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Spin control in reduced-dimensional chiral perovskites

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Hybrid organic-inorganic perovskites exhibit strong spin-orbit coupling¹, spin-dependent optical selection rules^{2,3}, and large Rashba splitting⁴⁻⁸. These characteristics make them promising candidates for spintronic devices⁹ with photonic interfaces. Here we report that spin polarization in perovskites can be controlled through chemical design as well as magnetic field. We obtain both spin-polarized photon absorption and spin-polarized photoluminescence in reduced-dimensional chiral perovskites through combined strategies of chirality transfer and energy funneling. A 3% spin-polarized photoluminescence is observed even in the absence of an applied external magnetic field owing to the different

emission rates of σ^+ and σ^- polarized photoluminescence. Three-dimensional perovskites achieve a comparable degree of photoluminescence polarization only under an external magnetic field of 5 T. Our findings pave the way for chiral perovskites as powerful spintronic materials.

Spintronics⁹ is an enabler of quantum information technology especially quantum computing^{10,11}. Whereas conventional electronics relies on the generation and transfer of charge, spintronics makes use of the electron's spin. Towards spintronic devices, it is necessary to control the number of electrons in the well-defined spin state, *i.e.*, to establish spin polarization control. Candidate materials should contain heavy atoms that exhibit a large spin-orbit interaction. Coupled with a non-centrosymmetric crystal structure, this will impart a magnetic moment to electrons moving in the electric field¹². This magnetic moment can also interact with spin-polarized (SP) light, changing the spin direction and thus building up a net spin in the material, leading to a spin-polarized current. The injection of spin-polarized current will also lead to spin-polarized photoluminescence (SPPL). These phenomena have been observed in gallium arsenide (GaAs), a benchmark material for spintronics^{13,14}. The development of low-temperature-fabricated, solution-processed spintronic materials will facilitate the deployment of these materials on a wide range of substrates and avoid the need of epitaxial growth.

Hybrid organic-inorganic perovskites (HOIP) have demonstrated attractive properties, including long-range balanced charge carrier diffusion lengths¹⁵, high dielectric constants¹⁶, low trap densities¹⁷, and tunable absorption and emission wavelengths¹⁸. These superior optical and electrical properties have prompted intensive research interest in HOIPs for high-performance

optoelectronics including in photovoltaics¹⁹⁻²¹, light-emitting diodes^{22,23}, lasers^{18,24}, and photodetectors^{25,26}.

The investigation of HOIPs in spintronics was launched only recently^{2,3,27-29}. For instance, perovskites have been found to exhibit strong spin-orbit coupling¹, spin-dependent optical selection rules^{2,3}, and large Rashba splitting⁴⁻⁸, and to exhibit significant magneto-photocurrent, magneto-electroluminescence, and magneto-photoluminescence responses^{1,30,31}. In particular, an unexpectedly long spin lifetime exceeding 1 ns, and ultra-long spin-diffusion lengths of ~85 nm, have recently been observed in HOIPs²⁷. These properties indicate HOIPs are promising materials towards the next generation spintronic devices.

The flexible crystal structure and ionic composition of HOIP suggest strategies to define materials properties at the time of design and synthesis. Specifically, HOIPs can potentially incorporate chiral organic ligands³². In 2006, Billing *et al.* reported the synthesis of chiral two-dimensional (2D) perovskite single crystals that incorporated chiral ligands³² and in 2017, thin films of chiral 2D perovskites were prepared and shown to absorb spin-polarized light³³. However, 2D perovskite films have so far exhibited poor photoluminescence quantum yields (PLQYs) owing to significant non-radiative recombination³⁴, and this significantly impedes their potential in optoelectronic applications.

Fortunately, quasi-2D (a.k.a. *Ruddlesden-Popper* structural) perovskites have recently shown high PLQYs for efficient photo- and electrically-induced light emission^{22,23}. Excitonic funneling assembled within quasi-2D perovskites is efficient for exciton transfer for radiative recombination, yet a question remains as to whether *chirality transfer* can be expected. We focus here on $\langle n \rangle = 2$ reduced-dimensional chiral perovskites (RDCP, where $\langle n \rangle$ is the average number

of inorganic layers separated by the bulky organic ligands) with the goal of maintaining a large fraction of the chiral organic component in the material and thus increasing the likelihood of chirality transfer.

In this study, for the first time, we have demonstrated that RDCP exhibit both circular dichroism and spin-polarized photoluminescence without the use of an external magnetic field.

We began by synthesizing pure chiral 2D perovskites ($\langle n \rangle = 1$) and reduced-dimensional chiral perovskites ($\langle n \rangle = 2$) by incorporating chiral organic ligands. In this case, *R*- and *S*-methylbenzylammonium bromide (*R*-MBABr and *S*-MBABr, chemical structures shown in Fig. 1) are employed as the chiral ligands, while racemic methylbenzylammonium bromide (*rac*-MBABr) is used to prepare achiral perovskites as controls. The introduction of these ligands forces the otherwise-3D perovskite into mixed reduced-dimensional layered structures^{22,23}. A distribution of $\langle n \rangle$ values present in the RDCP samples is expected to produce efficient energy funneling to the lowest-bandgap species^{22,23}.

Since $\langle n \rangle = 1$ perovskite contains the largest mole fraction of chiral ligands (as shown in Supplementary Fig. 1), it might be expected that chiral 2D perovskites ($\langle n \rangle = 1$) would exhibit the strongest chirality (as shown in Supplementary Fig. 2). However, no PL was observed for the pure chiral 2D (MBA)₂PbBr₄ ($\langle n \rangle = 1$) sample, in line with the very poor photoluminescence properties representative of many pure 2D perovskites³⁴. We focus here on $\langle n \rangle = 2$ reduced-dimensional chiral perovskites (RDCP, where $\langle n \rangle$ is the average number of inorganic layers separated by the bulky organic ligands) with the goal of maintaining a large mole fraction of the chiral organic component in the material and thus increasing the likelihood of chirality transfer.

We firstly applied circular dichroism (CD) spectroscopy to confirm the chirality of *R*- and *S*-MBABr bromide salts, the ellipticity (θ , unit: mdeg) is calculated based on Equation 1,

$$\theta \text{ (mdeg)} = \Delta A \left(\frac{\ln 10}{4} \right) \left(\frac{180000}{\pi} \right) \quad \text{Equation 1}$$

where ΔA is the absorption difference of the left-handed and right-handed spin-polarized light^{35,36}. As shown in Fig. 1b, opposite CD absorption features are observed in the two chiral ligands (the wider range linear absorption and CD spectra are shown in Supplementary Fig. 3). We conclude that the chiral ligands lead to the expected preferential absorption of the opposite handedness of spin-polarized light. The racemic blend of *R*- and *S*-MBABr ligands exhibits no absorption difference between left-handed and right-handed spin-polarized light. The CD signals for the chiral ligands do not extend past 280 nm; however, when they are incorporated into the RDCP, the resulting perovskites exhibit strongly spin-polarized absorption (induced circular dichroism) in the visible region (Fig. 1c). These observations indicate that the chirality of the organic ligands is successfully transferred to the perovskite quantum wells of which they are constituent. Here again the *rac*-RDCP sample exhibits no CD signal. For *R*- and *S*-RDCPs, the CD signals exhibit dispersive features centered around the absorption energy (Supplementary Fig. 4). This is known as the “Cotton effect”, due to coupling between degenerate transition dipoles, and has been observed for many types of chiral materials³⁵⁻³⁸. Conversely, no appreciable spin-polarized absorption peaks were observed for the higher dimensional species ($\langle n \rangle \geq 2$), revealing that the 2D component is the main contributor to the spin-polarized absorption.

We further examined the crystallinity and lattice orientations of perovskite domains using 2D grazing-incidence wide-angle X-ray scattering (2D-GIWAXS). As shown in Fig. 2a-2c, the GIWAXS results confirm that all three samples (*i.e.*, *rac*-RDCP, *R*-RDCP and *S*-RDCP) contain

domains with both $\langle n \rangle = 1$ and larger $\langle n \rangle$ values. The samples exhibit similar scattering patterns, suggesting that they share similar crystal types and components. The $(002)_{n=1}$ scattering of the $\langle n \rangle = 1$ perovskite domain (*i.e.*, $(\text{MBA})_2\text{PbBr}_4$) can be identified at $q = 0.42 \text{ \AA}^{-1}$, corresponding to the $\langle n \rangle = 1$ interlayer distance of $\sim 15 \text{ \AA}$ separated by the chiral ligands (Supplementary Fig. 5)³². In addition, the peak at $q = 0.63 \text{ \AA}^{-1}$ can be identified as the $(004)_{n=2}$ diffraction from the ($\langle n \rangle = 2$) quasi-2D perovskite layered domains with larger $\langle n \rangle$ numbers³⁹.

The presence of 2D and quasi-2D components in the RDCP films is further verified by the linear absorption spectra (Fig. 2d). The absorption feature at $\sim 380 \text{ nm}$ corresponds to the exciton peak of the 2D perovskite component (Supplementary Fig. 6), while the additional absorption extending to $\sim 525 \text{ nm}$ (absent in the pure 2D perovskite sample) corresponds to the higher $\langle n \rangle$ components ($\langle n \rangle \geq 2$).

These results confirm that all three samples (*i.e.*, *rac*-RDCP, *R*-RDCP and *S*-RDCP) contain domains with both $\langle n \rangle = 1$ and larger $\langle n \rangle$ components. We sought next to study whether energy funneling occurred among domains. We used ultrafast transient absorption spectroscopy (TAS), employing a 350-nm pump pulse ($10 \mu\text{J}/\text{cm}^2$, 1 kHz) to excite principally the $\langle n \rangle = 1$ component (Supplementary Fig. 7). From the spectra following a 1 ps delay (Fig. 2e), we observe a strong bleach at $\sim 511 \text{ nm}$, indicating that the energy has funneled down to the component having the lowest bandgap. Interestingly, the photoluminescence excitation (PLE) spectrum (Fig. 2f) reveals a dip at $\sim 380 \text{ nm}$, which belongs to the $\langle n \rangle = 1$ perovskite domains. This suggests that energy funneling from higher $\langle n \rangle$ components is more efficient than from the 2D perovskite component (*i.e.*, $\langle n \rangle = 1$). This may be related to the characteristically poor PL of 2D perovskites that arises from their fast nonradiative rates³⁴. The PLQY of the *rac*-RDCP was $\sim 36\%$ when photoexcited at 375 nm, while a higher PLQY of 76% was achieved when a 400-nm

incident excitation pump was applied. The same trend was also seen in *R*-RDCP and *S*-RDCP, but the PLQY reaches an impressive 90% under 400 nm excitation.

The spin-polarized photoluminescence of chiral and achiral RDCP was then measured using a fibre-based confocal microscope (Supplementary Fig. 8), and the details of the optical setup are shown in the Method section⁴⁰. The measurements were performed at a temperature of 2 K with an applied magnetic field that ranged from -7 T to 7 T perpendicular to the sample plane (Faraday configuration). As shown in Figure 3a, the degree of polarization (*DP*) scales linearly with the magnetic field for the *rac*-RDCP sample, and exhibits zero *DP* at 0 T while the degree of polarization for both *R*- and *S*-RDCP is non-zero at 0 T (Fig. 3b and 3c). Compared with prior work on 3D perovskites¹, the *rac*-RDCPs exhibit a similar degree of polarization controlled via magnetic field (Fig. 3a).

In order to explain the residual *DP* at $B = 0$ T observed from chiral perovskites, we refer to the energy level model illustrated in Figs. 4a and 4b. The model consists of the spin-up and spin-down electron minimum energy at the conduction band and its maximum energy at the valence band. Only the two spin-allowed transitions (*e.g.*, bright exciton transitions) are shown. In the case of achiral perovskite, these two transitions have the same spin-polarized emission rates; but this is not the case for chiral perovskites. Since the emission for RDCP only originates from one excited state (*i.g.*, the higher $\langle n \rangle$) to the ground state, the system is effectively a two-level system. For this case, based on Einstein coefficients⁴¹, the different absorption rate of the spin-polarized light (Figure 1c) for *R*-RDCP (or *S*-RDCP) implies a different spin-polarized emission rate (*e.g.*, $\gamma_{\text{exc}1} \neq \gamma_{\text{exc}2}$, as shown in Fig. 4). Thus, the *R*-RDCP (or *S*-RDCP) selectively emits σ^+ (or σ^-) polarized PL without the need of an external magnetic field.

The linear slope in Fig. 3 can be explained through the Zeeman effect. At non-zero magnetic field, the Zeeman effect breaks time-reversal symmetry in the system and gives rise to energy splitting of the spin-subbands. As shown in Fig. 4c, when a positive magnetic field is applied to *R*-RDCP, the spin-degeneracy is lifted by the Zeeman splitting. At the valence band, the spin-up level becomes shallower than the spin-down level, while it is reversed at the conduction band. Therefore, the spin-flipping from spin-down to spin-up becomes thermodynamically favorable. The synergistic effect of Zeeman splitting under a positive magnetic field and the asymmetric emission efficiency further enhances the degree of PL polarization with increasing positive magnetic field (Fig. 3b, region I, $B > 0$ T). The value is reversed once a negative magnetic field is applied. As shown in Figs. 4d and 4e, the energy splitting between spin-up and the spin-down levels becomes larger with increasing negative magnetic field. The direction of spin-flipping is reversed compared with that under a positive magnetic field, and the flipping from spin-up to spin-down energy level becomes energetically favorable. Since the influence of negative magnetic field and chirality transfer is opposite, the *DP* decreases with increasing negative magnetic field (Fig. 3b, region II and III, where $B < 0$ T). When B is applied to -2.8 T, the influence of chirality and Zeeman splitting cancels and zero *DP* is observed (Fig. 3b and Fig. 4d). Followed by the further increase in the strength of the negative magnetic field, Zeeman splitting effect gradually dominates, and the PL polarization changes correspondingly from σ^+ to σ^- with the emergence of a negative *DP* (Fig. 3b, region III, where $B < -2.8$ T and Fig. 4e). As for *S*-RDCP, the total process is the opposite. However, for *rac*-RDCP, there only exists the Zeeman-splitting (as observed in 3D perovskites) owing to their centrosymmetric nature¹.

The magnetic field dependence results for these three samples (Fig. 3) are fit following

Equation 2 (refer Supplementary Note 3 for the detailed derivation):

$$DP = \frac{g_{\text{eff}}\mu_B B}{k_B T} + DP_0 \quad (\text{Equation 2})$$

where g_{eff} is the effective g -factor of the spin-1/2 electron and hole in the spin-pair species (Supplementary Equation 9), μ_B is the Bohr magneton, B is the applied magnetic field, DP_0 is the degree of polarization introduced by the chirality in the absence of the magnetic field (Supplementary Equation 10), k_B is the Boltzmann constant and T is temperature. The g_{eff} of the R -, S - and rac -RDCP is 0.032, 0.031, and 0.027, respectively. The degree of polarization is $\sim 3\%$ for both R - and S -RDCP at 0 T, comparable to the previously reported experimental value of $\sim 3\%$ for 3D perovskites at 5 T¹.

In summary, we report the control of spin-polarized absorption and photoluminescence in perovskites through material design. By combining chirality transfer and energy funneling, we achieved 3% spin-polarized PL in reduced-dimensional chiral perovskite without the application of an external magnetic field. Compared with 3D perovskite, the same degree of PL polarization is obtained only under an external magnetic field of 5 T. Reduced-dimensional chiral perovskites, which now combine the excellent optoelectronic properties and the function of chirality, would be of great interest to the field of spintronics.

Methods

Thin-film fabrication

Pre-designed amount of PbBr_2 (183.5 mg, 0.5 mmol), $\text{CH}_3\text{NH}_3\text{Br}$ (5.6 mg, 0.05 mmol), CsBr (42.5 mg, 0.2 mmol) and MBABr (101 mg, 0.5 mmol) were put into a small vial with 0.5 mL dimethyl sulfoxide. The solution was stirred at room temperature in a nitrogen-filled glovebox for 4 hours, and then filtered through a polytetrafluoroethylene (PTFE) syringe filter (0.2 μm). The resulting solution was spin-coated onto the pre-cleaned substrate via a two-step process at 1000 r.p.m. (accelerate speed: 200 r.p.m.) and 5,000 r.p.m. (accelerate speed: 500 r.p.m.) for 10 sec and 60 sec, respectively. During the second spin step, 200 μL chlorobenzene was poured onto the substrate 20 sec after the spinning starts. The resulting films were then annealed at 90 $^\circ\text{C}$ for 10 min to improve crystallization. The thickness of the obtained perovskite film is \sim 600 nm.

Absorption, PL and PLE spectra and PLQY measurements

Optical absorption measurements were carried out in a Lambda 950 UV/Vis spectrophotometer. A Horiba Fluorolog system was used for photoluminescence (PL) measurements. A monochromatized Xe lamp was used as the excitation source for steady-state PL collection. The Fluorolog system was coupled to a Quanta-Phi integrating sphere with optical fibre bundles for absolute PL quantum yield (PLQY) measurements. Excitation and emission spectra were measured for three cases: the sample directly illuminated by the beam path in the integrating sphere, the sample indirectly illuminated within the integrating sphere, and the empty sphere. The Fluorolog was set to an excitation wavelength of 400 nm and 2-nm bandpass for both the excitation and emission slits. The detector and integrating sphere were calibrated with a Newport white light source for spectral variance. PL excitation (PLE) spectra were measured by monitoring the emission intensity as the excitation wavelength was varied. PLE spectra were normalized to the lamp intensity spectrum.

Circular dichroism spectra

The circular dichroism (CD) spectra were recorded on a JASCO J-810 circular dichroism spectrometer with 'Standard' sensitivity (100 mdeg) at 50 nm min^{-1} scan speed with 0.5 nm

resolution and response time of 1 s. All the measurements were performed at 20 °C.

Transient absorption measurements

Femtosecond laser pulses were created with a regeneratively amplified Yb:KGW laser at a 1 kHz repetition rate (Light Conversion, Pharos). A portion of the 1030 nm fundamental was passed through an optical parametric amplifier (Light Conversion, Orpheus) with the second harmonic of the signal pulse selected for 350 nm light. Both the pump and residual fundamental were sent into an optical bench (Ultrafast, Helios), where the fundamental was focused into a calcium fluoride crystal, generating a white light continuum. The time delay (resolution ~350 fs) was set by delaying the probe pulse optically, with time steps increasing exponentially. A chopper was employed to block every other pump pulse, and then the probe pulse was measured by a charge-coupled device (CCD) after being dispersed by a grating spectrograph (Ultrafast, Helios). Samples were spin-coated on a glass substrate, and they were translated at 1 mm s⁻¹ during the measurement. The pump fluences were held at 10 μJ cm⁻².

Spin-polarized photoluminescence measurement under magnetic field

We use a homemade fibre-based confocal microscope for polarization-resolved magneto-PL spectroscopy. The wavelength of the excitation is 473 nm. We install polarizers and quarter wave plates on the excitation and detection arm of the confocal microscope for polarization-resolved PL detection. The PL emission is directed by a multi-mode optical fibre into a spectrometer (Andor Technology). The samples are loaded into a magneto-cryostat (Cryomagnetics close-cycle cryostat) cooled down to 2 K. The magnetic field is applied perpendicular to the sample plane (Faraday configuration) ranging from -7 T to +7 T, and the SPPL was collected along the direction of magnetic field (Supplementary Fig. 8). The σ^+ and σ^- polarized excitations are employed (Supplementary Fig. 9), and the averaged degree of polarization under σ^+ and σ^- polarized excitation is shown in Fig. 3.

To extract the polarization of the PL emission, we rotate the quarter wave plate on the detection arm by 360 degree with a step of 10 degree. The PL intensity as a function of the rotation angle can be written as

$$I_{PL} = S_3 \sin 2\varphi + S_0 \quad \text{Equation 3}$$

Where S_3 and S_0 are the Stokes parameters corresponding to the circular polarization and the total intensity, respectively. φ is the angle of the quarter wave plate. The degree of polarization is therefore given by

$$DP = \frac{S_3}{S_0} = \frac{I_{\sigma^+} - I_{\sigma^-}}{I_{\sigma^+} + I_{\sigma^-}} \quad \text{Equation 4}$$

Where I_{σ^+} and I_{σ^-} are the areas of the left-handed and right-handed spin-polarized emission under photoexcitation, respectively.

Grazing-incidence wide-angle X-ray scattering (GIWAXS) measurement

All the GIWAXS measurements were conducted at the Hard X-ray MicroAnalysis (HXMA) beamline of the Canadian Light Source (CLS). An energy of 17.998 keV ($\lambda = 0.6888 \text{ \AA}$) was selected using a Si (111) monochromator. Incident angle was kept at 0.5° with respect to the sample plane. Patterns were collected on a SX165 CCD camera (Rayonix) placed at a distance of 175 mm from the sample. A lead beam stop was used to block the direct beam. Images were calibrated using LaB6 and processed via the Nika software package and the GIXSGUI MATLAB plugin.

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Author contributions

G.L., S.H. and E.H.S. conceived the idea and designed the experiments. G.L., R.S., Z.Y., W.G., Q.X. and E.H.S. wrote the manuscript. G.L. fabricated thin-films with help from L.Q. and J.X.; G.L. prepared chiral ammonium salts and performed measurements (CD, PL, PLE, PLQY, TAS and XRD) with help from R.S., G.W., M.W., X.G., Q.L. and D.S.; R.S. and G.X. analyzed the

TAS data, Z.Y. and R.Q. performed the GIWAXS measurement. C.J., W.G., X.L.W., Q.X., G.W. and H.Y. performed the SSPL measurement. C.J., A.R., W.G., M.W., G.L, X.W., O.V. and M.A. performed the SSPL data analyzing and discussion. A.R. built the mathematic model for magnetic field dependent SPPL for RDCP. All authors read and commented on the manuscript.

Competing financial interests

The authors declare no competing financial interests.

Additional information

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Figure 1 | Chirality transfer and energy funneling for efficient photoluminescence. **a**, Schematic illustration of the structures of reduced-dimensional chiral perovskites with different inorganic layers ($\langle n \rangle$). The chirality decreases with increasing the $\langle n \rangle$ layers, while strong photoluminescence can be obtained through efficient energy funneling to the higher $\langle n \rangle$ component. **b**, The CD spectra of the chiral ligands and its racemic mixture in DMF (0.5 mol/L), inset: the chemical structures of the chiral ligands (*R*-MBABr and *S*-MBABr) employed in this work. **c**, Thin film CD spectra of the reduced-dimensional chiral perovskites ($\langle n \rangle = 2$) prepared from the above chiral ligands.

Figure 2 | Structural and photophysical studies of reduced-dimensional chiral perovskites. The 2D-GIWAXS results of the RDCP ($\langle n \rangle = 2$): the *rac*-RDCP (**a**), *R*-RDCP (**b**) and *S*-RDCP (**c**). The linear absorption and photoluminescence spectra (**d**), and transient absorption spectra (**e**) of *rac*-RDCP, *R*-RDCP and *S*-RDCP. **f**, The photoluminescence excitation spectra and PLQY of *rac*-RDCP under excitation wavelength of 375 and 400 nm. Inset: a diagram is employed to show the energy funneling from $\langle n \rangle = 2$ component to the higher components is more efficient than that from the 2D perovskite component ($\langle n \rangle = 1$).

Figure 3 | Polarized PL studies of reduced-dimensional chiral perovskites at 2 K. The degree of PL polarization for *rac*-RDCP (**a**), *R*-RDCP (**b**) and *S*-RDCP (**c**) with magnetic field varied from -7 T to 7 T. The blue line is the fitting result based on Equation 2. The blue dashed line in (**a**) is the *DP* of 3D perovskite measured by Vardeny *et al.*¹ The graph of *R*-RDCP is divided into three regions: I, II and III. At $B = 0$ (*i.e.*, no external magnetic field), there exists a degree of polarization (DP_0) for *R*-RDCP. When a positive magnetic field is applied, the *DP*

increases with the magnetic field (region I). In region II, as a negative magnetic field is applied, the value of DP decreases accordingly until $DP = 0$. As a stronger negative magnetic field is applied, the DP changes sign from positive to negative (region III). Converse phenomena are observed for S -RDCP.

Figure 4 | Mechanism of SPPL in RDCPs and the influence of magnetic field on the energy levels and DP of R -RDCP. The spin-up and spin-down energy levels for R -RDCP (**a**) and S -RDCP (**b**) without magnetic field, and their relationship with the polarization of PL. **c**, When a positive magnetic field is applied, the synergistic effect of Zeeman splitting and the asymmetric emission efficiency of R -RDCP further enhances the PL polarization, and thus more σ^+ polarized PL is obtained (region I in Fig. 3b). (**d-e**) The DP decreases when applying a negative magnetic field (Fig. 3b, region II & III, where $B < 0$ T) since the influence of the negative magnetic field and the chirality are opposite. **d**, When B is applied to -2.8 T, the influence of the chirality transfer and Zeeman splitting cancels, and zero DP is observed (Fig. 3b). **e**, With further increase in the negative magnetic field, the influence of the Zeeman splitting becomes dominant. Therefore, the PL polarization changes from σ^+ to σ^- , and negative DP is observed (Fig. 3b, region III, where $B < -2.8$ T). The yellow arrow indicates σ^+ polarized emission while the black arrow stands for the σ^- polarized emission, and the intensity is demonstrated by the width of the arrow. The emission rates of σ^+ (γ_{exc1}) and σ^- (γ_{exc2}) polarized PL for RDCP are also shown in (**a**) and (**b**) for comparison.