; Beard, M. C. Control of Light, Spin and Charge with Chiral Metal Halide Semiconductors. *Nature Reviews Chemistry* **2022**, *6* (7), 470–485. https://doi.org/10.1038/s41570-022-00399-1.

2) What are the main factors that contributed to the significant increase in DOCP compared to a previous study [Science 2021, 371 (6534), 1129]?

Response: The enhanced DOCP compared to the previous Science study can be attributed primarily to the enhanced spin lifetime of the MQW system (100 ps; which we have measured and included in extended Fig 9.) relative to $CsPb(Br_{0.1}I_{0.9})_3$ (14 ps). The longer spin lifetime in the MQW system leads to more spin polarized carriers able to recombine and emit at a higher DOCP. We have added the following discussion to the main text of the manuscript:

"Our spin-LED has several advantages over previous literature reports of similar spin-LEDs enabled by CISS (Extended Data Table 1). In a previous report, we coupled c-HP with a non-chiral HP emitter layer. Spin-polarized holes were injected into the HP emitter to achieve DOCP of ~ 3%.[15] Here, we achieve a five-fold increase and the improved performance likely results from the improved spin lifetimes within the III-V emitter. We directly determined the spin lifetime in the AlGaInP MQW via time resolved circularly polarized spectroscopy (details in methods) to be ~100 ps (Extended Data Fig. 9), which is about a 5x time increase in the spin lifetime compared to the perovskite emitter layer."

3) Although the authors claim from the cross-sectional TEM images that a HOIS/III-V interface is formed with no oxide barrier, detailed elemental analysis should be performed by STEM-EDX. The results should provide strong evidence for the formation of oxide-free interface.

Response: We appreciate the reviewer's suggestion for acquiring a STEM-EDX spectrum from this interface, but unfortunately we could only perform minimal low temperature and low dose TEM imaging on the perovskite film. This is due to rapid breakdown of the thinned (~ 100 nm thick) thin film perovskite cross-sectional sample under exposure of the medium-voltage (300 kV) electron beam. The known sensitivity of HP layers to a focused electron and ion beams is why we employed careful protocols to create the cross-sectional sample under cryogenic conditions, as room temperature focused ion beam milling is too destructive to the thin-film perovskite (such milling can cause sublimation or void formation in the perovskite during imaging/milling). EDX performed in the SEM was severely damaging, creating 'bullet holes' in the perovskite at each position the beam collected a short map from. Therefore, STEM-EDX requires too high of beam exposure to the perovskite film to gain enough counts to produce an identifiable elemental map to identify an oxide barrier. It should be also noted that the sample was transferred into and out of the FIB/SEM through glovebox transfer without air exposure. The sample was transferred into the cryo TEM in the same manner, plunging the sample into a cryogenic bath from an inert environment. Therefore, we believe that the sample and interfaces were preserved during characterization. Cryogenic STEM for metal halide perovskites is complicated, since different formulations have different electron beam damage tolerances. We found that these samples were very sensitive to the 300 kV electron beam and could not sustain imaging at low beam doses (below 0.5 nA) for more than a few frames captured at image pixel values above 0.5 nm. Therefore, STEM-EDX mapping of the c-HP/III-V interface to capture a thin oxide layer was not possible on this sample without causing significant damage that would nullify the results of the EDX map.

4) The Hanle effect result shown in Fig. S5 seems poor evidence because the result of only one device is described. The decrease in DOCP due to the application of external magnetic field is small. The results of a number of devices should be shown as with the current dependence of DOCP. In addition, the DOCP at stronger magnetic fields should also be shown.

Response: Thank you for your comments. First, the magnitude of the decrease in DOCP in the Hanle experiments is likely related to the lack of strong magnetic field that can be applied in our current operating conditions. This is because the Hanle effect measurements were non-trivial compared to simple measurements of DOCP and the integration of a strong magnetic field while detecting EL intensity was challenging. We agree that further measurements would be informative in not only demonstrating reproducibility of the device, but also in characterizing further spin dependence such as angle dependence of the magnetic field. But inclusion of this initial Hanle experiment is meant to provide supporting evidence of the spin polarization, which is already supported by the DOCP we observe in devices. We have plans in the future to undertake this further study by assembling bespoke equipment to achieve the challenging measurements, but this deeper study is beyond the scope of the current manuscript.

5) In Fig. 2(e), the number of devices measured above 5 mA is decreasing. What could be the reason for this? Also, the authors claim that it was not possible to measure devices above 15 mA, explain why.

Response: Thank you for the acute observation. Yes, the devices have a higher probability in irreversible shunting at higher currents and as such, a limited number of measurements were completed for devices at higher currents before shunting. This shunting is not uncommon in devices containing halide perovskites, where poling can induce ion migration within the perovskite in the form of halide migration or adjacent materials migrating into the film (such as Au). Furthermore, the band offsets in the devices are not ideal, specifically the VB of the c-HP and the AlGaInP cladding layer. This contributes to the device breaking in the form of joule heating and requiring larger turn on voltages.

We have attempted to characterize this with time-of-flight secondary ion mass spectrometry (TOF-SIMS) on pristine (i.e. unoperated) devices (reviewer only Fig. 3) as well as devices which have been pushed beyond their stability (e.g. shunted / burned out devices) (reviewer only Fig. 4.). TOF-SIMS measures the distribution of atoms (in the form of ions) in a material system by sputtering into the material and collecting and characterizing the ions with mass spectrometry. Review only Fig. 3 and 4 show the IZO/$Al_2O_x$/TFB/perovskite on top of the AlGaInP. Careful comparison in review only Fig 5 shows a possible higher content of Al and Ga in the perovskite portion of the film in the "burned/shunted" device compared to the pristine/ unoperated device (overlapped are of Pb). We believe this is possible evidence of ions migrating under operation from the AlGaInP or $Al_2O_x$ into the perovskite contributing to the shunting. This ion migration should scale with current / voltage magnitude and is the reason a majority of our devices could not be operated above 15 mA (and sometimes below that in other devices).

We suspect that in future endeavors, optimizing the band offsets of the spin injection (CISS) layer and cladding layers will produce devices with better stability, less joule heating, and requiring lower currents/voltages to operate avoiding the breakdown issue.

We have added this caveat to the Fig. 2. description:

The decrease in the number of devices with higher currents is due to a higher probability of devices shunting above 15 mA, or in some cases at lower current.

6) On a related note, the P_CP-EL varies widely from device to device. What is the main reason for this? I am concerned that it may be differences in the quality of the c-HP/SC spin injection interface, which is the main issue of this study. This concern should be carefully investigated and clarified.

There are numerous possibilities for variations of the DOCP: First there are numerous layers impacting this device. The conformal coating of TFB, $Al_2O_x$, and Indium doped zinc oxide are not guaranteed and batch to batch variation may occur when depositing. The deposition of these materials is quite novel for our c-HP system and only have been optimized to a reasonable extent. An example of potential cause for variation, utilization of spiro-oMeTAD hole transport layers (an analog of TFB in our LEDs) in the perovskite solar cell field were hampered by difficult-to-control factors such as the degree of oxidation (and resulting doping) in the spiro-oMeTAD induced by exposure to ambient conditions and lead to significant variations in solar cell devices performance. Similar (or perhaps unrelated) processes that we cannot control for at this time may be impacting our device performance.

In addition, the c-HP/AlGaInP cladding layer interface was controlled to the best of our ability, including laboriously utilizing fresh deposition inks, the base LEDs being etched immediately prior to use, and exact spin coating deposition conditions noted in the methods with no deviation. However, reproducibility in the spin coating process is a notorious issue in the halide perovskite field, specifically parameters such as pinholes in the film can be difficult to control. In the early research on halide perovskite solar cells, the community experienced notorious issues with film processing reproducibility of film processing. These impediments were overcome through intense investigations into the crystallization of 3D halide perovskite and optimization of controllable parameters. Unfortunately, the insights for 3D perovskite are not directly translatable to 2D perovskites, and specifically the 2D chiral halide perovskites we use here, which undergo significantly different growth dynamics (see for example the spherulitic growth shown in extended data figure S1). We have not found a method of producing compact films that avoid this spherulitic growth, but we expect that avoiding this structure would improve our batch to batch variance. However, in light of the fact that this perovskite/III-V interface is novel and not previously demonstrated in any capacity (where a halide perovskite is in direct contact with a III-V and no buffer layers), we believe that the variance in this work is completely acceptable and within the expectations of a new system.

Some minor comments are as follows.
7) The following statement exists in the main text, but “Fig. S4” corresponding to this statement is not shown in the supplemental.
“In addition, we performed a pseudo in situ experiment, where the LED is continuously operated and the quarter waveplate was rotated selecting for RH and LH circular polarization (Fig. S4) over multiple cycles with continuous collection. While the overall EL intensity decreases with time due to joule-heating, the difference in intensity between RH and LH CP-EL remains > 10%.”

Response: Thank you. We have made sure what is now extended data Fig. 6 is present in our submission package.

8) For the caption in Fig. S3, "(A) Images....device." should be deleted.

Response: Thank you. We have corrected this error in the caption.

(a) Electroluminescence (EL) spectra (not polarized) with increasing applied current. (b) EL intensity vs. applied current showing linear increase. I-V curves of the LEDs in dark and under illumination: (c-d) is the LED with no (R/S-MBA)$_2$PbI$_4$ present and (e-f) is the full LED stack including (R/S-MBA)$_2$PbI$_4$.

9) For Figs. S6 and S7, units of “Polarization” should be described.

Response: Thank you. We have corrected this error in what is now extended data Fig. 4 & 5 to use DOCP.

10) For the results of B2 in Fig. S7, the vertical and horizontal axes are “Polarization (%)” and “Current (mA)”, respectively.

Response: Thank you. We have corrected this error in what is now extended data Fig. 5.

**Reviewer Reports on the First Revision:**

Referees' comments:

Referee #1 (Remarks to the Author):

The authors have made diligent efforts to further improve the presentation and quality of their manuscript. By conducting a series of new control experiments, the authors have provided detailed responses to the comments and fixed all the minor issues. I am generally satisfied with these responses except for one remaining question (see comment #4), although I also agree with the authors that the unusual Hanle curves at two field orientations are not the focus of this work. Overall, the revised manuscript is in good shape and thus I would like to recommend the publication of this work.

[1] Thanks for providing this information. I am glad that my comment also helps to elucidate the voltage/current dependence of DOCP in the device.

[2] Thanks for addressing this concern.

[3] I agree with this change in the main text which should not focus on the conductivity mismatch.

[4] The time-resolved circular dichroism spectroscopy indeed supports the data from the optical Hanle effect. However, I am slightly concerned about the non-trivial spin orientation injected into the III-V MQW from the c-HP. The authors stated that “This suggests that the spin orientation direction is non-trivial (i.e., neither along the a-b direction (parallel, out-of-plane) nor in the c direction (orthogonal, in-plane) of the c-HP)”. The CISS effect usually describes the generation of spin polarization parallel to the chiral axis, which is the out-of-plane direction of the c-HP thin film according to the CD spectra. This is because the hole carrier flows downward and injects into the III-V multiple quantum well. Why does such a perpendicular carrier flow generate a spin polarization in a different direction? Is this because this type of c-HP has more than one screw axis?

This Hanel measurement was taken at room temperature by applying a relatively small magnetic field. The Zeeman splitting induced by the external field (< 350 Oe) might not play an important role here.

[6] Thanks for addressing this comment.

Referee #2 (Remarks to the Author):

The authors' response to my previous comments is not very convincing, and there are still many issues to be addressed in this manuscript.

1. As a selling point, the authors claim a high spin injection efficiency throughout the paper, but they do not provide the actual value. The previous comments regarding the dynamics and efficiency of spin injection from the chiral perovskite to the cladding layer and subsequently to the MQWs have

not been addressed.

2. The claim of achieving a DCOP of EL up to 15% in the paper is also not adequately supported. The number of devices used in the study is indeed insufficient, with only three devices being tested (Fig. 2e). This limited sample size raises concerns about the statistical significance and reliability of the reported results. Additionally, when considering the average value from the three devices at 15 mA, the DCOP is actually 10%, which is lower than the reported values in recent papers on spin injection-induced polarization, such as the 12% reported in Advanced Materials 36.5 (2024): 2305604. It is important to note that at other currents, the DCOP values are even lower than 10%, further questioning the significance and advantage of this design when compared to reported spin injection into other materials.

3. Furthermore, the authors mentioned that the error bars in Extended Data Fig. 4 and 5 represent 1 standard deviation of 5 consecutive measurements (n=5). Obviously, there is a significant variation in the DOCP even for repeated measurements on a single device. The authors should clarify the sources of errors and the uncertainty associated with the measurements. Considering the large variation, the validity of the maximum 15% DCOP claimed by the authors is questionable.

4. Regarding the spin lifetime, the authors mentioned in response letter and manuscript that "We directly determined the spin lifetime in the AlGaInP MQW via time resolved circularly polarized spectroscopy (details in Methods) to be ~100 ps (Extended Data Fig. 9), which is about a 5x time increase in the spin lifetime compared to the previously used perovskite emitter layer.". Please provide experimental details and what is the pump fluence and injected carrier density, pump wavelength, probe wavelength and pump-probe spectrum. Furthermore, as the spins are injected from electrically driven, will the lifetime from optically injected spin of holes are valid? And also, if the author would like to demonstrate the improvement in spin lifetime, same measurements should be conducted on the control sample.

5. The statement that "high DCOP implies that the spin-injection process is highly efficient" is made without providing any evidence. This claim needs to be supported by experimental data or theoretical analysis.

6. It is difficult to observe an increase in DCOP with increasing current from Extended Data Fig. 4 and 5. This raises doubts about the validity of the conclusion that DCOP increases with the driven current. Additionally, in the authors' previous work (Ref 15), spin lifetime decreased with increased carrier density, so it is unclear why DCOP would increase with the driven current in this study.

7. The authors need to explain how they determined the doping concentration and dielectric constant of c-HP. Additionally, they should clarify whether these values are feasible and reliable. The reliability of the estimated drift velocity is also a concern related to the accuracy of the determined doping concentration.

8. The concepts of spin accumulation and spin injection are easily confused in the manuscript. The authors should provide clear definitions and explanations to avoid confusion and clearly state which concept contributes to DCOP.

9. The statement that "the spin orientation produced via the CISS mechanism is parallel to the direction of current, and the light emission is also parallel to the currentdirection due to the small escape cone of the III-V" needs to be supported by evidence. The authors should provide experimental data or theoretical analysis to support this claim.

10. The term "collapsing depletion region" is not clear. In Fig. 3b, the width of the depletion region in c-HP for a bias of 3 V remains unchanged compared to that of 0 V. Therefore, the proposed mechanism for low DCOP under lower bias is not valid. The authors should provide a clear and

accurate explanation of the phenomenon observed in the figure.
11. The energy levels used in the paper are extracted from literature sources. However, it is unclear whether these values can be directly applied to the current study, as the energy levels might be different due to variations in the fabrication process and doping. The authors should address this concern and discuss the potential impact of fabrication process variations on the energy levels.
12. There are numerous typos throughout the manuscript, and the English and writing style need improvement. The authors should carefully proofread and polish their writing to enhance the clarity and readability of the manuscript.
13. Lastly, the novelty and importance of this work are still not strong. The use of III-Vs for spin injection is not as novel or important as the authors suggest. There have been many reports on the use of chiral perovskites for spin injection to other materials (e.g., perovskite film, QDs, 2D materials (Nano Lett. 24, 1001, 2024), etc) with high spin injection efficiency (80%; Adv. Mater. 36, 2305604, 2024) and high DOCP. These materials offer advantages such as low-cost fabrication, high PLQY, high EQE, and flexibility. In contrast, commercial III-V materials require high-cost fabrication, and the EQE demonstrated in this paper is extremely low (<0.1%). This significantly limits its application and importance. Furth more, it's important to note that chiral perovskites can be used even as standalone spintronic devices. This raises questions about the uniqueness and significance of the proposed chiral perovskite/III-V spin injection approach.
Overall, given the lack of novelty and striking advance, the poor quality of the data with many technical shortcomings, the large variation and over-explanation of the 15% DCOP, the extremely low EQE, the lack of solid experiments and measurements to support their assumptions and conclusions, and an unclear explanation of the mechanism as listed above, I am therefore unable to support this paper for publication in Nature.

Referee #3 (Remarks to the Author):

The authors responded appropriately to the reviewers' comments and the manuscript was sufficiently revised. This achievement will accelerate the research on integration of chiral-perovskite with common III-V semiconductors. Therefore, I recommend this revised manuscript for publication in Nature.

**Author Rebuttals to First Revision:**

Code:

Blue: Comment discussing the reviewer's question

Orange: Changes made to the main text

Referees' comments:

Referee #1 (Remarks to the Author):

The authors have made diligent efforts to further improve the presentation and quality of their manuscript. By conducting a series of new control experiments, the authors have provided detailed responses to the comments and fixed all the minor issues. I am generally satisfied with these responses except for one remaining question (see comment #4), although I also agree with the authors that the unusual Hanle curves at two field orientations are not the focus of this work. Overall, the revised manuscript is in good shape and thus I would like to recommend the publication of this work.

Thank you for the positive support of this manuscript. Your suggestions significantly improved the quality of the work.

[1] Thanks for providing this information. I am glad that my comment also helps to elucidate the voltage/current dependence of DOCP in the device.

[2] Thanks for addressing this concern.

[3] I agree with this change in the main text which should not focus on the conductivity mismatch.

[4] The time-resolved circular dichroism spectroscopy indeed supports the data from the optical Hanle effect. However, I am slightly concerned about the non-trivial spin orientation injected into the III-V MQW from the c-HP. The authors stated that "This suggests that the spin orientation direction is non-trivial (i.e., neither along the a-b direction (parallel, out-of-plane) nor in the c direction (orthogonal, in-plane) of the c-HP)". The CISS effect usually describes the generation of spin polarization parallel to the chiral axis, which is the out-of-plane direction of the c-HP thin film according to the CD spectra. This is because the hole carrier flows downward and injects into the III-V multiple quantum well. Why does such a perpendicular carrier flow generate a spin polarization in a different direction? Is this because this type of c-HP has more than one screw axis?

This Hanel measurement was taken at room temperature by applying a relatively small magnetic field. The Zeeman splitting induced by the external field (< 350 Oe) might not play an important role here.

We thank the referee for this important question. We apologize for the confusing statement in our response to the reviewers on the potential for a non-trivial spin orientation. First, we would like to note in the manuscript we do not propose this conjecture of non-trivial spin orientation and only discussed that possibility in the reviewer response. We agree with the reviewer that the spin orientation must be along the chiral axis of the chiral perovskite (i.e. out of plane). It is true that the c-HP has an in-plane screw axis (actually both in-plane directions have screw axis). But the current flow is out of plane and the in-plane axis should not impact the out-of-plane polarization. There is some possibility that the axis is not perfectly aligned with the substrate. However, we conjecture that the complicated Hanle measurements reflect a more complicated spin-dynamics within the AlInGaP MQWs and may not reflect directly the spin-orientation from CISS, i.e., there the Hanle measurements are a convolution of the CISS injection and the spin-dynamics in the III-V MQWs. For example, localization at defects, trion formation, and interactions with the spin of the nuclei are all possible in the III-V MQWs and could explain the non-trivial Hanle results.

The main point we want to make for this manuscript is that there *is* a Hanle effect in the polarization which can only be a result of spin accumulation and spin-dynamics in the III-V MQW and thus proves that spins are injected from the CISS into AlInGaP emitter. The high measured DOCP is a result of the spin-accumulation in the III-V and the only spin injection mechanism available is the c-HP, i.e., there are no magnets or ferromagnets present. We do find the Hanle type measurements very interesting and plan on exploring these measurements for CISS in future experiments.

In the manuscript we did not bring up this point only using the Hanle measurements to demonstrate that the DOCP is results of spins.

“To further confirm that the CP-EL is a result of spin polarized accumulation into the SC we measured quenching of the DOCP under an applied magnetic field (i.e. optical Hanle effect). Application of external magnetic field leads to spin precession around the field direction, causing a decrease in the DOCP (Extended Data Fig. 8).[25,26] In our measurement, a LED with 6.5% DOCP at 0 mT decreases to ~4% at 130 mT.”

[6] Thanks for addressing this comment.

Referee #2 (Remarks to the Author):

The authors' response to my previous comments is not very convincing, and there are still many issues to be addressed in this manuscript.

Thank you for taking the time to read our manuscript again to determine further concerns you may have. We hope the clarifications provided here of the number of devices and statistical variance are adequately discussed and that the quality of the manuscript is improved overall.

1. As a selling point, the authors claim a high spin injection efficiency throughout the paper, but they do not provide the actual value. The previous comments regarding the dynamics and efficiency of

spin injection from the chiral perovskite to the cladding layer and subsequently to the MQWs have not been addressed.

We apologize for the confusion. We wanted to focus our report on the c-HP CISS spin injection into the III-V and not focus too much on spin-dynamics in the III-V MQW. However, we do recognize that we can provide more specific information about the spin-injection efficiency and we can also clearly distinguish between spin-injection efficiency and spin accumulation. So we have modified the manuscript to be more precise about these terms and we thank the reviewer for bringing this point to our attention.

The DOCP Is a direct result of spin accumulation and is related to the spin injection via the following: DOCP = $\alpha \cdot F \cdot P_{inj}$, where $\alpha$ is related to the optical selection rules of the III-V MQWs, F is a factor that represents the fraction of spin-polarized carriers that emit prior to losing their spin polarization, $F = 1/(1+\tau/\tau_s)$, where $\tau$ is the total carrier lifetime and $\tau_s$ is the spin lifetime, and $P_{inj}$ is the spin injection efficiency, i.e. the fraction of injected carriers into the MQWs that are spin polarized. The spin injection we are referring to is the injection of spin polarized carriers across an interface, in our case the c-HP into the AlInGaP MQW emitter. So naturally that term also depends upon the spin injection into the cladding layer, transport across the cladding layer and subsequent injection into the MQW. Spin accumulation is the build-up of spin polarized carriers under steady state conditions in the AlInGaP MQW emitter layer. Thus, the spin accumulation is $F \cdot P_{inj}$ and consists of the spin-injection multiplied by the fraction of spin polarized carriers in the emitter layer. The DOCP value represents the spin polarized charge carriers that successfully recombine in the MQWs as a result of the spin injection and subsequent spin accumulation to produce circularly polarized light as detected by our setup.

We can estimate the F factor from the spin-lifetime measurements and the carrier measurements. Note that both the spin lifetime and the carrier lifetime are dependent on the carrier density. We can estimate that under working conditions (15 mA) the carrier density is ~ $10^{14}$ – $10^{15}$ $cm^{-3}$ (device area is 4 $mm^2$). We estimate that the carrier lifetime (from TRPL measurements now included in extended figure 9b) is ~ 60 ps and the spin-lifetime is ~ 100 ps providing a lower bound of F to be ~ 0.625. Thus since $\alpha$ is 0.5 and DOCP is 0.15, the $P_{inj}$ is ~ 0.48 or 48%.

We have modified the manuscript as follows (noted in orange):

> "The DOCP is a direct measure of spin accumulation in the MQW and is proportional to and limited by the spin injection efficiency ($P_{inj}$) i.e. the fraction of injected carriers that are spin polarized. The DOCP is related $P_{inj}$ through the following, DOCP = $\alpha \cdot F \cdot P_{inj}$,[23] where $\alpha$ is related to the optical selection rules of the III-V MQWs and can be $0.5 \leq \alpha \leq 1$ depending on the degree of quantum confinement in the MQW.[24] $F$ is a renormalization factor that represents the fraction of spin-polarized carriers that emit prior to losing their spin polarization, $F = 1/(1+\tau/\tau_s)$, where $\tau$ is the total carrier lifetime and $\tau_s$ is the spin lifetime. Due to the lack of confinement that would modify the band edge electronic structure in the 10 nm MQWs (as shown by the lack of blueshifted PL), $\alpha$ is estimated to be 0.5. This is due to the optical selection rules in the III-V semiconductor and transition probabilities favoring the heavy-hole over light-hole sub band in a 3:1 ratio, producing 3 right (left) handed to 1 left (right) handed circularly polarized photons when 100% spin polarized carriers are introduced.[24,25] Since $\alpha$ is 0.5 the spin accumulation is 2*DOCP. We measured the spin lifetime, $\tau_s$, using circularly polarized transient absorbance (extended Data Fig. 9a) to be ~100 ps and independent

of carrier density (over 1 order of magnitude), $\tau$=60 ps at low carrier densities as determined by time resolved photoluminescence spectroscopy (extended Data Fig. 9b). Thus $P_{inj}$= 0.48 meaning that 48% of carriers injected are spin polarized."

"Here we assign the voltage dependent DOCP to a voltage dependent $P_{inj}$, since both $\alpha$ and $F$ should depend weakly on voltage. $P_{inj}$ can be further separated into a product of the injection efficiency from the c-HP into the cladding layer ($P_{Chiral}$) and a normalization factor to describe losses of spin polarization during traverse through the p-cladding layer ($D_{tr}$). Most reports of $P_{Chiral}$ do not find a strong voltage dependence[9], thus the voltage dependence is likely a result of $D_{tr}$; $P_{inj}(V) = P_{Chiral} \cdot D_{tr}(V)$. We considered two possible sources of $D_{tr}(V)$. (1) The poorly aligned type-II bands (Fig 3a) at the c-HP/AlGaInP interface. When the carriers equilibrate (at 0 V bias, Fig. 3b), there is a large depletion region into the c-HP with low carrier concentration, which allows for the formation of a 2D hole gas within the c-HP at the interface. A large depletion region and the corresponding 2D hole gas provides opportunities for spin scattering during spin-injection.[29] However, a higher bias (3V is shown in Fig. 3b) reduces the width of the 2D hole gas, therefore reducing the number of quantized states and gives injected carriers more energy resulting in less spin-scattering.[28,30] (2) The voltage dependence arises due to spin scattering/relaxation as holes traverse the 200 nm p-type cladding layer residing between the c-HP and MQW. We estimate the traverse time of carriers across the p-cladding layer to be <1.9 ps, which shortens with increased applied bias (see Methods for calculation details). Low temperature measurements in related III-V semiconductors suggest hole spin relaxation is on the ps time scale at room temperature, close to the carrier traverse time.[31,32] As traverse time shortens with the increase applied bias, there is less time during transport for spin relaxation and more carriers maintain their spin polarization causing the increase in the DOCP at higher bias."

We also note that this device design can be further optimized to produce a large DOCP, including minimizing the p-cladding layer size and fabricating the MQWs as well confined QDs among other possibilities.

2. The claim of achieving a DCOP of EL up to 15% in the paper is also not adequately supported. The number of devices used in the study is indeed insufficient, with only three devices being tested (Fig. 2e). This limited sample size raises concerns about the statistical significance and reliability of the reported results. (we have split this into two questions to clearly address both concerns)

We can hardly agree with this statement and are confused by the wording of 'not adequately' supported. Yes. There is some variability in the DOCP across the number of devices that we tested and measured. But the 15% is clearly measured with low measurement error and is adequately supported by our measurements. We have not claimed that the average value was 15% only that we are able to achieve this. As far as the number of devices shown, 6 devices characterized at multiple current densities (2 in Figure 2, 4 in extended data figure 4 and 5 combined) is a very reasonable and often common number for reports on III-V devices, which are not high throughput solution processed as is the case with solution processed QD LEDs. Growth of large area III-Vs is challenging and time intensive on the small boutique scale of a laboratory (while commercial manufacturing at scale is highly efficient). This is represented well in the spin LED literature utilizing

III-Vs, where a handful of samples is very common to investigate the underlying physics of their spin processes (some citations in main text: 28 - 1 device; 32 - 4 devices (3 with variations and 1 control); 41 - 4 devices (3 the same, 1 control); 42 – 1 device;). As such, we have confidence in our 6 devices, which all have circular polarization demonstrating spin injection into III-Vs. Each of these devices were measured across multiple currents, although not all were able to be characterized at 15 mA and broke before (justification of 3 data points at 15 mA). As discussed in the previous round of revisions, the variance of these devices can be attributed to processing of the TFB, Al2O3, Perovskite, IZO etc. as is common in integration of new materials into a device.

Reporting of a champion device provides impetus to the community to continue working to further improve upon the results. Our measurements clearly show that this is a promising direction to pursue and we have also suggested several ways where the polarization efficiency could be further improved. However, to our knowledge this is the first report showing that a HP layer can be successfully integrated with traditional opto-electronics (let alone a spin-LED) and the first report which shows CISS can be successfully integrated into a well established opto-electronic platform.

Additionally, when considering the average value from the three devices at 15 mA, the DCOP is actually 10%, which is lower than the reported values in recent papers on spin injection-induced polarization, such as the 12% reported in Advanced Materials 36.5 (2024): 2305604. It is important to note that at other currents, the DCOP values are even lower than 10%, further questioning the significance and advantage of this design when compared to reported spin injection into other materials.

Thank you for the comment and hopefully it does not come across in our manuscript that a champion DOCP is the goal of this work, but it is important to mention our champion device. We use DOCP as a convenient method of detecting spin in semiconductors, produced by the CISS effect. The aim of this work is to effectively integrate CISS spin injection with conventional semiconductors (III-Vs in this case) which is a more valuable and not previously demonstrated goal. We did not attempt to optimizing the DOCP. In fact, we were quite surprised that we could take a 'off the shelf' LED platform and successfully integrate the c-HP and get out any polarized emission (let alone 15%!). So fully expect that this value could be improved but that the improvement is a scientific community exercise. We hope that our report will spur many more scientist to also pursue this activity.

*However, we do agree that it is important to accurately represent the efficiency of the circular polarization and appreciate the constructive criticism that it may be unclear as presented to the reader*. To address the concern that the DOCP in one device is 15% being an issue we have added in the main text the following:

"…reaches up to 15±4% at the highest drive currents in this champion device. An average circular polarization of 10±5 is achieved at 15 mA across multiple devices"

to clarify that this is the maximum we achieved in one device and represent the average device measured as shown in figure 2e, which should be a transparent representation of our device's operation. We have also added the error throughout the main text as 15±4% to be fully transparent.

The Advanced Materials 36.5 (2024): 2305604 report is cited in our extended data table 1 with it's g_CP-EL of $1.6\times10^{-2}$ (DOCP =0.8%) as well as the advanced *Adv. Mater.* **2024**, *36* (5), 2309335 report with the shown 12% DOCP (we believe this is the one the reviewer is referring to). We find the *Adv. Mater.* **2024**, *36* (5), 2309335 report very creative, but would like to note that this is likely a champion device and operating condition achieving the 12% DOCP, as a statistical distribution or the number of devices is not discussed in the text to our knowledge.

We have already included the following in the main text, pointing out that high DOCP can be achieved with other systems, specifically the *Adv. Mater.* **2024**, *36* (5), 2309335 and discuss the likely source of their large DOCP as well as advantages of our III-V system:

"Our spin-LED has several advantages over previous literature reports of similar spin-LEDs enabled by CISS (Extended Data Table 1). In a previous report, we coupled c-HP with a non-chiral HP emitter layer. Spin-polarized holes were injected into the HP emitter to achieve DOCP of ~ 2.6%.[15] Here, we achieve a five-fold increase and the improved performance likely results from the improved spin lifetimes within the III-V emitter, the measured $\tau_s$ ~100 ps (Extended Data Fig. 9a), is about a 5x time increase in the spin lifetime compared to the previously used perovskite emitter layer. An example of another approach is that of Jang et. al. who reported a DOCP of ~ 12% at room temperature when they incorporated a core/shell HP nanocrystal emitter layer, where the shell consists of a 2D c-HP, into a LED.[50] In contrast, the spin-LEDs developed here also demonstrate a large DOCP and more importantly demonstrates that c-HP can be integrated with traditional III-V or IV semiconductor platforms which can be easily integrated into new spintronic platforms beyond spin LEDs."

3. Furthermore, the authors mentioned that the error bars in Extended Data Fig. 4 and 5 represent 1 standard deviation of 5 consecutive measurements (n=5). Obviously, there is a significant variation in the DOCP even for repeated measurements on a single device. The authors should clarify the sources of errors and the uncertainty associated with the measurements. Considering the large variation, the validity of the maximum 15% DCOP claimed by the authors is questionable.

The error associated with our 5 consecutive measurements at each data point can be attributed to Joule heating during device operation causing fluctuations in EL intensity (shown in extended data Fig. 6) and subsequent error in DOCP determination. We have added the following to the caption of Extended Data Fig. 4 and 5:

The source of the variation in the devices can be attributed to the Joule heating as described in extended data Fig. 6.

The maximum 15±4% is accurately represented with error bars in the figures and now the main text as well (see above comment). We chose not to take the maximum of an individual measurement and represent that as our champion efficiency, as averaging over 5 consecutive measurements is a more reliable and transparent method. The error is also represented by shading in Figure 2ab, as noted in the figure caption, though there was low deviation on the scale of the plot. Having devices outside of this champion device with lower DOCP does not change our conclusion, that CISS can inject spin polarized current into III-Vs. We feel that this is a very common practice when both developing a new field as well as (as in our case) when introducing a completely new concept and idea. Generally, as the field better understands and develops the ideas the efficiency can be improved upon. The value of reporting champion device results can not be overstated in our opinion. For example, in the area of PV the champion device efficiencies are reported (and tabulated by NREL). These values provide enormous value to the community because the demonstrate the potential and provide the impetus to continue developing a field or direction. Needless to say the solar cells that are on my roof are a far cry from the champion results (even for silicon solar cells with record efficiencies well over 26%) the solar cells on my roof are only 21% under ideal testing conditions.

4. Regarding the spin lifetime, the authors mentioned in response letter and manuscript that “We directly determined the spin lifetime in the AlGaInP MQW via time resolved circularly polarized spectroscopy (details in Methods) to be ~100 ps (Extended Data Fig. 9), which is about a 5x time increase in the spin lifetime compared to the previously used perovskite emitter layer.”. Please provide experimental details and what is the pump fluence and injected carrier density, pump wavelength, probe wavelength and pump-probe spectrum. Furthermore, as the spins are injected from electrically driven, will the lifetime from optically injected spin of holes are valid? And also, if the author would like to demonstrate the improvement in spin lifetime, same measurements should be conducted on the control sample.

We apologize for not including more details about the spin-lifetime measurements. We have added that to methods section. We followed standard procedures for measuring the spin-lifetime in III-V quantum wells (we provided a reference to that as well).

Text added:

“The spin lifetime measurements were performed on a MQW sample where the GaAs substrate was back etched and resulting free standing MQW was supported on glass substrate. To remove the AlGaInP heterostructure from the GaAs substrate, the top of the AlGaInP heterostructure was first fixed to a glass substrate with epoxy. The GaAs substrate was then removed in a 1:1 NH3OH:H2O2 etchant, which is selective to etching arsenides only. The measurements were done in transmission mode using a home-built time-resolved Faraday rotation setup[Doi:10.1016/j.physrep.2010.05.001], but with no applied magnetic field. The pump and probe beams are generated from a 1kHz amplified laser source Ti: sapphire laser amplifier (Coherent Astrella, 800 nm, pulse duration ~60 fs, ~5 mJ/pulse and 1kHz repetition rate). The fundamental beam (800 nm) is split into two beams. One beam is sent to an optical parametric amplifier (OPA) to generate the pump pulse with tunable wavelength, and its intensity is attenuated by two neutral density filter wheels. The other 800 nm beam was focused into a sapphire to generate white light probe. The time delay between pump and probe is tuned by a delay line. The pump beam excitation wavelength was set to be 555 nm and it’s polarization was set to either right or left circularly polarization by a Glan-Thompson prism polarizer and a broadband visible $\lambda/4$ waveplate, both polarizations gave the same spin lifetime while linear polarized light, i.e., $\lambda/4$ set at 0 gave no measureable signal. The white light probe was linearly polarized using a broadband sheet polarizer. The white light probe is passed through the sample and overlapped with the pump beam at the sample. The pump and probe were cross at a $<10^{o}$ angle. A broad band $\lambda/4$ plate and Wollaston prism is used to analyze the rotation of the probe beam polarization, the two orthogonal polarizations are sent to matched broadband detectors. The pump fluence was varied between 17 and 7 $\mu J/cm^2$/pulse and no fluence dependence was observed. The samples all were measured under ambient conditions and peak maximum was at 564 nm.”

Yes. The spin lifetimes measured optically are relevant to the electrically driven case. The only point that could be different is the electrical or optical injected carrier densities as these may be different and it’s hard to estimate the carrier density under operating conditions in the LED. However, we think our carrier densities are close and that the spin-lifetime in the low carrier density regime should be weakly dependent on carrier density.

We are not trying to 'improve the spin-lifetime' of the emitter layer. We are only suggesting that the improvement in the DOCP could arise from the better spin lifetime in the III-V MQWs. The AlGaInP MQWs were measured with the similar method as the previously used perovskite emitter layer (*Science* **2021**, *371* (6534), 1129–1133): circularly polarized transient absorbance. This allows for a direct comparison with the previously used perovskite emitter layer, $CsPb(Br_{0.1}I_{0.9})_3$ which was measured by us, with the same experimental setup making for a suitable comparison. We are referring to a previously measured value of spin-lifetime in perovskite emitters.

Improving the spin lifetime in the emitter layer is an interesting research direction and one we are also working on. However, that is not the focus of this work on that it likely is the reason for the measured higher DOCP and still one of the limitations for achieving an even higher DOCP.

5. The statement that "high DCOP implies that the spin-injection process is highly efficient" is made without providing any evidence. This claim needs to be supported by experimental data or theoretical analysis.

Yes we apologize for being a little vague and we addressed most of this in our response to questions 1. We have provided an estimate of the spin-injection efficiency and what limits it (transport across the cladding layer). Our purpose was to be focused on the CISS layer and not the III-V, however, we do thank the reviewer for pointing out this confusion which we hope now to have fixed.

6. It is difficult to observe an increase in DCOP with increasing current from Extended Data Fig. 4 and 5. This raises doubts about the validity of the conclusion that DCOP increases with the driven current. Additionally, in the authors' previous work (Ref 15), spin lifetime decreased with increased carrier density, so it is unclear why DCOP would increase with the driven current in this study.

Figure 2e. provides the averages of all devices reliably measured at a specific current. As mentioned in the previous rounds of review, we had issues with devices breaking, so it is not a uniform number of devices measured at each current. The best operating device shown in figure 2 gave us the idea of a possible power dependence. To better elucidate this, we took the DOCP of each device reliably measured device at each current and averaged them, where we were able to observe the power dependence. The Joule heating and subsequent variation in these devices is unfortunate, that it makes a comparison of this phenomena difficult to measure in a single device, but we find this average devices DOCP at each current to be strong evidence of current dependence and is the best we can show with the devices as fabricated.

As far as the change in behavior compared to the previous work, that work here has two important features that are different, which are unrelated to spin lifetime. 1. The band offsets are not an issue in the previous work and are here as we have discussed in the main text. 2. That device does not have a cladding layer for carriers to traverse, where a power dependence can affect the traverse time. It is possible that there will be a current density where this increasing DOCP trend flips, but as mentioned the devices breaking make this not possible to investigate.

Regarding the carrier density dependent spin-lifetime. In our previous work the spin lifetime was very much dependent on the carrier density. However, that is a characteristic of the metal-halide perovskite and the different spin scattering mechanism at play (under different carrier densities) compared to the III-V. Here we did not see a large different in spin lifetime over the carrier densities that we tested. However, we do think that at higher drive currents the DOCP would and should go down because the spin lifetime would be short. We briefly discuss this in the context of other reports on III-V semiconductors who also report an increase in DOCP with bias and then a higher bias a decrease. We expect the same behavior here – but could not test much high biases for these LEDs.

7. The authors need to explain how they determined the doping concentration and dielectric constant of c-HP. Additionally, they should clarify whether these values are feasible and reliable. The reliability of the estimated drift velocity is also a concern related to the accuracy of the determined doping concentration.

We used a dielectric constant of 4.4 which was measured in a previous report for the related (Phenylethylammonium)$_2$PbI$_4$ compound.
https://journals.aps.org/prb/pdf/10.1103/PhysRevB.45.6961

The doping concentration of the c-HP is actually quite complicated. 2D halide perovskites, in single crystal form have extremely low self-doping. Based on electrical measurements, and noise in photodetectors there is more self-doping in the 2D perovskite *films* *https://pubs.acs.org/doi/10.1021/acs.nanolett.7b01475* . First, we tested a range of dopant (p-type, per literature) concentrations of $10^{14}$, $10^{15}$, $10^{16}$. As the depletion region in the perovskite is quite large due to its lower doping concentration than the adjacent well doped AlGaInP, there was no effect with our simple simulation on the depletion region regardless of the doping concentration. Based on the above literature, for the simulation presented we used an extremely low doping concentration of $10^{14}$. The band bending simulation shown is reasonable and the electric field built up at the interface, is only an order of magnitude different then the SPV-KPFM electric field suggested, albeit at 1.5 V (SPV-KPFM) vs 3 V (simulated) applied across the device. Furthermore, we believe the estimated traverse time is completely reasonable in light of the higher potentials used for device operation compared to the SPV-KPFM and simulated band diagrams as mentioned in the previous review.

8. The concepts of spin accumulation and spin injection are easily confused in the manuscript. The authors should provide clear definitions and explanations to avoid confusion and clearly state which concept contributes to DCOP.

Spin injection is injection of spin polarized carriers across interfaces and spin accumulation is the build up of spin polarized carriers in the device. We significantly modified the text to define these two terms explicitly (see response to #1). We thank the reviewer for pointing out this confusion. Too make sure we have carefully checked the manuscript and have used spin injection and spin accumulation accurately in each instance and specified where relevant we are referring to spin injection into the MQWs.

9. The statement that "the spin orientation produced via the CISS mechanism is parallel to the direction of current, and the light emission is also parallel to the currentdirection due to the small escape cone of the III-V" needs to be supported by evidence. The authors should provide experimental data or theoretical analysis to support this claim.

We apologize for the confusion. We are not claiming that this contributes to anything measured here only that it is clearly an advantage to the CISS method of producing spins (out of plane polarization). Producing an out-of-plane spin polarization with Ferromagnets has been a topic of the condensed matter physics communities for a long time mostly for the same reason (i.e. take advantage of the escape cone and circularly polarized light emission optical selection rules). The act we get this for 'free' with CISS is a major selling point.

The escape cone of the III-V is a well-known property found in many semiconductor textbooks. The CISS mechanism of spin orientation being parallel to current is shown convincingly in the literature and specifically well described in this recent work: https://arxiv.org/abs/2312.15466 which we have now cited. The spin orientation must be along the chiral axis of the injection via symmetry arguments.

For light emission the circularly polarization is along the light propagation direction is also a textbook concept. Therefore, it would not be appropriate for us to provide any further theoretical analysis in the manuscript.

10. The term "collapsing depletion region" is not clear. In Fig. 3b, the width of the depletion region in c-HP for a bias of 3 V remains unchanged compared to that of 0 V. Therefore, the proposed mechanism for low DCOP under lower bias is not valid. The authors should provide a clear and accurate explanation of the phenomenon observed in the figure.

The reviewer brings up a good point here. As the band diagram shows, the c-HP can be described as fully depleted at both bias conditions. However, we should point out that what does collapse is the region for the 2D hole gas (2DHG). As can be seen, the higher bias condition collapses the width of the well which the 2DHG resides thus reducing the number of states in the 2DHG. The field also increases as is stated giving the holes far more energy to overcome scattering at this barrier.

In response to this, we have removed the phrase about the collapsing depletion width and modified it:

"We considered the possible sources of the current/bias dependence of the DOCP. (1) It likely arises due to the barriers from poorly aligned type-II bands (Fig 3a) at the c-HP/AlGaInP interface. When the carriers equilibrate (at 0 V bias, Fig. 3b), there is a large depletion region of the c-HP with low carrier concentration, which allows for the formation of a 2D hole gas within the c-HP at the interface. A large depletion region and build up of a 2D hole gas provides opportunities for spin scattering during spin-injection.[31] However, a higher bias (3V is shown in Fig. 3b) reduces the width of the 2D hole gas, therefore reducing the number of quantizied states and ~~collapses the depletion region~~ and gives injected carriers more energy to reduce interactions at the interface. Similar mechanisms of spin scattering due to depletion region and interface barrier heights have been suggested previously.[30,32] (2) It arises due to spin scattering/relaxation as holes traverse the 200 nm p-type cladding layer residing between the c-HP and MQW."

11. The energy levels used in the paper are extracted from literature sources. However, it is unclear whether these values can be directly applied to the current study, as the energy levels might be different due to variations in the fabrication process and doping. The authors should address this concern and discuss the potential impact of fabrication process variations on the energy levels.

As with any model, the model is only as good as the assumptions. While any band diagram is prone to some error, we have utilized the best values available for simulating our interface and it provides adequate detail to describe the action we are seeing. The energy levels, shown from literature, correctly point out that there is a large valence band mismatch between the perovskite and the III-V, which is the main point of showing the energy levels. A 0.9 eV shift (the difference of AlGaInP VBM and c-HP VBM) due to variations in the fabrication process is not realistic and any reasonable shift would not change our conclusion: the valence bands are offset. We do not believe the discussion that the processing conditions effect materials is valuable.

12. There are numerous typos throughout the manuscript, and the English and writing style need improvement. The authors should carefully proofread and polish their writing to enhance the clarity and readability of the manuscript.

We have attempted to clarify and fix any typos and thank the reviewer for pointing those out to us. We apologize for that and will further work with the editors to polish the manuscript if approved for publication.

13. Lastly, the novelty and importance of this work are still not strong. The use of III-Vs for spin injection is not as novel or important as the authors suggest. There have been many reports on the use of chiral perovskites for spin injection to other materials (e.g., perovskite film, QDs, 2D materials (Nano Lett. 24, 1001, 2024), etc) with high spin injection efficiency (80%; Adv. Mater. 36, 2305604, 2024) and high DOCP. These materials offer advantages such as low-cost fabrication, high PLQY, high EQE, and flexibility. In contrast, commercial III-V materials require high-cost fabrication, and the EQE demonstrated in this paper is extremely low (<0.1%). This significantly limits its application and importance. Furth more, it's important to note that chiral perovskites can be used even as standalone spintronic devices. This raises questions about the uniqueness and significance of the proposed chiral perovskite/III-V spin injection approach.

We must disagree on this topic. This is, of course, a matter of perspective. The previous reports shown do not inject spin polarized carriers into III-Vs, which are the dominant material used in the LED industry: https://www.ledsmagazine.com/leds-ssl-design/materials/article/16701292/what-is-an-led. In fact, the AlGaInP compositions we use in this work are the standard for yellow-red LEDs available for purchase: https://shorturl.at/pquT6 (see data sheet) while other III-Vs color the rest of the color gamut. We are very excited about being able to successfully inject spin into a commercially produced architecture. Furthermore, this demonstration can open numerous spintronics applications beyond spin LEDs, where spin injection into III-V (or related group IV) semiconductors can enable demonstrations of spin-FETs, semiconductor spin torque devices, and other creative technologies enabled by the excellent processing control the semiconductor research field has garnered over the previous 70 years in these materials. We have not seen any literature integrating CISS perovskites with III-Vs in an electronic device. Although CISS has been integrated with other emerging technologies (perovskite) by us and others, integrating CISS with III-Vs is an important not obvious demonstration that can be very valuable to academics and industry interested in exploring spintronic platforms. A very specific example could be the integration of CISS with III-V based vertical-cavity surface-emitting Lasers used in telecommuncations for circular polarization and enhanced information encoding. We hope this initial demonstration will enable investigation in similar devices utilizing conventional semiconductors.

We do not see our low EQE as an issue. EQE is excellent for evaluating new emitters and device architectures, but phosphide III-Vs are a well-established technology with high EQE and wall-plug efficiency (the industrial metric) when optimized for luminance. Our design here is not optimized for EQE as noted in the previous round. Industry optimizes their LEDs for EQE (or more importantly, wall-plug efficiency) by adding light extraction features we are not capable of producing at this time. In our integrating sphere experiment, the back contact (GaAs) dramatically decreases our EQE as noted in the previous reviews.

We are happy to see that the Adv. Mater. 36, 2305604, 2024 report shows a large 80% spin polarized current measurement, in great agreement with our previous result: https://www.science.org/doi/full/10.1126/sciadv.aay0571 These are the same materials, (R/S-MBA)$_2$PbI$_4$ used as a CISS layer for spin injection as we have used in our device in this work, indicating the large spin polarized currents that they can produce.

Overall, given the lack of novelty and striking advance, the poor quality of the data with many technical shortcomings, the large variation and over-explanation of the 15% DCOP, the extremely low EQE, the lack of solid experiments and measurements to support their assumptions and conclusions, and an unclear explanation of the mechanism as listed above, I am therefore unable to support this paper for publication in Nature.

Referee #3 (Remarks to the Author):

The authors responded appropriately to the reviewers' comments and the manuscript was sufficiently revised. This achievement will accelerate the research on integration of chiral-perovskite with common III-V semiconductors. Therefore, I recommend this revised manuscript for publication in Nature.

Thank you for your suggestions in the previous round of reviews and we are glad o see the revisiosn were sufficient. We sincerely believe you suggestions have improved our manuscript.

**Reviewer Reports on the Second Revision:**

Referees' comments:

Referee #1 (Remarks to the Author):

The authors have answered all my questions. This is a milestone work to bridge the CISS and III-V semiconductors and their opto-spintronic device applications. The impact of this work will be marvelous. Thus I am confident to recommend the publication of this work in Nature.

I noticed that most of reviewer 2’s comments are about the validation of injected spin polarization degree (2.1), maximum DOCP (a figure of merit device, 2.2), error bars and statistical concerns (2.3), and the spin lifetime (2.4). I think all these comments have been properly addressed in the revised manuscript by the authors by providing extra descriptions in the main text and formula that improved the presentation of this work. Reviewer 2 also captured a couple of confused definitions about spin accumulation vs. spin injection (2.8), CISS-induced spin polarization direction (2.9), collapsing depletion region (2.10), energy level (2.11) which have been described in CISS and III-V literature reports elsewhere, although elucidating these terms for audiences will indeed improve the quality of this work.

As for 2.13, I want to clarify that the circularly polarized emission from a single chiral layer should not be attributed to the CISS effect. This is the common misunderstanding between the CISS effect and ordinary chiroptical response. Most of them are just circularly polarized light-emitting devices or CP-LEDs. Their circularly polarized EL (larger or smaller than the current report values) is caused by a trivial CD response of chiral materials instead of spin injection via the CISS effect (spin-LEDs) as demonstrated in this study. The impact of the listed references and the current work should be differentiated. The physical mechanism of the CISS effect does not allow the spin-polarized carrier injection to occur in a single chiral layer. In these CP-LED device geometries, holes and electrons are electrically injected from opposite ends to the same blend. The structural chirality is invariant to the rotation operation. Thus, reversing the carrier flow does not reverse the spin polarization of the CISS effect (if it occurs) as reported in many mc-AFM experiments. It means that both holes and electrons would be polarized to the same spin orientation. This triplet-like electron-hole pair cannot radiatively recombine and emit CP-EL since this violates the optical selection rules.

The demonstrated study here offers a novel opportunity to realize a high-performance spin-LED efficiency that may triumph over individual existing organic and perovskite-based CP-LEDs by utilizing both large spin polarization of the injected spin at the hybrid perovskite/MQW interface compatible with stable, wafer-scale III-V semiconductor heterostructures.

Referee #2 (Remarks to the Author):

The revised version of the paper shows improvement; however, the results and concepts presented do not meet the exceptional quality required by Nature. The manuscript fails to demonstrate, either experimentally or through a novel strategy, a significant advancement in chiral materials or chirality-related spintronics. The main reasons for this are as follows:

1. Chirality-induced spin selectivity (CISS) and the use of chiral perovskite as a spin injector have been extensively reported in previous studies, including the authors' previous work. This paper does not provide any new physical insights into CISS. The successful demonstration of using chiral materials as spin injectors/filters in III-V devices at room temperature has already been achieved (e.g., "Electric Field-Controlled Magnetization in GaAs/AlGaAs Heterostructures–Chiral Organic Molecules Hybrids," J. Phys. Chem. Lett. 2019, 10, 5, 1139). In this manuscript, the authors only demonstrate the use of chiral perovskite for spin injection in III-V materials, which is not a ground-breaking result.
2. The most significant unresolved issue with chiral materials used in spintronic devices is the inability to control chirality electrically or optically to switch the spin polarization direction for spintronic application. This limitation greatly restricts the application of chiral materials, including chiral perovskite, in spintronic devices. It is worth noting that ferromagnetic film with 100% spin polarization can be used for highly efficient spin injection into III-V materials/devices and can control/switch the spin polarization at room temperature. For example, an electrically driven circular polarization of 8% (0T, 300K) has been demonstrated in a GaAs/InGaAs quantum well spin LED with CoFeB as the spin injector ("Large and robust electrical spin injection into GaAs at zero magnetic field using an ultrathin CoFeB/MgO injector," Physical Review B 90, 085310 (2014)). Furthermore, a recent paper published in Nature ("Controlling the helicity of light by electrical magnetization switching," Nature, 627, 783, 2024) has already demonstrates that a single ferromagnetic layer (CoFeB) injects electron spins into a GaAs/InGaAs QD LED, and a commercially established spin–orbit torque (SOT) electrically switches the magnetization, thereby controlling spin polarization at room temperature and zero applied magnetic field. The circular polarization of electroluminescence can reach 36% (0T, 300K). When compared to these published works, the current manuscript falls significantly below the standard expected by Nature.

Additional technical comments:

1. There are discrepancies in the relative energy level differences between different layers in Figure 3a and 3b. For example, in Figure 3a, there is a significant VBM energy barrier between the perovskite and cladding layer.
2. It is unclear why the voltage is denoted as "-3V" instead of "3V." Clarification is needed.
3. If spin-polarized holes from chiral perovskite can be injected into AlGaInP quantum wells (QWs) via electrical injection, resulting in circularly polarized electroluminescence (CP-EL), it can be expected that even without using chiral perovskite, under circularly polarized light excitation of QWs, spin-polarized carriers can be injected into the QWs. The authors should demonstrate whether circularly polarized PL can be observed in AlGaInP QWs under circularly polarized light excitation.
4. The basic characterizations of LED are missing, eg. Luminance intensity-voltage and current intensity-voltage curves should be provided.
5. For the formula "DOCP = $\alpha \cdot F \cdot Pinj$, 23", I did not find this equation in the Ref 23. And how is this DOCP related with injected spin hole polarization? What is the effect of injected electron?
6. Does the measured spin lifetime of AlGaInP MAW refer to electron or hole spin lifetime? To what extent is the estimated spin injection efficiency affected since only hole spins are injected?
7. The figure caption and main text for Fig. 2c,d,e do not even mention the sample! Are they from (R-MBA)2PbI4 or (S-MBA)2PbI4? Why is the measured DOCP for a specific chiral material inverse to

other reports such as Adv. Mater. 2024, 36, 2305604 and Science 2021, 371, 1129 and Adv. Mater. 2024, 36, 2309335)?? In the previous works, even including the authors' paper (Science 2021, 371,1129), DOCP is positive for (R-MBA)2PbI4, why in this manuscript, line 110, "The measured DOCP reaches > 10% when (S-MBA)2PbI4"?
8. What is the width of the 2D hole gas to which the authors refer? Why should the width of the 2D hole gas decrease with increased bias, since the width of the depletion region in the c-HP layer remains unchanged?
9. As mentioned by the authors, there is an order of magnitude difference between the simulated and measured electric field. The estimated drift velocity and transverse time are therefore not reliable. Meanwhile, only the measured potential difference in the c-HP layer is in slight agreement with the simulated results, while those in the MQW and the p-clad layer are not. Furthermore, the potential drop is not uniform across the p-cladding layer and is much larger at the interface (Figure 3).

Referee #3 (Remarks to the Author):

The authors carefully studied the comments raised by Referee 1 and 2, and appropriately revised the manuscript in addition to the sufficient responses to them.
In particular, the quantitative evaluation of the spin injection efficiency significantly improved the quality of the study.
On the other hand, I had similar questions about the large variation in DOCP pointed out by Referee 2.
However, as the author claimed, the breakthrough of this study is the integration of CISS perovskites with traditional III-V semiconductors.
I believe that the improvements in device design and device fabrication in the near future will greatly improve the performance, repeatability and thermal stability.
Therefore, I would like to recommend the publication of the revised manuscript in Nature.

**Author Rebuttals to Second Revision:**

Code:

Blue: Comment discussing the reviewer's question

Orange: Changes made to the main text

Referee #1 (Remarks to the Author):

The authors have answered all my questions. This is a milestone work to bridge the CISS and III-V semiconductors and their opto-spintronic device applications. The impact of this work will be marvelous. Thus I am confident to recommend the publication of this work in Nature.

Thank you for the support of this work.

I noticed that most of reviewer 2's comments are about the validation of injected spin polarization degree (2.1), maximum DOCP (a figure of merit device, 2.2), error bars and statistical concerns (2.3), and the spin lifetime (2.4). I think all these comments have been properly addressed in the revised manuscript by the authors by providing extra descriptions in the main text and formula that improved the presentation of this work. Reviewer 2 also captured a couple of confused definitions about spin accumulation vs. spin injection (2.8), CISS-induced spin polarization direction (2.9), collapsing depletion region (2.10), energy level (2.11) which have been described in CISS and III-V literature reports elsewhere, although elucidating these terms for audiences will indeed improve the quality of this work.

Thank you for taking the time to read through each of these concerns and our responses. We will continue to improve the definitions in the main text specifically regarding CISS terms.

As for 2.13, I want to clarify that the circularly polarized emission from a single chiral layer should not be attributed to the CISS effect. This is the common misunderstanding between the CISS effect and ordinary chiroptical response. Most of them are just circularly polarized light-emitting devices or CP-LEDs. Their circularly polarized EL (larger or smaller than the current report values) is caused by a trivial CD response of chiral materials instead of spin injection via the CISS effect (spin-LEDs) as demonstrated in this study. The impact of the listed references and the current work should be differentiated. The physical mechanism of the CISS effect does not allow the spin-polarized carrier injection to occur in a single chiral layer. In these CP-LED device geometries, holes and electrons are electrically injected from opposite ends to the same blend. The structural chirality is invariant to the rotation operation. Thus, reversing the carrier flow does not reverse the spin polarization of the CISS effect (if it occurs) as reported in many mc-AFM experiments. It means that both holes and electrons would be polarized to the same spin orientation. This triplet-like electron-hole pair cannot radiatively recombine and emit CP-EL since this violates the optical selection rules.

Thank you for the detailed response. We do believe a value of our submitted work is the "cleanliness" of our junction, where convoluted effects of directionality etc. mentioned above are largely absent.

The demonstrated study here offers a novel opportunity to realize a high-performance spin-LED efficiency that may triumph over individual existing organic and perovskite-based CP-LEDs by utilizing both large spin polarization of the injected spin at the hybrid perovskite/MQW interface compatible with stable, wafer-scale III-V semiconductor heterostructures.

Referee #2 (Remarks to the Author):

The revised version of the paper shows improvement; however, the results and concepts presented do not meet the exceptional quality required by Nature. The manuscript fails to demonstrate, either experimentally or through a novel strategy, a significant advancement in chiral materials or chirality-related spintronics. The main reasons for this are as follows:

1. Chirality-induced spin selectivity (CISS) and the use of chiral perovskite as a spin injector have been extensively reported in previous studies, including the authors' previous work. This paper does not provide any new physical insights into CISS. The successful demonstration of using chiral materials as spin injectors/filters in III-V devices at room temperature has already been achieved (e.g., "Electric Field-Controlled Magnetization in GaAs/AlGaAs Heterostructures–Chiral Organic Molecules Hybrids," J. Phys. Chem. Lett. 2019, 10, 5, 1139). In this manuscript, the authors only demonstrate the use of chiral perovskite for spin injection in III-V materials, which is not a ground-breaking result.

We disagree with this assessment. The approach we have taken here, allows integration of CISS based spin injection in an ‘off-the-shelf’ optoelectronic device. The previous work on GaAs/AlGaAs demonstrates electric field induced ferromagnetism in a GaAs/AlGaAs heterostructure, which is an exciting result, but differs significantly from our work. Furthermore, our approach demonstrates a new semiconductor/semiconductor interface, which we believe will be key to integrating CISS devices in various applications, where monolayers of organics (above cited work) are limited in the processibility and thus utility.

2. The most significant unresolved issue with chiral materials used in spintronic devices is the inability to control chirality electrically or optically to switch the spin polarization direction for spintronic application. This limitation greatly restricts the application of chiral materials, including chiral perovskite, in spintronic devices. It is worth noting that ferromagnetic film with 100% spin polarization can be used for highly efficient spin injection into III-V materials/devices and can control/switch the spin polarization at room temperature. For example, an electrically driven circular polarization of 8% (0T, 300K) has been demonstrated in a GaAs/InGaAs quantum well spin LED with CoFeB as the spin injector ("Large and robust electrical spin injection into GaAs at zero magnetic field using an ultrathin CoFeB/MgO injector," Physical Review B 90, 085310 (2014)). Furthermore, a recent paper published in Nature ("Controlling the helicity of light by electrical magnetization

switching," Nature, 627, 783, 2024) has already demonstrates that a single ferromagnetic layer (CoFeB) injects electron spins into a GaAs/InGaAs QD LED, and a commercially established spin–orbit torque (SOT) electrically switches the magnetization, thereby controlling spin polarization at room temperature and zero applied magnetic field. The circular polarization of electroluminescence can reach 36% (0T, 300K). When compared to these published works, the current manuscript falls significantly below the standard expected by Nature.

We are well aware of the progress being made using ferromagnetic spin injectors represented by two papers cited by the reviewer here, yet they are clearly distinguished from our submitted manuscript and the use of chirality to control spin populations.

1. First, this work is the first demonstration using the CISS effect for spin injection in III-V spin LEDs, which is completely new concept compared to the traditional ferromagnetic spin injector.

2. Second, for FM injector, the impedance mismatch between metal and semiconductor is long-term detrimental problem for spin injection. One has to sophistically engineer the interface by adding a thin tunneling barrier to enhance the spin injection. However, based on the intrinsic semiconducting property of the chiral perovskite based semiconductor, the CISS injector can avoid the impedance mismatch problem and the spin injection efficiency does not rely on the interface but to the robust bulk CISS effect, which greatly reduces the difficulty of obtaining high-efficiency of spin injection. The spin injector can be fabricated by solution-based spin coating method, which is suitable for low cost mass production compared to the FM injector fabrication with UHV MBE or sputtering.

3. Third, FM injector has limited spin polarization. It is very difficult to achieve higher circular polarization than 50% without using sophistically designed optical cavity. Even the people already tried with half metallic spin injector (100% spin injection) (Applied Physics Letters 98, 162508 2011), the spin injection efficiency is not as high as the traditional FM injector since the interface problem is detrimental for FM injector. In addition, one has to fulfill perpendicular magnetic anisotropy for spin injection without magnetic field (in Faraday geometry). Compared to these weakness, CISS injector possesses not only high spin polarization (30nm to achieve 80-90% spin polarization) but also out-of-plane polarization direction, which ensures a high circular polarization with zero magnetic field.

Additional technical comments:
1. There are discrepancies in the relative energy level differences between different layers in Figure 3a and 3b. For example, in Figure 3a, there is a significant VBM energy barrier between the perovskite and cladding layer.

For drawing the equilibrium band diagram, we utilized the online free software package titled “Energy Band Diagram Program” (Boise State College of Engineering) we input the appropriate VBM and Eg values (as described in figure 3a). The software then constructs the equilibrium band diagram and that for various applied biases. The reduced step height is likely a resolution limit where strong interfacial bending at smaller intervals than the point step leads to the graph presented in the figure. Since the exact band positions shown in Fig 3a were used to generate the band diagram, there are not inconsistencies in the analysis, only in the appearance of the output band diagram graph. Thank you for pointing this out.

In the manuscript we have added a note in the methods describing the band simulation that “The band diagram shown has a step width that may underrepresent the spike at the Perovskite/AlInGaP interface.”

2. It is unclear why the voltage is denoted as "-3V" instead of "3V." Clarification is needed.

In the “Energy Band Diagram Program” software we utilized, the defined polarity had to be flipped due to the software limitations (direction of the layers require negative potential to reflect experimental conditions). We will leave it as such, as those were the input parameters.

3. If spin-polarized holes from chiral perovskite can be injected into AlGaInP quantum wells (QWs) via electrical injection, resulting in circularly polarized electroluminescence (CP-EL), it can be expected that even without using chiral perovskite, under circularly polarized light excitation of QWs, spin-polarized carriers can be injected into the QWs. The authors should demonstrate whether circularly polarized PL can be observed in AlGaInP QWs under circularly polarized light excitation.

This is a well known phenomena in III-V semiconductors as discussed in our section describing the optical selection rules. We do not believe there is value in demonstrating this at this time.

4. The basic characterizations of LED are missing, eg. Luminance intensity-voltage and current intensity-voltage curves should be provided.

We have mentioned the complications of providing quantitative electroluminescence data on our devices in the previous rounds of reviews. These experiments will become more valuable as the technology matures, but do not believe it is necessary in this initial demonstration and detracts from our focus on spin polarization and spin accumulation.

5. For the formula “DOCP = $\alpha \cdot F \cdot Pinj$, 23”, I did not find this equation in the Ref 23. And how is this DOCP related with injected spin hole polarization? What is the effect of injected electron?

We apologize for this typo and appreciate that the reviewer brought this to our attention. We meant to cite a very similar work by the same lead and corresponding author and have inserted the correct citation. https://journals.aps.org/prapplied/pdf/10.1103/PhysRevApplied.16.014034 where we have adapted equation 1 and 2 for our system (replace ferromagnet with Pinj for CISS).

We are injecting holes through the CISS layer. As such our DOCP is related to our spin hole polarization. Electrons injected from the backside do not have spin polarization (transport through non-ciss/FM layers).

Related ot this comment, we also added the further parameterization of this equation by providing Pinj for varying alpha parameters:

as determined by time resolved photoluminescence spectroscopy (Extended Data Fig. 9b). The 10 nm MQW samples utilized here are close to the size of confinement (analogous InP exciton radii is ~10 nm[25]), however there is no blue shifting in the PL compared to predicted bulk $E_g$.[22] If the structure is not confined, α is estimated to be 0.5, due to the optical selection rules in the III-V semiconductor and transition probabilities favoring the heavy-hole over light-hole sub band in a 3:1 ratio, producing 3 right (left) handed to 1 left (right) handed circularly polarized photons when 100% spin polarized carriers are introduced.[26,27] With α = 0.5 the spin accumulation is 2*|DOCP|. Thus $P_{inj} = 0.48$ meaning that 48% of carriers injected are spin polarized. However, since the structures are close to the confinement size, there is a possible lifting of the degeneracy favoring the heavy-hole over light-hole sub band, in that case α = 1 and would yield $P_{inj} = 0.24$.

6. Does the measured spin lifetime of AlGaInP MAW refer to electron or hole spin lifetime? To what extent is the estimated spin injection efficiency affected since only hole spins are injected?

The measured spin lifetime is of the exciton (i.e., both electron and hole). However, we believe that our measurement is applicable to the spin-LED case. Emission requires both electrons and holes and the light emission process will obey the same optical selection rules no matter how the carriers are generated. Depolarization of either electron or hole will contribute to the overall depolarization in both the photoexcited case and the electrically injected. Thus the polarization lifetime should be similar for both as long as the carrier density is similar and/or the lifetime is not dependent on the carrier density.

For the transport discussion on the other hand can be different because in this case the holes are injected without electrons present so optically excited situation is not the same for the cladding layer. Therefore, in that case we use literature values as a comparison to be as conservative as possible:

"We estimate the traverse time of carriers across the p-cladding layer to be <1.9 ps, which shortens with increased applied bias (see Methods for calculation details). Low temperature measurements in related III-V semiconductors suggest hole spin relaxation is on the ps time scale at room temperature, close to the carrier traverse time.[31,32]"

We have also added a note in the methods section clarifying this: "We would like to note that the measurement here is ambipolar and thus likely the measurement of the exciton spin lifetime."

7. The figure caption and main text for Fig. 2c,d,e do not even mention the sample! Are they from (R-MBA)2PbI4 or (S-MBA)2PbI4? Why is the measured DOCP for a specific chiral material inverse to other reports such as Adv. Mater. 2024, 36, 2305604 and Science 2021, 371, 1129 and Adv. Mater. 2024, 36, 2309335)?? In the previous works, even including the authors' paper (Science 2021, 371,1129), DOCP is positive for (R-MBA)2PbI4, why in this manuscript, line 110, "The measured DOCP reaches > 10% when (S-MBA)2PbI4"?

We apologize for any confusion and appreciate bringing this to our attention.

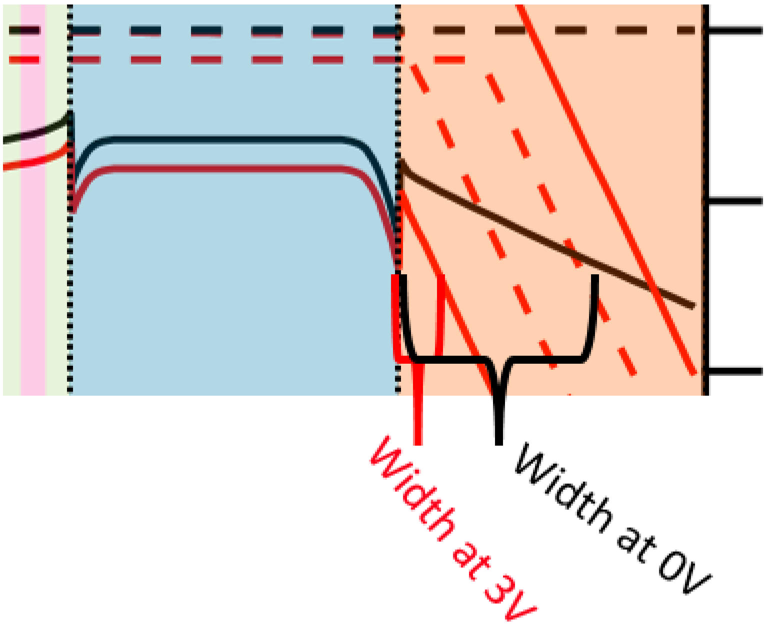
The DOCP is consistent with previous reports. $(R\text{-}MBA)_2PbI_4$ produces stronger LHCP (positive DOCP), same as the previous reports. (Figure 2a)

At some point in the figure making process, labels in figure 2c and 2d were removed inadvertently and we have added them back in.

Line 110 is a typo, although the magnitude is probably more important. We have modified the text to make that when we discuss the DOCP we are talking about the magnitude and not the sign. (i.e., a larger DOCP means either greater if its positive or more negative if its negative.

8. What is the width of the 2D hole gas to which the authors refer? Why should the width of the 2D hole gas decrease with increased bias, since the width of the depletion region in the c-HP layer remains unchanged?

The width of the 2DHG is shown in this image at different potentials and the description in the text is provided below. We believe this is clear as written.



“When the carriers equilibrate (at 0 V bias, Fig. 3b), there is a large depletion region into the c-HP with low carrier concentration, which allows for the formation of a 2D hole gas within the c-HP at the interface. A large depletion region and the corresponding 2D hole gas provides opportunities for spin scattering during spin-injection.[29] However, a higher bias (3V is shown in Fig. 3b) reduces the width of the 2D hole gas, therefore reducing the number of quantized states and gives injected carriers more energy resulting in less spin-scattering.[28,30]”

9. As mentioned by the authors, there is an order of magnitude difference between the simulated and measured electric field. The estimated drift velocity and transverse time are therefore not reliable. Meanwhile, only the measured potential difference in the c-HP layer is in slight agreement with the simulated results, while those in the MQW and the p-clad layer are not. Furthermore, the potential drop is not uniform across the p-cladding layer and is much larger at the interface (Figure

3).

This comment does not allow for the limitations of measurements and simulations. Cross-section measurements done with KPFM measures surfaces that are not exposed in actual device operation. Furthermore, there are always limitations with the resolution in such a measurement. Simulations do not perfectly model devices, especially with novel semiconductors such as chiral halide perovskite where interfaces and general transport are not well understood. However, we feel we have been conservative in our estimates of the transverse time, e.g., the simulations are for -3V – the device is operating at much higher voltage and we use a conservative value of the hole spin lifetime in the cladding layer. We fully acknowledge in the manuscript (as the reviewer points out) that there are discrepancies between the model and the actual data.

Referee #3 (Remarks to the Author):

The authors carefully studied the comments raised by Referee 1 and 2, and appropriately revised the manuscript in addition to the sufficient responses to them.
In particular, the quantitative evaluation of the spin injection efficiency significantly improved the quality of the study.
On the other hand, I had similar questions about the large variation in DOCP pointed out by Referee 2.
However, as the author claimed, the breakthrough of this study is the integration of CISS perovskites with traditional III-V semiconductors.
I believe that the improvements in device design and device fabrication in the near future will greatly improve the performance, repeatability and thermal stability.
Therefore, I would like to recommend the publication of the revised manuscript in Nature.

Thank you for the support. We are glad to see readers of our manuscript are receptive to our main point, of the integration of two unique materials to enhance functionality.