Supplementary Information

Magnetic-field manipulation of circularly polarized photoluminescence in chiral perovskites

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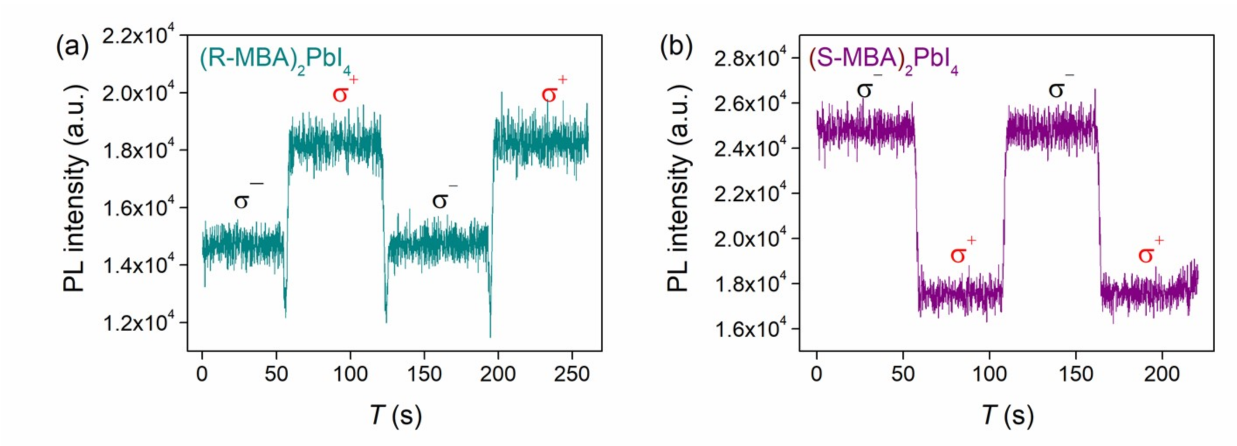
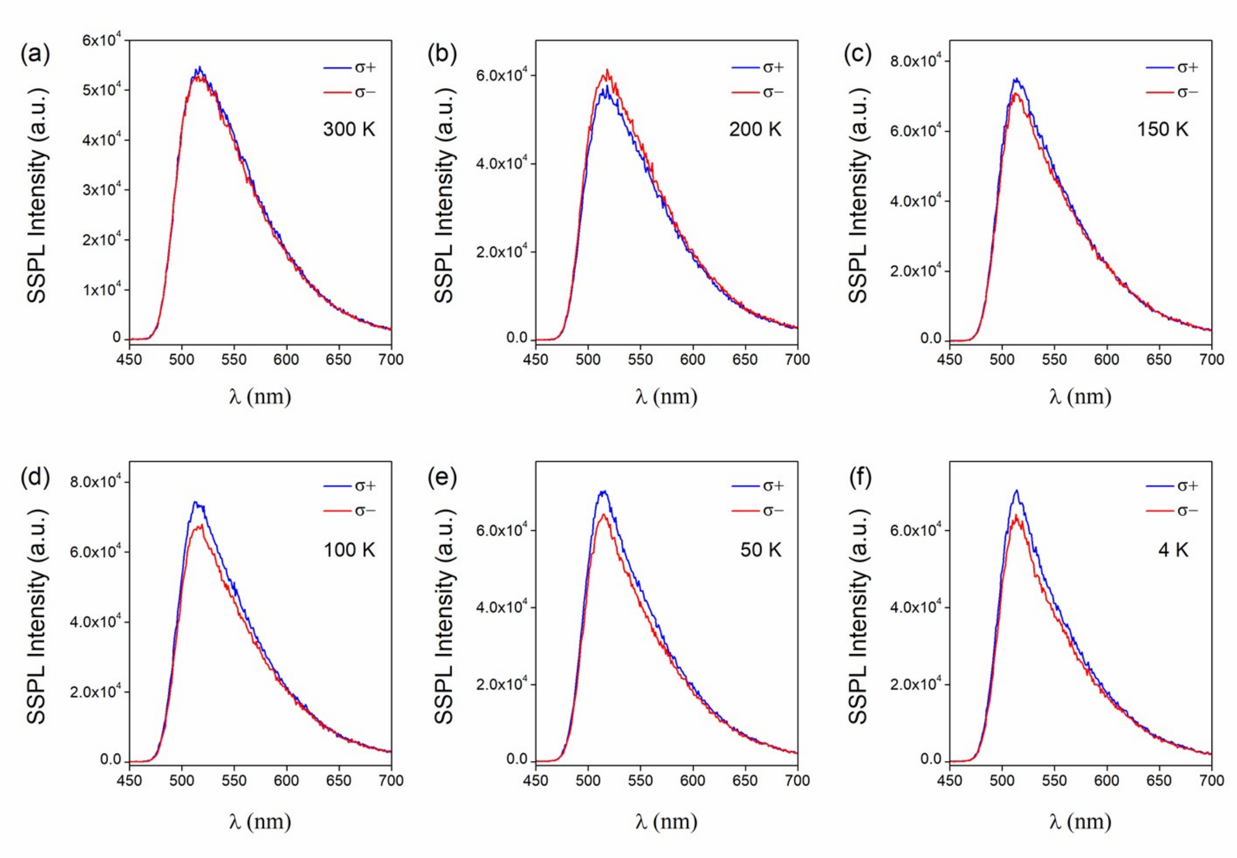
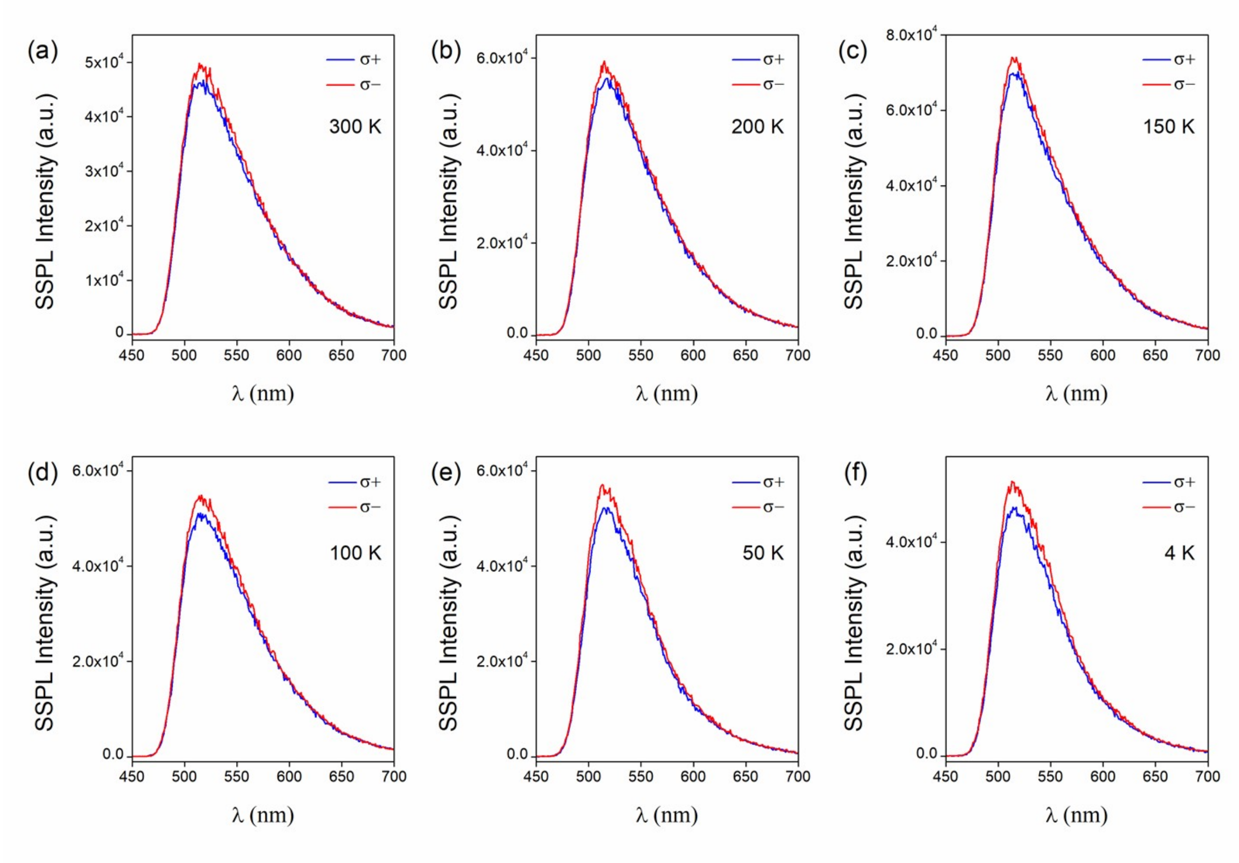
Part I – Experimental Results



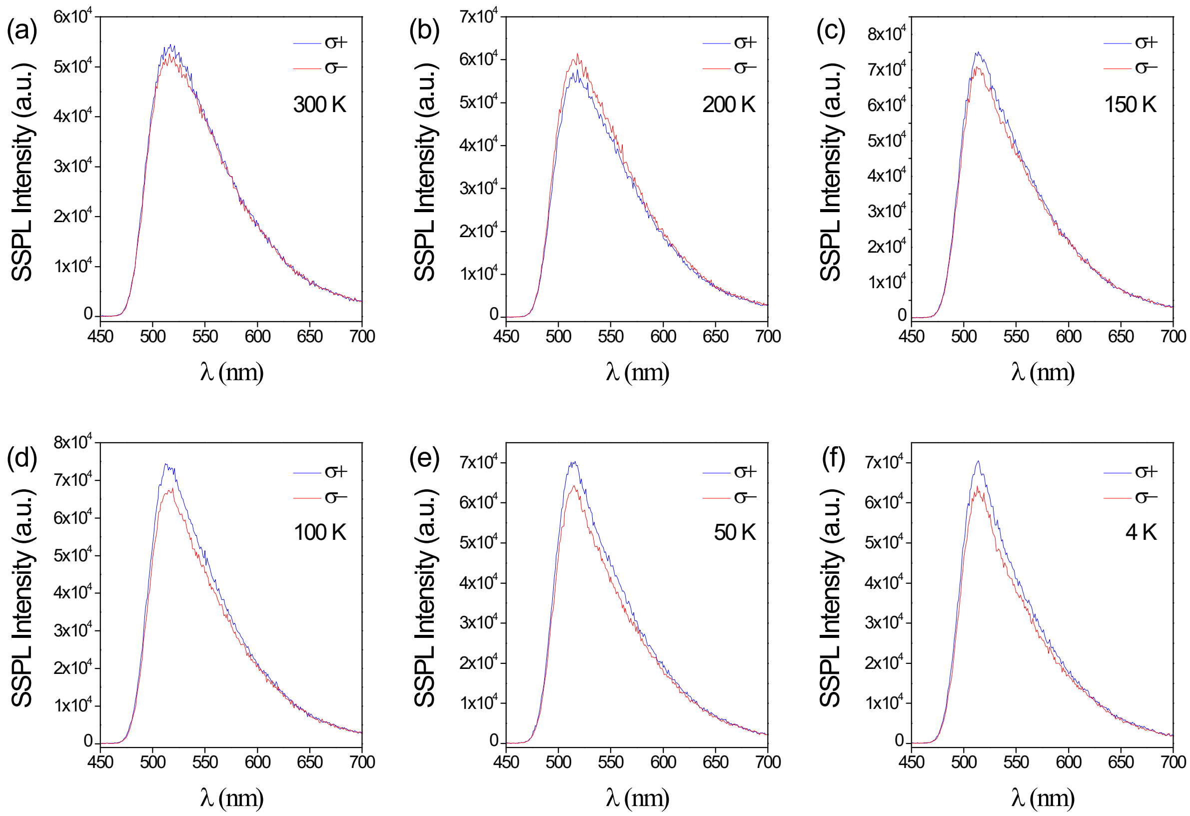
S-Fig. 1 Variation of PL intensity due to the left (σ^+) and right (σ^-) circularly polarized photoexcitation for (a) $(R\text{-}MBA)_2PbI_4$ and (b) $(S\text{-}MBA)_2PbI_4$ respectively. The photoexcitation wavelength is 405 nm and the power is set to be 90 mW.



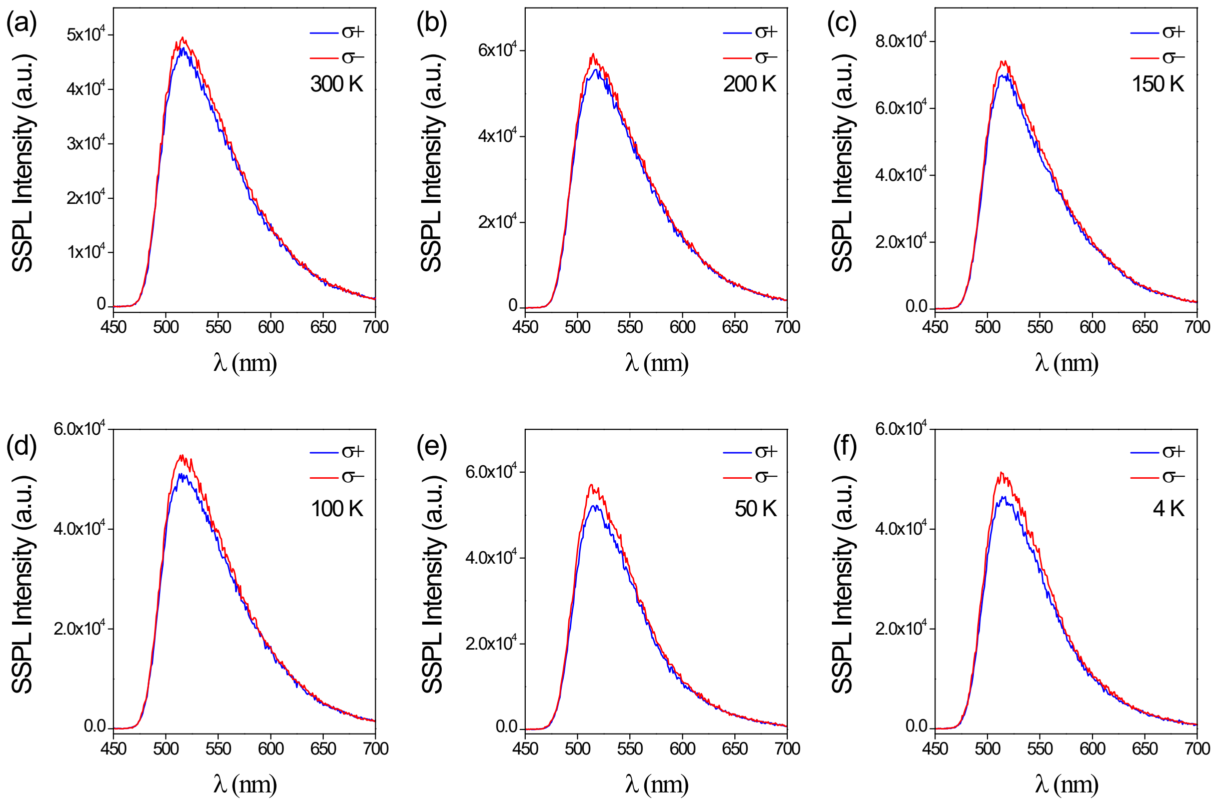
S-Fig. 2 (a)-(f) Experimental results of temperature dependent CPL for the solution processed (R-MBA)$_2$PbI$_4$ thin film.



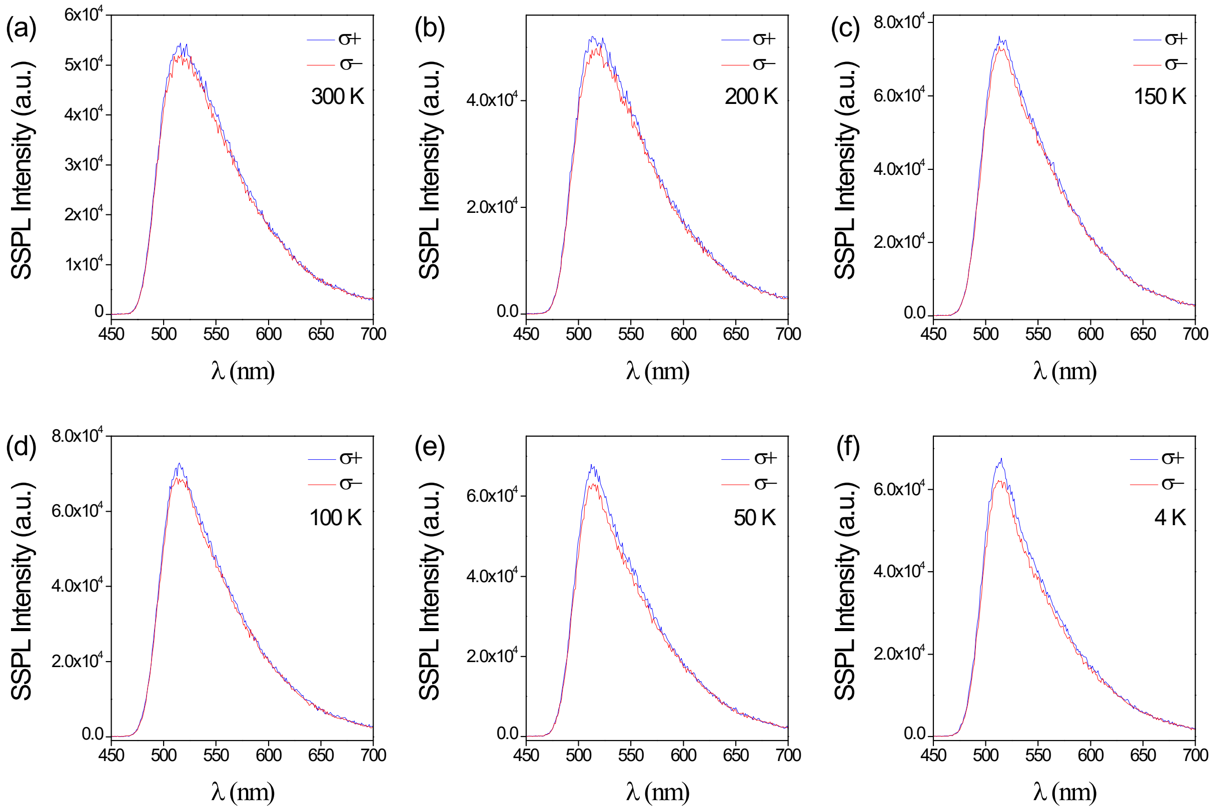
S-Fig. 3 (a)-(f) Experimental results of the temperature dependent CPL for the solution processed (S-MBA)$_2$PbI$_4$ thin film.



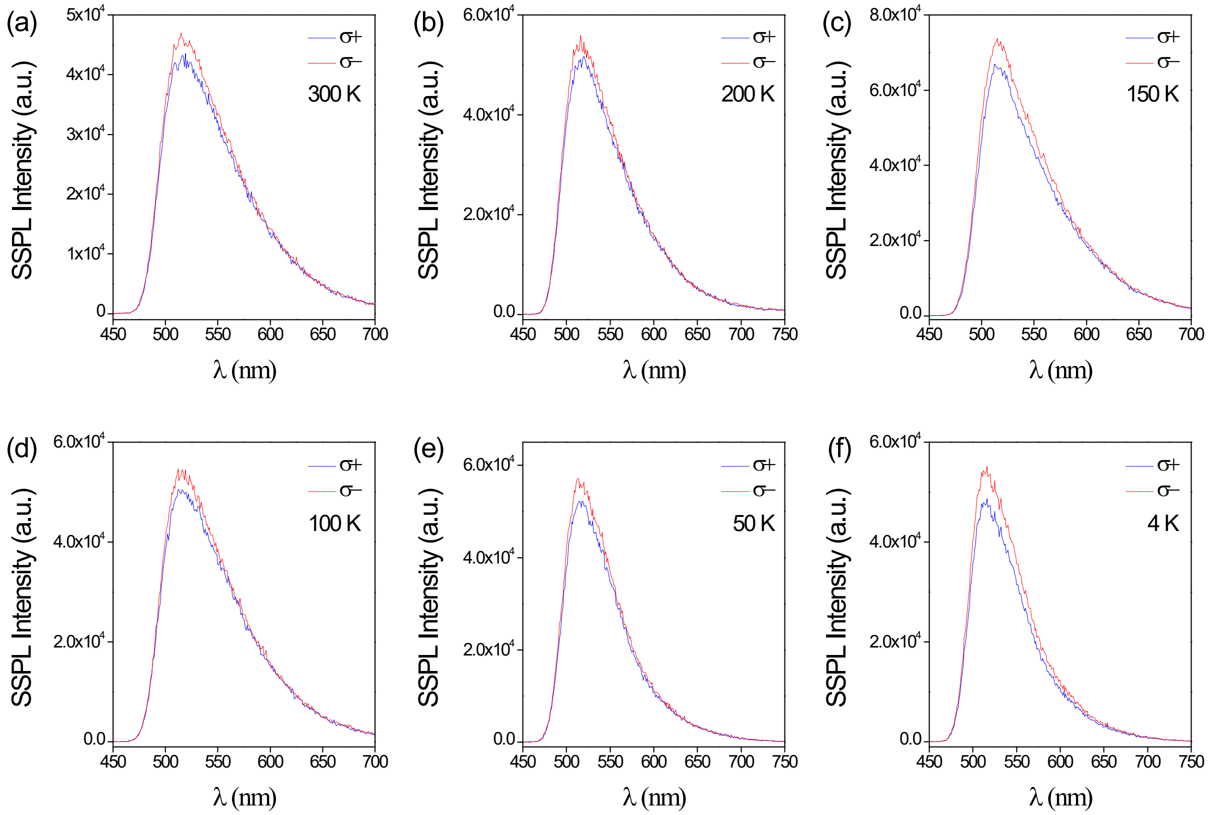
S-Fig. 4 Experimental results of temperature dependent CPL for the solution processed $(R\text{-}MBA)_2PbI_4$ thin film at 900 mT.



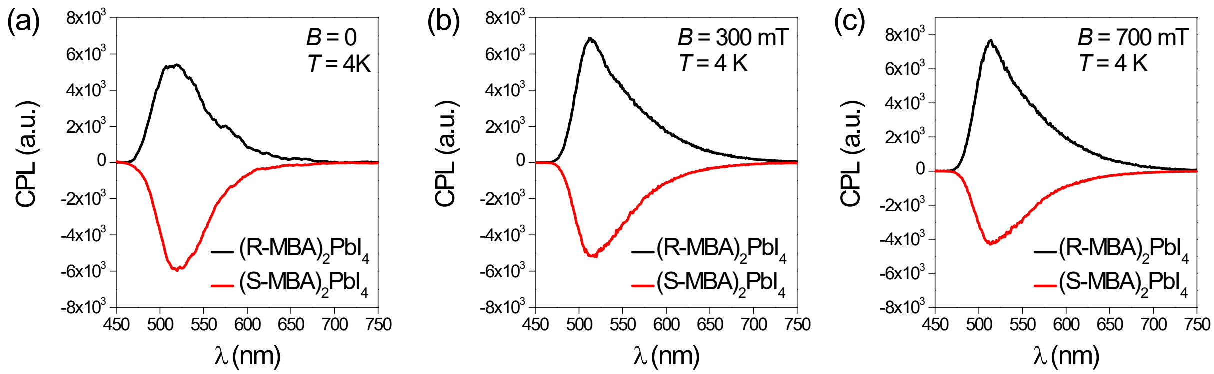
S-Fig. 5 (a)-(f) Experimental results of temperature dependent CPL for the solution processed (S-MBA)$_2$PbI$_4$ thin film at 900 mT.



S-Fig. 6 Experimental results of temperature dependent CPL for the solution processed $(R\text{-}MBA)_2PbI_4$ thin film at -900 mT.



S-Fig. 7 Experimental results of temperature dependent CPL for the solution processed $(S\text{-}MBA)_2PbI_4$ thin film at -900 mT.



S-Fig. 8 CPL spectra for $(R\text{-}MBA)_2PbI_4$ and $(S\text{-}MBA)_2PbI_4$ thin films measured at T = 4 K with the applications of magnetic fields at (a) 0 mT, (b) 300 mT, and (c) 700 mT respectively.

Part II - Theoretical Model

1. Exciton states

The exciton states for OIHPs have: Γ_1 (dark), Γ_2 (polarized light emission along the *z*-axis), and $\Gamma_5^{\pm}$ (doubly degenerate, CPL emission). If we use $c_{\pm}$ and $\bar{v}_{\pm}$ to denote electron and hole spin states respectively, in which ± represents the up- $(\uparrow)$ and down- $(\downarrow)$ components of (pseudo) spins $j_e = 1/2$ and $s_h = 1/2$. The exciton states for Γ_1, Γ_2, and $\Gamma_5^{\pm}$ can be written as:

$$|\Gamma_1\rangle = \frac{1}{\sqrt{2}}(|c_+\bar{v}_-\rangle - |c_-\bar{v}_+\rangle), \; |\Gamma_2\rangle = \frac{1}{\sqrt{2}}(|c_+\bar{v}_-\rangle + |c_-\bar{v}_+\rangle), \; |\Gamma_5^{\pm}\rangle = |c_{\pm}\bar{v}_{\pm}\rangle, \quad \text{(S1)}$$

The four possible spin configurations are $c_+\bar{v}_+$, $c_-\bar{v}_-$, $c_+\bar{v}_-$ and $c_-\bar{v}_+$ for an exciton. The energy states can be characterized by the total angular momentum $J = j_e + s_h$. In this case, the exciton states, Γ_1, Γ_2, and $\Gamma_5^{\pm}$, correspond to $|J^{ex}, J_z^{ex}\rangle = |0,\ 0\rangle$, $|1,\ 0\rangle$, and $|1,\ \pm\rangle$ respectively. J_z^{ex} denotes the projection of J^{ex} on the *z*-axis.

Note that for the conduction electrons $j_e = l + s_e$ with $l = 1$ and one should not be confused j_e with s_e. When discussing electron g-factors and exchange coupling, the relevant property is the pseudo spin j_e. Whereas in discussing optical selection, it is the real spin that is preserved in the electric-dipole transitions.

2. Exchange coupling

There exists a short-range exchange coupling between the electron and hole pseudo spins, the corresponding Hamiltonian (H_{ex}) for the exchange coupling can be written as:

$$H_{ex} = J_{\parallel}\sigma_{ez}\sigma_{hz} + J_{\perp}(\sigma_{ex}\sigma_{hx} + \sigma_{ey}\sigma_{hy}) \equiv J_{\parallel}\sigma_{ez}\sigma_{hz} + 2J_{\perp}(\sigma_{e-}\sigma_{h+} + \sigma_{e+}\sigma_{h-}), \quad \text{(S2)}$$

where σ_{ex}, σ_{ey}, σ_{ez} are the Pauli spin matrices of *x*, *y* and *z* components for electrons. σ_{hx}, σ_{hy}, σ_{hz} are the Pauli spin matrices of *x*, *y* and *z* components for holes. $J_{\parallel}$ and $J_{\perp}$ are the exchange coefficients, in parallel and perpendicular to the C-axis (tetragonal, β phase, symmetry axis of C_{4v}). It breaks the energy degeneracy among the four exciton states. Here $\sigma_{e(h)\pm} = (\sigma_{e(h)x} \pm i\sigma_{e(h)y})/2$. The exciton energies, with H_{sr} included, become,

$$E_1 = -J_{\parallel} - 2J_{\perp}, \; E_2 = -J_{\parallel} + 2J_{\perp}, \; E_5 = J_{\parallel}, \quad \text{(S3)}$$

If $J_{\parallel} \neq J_{\perp}$, $E_2 \neq E_5$, i.e., there is an energy splitting between $(J, J_z) = (1,0)$ and $(1, \pm 1)$.

3. Zeeman energy

In the presence of a magnetic field ***B***, the Hamiltonian associated Zeeman energy (H_Z) can be written as:

$$H_Z = \frac{1}{2}\mu_B[g_{e\perp}(\sigma_{ex}B_x + \sigma_{ey}B_y) + g_{e\parallel}\sigma_{ex}B_z + g_{h\perp}(\sigma_{hx}B_x + \sigma_{hy}B_y) + g_{h\parallel}\sigma_{hz}B_z] \quad \text{, (S4)}$$

in which, μ_B is the Bohr magneton. It is known that a free electron has only the intrinsic spin magnetic moment with a g-factor of approximately 2.0023. The orbital motion of the electron can create an additional magnetic moment and couple with the spin moment. Eventually, it yields an effective g-factor. H_Z has taken into account the anisotropic g-factors for the electron and hole. In equation S4, $g_{e\perp}$ and $g_{e\parallel}$ denote the g-factor of the conduction band-edge in perpendicular and parallel to the C-axis respectively; while, $g_{h\perp}$ and $g_{h\parallel}$ denote the g-factor of the valence band-edge in perpendicular and parallel to the C-axis respectively. For a magnetic field having an angle θ with respect to the crystallographic axis, the measured g-factors for an electron or hole $(g_{e(h)})$ should be expressed as:

$$g_{e(h)}(\theta) = (g_{e(h)\parallel}cos^2\theta + g_{e(h)\perp}sin^2\theta)^{1/2} \quad \text{, equation (S5)}$$

By using the basis set (Γ_5^+, Γ_5^+, Γ_1, Γ_2), we can write $H_{ex} + H_Z$ as:

$$H_{ex} + H_Z = \begin{pmatrix} J_\parallel + \frac{\mu_B}{2}(g_{e\parallel} + g_{h\parallel})B_z & 0 & \frac{\mu_B}{2\sqrt{2}}(g_{h\perp} - g_{e\perp})B_- & \frac{\mu_B}{2\sqrt{2}}(g_{e\perp} + \\ 0 & J_\parallel - \frac{\mu_B}{2}(g_{e\parallel} + g_{h\parallel})B_z & \frac{\mu_B}{2\sqrt{2}}(g_{e\perp} - g_{h\perp})B_+ & \frac{\mu_B}{2\sqrt{2}}(g_{e\perp} + \\ \frac{\mu_B}{2\sqrt{2}}(g_{h\perp} - g_{e\perp})B_+ & \frac{\mu_B}{2\sqrt{2}}(g_{e\perp} - g_{h\perp})B_- & -J_\parallel - 2J_\perp & \frac{\mu_B}{2}(g_{e\parallel} - \\ \frac{\mu_B}{2\sqrt{2}}(g_{h\perp} + g_{e\perp})B_+ & \frac{\mu_B}{2\sqrt{2}}(g_{h\perp} + g_{e\perp})B_- & \frac{\mu_B}{2}(g_{e\parallel} - g_{h\parallel})B_z & -J_\parallel + \end{pmatrix}$$

(S6)

where $B_\pm = B_x + iB_y$.

We can write the effective Hamiltonian $(\tilde{H})$ between Γ_5^+ and Γ_5^- as:

$$\tilde{H} = \begin{pmatrix} \frac{\Delta E}{2} + \frac{\mu_B}{2}(g_{e\parallel} + g_{h\parallel})B_z & \gamma B_-^2 \\ \gamma B_+^2 & -\frac{\Delta E}{2} - \frac{\mu_B}{2}(g_{e\parallel} + g_{h\parallel})B_z \end{pmatrix}, \text{(S7)}$$

where,

$$\gamma = \frac{1}{16}\mu_B^2\left[\frac{(g_{e\perp} + g_{h\perp})^2}{J_\parallel - J_\perp} - \frac{(g_{e\perp} - g_{h\perp})^2}{J_\parallel + J_\perp}\right], \text{(S8)}$$

Again we solve the Bloch equation of the density matrix $\hat{\rho} = \sum_{\pm} \rho_{\pm,\pm} |\Gamma_5^{\pm}\rangle\langle\Gamma_5^{\pm}|$,

$$\frac{\partial\hat{\rho}}{\partial t} = \frac{i}{\hbar}[\rho,\tilde{H}] + \left(\frac{\partial\hat{\rho}}{\partial t}\right)_g - \frac{\hat{\rho}}{\tau} - \left(\frac{\partial\hat{\rho}}{\partial t}\right)_{sr}, \text{(S9)}$$

Here we have explicitly included spin relaxation, which can be described by T_1 and T_2,

$$\left(\frac{\partial(\rho_{++} - \rho_{--})}{\partial t}\right)_{sr} = -\frac{\rho_{++} - \rho_{--}}{\mathrm{T}_1}, \text{(S10)}$$

$$\left(\frac{\partial\rho_{+-}}{\partial t}\right)_{sr} = -\frac{\rho_{+-}}{\mathrm{T}_2}, \text{(S11)}$$

4. Optical selection rules

The optical selection rules of these exciton states can be derived from the matrix elements of the momentum operator, $e \cdot p$ with e being the electric-field polarization of the electromagnetic wave. According to the effective-mass model, we have,

$$\langle\Gamma_1|\, e \cdot p|G\rangle = 0, \text{(S12)}$$

$$\langle\Gamma_2|\, e \cdot p|G\rangle = i\frac{m}{\hbar}sin\xi P_\parallel e_z, \text{(S13)}$$

$$\langle\Gamma_5^{\pm}|\, e \cdot p|G\rangle = i\frac{m}{\hbar}cos\xi P_\perp e_\pm, \text{(S14)}$$

where m is the free-electron mass, $P_\parallel$ and $P_\perp$ and are the Kane parameters.

5. Orientation average

For a tilted angle θ, a right circularly polarized emission has both right and left circularly polarized components, with amplitudes:

$$p_{\pm} \equiv \left(\frac{1 \pm \cos\theta}{2}\right)^2, \text{(S15)}$$

Thus the circular polarization degree is:

$$P_c = \frac{\left(I_L^0 p_+ + I_R^0 p_-\right) - \left(I_L^0 p_- + I_R^0 p_+\right)}{\left(I_L^0 p_+ + I_R^0 p_-\right) + \left(I_L^0 p_- + I_R^0 p_+\right)} = \frac{\cos\theta}{1 + COS^2\theta} \frac{I_L^0 - I_R^0}{I_L^0 + I_R^0} = \frac{\cos\theta}{1 + COS^2\theta} \tan h \frac{\Delta E + g_{ex}\mu_B B \cos\theta}{2\kappa_B \mathrm{T}},$$

(S16)

We perform the orientation average:

$$P_c = \int_0^{\pi/2} d\theta \sin\theta \frac{\cos\theta}{1 + COS^2\theta} \frac{\Delta E + g_{ex}\mu_B B \cos\theta}{2\kappa_B \mathrm{T}}, \text{(S17)}$$

$$P_c = \frac{1}{2\kappa_B \mathrm{T}} \left[\Delta E \frac{log2}{2} + g_{ex}\mu_B B\left(1 - \frac{\pi}{4}\right)\right], \text{(S18)}$$

Thus the Hamiltonian for Γ_2 and Γ_{5x} is:

$$H' = H_{ex} + H_Z = \begin{pmatrix} -J_{\parallel} + 2J_{\perp} & i(g_{e\perp} + g_{h\perp})\mu_B B_x/2 \\ -i(g_{e\perp} + g_{h\perp})\mu_B B_x/2 & J_{\parallel} \end{pmatrix}, \text{(S19)}$$

Population dynamics can be obtained by solving the Bloch equation of the density matrix.

$$\frac{\partial\hat{\rho}}{\partial t} = \frac{i}{\hbar}[\rho, H'] + \left(\frac{\partial\hat{\rho}}{\partial t}\right)_g - \frac{\hat{\rho}}{\tau}, \text{(S20)}$$

where $\hat{\rho}$ is a 2×2 density matrix spanned by Γ_2 and Γ_{5x}, $\hat{\rho} = \sum_{m,n} \rho_{mn} |\psi_m\rangle \langle\psi_n|\ with\ m,n = 1, 2\ and\ \psi_{1(2)} = \Gamma_{2(5x)} \cdot (\partial\rho/\partial t)_g$ represents the generation of the exciton states, which is finite only for diagonal terms, $(\partial\rho_{mn}/\partial t)_g = F_m \delta_{mn}$, because the PL in the MFE measurements is not resonantly excited. τ is the recombination life time of these exciton states.