

Spin quantum dot light-emitting diodes enabled by two-dimensional chiral perovskite with spin-dependent carrier transport

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Abstract:

Chiral-induced spin selectivity (CISS) effect provides innovative approach to spintronics and quantum-based devices for chiral materials. Different from the conventional ferromagnetic devices, the application of CISS effect is potential to operate under room temperature and zero applied magnetic field. Low dimensional chiral perovskites by introducing chiral amines are beginning to show significant CISS effect for spin injection, but research on chiral perovskites is still in its infancy, especially on spin-light emitting diode (spin-LED) construction. Here we report the spin-QLEDs enabled by two-dimensional (2D) chiral perovskites as CISS layer for spin-dependent carrier injection and CdSe/ZnS quantum dots (QDs) as light emitting layer. The regulation pattern of the chirality and thickness of chiral perovskites, which affects the circularly polarized electroluminescence (CP-EL) emission of spin-QLED, has been discovered. Notably, the spin injection polarization of 2D chiral perovskites is higher than 80% and the CP-EL asymmetric factor (g_{CP-EL}) achieves up to 1.6×10^{-2} . Consequently, this work opens up a new and effective approach for high-performance spin-LEDs.

1. Introduction

Spin light-emitting diodes (spin-LED), as an important component in spintronics, have great potentials in optical communication, quantum-based computing and information processing, tomography, encryption and three-dimensional (3D) display.[1-7] Different from circularly polarized (CP) LEDs,[8] in spin-LEDs, the emitted left-handed or right-handed CP light (LCP or RCP) is the expression of carrier spin polarization information in the hierarchy.[9, 10] The recombination of electrons and holes complies with the optical selection rules,[11] that is the change of magnetic quantum number (Δm_j) is +1 or -1, resulting in the emission of CP light σ^- or σ^+ . By governing the injection of carrier populations ($n_\uparrow$ for spin up and $n_\downarrow$ for spin down), different polarization of emission light can be achieved ($n_\uparrow = n_\downarrow$ for unpolarized).[12]

Spin-dependent carrier transport can occur in chiral materials at ambient conditions, which is termed as chiral-induced spin selectivity (CISS).[13-16] When an electron moves in chiral materials, the chiral molecules apply effective magnetic field on the electron. Since the electron has a magnetic dipole, the two spin states split and the electron becomes spin-polarized.[17-19] In 2019, Lu *et al.* found spin-dependent charge transport in 2D chiral hybrid lead-iodide perovskites (*R/S*-MBA₂PbI₄).[20] The authors performed magnetic conductive probe atomic force microscopy (mCP-AFM) experiments and uncovered the CISS effect of 2D chiral perovskites. The results exhibited that in 2D chiral perovskites with ~50 nm thickness, the spin selectivity of electrons could be even much stronger than a large DNA molecule. The spin polarizations were 86% for R sample and -84% for S sample at 2V respectively. Later, 2D chiral tin-iodide perovskites (*R/S*-MBA₂SnI₄) were reported by the same group.[21] The octahedra of [SnI₆]⁴⁻ in these chiral tin-iodide perovskites were highly distorted. As a result, the spin polarization measured through mCP-AFM was up to 94%. Then one-dimensional lead-iodide perovskites (*R/S*-MBAPbBr₃) were investigated by Lu *et al.*[22] Benefiting from the much more distorted crystal structure and more ratio of chiral cations in the crystal lattices compared with the 2D counterpart, the spin polarization of the 1D chiral perovskites achieved 90% at voltage of 1V. All those pioneer works exhibit remarkable spin-dependent charge transport in chiral perovskites, indicating the great potential of chiral perovskites acting as spin filter in spin-based devices.

The chiral-optical properties of chiral perovskites were firstly studied in 2017, Ahn *et al.* investigated the absorption differences of CP-light (circular dichroism, CD) of *R/S*-MBA₂PbI₄, but the emission differences of CP-light (circularly polarized luminescence, CPL) was not mentioned in this work.[23] Since then, studies on CD and CPL of chiral perovskites have emerged and prospered rapidly. With continuous advance of research, a contradictory problem appears, that is the introduction of chirality reduces the photoluminescence quantum yield (PLQY). Not all the works on chiral perovskites reported the CPL results or even PL. The poor PL property in those low-dimensional chiral perovskites may attribute to the significant non-radiative recombination in the thin films and the defects caused by the lattice distortion.[24] Perovskite nanocrystals are promising in LED devices and display applications.[25-27] However, the same issue appeared in perovskite nanocrystals when

chirality is introduced. The contradiction between chirality and PL performance becomes a great challenge and impedes the application of chiral perovskites in optoelectronics. Since the CISS effect enables chiral perovskites remarkable spin-dependent charge transport as spin filter, one effective approach to meet the challenge is to apply the chiral perovskites as a functional interface to inject spin-polarized electrons or holes. Kim *et al.* firstly applied 2D chiral perovskites as spin filter layer to construct spin-LED with CsPbBr₃/I₃ nanocrystals as light-emitting layer.[28] Spin-polarized holes were successfully injected into the device and as a result, CP-light were emitted with polarization of $\pm 2.6\%$. Later, Yu *et al.* fabricated perovskites core-shell nanocrystals with 2D chiral perovskite shells and 3D achiral perovskite cores.[29] The nanocrystal is type II heterojunction with spin-polarized electrons injecting and recombining in the core. The polarization was judged by asymmetry factor (g_{CP-EL} , calculated by twice difference of intensity between LCP and RCP divided by their sum) and the devices exhibited $|g_{CP-EL}|$ of 6.0×10^{-3} (0.3% of polarization). These studies effectively apply CISS effect of chiral perovskites in spin injection enabling spin-LED at room temperature and zero magnetic field.

In our previous study, the QDs/chiral perovskites thin film exhibited CPL asymmetry factor (g_{lum}) of 9.06×10^{-3} . [30] Since the spin injection of chiral perovskites are significantly effective, we believe QDs/chiral perovskites thin film could be promising in spin-QLED. Here, in this work, we apply 2D chiral perovskites as spin injection layer and CdSe/ZnS quantum dots (QDs, TEM images shown in Figure S1) as active layer to construct spin-QLED. The schematic illustration of the spin-QLED is shown in Figure 1. The chiral perovskite is inserted into the classic QLED device between TFB and QDs. The CISS effect of chiral perovskites endows spin polarization to the injected holes and is investigated by mCP-AFM. The spin-polarized holes recombine with related electrons based on the optical selection rules, resulting CP-EL emission. By modifying the chiral perovskites layer, the spin-QLED devices achieve g_{CP-EL} of 1.6×10^{-2} . From the simulation of device, we can know that the recombination center is close to the chiral perovskites/QDs interface, which benefits the g_{CP-EL} of the spin-QLED device.

2. Octahedra distortion of chiral MBA_2PbI_4

First of all, we fabricated $R/S\text{-MBA}_2\text{PbI}_4$ crystals through hydroiodic acid solution method developed by Kanatzidis with some modifications.[31] The crystal structures shown in Figure 2a and 2d were measured by single crystal XRD. Detailed crystal data and structure refinement information are given in Table S1. The structure is classic 2D Rudlesden-Popper perovskite (2D-RPP). Corner shared $[\text{PbI}_6]^{4-}$ octahedra and MBA cations stack alternatively with one layer of octahedra and two layer of MBA cations. The crystal structure and octahedra stacking are similar. Both of them has orthorhombic crystal system and the arrangement of atoms in the crystal can be index to space group of $\text{P2}_1\text{2}_1\text{2}_1$ which is a chiral space group. The lack of symmetry is the fundamental of chirality[32, 33] In this case, the introduction of chiral organic cations leads to the highly distorted octahedra which is responsible for the chirality. The distortion includes two parts, inter-octahedra and inner-octahedra. The corner sharing Pb-I-Pb angles between two octahedra in both enantiomers are 155.47° and 151.21° for $R\text{-MBA}_2\text{PbI}_4$ and 155.50° and 151.30° for $S\text{-MBA}_2\text{PbI}_4$ (Figure 1b and 1e) which are significantly different from 180° (in achiral perovskite). Besides, the octahedron itself is also highly distorted. As shown in Figure 1c and 1f, the I-Pb-I angles between the adjacent I atoms are ranging from 81.99° to 97.29° for $R\text{-MBA}_2\text{PbI}_4$ and 82.22° to 97.32° for $S\text{-MBA}_2\text{PbI}_4$. The length of different Pb-I bonds is approximate, ranging from $3.176 \text{ \AA}$ to $3.313 \text{ \AA}$ for $R\text{-MBA}_2\text{PbI}_4$ and $3.177 \text{ \AA}$ to $3.3094 \text{ \AA}$ for $S\text{-MBA}_2\text{PbI}_4$ (details can be seen in Table S2).

To quantify the distortion, we introduce the bond length distortion index (D) [34] and bond angle variance (σ_2) [35]. The equations are as follows:

$$D = \frac{1}{6} \sum_{i=1}^6 \frac{|d_i - d_0|}{d_0} \dots\dots\dots(1)$$

$$\sigma^2 = \frac{1}{11} \sum_{i=1}^{12} (\theta_i - 90)^2 \dots\dots\dots(2)$$

where d_i is Pb-I bond lengths, d_0 is the average Pb-I bond length, and θ_i corresponds to the octahedra I-Pb-I bond angles. Both D and σ_2 would be zero in an ideal octahedron. The calculated D and σ_2 of two chiral 2D-RPP are approximate to each other. The distortion index is 0.018 for R and

0.017 for S and the angle variance is 17.50 for R and 16.07 for S. But when it comes to achiral 2D-RPPs and 3D perovskites, both D and σ^2 become much smaller (more details can be seen in Table S3). Thus, the synergic effect of inter- and inner-octahedra distortion leads to the chirality of the chiral 2D-RPP.

3. Spin-dependent charge transport

As we mentioned, the chiral materials apply an effective magnetic field on the passing through electrons, resulting in spin-polarization of the electrons. To evaluate the spin-dependent charge transport which is also termed as CISS effect, AFM measurements with contact mode was carried out. Before the measurement, the magnetic tip (MESP-V2, Co/Cr coated) was magnetized by the N pole or S pole of a magnet for 1h. I-V curves were collected with the magnetized tips (the experimental schematic diagram displayed in Figure 3a and 3e). Since the thin films of $R/S\text{-MBA}_2\text{PbI}_4$ were not ideally uniform, we averaged more than 50 curves on different areas of the thin films. We denoted spin-up current ($I_{\text{spin-up}}$) for the current obtained with N pole magnetized tip and spin-down current ($I_{\text{spin-down}}$) for the S pole magnetized tip. Thus, we can calculate the spin polarization P defined as the following equation:[36]

$$P = \frac{I_{\text{spin-up}} - I_{\text{spin-down}}}{I_{\text{spin-up}} + I_{\text{spin-down}}} \times 100\% \dots \dots \dots (3)$$

Chiral $R/S\text{-MBA}_2\text{PbI}_4$ thin films deposited on ITO glass were investigated first and the results are shown in Figure 3b-3d. The curves are averaged from more than 50 curves and the error bars reflect the deviation of the results. For R sample, the spin-up current is much higher than the spin-down current when the applied bias is higher than 1V (Figure 3b). From what is known about CISS effect, the S sample should exhibit opposite result, that the spin-down current is larger. Our experimental result of S sample complies with the CISS effect (Figure 3c) and the spin polarization as a function of voltage is plotted in Figure 3d. We can see that the spin polarization of R sample is 83.1% and of S sample is -80.3% at bias of 2V, indicating the spin-up injection for R sample and spin-down injection

of *S* sample. Then we measured the CISS effect of *R/S*-MBA₂PbI₄ thin films deposited on hole transport layer (Figure 3f and 3g). The structure of the samples is ITO/PEDOT:PSS/TFB/ (*R/S*-MBA₂PbI₄), which is the hole transport part of a complete QLED device. In this case, the spin polarization is 98.9% and -83.5% for *R* and *S* sample at bias of 2V, respectively (Figure 3h). We can notice that the current measured in this structure is lower than the pure *R/S*-MBA₂PbI₄ sample which is easy to make sense that the resistance of chiral perovskites deposited on hole transport layer is larger. Besides, the wetting property of chiral perovskites precursors on TFB is rather poor that we had to modify the TFB layer with nano Al₂O₃ to make sure the good film quality of the deposited chiral perovskites. The spin polarization of the chiral perovskites on hole transport layer is consistent with the pure chiral perovskites. As can be seen in Figure 3d and 3h, the values of *P* for *R* samples are around 80% and around -80% for *S* samples at bias range from 1 V to 2 V. These results indicate the high injection efficiency of spin charge carriers generated by chiral perovskites.

4. Spin-QLED fabrication, characterization and simulation.

With encouraging results of spin injection of chiral perovskites as hole transport layer, we fabricated spin-QLEDs by inserting chiral perovskites as CISS layer into the red CdSe QLED device. The device structure is ITO/PEDOT:PSS/TFB/(*R/S*-MBA₂PbI₄)/(CdSe/ZnS) QDs/ZnO/Ag and the energy band diagram is shown in Figure 4a.[37] We put *R*-MBA₂PbI₄ as represent since the energy band difference between *R*-MBA₂PbI₄ and *S*-MBA₂PbI₄ is little[30]. We choose CdSe/ZnS QDs as light emitter because the QDs are dispersed in a nonpolar solvent octane which does not dissolve the chiral perovskites. Besides, the energy band of chiral perovskites suits well in this device structure while stable and efficient red CdSe QLEDs are routinely obtained.[38] The cross-section image (Figure 4b) of the *R*-device exhibit that the whole device is about 300 nm thick. Figure 4c is a photograph of working spin-QLED device. The detailed parameters of the devices are summarized in Table 1 and related J-V-L curves, EQE as a function of current density and normalized EL spectra of the devices are shown in Figure 4 (Figure 4d-4f for *R* devices and Figure 4g-4i for *S* devices). *R*-0.05M represents the device with CISS layer deposited with 0.05 M concentration of *R*-MBA₂PbI₄ and *R*-0.1M device is prepared with 0.1 M of *R*-MBA₂PbI₄. The *S*-0.05M and *S*-0.1M represent the same with their *R* counterparts.

The lower concentration of precursor leads to thinner CISS layer, 0.05 M leads to thickness less than 20 nm and 0.1 M leads to thickness less than 60 nm (Figure S2). The R-0.05M device exhibits turn-on voltage of 1.9 V, luminance of 5638 cd m⁻² and maximum EQE of 2.7%, and S-0.05M device exhibits turn-on voltage of 2.1 V, luminance of 3122 cd m⁻² and maximum EQE of 1.8%. Meanwhile, the devices with thicker CISS layer exhibit poorer EL performance. The R-0.1M device has a turn-on voltage of 3.8 V, luminance of 610 cd m⁻² and maximum EQE of 0.9%, and S-0.05M device exhibits a turn-on voltage of 3.2 V, luminance of 600 cd m⁻² and maximum EQE of 1.0%. These results are significantly deficient comparing with the QLED device without chiral perovskites (Figure S3). The control QLED device has a turn-on voltage of 1.7 V, luminance of 101321 cd m⁻² and maximum EQE of 14.8%. We shall explain the EL performance deterioration with introduced perovskite CISS layer from three aspects.

First, in bottom-emitting CdSe QLEDs with normal structure as illustrated in Figure 5a, the injection and transport of electrons are more efficient than holes because of the higher mobility of electron transport material and smaller injection barrier at the interfaces.[39] However, the introduction of perovskite CISS layer between hole transport layer and QDs should further aggravate the carrier injection imbalance because of its finite mobility. The Hall mobility of the chiral perovskite was measured through a four-point-probe approach. For *R*-MBA₂PbI₄, the sheet Hall coefficient and sheet resistance are $-2.14 \times 10^9 \text{ m}^2 \text{ C}^{-1}$ and $-9.337 \times 10^{10} \Omega \text{ sq}^{-1}$. The calculated Hall mobility is $2.29 \times 10^{-2} \text{ cm}^2 (\text{V s})^{-1}$, which is 2 orders less than the achiral 2D-RPP (PEA₂PbI₄).[40] As a result, the hampered hole injection would lead to stronger Auger combination that deteriorates the EL performance. We conducted an electrical simulation showing the recombination distribution in spin-QLEDs with different thickness of perovskite CISS layer as shown in Figure S4, in which the recombination centre is always at the perovskite/QDs interface but its rate is significantly reduced with thicker perovskite, which is also confirmed by experimentally observed luminance decline from R-0.05M sample to R-0.1M one.

Second, the light extraction efficiency (LEE) is also reduced with the introduced perovskite CISS layer. The refractive index of $R/S\text{-MBA}_2\text{PbI}_4$ is about 2.4 at 629 nm as shown in Figure S5, which is higher than those of QDs (~ 2.0) and TFB (~ 1.7).^[41] Consequently, a significant waveguide mode induced by total internal reflection (TIR) with inserted perovskite is observed from the optical mode simulation as shown in Figure S6, leading to reduced LEE marked as “outcoupled” in the figure. The external quantum efficiency (EQE) of a QLED is determined by the combination of the light extraction efficiency (LEE) and the internal quantum efficiency (IQE). When the perovskite is inserted into the QLED structure, the decrease in EQE is not solely caused by the TIR induced LEE reduction, but also by the simultaneous unbalanced carrier injection and deterioration of the interface/film quality, which subsequently reduces the IQE. As we mentioned in the main text, the mobility of 2D chiral perovskite is much less than achiral one PEA_2PbI_4 (PEA is an isomer of MBA). Besides, the chiral MBA_2PbI_4 has more defects than PEA_2PbI_4 since the crystal structure is largely distorted. All these lead to the reduction of IQE, which is the most significant role in the reduction of EQE. Based on simulations, the LEE for the control sample without perovskite was estimated to be 19.1%. By comparing this with the measured EQE of 14.8%, we can deduce a maximum IQE of 77.5% for the control sample. In contrast, when a 30 nm R-perovskite layer (referred to as R-0.1 in the paper) was introduced into the QLED, the simulated LEE decreased to 13.0%, and the measured EQE dropped significantly to 0.9%. This suggests that the IQE also decreased to 6.9%. Another simulation result with fixed perovskite thickness of 50 nm and various refractive indices (real part, n) from 2.0 to 3.0 is given in Figure S7. What’s more, the LEE dispersion with $n(\text{perovskite}) \sim 2.4$ and different perovskite thickness from 0 to 100 nm is illustrated in Figure S8. The light with longer wavelength exhibits larger LEE than that with shorter wavelength because of its larger penetration depth of the evanescent wave which makes it more likely to bypass the TIR and penetrate through the perovskite by optical tunnelling.^[41]

Third, the interface/film quality in QLED is affected by the introduction of perovskite. From the SEM images (Figure S9) of the chiral perovskites on TFB we can see the thin films are dense and the roughness measured by AFM (Figure S10) is 2.0 nm for R-0.05M sample and 3.4 nm for R-0.1M sample respectively (3.9 nm for S-0.05M and 13.6 nm for S-0.1M). After CdSe/ZnS QDs are deposited

on the chiral perovskites, we see the small dots stacking tightly to each other, but some pinholes and cracks can also be observed which may be one reason for the poor device performance. Besides, the orientation of chiral perovskites is parallel to the substrate, indicating the organic and inorganic layers are stacking alternatively which may seriously impede the holes injection of the device.

The results discussed above are strong evidence to explain why the EL performance is deteriorated when the perovskite is inserted into the QLEDs from the perspectives of carrier injection, light extraction and film quality, which could also be guidance to improve the spin-QLEDs EL characteristics. However, despite the relatively poor performance of spin-QLEDs compared with the control sample, its luminance is high enough for CP-EL measurements. More importantly, a thicker perovskite CISS layer is necessary for strongly polarized EL emission. The results were collected by JASCO CPL-300 spectrophotometer with some modifications, mounting the device on the centre of the sample holder and covering the light source with black sheets. The results of R- and S-0.05M are shown in Figure 5c-5d, while R- and S-0.1M are shown in Figure 5e-5f. Ideally, the $|g_{CP-EL}|$ of R-0.1M sample should be higher than S-0.1M sample. However, various factor could affect chirality of the samples, such as thickness, homogeneity, crystal growth orientation and stacking behavior of the film. Besides, the optical purity of the precursor would also affect the chirality. Among those, the orientation and stacking behavior would affect the chirality most.[42, 43] Highly oriented chiral perovskite films lead to stronger chirality which may exhibit higher values in CD, CPL, CISS *et al.* Stacking behavior implies the possible self-organization of chiral perovskite. Different self-organization direction may lead to inversion of chirality. Thus, the thickness and $|g_{CP-EL}|$ are not strict positive correlation. The statistics exhibit that the thicker the film is, the higher $|g_{CP-EL}|$ will be. We can see the devices with thinner CISS layer have lower g_{CP-EL} , 0.001 for R-0.05M and -0.002 for S-0.05M, and the devices with thicker CISS layer achieve higher g_{CP-EL} , 0.016 for R-0.1M and -0.005 for S-0.1M. The statistics of 25 devices for both 0.05M and 0.1M are shown in Figure 5b. Overall, most of 0.05M devices have EQE higher than 1%, but $|g_{CP-EL}|$ less than 0.001. On the contrary, most of 0.1M devices have EQE lower than 1%, but $|g_{CP-EL}|$ more than 0.001, close to 0.01. An irreconcilable contradiction appears that thicker CISS layer leads to higher g_{CP-EL} but worse EL performance. Notably, in Figure 5c and 5d, the CP-EL and g_{CP-EL} results of QLED without chiral perovskite (magenta

hollow circles) exhibit that the emitting light of standard QLED has no polarization. Figure 5a shows the schematic illustration of spin-QLED emission. When passing through the CISS layer, the holes become spin-polarized because of the CISS effect. Then the spin-polarized holes are injected to the QDs and recombine with the corresponding electrons injected from ZnO. This recombination leads to the CP-EL emission. However, the spin-polarized holes will depolarize very fast in QDs and recombine with the electrons. This route for recombination is just the same with the recombination in normal QLED and emits unpolarized light. The second part is dominant in the spin-QLED and that is the reason for the asymmetric factor, $|g_{CP-EL}|$, is from 10^{-3} to 10^{-2} . Perovskite-based spin-LEDs are summarized in Table S3, from which we can see that our device has great improved the luminance of CISS-based spin-LED.

Generally, the spin relaxation time (τ_{spin}) is much shorter (3 to 4 orders) than carrier lifetime ($\tau_{carrier}$) under ambient conditions. The carrier lifetime ($\tau_{carrier}$) of our QDs/chiral perovskites is only ~ 3 ns[30], considering the interfacial effect between QDs and ZnO, the carrier lifetime in the device will be shorter. In different CdSe QDs, the carrier lifetime varies from $\sim 10^0$ to $\sim 10^2$ ns.[44-48] The spin relaxation time (τ_{spin}) of different CdSe samples at ambient conditions in reported articles is ranging from $\sim 10^0$ to $\sim 10^1$ ps.[49-53] An approximate method to calculate the polarization of the spin-QLED is τ_{spin} divided by $\tau_{carrier}$ when the spin injection is highly polarized. Thus, the calculated result of in this hierarchy ranges from 10^{-5} to 10^{-2} . Another factor affecting the g_{CP-EL} of the device is the spin diffusion length (L_{spin}) of the CdSe/ZnS QDs. The calculation of L_{spin} is similar to the carrier diffusion length (L) which can be interpreted as following equations:[54]

$$L = \sqrt{D\tau} \dots \dots \dots (2)$$

$$D = \frac{\mu k_B T}{q} \dots \dots \dots (3)$$

where D is diffusion coefficient, τ is carrier lifetime, μ is the mobility, k_B is Boltzmann constant, T is temperature (300K) and q is the elementary charge. To calculate L_{spin} , τ should be replaced by τ_{spin} , which is spin relaxation time. Generally, the mobility of CdSe/ZnS QDs thin film is less than $0.1 \text{ cm}^2 (\text{V s})^{-1}$. [55] By substituting all the related parameters, the calculated spin diffusion length in the device

is only about $\sim 10^{-1}$ to $\sim 10^1$ nm, indicating the recombination center of the spin polarized carriers mainly distributes close to the interface between chiral perovskites and CdSe/ZnS QDs. To achieve a higher g_{CP-EL} , analysis and manipulation of recombination center in spin-QLEDs are necessary.

As we discussed above, the electrons should be over-injected while the hole injection and transport are insufficient in our spin-QLEDs. The recombination center should be at perovskite/QDs interface because of the spread of over-injected electrons through QD layers. Furthermore, to give an insight of the carrier recombination distribution, we conducted an electrical simulation with Setfos. The simulated recombination rate distribution under bias from 0 to 8 V is illustrated in Figure 6a, where the recombination rate at perovskite/QDs interface strongly outcompetes that at QDs/ZnO interface regardless of the applied bias. The recombination rates at both interfaces increase with larger bias, but the increment at perovskite/QDs interface is more significant. For example, the peak recombination rate at perovskite/QDs interface is enhanced by more than 7 orders from $2.2 \times 10^{14} \text{ cm}^3 \text{ s}^{-1}$ to $7.3 \times 10^{21} \text{ cm}^3 \text{ s}^{-1}$ when the bias is increased from 1 V to 8 V. In contrast, the peak recombination rate at QDs/ZnO interface is only increased from $9.0 \times 10^{11} \text{ cm}^3 \text{ s}^{-1}$ to $3.8 \times 10^{17} \text{ cm}^3 \text{ s}^{-1}$, corresponding to a smaller improvement of less than 6 orders. Interestingly, we found the increment of recombination rate is non-linear. As shown in Figure 6b, the simulated J-V-L curves exhibit inflection points at about 1.8 V, indicating a similar turn-on characteristic with that shown in the experiment results (see in Figures 4d and 4g). We should note that the demonstrated dominant recombination at perovskite/QDs interface is desirable to achieve strongly polarized EL because the spin polarized carriers/excitons could recombine as soon as possible within the spin diffusion length of only about $\sim 10^{-1}$ to $\sim 10^1$ nm. We also measured the *g-factor* as a function of bias, the results are shown in Figure S11. As we can see, the *g-factor* decreases slightly with the increasing of the applied voltage. The decrease of *g-factor* may attribute to the high voltage since metal halide perovskite is not stable at too high voltage.

Moreover, we found that the recombination center approaching the perovskite/QDs interface is also beneficial to improve the LEE. The dipole position dependent LEE is illustrated in Figure S12. We

should note that although the simulated recombination centre is at the perovskite/QDs interface, the actual centre should be at the CdSe core of the QDs layer nearby. In this case, a peak LEE of 8.3% can be obtained if the dipole is positioned in the CdSe core region of QDs near the perovskite. Otherwise, if the recombination centre is in the CdSe core of QDs layer close to ZnO electron transport layer, the LEE shall be decreased to 7.5%.

5. Conclusion

In summary, we have demonstrated a spin-QLED with 2D chiral perovskite as spin injection layer based on CISS effect at room temperature and zero applied magnetic field with a g_{CP-EL} of 1.6×10^{-2} . The introduction of chiral amine leads to the distortion of octahedra in perovskite, as a result, CISS effect is endowed to the 2D chiral perovskites. According to the electrical simulation, the recombination center locates close to the chiral perovskite/QDs interface, which is beneficial to achieve strongly polarized EL and relatively efficient light extraction. The introduced 2D chiral perovskite for CP emission is responsible for the deteriorated EL performance of the device since it significantly influences the carrier injection, light extraction and film quality of the QLED. When the injected spin-polarized carriers transport in the light emitting layer, spin relaxation will happen since the carrier spin lifetime is rather fast in CdSe/ZnS QDs. The upper limit of g_{CP-EL} depends on the carrier spin lifetime (τ_{spin}) of light emitting layer. The higher the carrier spin lifetime is, the longer the spin diffusion length will be. Thus, the spin-polarized carriers could recombine radiatively before spin relaxation. Therefore, improving the carrier spin lifetime in QDs (that is spin manipulation) will be the most critical issue to achieve high asymmetric factor spin-LEDs. QDs with strong spin-orbital coupling will be beneficial. Besides, chiral perovskites with excellent photoluminescence properties may also be an effective solution. Future works should focus on spin manipulation of the QDs and novel preparation strategies on chiral perovskites.

6. Method

Materials: R- α -methylbenzylamine (R-MBA, TCI), S- α -methylbenzylamine (S-MBA, TCI), lead iodide (PbI₂, TCI), hydriodic acid (HI, 55 wt.%-58 wt.% in aqueous solution, Aladdin Ltd, Shanghai, China), hypophosphorous acid (H₃PO₂, MACKLIN Company, Shanghai, China), *N,N*-dimethylformamide (DMF, anhydrous, 99.8%, Sigma-Aldrich), CdSe/ZnS QDs (Mesolight Company, Suzhou, China), PEDOT:PSS (P-OLED Technology Company, Shanghai, China), TFB (American Dye Source, Inc).

Growth of R/S-MBA₂PbI₄ crystals: 2.305 g (5 mmol) of PbI₂ was dissolved into the mixture of 10 mL HI and 5 mL H₂PO₃ at the temperature of 90 °C with continuous stirring in a three-neck flask. In another beaker, 1.289 mL (10 mmol) of R/S-MBA was added into 5 mL of HI by drops in an ice bath under magnetic stirring for 3 h. The as-prepared R/S-(MBA)I was then added into the flask. The temperature was increased to 130 °C and kept stirring for 2 h. Then the stirring was stopped and the temperature was cooling to 25 °C with the rate of 0.5 °C min⁻¹. The echinoid-like orange crystals were collected after washing by ethyl ester and drying in vacuum over night under temperature of 60 °C.

Materials characterization: Crystal structure was measured by Bruker D8 VENTURE single crystal X-ray diffraction. SEM images were collected by Gemini 300 scanning electron microscopy. AFM images were collected by MFP-3D Stand Alone atom force microscopy. CISS effect was measured by AFM with contact mode. Before the measurement, the magnetic tip (MESP-V2, Co/Cr coated) were magnetized by the N pole or S pole of a magnet for 1h. More than 50 I-V curves were collected on different areas of the thin films. If the measurements lasted longer than 1h, the tip should be magnetized again.

Device preparation: Patterned ITO glass was sonicated in deionized water, acetone, isopropanol for 20 min consecutively. The cleaned substrate was blown by the nitrogen and dried at 130 °C for 10 min, followed by UV-ozone treatment for 10 min. PEDOT:PSS (filtrated before use) was spin-coated on the substrate at 3000 rpm for 60 s, followed by 130 °C drying on hotplate for 30 min. Then the

substrate was transferred into glovebox filled with nitrogen. TFB (dissolved in chlorobenzene, 20 mg mL⁻¹), chiral perovskite (dissolved in DMF, 0.1 or 0.05 mol L⁻¹), CdSe/ZnS QDs (10 mg mL⁻¹) and ZnO (dissolved in ethanol, 20 mg mL⁻¹, fabricated according to the reported method)[56] were spin-coated in sequence. The spin-coating and following annealing conditions were 3000 rpm, 100 °C for 10 min; 3000 rpm, 100 °C for 10 min; 3000 rpm, 80 °C for 5 min; 3000 rpm, 120 °C for 10 min, respectively. 100 nm Ag was then evaporated under pressure of 5×10^{-4} pa. The as-prepared device was encapsulated before further characterization.

Device characterization: Cross-section images of the devices were measured by ORION NanoFab helium ion microscopy. The current density-voltage-luminance-external quantum efficiency (J-V-L-EQE) of the device were measured by a LED characterization system XPQY-EQE-350-1100 (Guangzhou Xi Pu Optoelectronics Technology Co., Ltd.) combined with an integrated sphere GPS-4P-SL (Labsphere), a spectrometer USB2000+ (Ocean Optics), and a photodetector S7031-1006 (Hamamatsu Photonics). The CP-EL was measured by JASCO CPL-300. All measurements are performed under room temperature and zero applied magnetic field.

Numerical simulation: The optical and electrical simulation are performed by Setfos 5.0. The material parameters including thickness, highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), work function (WF), electron- and hole-mobility (μ_e and μ_h), real- and imaginary-part of refractive index (n and k at 629 nm) of different layers used in the simulation are given in Table S4. The dipole orientation is set to isotropic because the CdSe QDs we used are symmetric in structure. For optical simulation, the transfer matrix approach is used to calculate passive optical properties of thin multilayer structures while the Mie or Rayleigh scattering from QDs is neglected. The dispersion of n and k for each material is considered. For example, the wavelength-dependent n and k of MBA_2PbI_4 perovskite can be found in Figure S5. For electrical simulation, the μ_e and μ_h of each material are set to constant while the Poole-Frenkel effect that describes the field-dependent mobility is neglected. The carrier injection at the ITO/PEDOT:PSS interface is the thermionic-type as the injection barrier is relatively large (~ 0.7 eV) while that at the ZnO NPs/Ag

interface is set to ohmic because of its small barrier (~ 0.2 eV). Charge drift-diffusion model is used to simulate the electrical characteristics of the spin-QLED.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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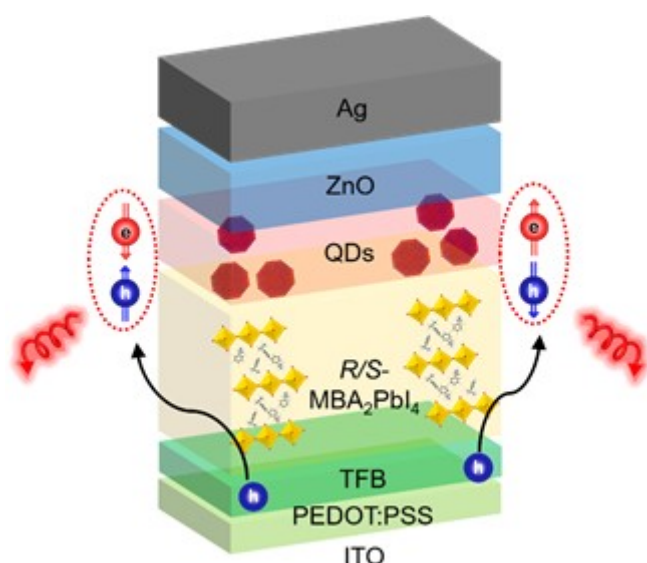


Figure 1. Schematic illustration of chiral-induced spin selective charge injection for CP-EL emission for spin-QLED.

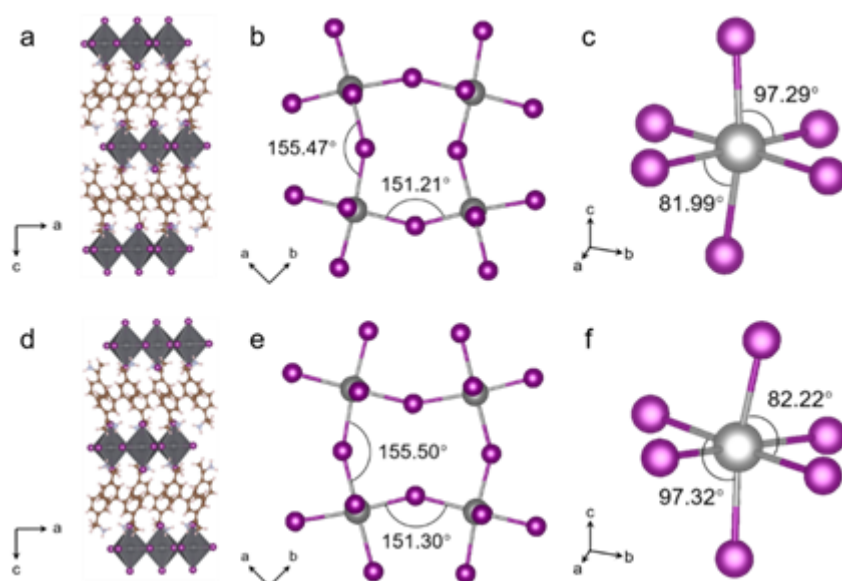


Figure 2. Crystal structure of *R*- (a) and *S*-MBA₂PbI₄ (d) measured by single crystal XRD and related inter- (b for *R*, e for *S*) and inner-octahedra (c for *R*, f for *S*) distortion.

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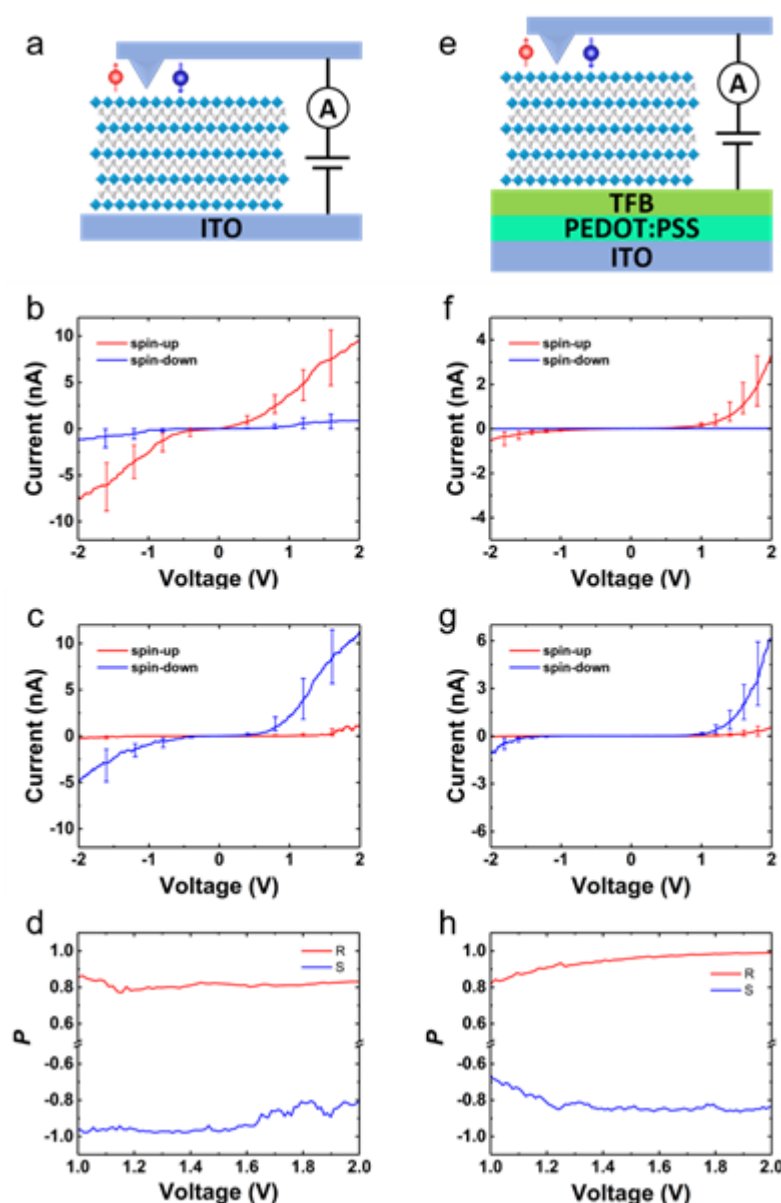


Figure 3. Schematic illustration of mCP-AFM of chiral perovskites on ITO (a) and hole transport layer (e). The tip is coated by Co/Cr, and before the measurement, the tip is pre-magnetized by N or S pole of a magnet. I-V curves are measured, (b) for ITO/R-MBA₂PbI₄, (c) for ITO/S-MBA₂PbI₄, (f) for ITO/PEDOT:PSS/TFB/R-MBA₂PbI₄, (g) for ITO/PEDOT:PSS/TFB/S-MBA₂PbI₄ and spin polarization

calculated by the currents, (d) for ITO/(R/S-MBA₂PbI₄) and (f) for ITO/PEDOT:PSS/TFB/(R/S-MBA₂PbI₄).

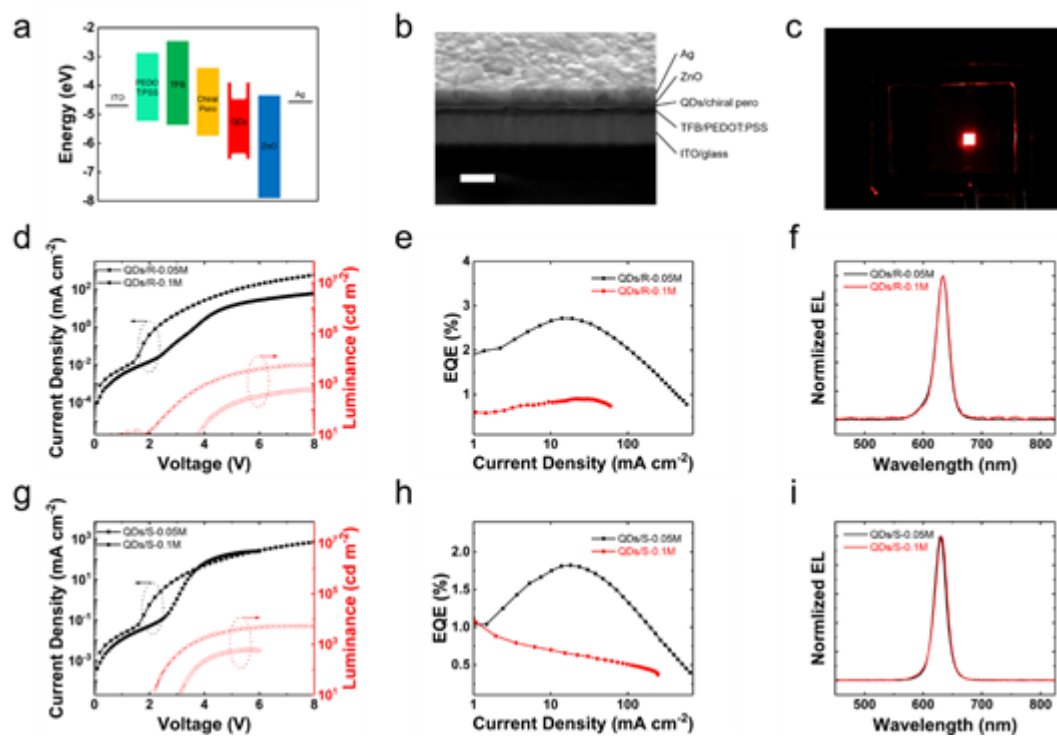


Figure 4. Energy band diagram of spin-QLED (a), cross-section SEM image (b, the scale bar is 200 nm), photograph of a R-device (c), J-V-L curves of R/S device (d, g); EQE as a function of current density (e, h), normalized EL as a function of wavelength (f, i).

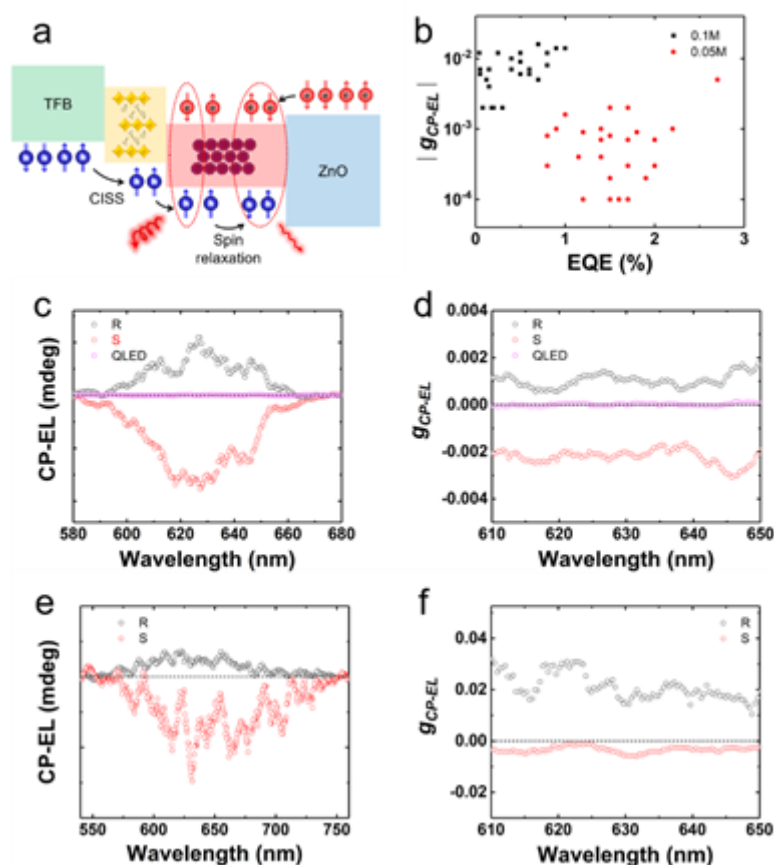


Figure 5. The schematic illustration of CP-EL emission in the spin-QLED (a), statistics of $|g_{CP-EL}|$ and EQE of spin-QLEDs (b), CP-EL degrees as a function of wavelength and related g_{CP-EL} , (c) and (d) for the devices prepared with 0.05 M of chiral perovskite precursors, (e) and (f) for the devices prepared with 0.1 M of chiral perovskite precursors. The inset in (d) is the S sample with magnified scale of g_{CP-EL} axis, from 0 to -0.0004. The magenta plots in (c) and (d) are CP-EL and g_{CP-EL} of pure QLED device without chiral perovskite.

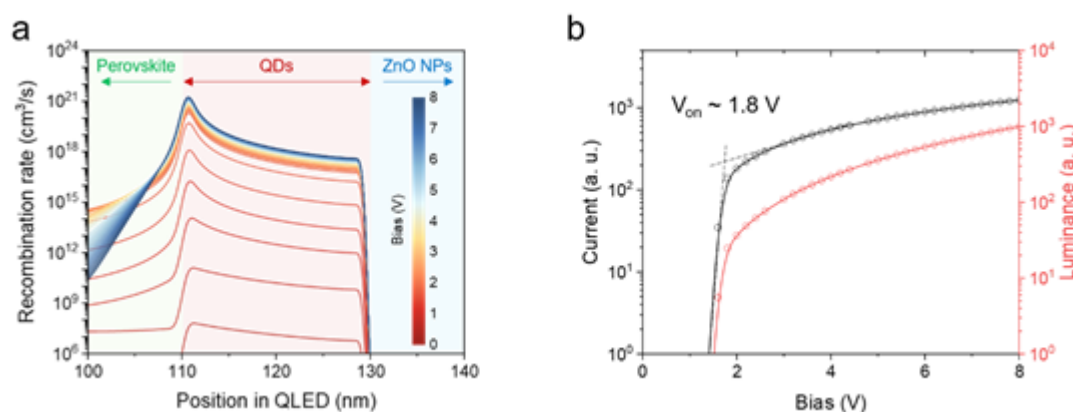


Figure 6. Simulation of carrier recombination rate distribution (a) and J-V-L curve (b) of the spin-QLED device.

Table 1. Summary of device EL parameters with R or S chiral perovskite as CISS layer.

	Turn-on voltage (V)	Luminance _{max} (cd m ⁻²)	EQE _{max} (%)
R-0.05	1.9	5638	2.7
S-0.05	2.1	3122	1.8
R-0.1	3.8	610	0.9
S-0.1	3.2	600	1.0

Spin quantum dot light emitting diode (spin-QLED) emitting circularly polarized light is achieved by introducing chiral perovskite with chiral induced spin selectivity (CISS) effect. The spin polarized holes generated by the CISS effect of chiral perovskite recombine with correspondent electrons according to the optical selective rules and directly emit left- or right-handed circularly polarized light.

