

# SUPPLEMENTARY INFORMATION

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## Supplementary information for:

### Bright triplet excitons in caesium lead halide perovskites

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## S1. EXCITON FINE STRUCTURE IN THE EFFECTIVE-MASS MODEL

### A. Four-band model

To calculate optical transition energies, exciton fine structure, polarization properties, as well as exciton and trion radiative lifetimes for perovskite nanocrystals, we need a multi-band effective-mass Hamiltonian that describes the carrier energies in the vicinity of the bandgap edge in bulk perovskite semiconductors. Effective energy-band parameters for this Hamiltonian can be extracted from the predicted electron and hole dispersion obtained via first-principle descriptions of the bulk energy structure for these semiconductors. Then, all the critical characteristics of perovskite nanocrystals can be calculated within this multi-band effective-mass Hamiltonian. The goal of this and the next subsection is to develop this effective-mass Hamiltonian.

The R-point of the Brillouin zone is isomorphic to the  $\Gamma$ -point in cubic semiconductors [S1]. As a result, the dispersion of electrons and holes at the R-point is described by the familiar 8x8  $\mathbf{k} \cdot \mathbf{p}$  Hamiltonian matrix that characterizes the band edge of direct-gap cubic semiconductors at the  $\Gamma$ -point. In the perovskites studied here, due to large spin-orbit coupling, a good description of the electron and hole dispersion is obtained by extracting the 4x4 part related to the  $\Gamma_6^-$  and  $\Gamma_6^+$  bands of the conduction and valence bands [S2, S3]. Using the same standard semiconductor notation [S4, S5] introduced in the main text, the Bloch wavefunctions of the corresponding band-edge states can be written as:

$$\begin{aligned}
 |\uparrow\rangle_e &= -\frac{1}{\sqrt{3}} [(|X\rangle + i|Y\rangle)|\downarrow\rangle + |Z\rangle|\uparrow\rangle] \\
 |\downarrow\rangle_e &= \frac{1}{\sqrt{3}} [|Z\rangle|\downarrow\rangle - (|X\rangle - i|Y\rangle)|\uparrow\rangle] \\
 |\uparrow\rangle_h &= |S\rangle|\uparrow\rangle \\
 |\downarrow\rangle_h &= |S\rangle|\downarrow\rangle .
 \end{aligned} \tag{S1}$$

Note the different phases of the basis functions in comparison with ref. S2. The Hamiltonian in our basis is

$$\hat{H} = \begin{pmatrix} E_c + \gamma_e \frac{p^2}{2m_0} & 0 & -\frac{1}{m_0} \frac{iP}{\sqrt{3}} p_z & -\frac{1}{m_0} \frac{iP}{\sqrt{3}} p_- \\ 0 & E_c + \gamma_e \frac{p^2}{2m_0} & -\frac{1}{m_0} \frac{iP}{\sqrt{3}} p_+ & \frac{1}{m_0} \frac{iP}{\sqrt{3}} p_z \\ \frac{1}{m_0} \frac{iP}{\sqrt{3}} p_z & \frac{1}{m_0} \frac{iP}{\sqrt{3}} p_- & E_v - \gamma_h \frac{p^2}{2m_0} & 0 \\ \frac{1}{m_0} \frac{iP}{\sqrt{3}} p_+ & -\frac{1}{m_0} \frac{iP}{\sqrt{3}} p_z & 0 & E_v - \gamma_h \frac{p^2}{2m_0} \end{pmatrix}, \tag{S2}$$

where  $\hat{\mathbf{p}}$  is the momentum operator,  $P = -i\langle S|p_z|Z\rangle$  is the Kane matrix element,  $p_{\pm} = p_x \pm ip_y$ ,  $p^2 = p_x^2 + p_y^2 + p_z^2$ ,  $E_{c,v}$  are the band-edge energies, and  $\gamma_{e,h}$  are the remote-band contributions to the electron and hole effective masses. Note that in the perovskites considered the band structure is reversed compared to many typical semiconductors in the sense that the valence band (instead of the conduction band) is *s*-like. The energy gap,  $E_g = E_c - E_v$ , is connected with the energy gap  $E'_g$  and the spin-orbit splitting  $\Delta$  of the standard 8-band model as  $E_g = E'_g - |\Delta|$ , because  $\Delta$  in these perovskites is negative.

The energy spectrum of the carriers is isotropic at the R-point of the Brillouin zone and can be easily found by taking  $\mathbf{p}$  along the *z* axis. In this case, the  $4 \times 4$  matrix is composed of two identical  $2 \times 2$  blocks decoupled from each other, determined as,

$$\begin{pmatrix} E_g - \mathcal{E} + \frac{\gamma_e}{2m_0}p^2 & \frac{i}{\sqrt{3}}\frac{P}{m_0}p \\ -\frac{i}{\sqrt{3}}\frac{P}{m_0}p & -\mathcal{E} - \frac{\gamma_h}{2m_0}p^2 \end{pmatrix}. \quad (\text{S3})$$

The usual procedures lead to the dispersion relation

$$\mathcal{E}_{\pm} = \frac{1}{2} \left[ E_g + (\gamma_e - \gamma_h) \frac{p^2}{2m_0} \right] \pm \sqrt{\frac{1}{4} \left[ E_g + (\gamma_e + \gamma_h) \frac{p^2}{2m_0} \right]^2 + E_p \frac{p^2}{6m_0}}, \quad (\text{S4})$$

where we have used the Kane energy  $E_p = 2P^2/m_0$ .

## B. Estimating the energy-band parameters of the four-band model

To describe the energy spectra and radiative lifetimes in nanocrystals we need the parameters  $E_p$  and  $\gamma_{e,h}$  of the four-band model for the cubic perovskites, Eq. (S4). We determine these parameters by fitting the first-principles calculations presented in Fig. 1b in the main text and Extended Data Fig. 1. In particular,  $E_p$  and  $\gamma_{e,h}$  are connected to the effective masses of the electrons and holes,  $m_e$  and  $m_h$ , at their respective band edges by the following relationships:

$$\frac{m_0}{m_e} = \gamma_e + \frac{E_p}{3E_g}, \quad \frac{m_0}{m_h} = \gamma_h + \frac{E_p}{3E_g}. \quad (\text{S5})$$

These expressions are derived from the parabolic approximation to Eq.(S4) applied for small  $p$  and using  $E_p \gg E_g$ . To extract  $E_p$ , we take the asymptotic limit of Eq.(S4) at large  $p$ , such that  $p^2 E_p \gg 6m_0 E_g^2$ . Assuming that  $E_p$  is sufficiently large that  $p^2 \ll m_0 E_p / (\gamma_e \pm \gamma_h)$ , which is satisfied for a very wide range of energies in the conduction and

	CsPbCl <sub>3</sub>	CsPbBr <sub>3</sub>	CsPbI <sub>3</sub>
$E_g$ exp (eV)	3.04 [S6]	2.36 [S6]	1.67 [S7]
$E_p$ (eV)	40.1	39.9	41.6
$\gamma_e$	0.77	1.85	3.27
$\gamma_h$	1.51	2.21	2.58
$m_e/m_0$	0.194	0.134	0.086
$m_h/m_0$	0.170	0.128	0.095
$\epsilon_{in}$ exp.	4.5	4.8	5.0

TABLE S1. Parameters of the four-band model, describing the dispersion of the conduction and valence bands in the vicinity of the R-point of the Brillouin zone, and the high-frequency dielectric constants of the CsPbX<sub>3</sub> (X=Cl, Br, and I) perovskites used in calculations of the exciton lifetimes. The band parameters were extracted from first-principles calculations of the perovskite band structures. The high-frequency dielectric constants were obtained from an analysis of the exciton binding energy and the refractive index.

valence bands, we obtain,

$$\mathcal{E} \approx \frac{1}{2}E_g \pm \sqrt{\frac{E_p}{6m_0}p}, \left( p^2 \gg \frac{6m_0E_g^2}{E_p} \right). \quad (\text{S6})$$

Extended Data Fig. 7 shows the slope  $\sqrt{E_p/6m_0}$  according to Eq.(S6), which is calculated as the energy difference  $\mathcal{E} - E_g/2$  divided by the corresponding difference in momentum,  $p = \hbar\Delta k$ , where  $\Delta k$  is the wave number shown in nm<sup>-1</sup>. The results of this fitting procedure are summarized in the Table S1 along with the energy gaps  $E_g$  of the bulk perovskites CsPbX<sub>3</sub> taken from experimental data.

The last parameter needed to analyze the exciton radiative lifetimes is the high-frequency dielectric constant for each material. Using the effective masses summarized in Table S1 we can calculate the high-frequency dielectric constant from the exciton Rydberg when it is known. Taking the measured Rydberg for CsPbCl<sub>3</sub> and CsPbBr<sub>3</sub>, 60 meV and 34 meV, respectively [S6], we find  $\epsilon_{in} = 4.5$  for CsPbCl<sub>3</sub> and  $\epsilon_{in} = 4.8$  in CsPbBr<sub>3</sub>. The Rydberg has not been measured for CsPbI<sub>3</sub>. Noting that the dielectric constants determined for CsPbCl<sub>3</sub> and CsPbBr<sub>3</sub> are very close to those measured in methylammonium (MA) lead halide perovskites [S8] ( $\epsilon_{in} = 4.0$  in MAPbCl<sub>3</sub> and  $\epsilon_{in} = 4.7$  in MAPbBr<sub>3</sub>), we have taken the dielectric constant of MAPbI<sub>3</sub>,  $\epsilon_{in} = 5.0$  [S8], for CsPbI<sub>3</sub>. The dielectric constants

and the energy-band parameters from Table S1 are used in the calculations of the radiative lifetimes.

### C. Exciton fine structure in nanocrystals with cubic lattice structure

The total wavefunction of the electron and hole states in nanocrystals can be found using the parabolic-band effective-mass approximation [S9, S10]. They generally can be written as a product of the Bloch functions defined in Eq.(S1) and envelope functions, *i.e.* products of the form:  $\Psi_{\uparrow,\downarrow}^e(\mathbf{r}_e) = F_e(\mathbf{r}_e)|\uparrow,\downarrow\rangle_e$  and  $\Psi_{\uparrow,\downarrow}^h(\mathbf{r}_h) = F_h(\mathbf{r}_h)|\uparrow,\downarrow\rangle_h$  for electron and hole states, respectively, where  $F_{e,h}$  are the electron or hole envelope functions.

The total exciton wavefunctions in nanocrystals are the product of the Bloch functions defined in Eqs.(2) and (3) in the main text and the exciton envelope function  $v(\mathbf{r}_e, \mathbf{r}_h)$ , which describes spatial motion of the exciton confined in the nanocrystal. The resulting wavefunctions of the exciton  $\Psi_{J,J_z}^{ex}$  with momentum  $J$  and momentum projection  $J_z$  have the following form:

$$\begin{aligned}\Psi_{0,0}^{ex} &= \frac{1}{\sqrt{2}} (|\downarrow\rangle_e|\uparrow\rangle_h - |\uparrow\rangle_e|\downarrow\rangle_h) v(\mathbf{r}_e, \mathbf{r}_h), \quad \Psi_{1,+1}^{ex} = |\uparrow\rangle_e|\uparrow\rangle_h v(\mathbf{r}_e, \mathbf{r}_h), \\ \Psi_{1,0}^{ex} &= \frac{1}{\sqrt{2}} (|\downarrow\rangle_e|\uparrow\rangle_h + |\uparrow\rangle_e|\downarrow\rangle_h) v(\mathbf{r}_e, \mathbf{r}_h), \quad \Psi_{1,-1}^{ex} = |\downarrow\rangle_e|\downarrow\rangle_h v(\mathbf{r}_e, \mathbf{r}_h).\end{aligned}\quad (S7)$$

The electron–hole exchange interaction [S1],  $H_{\text{exch}} = -\alpha_{exc} \Omega_0 (\boldsymbol{\sigma}^e \cdot \boldsymbol{\sigma}^h) \delta(\mathbf{r}_e - \mathbf{r}_h)$ , where  $\boldsymbol{\sigma}^{e,h}$  are the electron and hole Pauli operators,  $\alpha_{exc}$  is the exchange constant, and  $\Omega_0$  is the volume of the unit cell, conserves the two-particle angular momentum,  $\mathbf{J} = \frac{1}{2}(\boldsymbol{\sigma}^e + \boldsymbol{\sigma}^h)$ . This exchange interaction splits the fourfold degenerate exciton ground state into an optically passive singlet ( $J = 0$ ) and a threefold degenerate optically active triplet state ( $J = 1$  with three momentum projections  $J_z = \pm 1, 0$ ).

The singlet–triplet splitting of the exciton levels can be shown to be equal to  $4\eta$ , where  $\eta = \alpha_{exc}\Theta$ , with  $\Theta = \Omega_0 \int d^3r v^2(r, r)$ . It is known that the splitting is enhanced by spatial confinement [S11], which is included via the parameter  $\Theta$ . In the strong-confinement regime:  $\Theta \sim \Omega_0/V$  and is inversely proportional to the nanocrystal volume,  $V$ . In the bulk and in the weak-confinement regime:  $\Theta = \Omega_0/\pi a_B^3$ .

It is easy to demonstrate that the singlet level  $|\Psi_{0,0}\rangle$  is optically passive. This is because the transition-dipole matrix element taken between this state and the vacuum state  $|0\rangle = \delta(\mathbf{r}_e - \mathbf{r}_h)$  is zero:  $\langle 0|\hat{\mathbf{p}}|\Psi_{0,0}\rangle = 0$ . In the optical matrix element,  $\hat{\mathbf{p}}$  acts only on the

conduction-band Bloch functions. Thus, the exciton wavefunction  $|\Psi_{0,0}\rangle$  from Eq.(2) in the main text should be transformed to the electron–electron representation. In this case, using the time-reversal operator  $\hat{K}$  for transformation of the hole wavefunction to the electron form, one can show that

$$\begin{aligned}
 \langle 0|\hat{\mathbf{p}}|\Psi_{0,0}\rangle &= \int d^3r \frac{1}{\sqrt{2}} \left( (\hat{K}|S\rangle|\uparrow\rangle)\hat{\mathbf{p}}\frac{1}{\sqrt{3}} [ |Z\rangle|\downarrow\rangle - (|X\rangle - i|Y\rangle)|\uparrow\rangle] \right. \\
 &\quad \left. - (\hat{K}|S\rangle|\downarrow\rangle)\hat{\mathbf{p}}\left( -\frac{1}{\sqrt{3}} [(|X\rangle + i|Y\rangle)|\downarrow\rangle + |Z\rangle|\uparrow\rangle] \right) \right) \\
 &= \frac{1}{\sqrt{6}} \int d^3r (\langle S|\langle\downarrow|\hat{\mathbf{p}}[|Z\rangle|\downarrow\rangle - (|X\rangle - i|Y\rangle)|\uparrow\rangle] \\
 &\quad + \langle S|\langle\uparrow|\hat{\mathbf{p}}[-(|X\rangle + i|Y\rangle)|\downarrow\rangle + |Z\rangle|\uparrow\rangle]) \\
 &= \frac{1}{\sqrt{6}} \int d^3r (\langle S|\hat{\mathbf{p}}|Z\rangle - \langle S|\hat{\mathbf{p}}|Z\rangle) = 0 .
 \end{aligned} \tag{S8}$$

Here we used the following properties of the time-reversal operator  $\hat{K}$ :  $\hat{K}|\uparrow\rangle = |\downarrow\rangle$  and  $\hat{K}|\downarrow\rangle = -|\uparrow\rangle$ . Similar calculations show that all three triplet states are optically active.

#### D. The order of the singlet and triplet excitons in perovskite nanocrystals

The sign of the exchange-interaction constant  $\alpha_{exc}$  affects the level order of the singlet and triplet exciton states. In the absence of spin–orbit coupling, both  $\alpha_{exc}$  and  $\eta$  are always positive, resulting in an optically passive spin-triplet exciton ground state. This is the case for organic semiconductors. When strong spin–orbit coupling exists in only one band (for which the corresponding band-edge Bloch functions are described by Eq. 1 of the main text and above), the parameters  $\alpha_{exc}$  and  $\eta$  are negative leading to an *optically passive singlet exciton ground state*. Ignoring the Rashba effect for the moment (see the next subsection, Section S1.E), this optically passive singlet would be the expected exciton ground state for perovskites and perovskite nanocrystals [S12–S16]. The splitting in this case was intensively analyzed theoretically [S17–S19] in connection with CuCl, for which the conduction and valence band edges have symmetry  $\Gamma_6$  and  $\Gamma_7$ , respectively, with Bloch functions as in Eq. (S1), but with the band labels reversed. The triplet–singlet splitting,  $4\eta$  can be expressed in terms of the Bloch functions of the conduction and valence bands [S18]:  $4\eta = (2/3)(\Theta/\Omega_0^2) \int d^3r_1 d^3r_2 S^*(\mathbf{r}_1)X^*(\mathbf{r}_2)V(\mathbf{r}_1 - \mathbf{r}_2)S(\mathbf{r}_2)X(\mathbf{r}_1)$ , where the Bloch functions are normalized to the unit-cell volume,  $\Omega_0$ , the integrals are taken over one unit

TABLE S2. Calculated exchange constant  $\alpha_{exc}$ ,  $\Theta$ , and singlet–triplet splitting  $4\eta = 4\alpha_{exc}\Theta$  in  $\text{CsPbX}_3$  (X=Cl, Br, and I).

Perovskite	$4\alpha_{exc}$ (meV)	$\Theta$	singlet–triplet splitting, $4\eta$ (meV)
CsPbCl <sub>3</sub>	354	0.00313	1.11
CsPbBr <sub>3</sub>	267	0.00110	0.29
CsPbI <sub>3</sub>	204	0.00038	0.078

cell, and  $V(\mathbf{r}_1 - \mathbf{r}_2) = e^2/(\epsilon_{\text{in}}|\mathbf{r}_1 - \mathbf{r}_2|)$  is the Coulomb potential between two electrons. This exchange integral is *always* positive and the optically active triplet *always* has higher energy.

To quantify the exchange splitting for perovskite nanocrystals (still ignoring the Rashba effect), we conducted first-principles calculations of the band-edge Bloch functions using the Heyd-Scuseria-Ernzerhof HSE06 hybrid functionals, which mix exact Hartree-Fock exchange with conventional DFT (see Methods). From these wavefunctions and the expression above for  $\eta$  we calculated the exchange constant  $\alpha_{exc}$  for all three  $\text{CsPbX}_3$  halide perovskites (X=Cl, Br, and I). The resulting short-range exchange splittings of the singlet–triplet exciton are listed in the third column of Table S2.

Our experimentally studied  $\text{CsPbX}_3$  nanocrystals are known to exhibit an orthorhombic lattice distortion [S20]. The reduction of the nanocrystal symmetry generally splits the threefold degenerate triplet states into three exciton sublevels. To find these splittings in  $\text{CsPbBr}_3$  nanocrystals, we used  $G_0W_0$  first-principle calculations (see Methods). Our calculations predict an expected orthorhombic splitting for the triplet with  $\Delta_1 = 1.9 * 0.004388 = 0.008$  meV and  $\Delta_2 = 3.9 * 0.004388 = 0.017$  meV (see inset to Fig. 3i in the main text for definitions of  $\Delta_1$  and  $\Delta_2$ ). These splittings are hundreds of times smaller than the splittings measured experimentally ( $\sim 1$  meV) in our perovskite nanocrystals (see Fig. 3 in the main text). This suggests that the orthorhombic distortion is not responsible for the observed splittings.

### E. Effect of Rashba terms on the exciton fine structure

We now consider the influence of the Rashba effect on the observed exciton fine structure. This effect can arise due to inversion-symmetry breaking in  $\text{CsPbBr}_3$ , for example due to

the instability of  $\text{Cs}^+$  ions in the lattice [S21]. Instabilities in the ion positions can result in lattice polarization, which creates Rashba terms in the Hamiltonians describing the electrons and holes.

The Rashba spin-orbit term was first written for wurtzite crystals [S22]. For electrons and holes in a nanocrystal made from a cubic crystal lattice, the Rashba effect can be described as [S23]:

$$\hat{H}_R^c = \alpha_{R,c} [(\sigma_x p_y - \sigma_y p_x) n_z + (\sigma_z p_x - \sigma_x p_z) n_y + (\sigma_y p_z - \sigma_z p_y) n_x], \quad (\text{S9})$$

where  $\alpha_{R,c}$  represents either the conduction- or valence-band Rashba coefficient for nanocrystals with cubic lattice structure ( $\alpha_{R,c}^e$  and  $\alpha_{R,c}^h$ , respectively), and  $\sigma_i$  are the projections of the Pauli operators for the electron total momentum operator for  $J = 1/2$  and for the hole spin  $s = 1/2$ , ( $\sigma_i^e$  and  $\sigma_i^h$  respectively). In Eq. (S9),  $n_{x,y,z}$  are the projections on the cubic axes of a unit vector  $\mathbf{n}$  defining the direction of the symmetry breaking (see, for example, the inset in Fig. 1c of the main text).

From Eq. (S9) we can write the most general Rashba Hamiltonian for nanocrystals with orthorhombic symmetry:

$$\begin{aligned} \hat{H}_R^o &= \alpha_{R,xy}^z \sigma_x p_y n_z - \alpha_{R,yx}^z \sigma_y p_x n_z + \alpha_{R,zx}^y \sigma_z p_x n_y - \alpha_{R,xz}^y \sigma_x p_z n_y \\ &+ \alpha_{R,yz}^x \sigma_y p_z n_x - \alpha_{R,zy}^x \sigma_z p_y n_x. \end{aligned} \quad (\text{S10})$$

As one can see from Eq. (S10), the Rashba effect for both electrons and holes is fully described with six independent parameters:  $\alpha_{R,xy}^{z,e;h}$ ,  $\alpha_{R,yx}^{z,e;h}$ ,  $\alpha_{R,zx}^{y,e;h}$ ,  $\alpha_{R,xz}^{y,e;h}$ ,  $\alpha_{R,yz}^{x,e;h}$ , and  $\alpha_{R,zy}^{x,e;h}$ , respectively, which reflect the material properties and symmetry of the nanocrystal, while again the projections  $n_x, n_y, n_z$  of the unit vector  $\mathbf{n}$  define the Rashba symmetry-breaking direction. For calculations it is convenient to re-write the Rashba Hamiltonian in Eq. (S10) acting on the exciton as a sum of the three terms  $\hat{H}_R^o = \hat{H}_x n_x + \hat{H}_y n_y + \hat{H}_z n_z$ :

$$\begin{aligned} \hat{H}_z &= \alpha_{R,xy}^{z,e} \sigma_x^e p_y^e - \alpha_{R,yx}^{z,e} \sigma_y^e p_x^e + \alpha_{R,xy}^{z,h} \sigma_x^h p_y^h - \alpha_{R,yx}^{z,h} \sigma_y^h p_x^h, \\ \hat{H}_y &= \alpha_{R,zx}^{y,e} \sigma_z^e p_x^e - \alpha_{R,xz}^{y,e} \sigma_x^e p_z^e + \alpha_{R,zx}^{y,h} \sigma_z^h p_x^h - \alpha_{R,xz}^{y,h} \sigma_x^h p_z^h, \\ \hat{H}_x &= \alpha_{R,yz}^{x,e} \sigma_y^e p_z^e - \alpha_{R,zy}^{x,e} \sigma_z^e p_y^e + \alpha_{R,yz}^{x,h} \sigma_y^h p_z^h - \alpha_{R,zy}^{x,h} \sigma_z^h p_y^h. \end{aligned} \quad (\text{S11})$$

The wavefunction of the exciton ground state in cube-shaped nanocrystals in the weak confinement regime (which we use to approximate our experimental samples), can be written as:

$$\Psi_{gr}^{J,J_z}(\mathbf{R}, \mathbf{r}) = \psi_{100}(\mathbf{r}) \Psi_0(\mathbf{R}) U_{J,J_z} \quad (\text{S12})$$



Here  $\psi_{100}(\mathbf{r})$  is the hydrogen-like function that describes the relative motion of the exciton ground state with  $\mathbf{r} = \mathbf{r}_h - \mathbf{r}_e$ . For the ground state, the wavefunction of the exciton relative motion can be written:

$$\psi_{100}(\mathbf{r}) = 2 \left( \frac{1}{a_B} \right)^{3/2} e^{-r/a_B} Y_{0,0}, \quad (\text{S13})$$

where  $a_B = \epsilon_{\text{in}} \hbar^2 / (e^2 \mu)$  is the exciton Bohr radius with  $\mu = 1/[1/m_e + 1/m_h]$  as the reduced exciton effective mass, and  $Y_{0,0}$  is the spherical harmonic with  $l = 0$ .  $\Psi_0(\mathbf{R})$  describes the wavefunction of the exciton center-of-mass motion, with  $\mathbf{R} = [m_e \mathbf{r}_e + m_h \mathbf{r}_h]/M$ , where  $m_e$  and  $m_h$  are the electron and hole effective masses, and  $M = m_e + m_h$ . For the exciton ground state, the wavefunction of the exciton center-of-mass motion can be written:

$$\Psi_0(\mathbf{R}) = \sqrt{\frac{8}{L_x L_y L_z}} \cos(\pi X/L_x) \cos(\pi Y/L_y) \cos(\pi Z/L_z), \quad (\text{S14})$$

where  $L_x$ ,  $L_y$ , and  $L_z$  are the edge lengths of the cube-shaped nanocrystal. Finally  $U_{J,J_z}$  in Eq.(S12) is the spin part of the exciton function, which for  $J = 0$  and  $J = 1$  (singlet and triplet states, respectively) can be written as:

$$|0, 0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle) \quad (\text{S15})$$

$$|1, +1\rangle = |\uparrow\rangle|\uparrow\rangle, \quad |1, 0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle|\downarrow\rangle + |\downarrow\rangle|\uparrow\rangle), \quad |1, -1\rangle = |\downarrow\rangle|\downarrow\rangle. \quad (\text{S16})$$

Corrections to the exciton ground state from the Rashba terms in Eqs. (S11) vanish in first-order perturbation theory. In second-order perturbation theory, however, we find corrections that describe coupling among the spin sublevels of the exciton. The resulting coupling matrix contains spin–spin coupling terms and is similar in that respect to an effective exchange Hamiltonian. In second-order perturbation theory this matrix can be written [S24]:

$$M_{J,J_z}^{J',J'_z} = \sum_{m; J'', J''_z} \frac{\langle \Psi_{gr}^{J,J_z} | \hat{H}_R | \Psi_m^{J'', J''_z} \rangle \langle \Psi_m^{J'', J''_z} | \hat{H}_R | \Psi_{gr}^{J', J'_z} \rangle}{E_{gr} - E_m}, \quad (\text{S17})$$

where the sum goes over all intermediate spatial states  $m$  and all spin states  $J''$  and  $J''_z$ . However, significant simplifications arise because the energies of the intermediate states in this expression are independent of spin. One can sum over all intermediate  $J'', J''_z$  states, resulting in a 4x4 coupling matrix.

To estimate the matrix in Eq. (S17) we take into account just the first few excited states of the exciton center-of-mass and relative motions. In the later case, the wavefunction can be written as:

$$\Psi_{1m}^{r;J,J_z}(\mathbf{R}, \mathbf{r}) = \psi_{21m}(\mathbf{r})\Psi_0(\mathbf{R})U_{J,J_z}, \quad (\text{S18})$$

where  $\psi_{21m}(\mathbf{r})$  is the hydrogen-like wavefunction of the 1P exciton level with angular momentum  $l = 1$  and momentum projections  $m = 0, \pm 1$ . These wavefunctions can be written as:

$$\psi_{21m}(\mathbf{r}) = \frac{1}{2\sqrt{6}} \left( \frac{1}{a_B} \right)^{3/2} \frac{r}{a_B} e^{-r/2a_B} Y_{1,m}(\theta, \phi), \quad (\text{S19})$$

where  $Y_{1,m}$  are the spherical harmonics with  $l = 1$  [S24]. The energy distance for the 1P level is  $0.75e^4\mu/\hbar^2\epsilon_{\text{in}}^2$ .

For the first three excited levels connected with the exciton center-of-mass motion we can write:

$$\Psi_{x,y,z}^{R;J,J_z}(\mathbf{R}, \mathbf{r}) = \psi_{100}(\mathbf{r})\Psi_{x,y,z}(\mathbf{R})U_{J,J_z}, \quad (\text{S20})$$

where the excited wavefunction of the exciton center-of-mass motion  $\Psi_{x,y,z}$  can be written:

$$\begin{aligned} \Psi_x(\mathbf{R}) &= \sqrt{\frac{8}{L_x L_y L_z}} \sin(2\pi X/L_x) \cos(\pi Y/L_y) \cos(\pi Z/L_z), \\ \Psi_y(\mathbf{R}) &= \sqrt{\frac{8}{L_x L_y L_z}} \cos(\pi X/L_x) \sin(2\pi Y/L_y) \cos(\pi Z/L_z), \\ \Psi_z(\mathbf{R}) &= \sqrt{\frac{8}{L_x L_y L_z}} \cos(\pi X/L_x) \cos(\pi Y/L_y) \sin(2\pi Z/L_z). \end{aligned} \quad (\text{S21})$$

The energy distances between the ground and excited exciton states are  $3\hbar^2\pi^2/2ML_x^2$ ,  $3\hbar^2\pi^2/2ML_y^2$ , and  $3\hbar^2\pi^2/2ML_z^2$ , respectively.

Let us now calculate the effective electron–hole spin-coupling Hamiltonian created by the

Rashba term. Substituting  $\hat{H}_R^o$  into Eq. (S17) we obtain:

$$\begin{aligned}
M_{J,J_z}^{J',J'_z} = & \\
& - \frac{2m_e}{M} (A_R^c m_e + A_R^r m_h) \left[ (\tilde{\alpha}_{R,zx}^{y,e})^2 + (\tilde{\alpha}_{R,yx}^{z,e})^2 + (\tilde{\alpha}_{R,xy}^{z,e})^2 + (\tilde{\alpha}_{R,zy}^{x,e})^2 + (\tilde{\alpha}_{R,yz}^{x,e})^2 + (\tilde{\alpha}_{R,xz}^{y,e})^2 \right] \\
& - \frac{2m_h}{M} (A_R^c m_h + A_R^r m_e) \left[ (\tilde{\alpha}_{R,zx}^{y,h})^2 + (\tilde{\alpha}_{R,yx}^{z,h})^2 + (\tilde{\alpha}_{R,xy}^{z,h})^2 + (\tilde{\alpha}_{R,zy}^{x,h})^2 + (\tilde{\alpha}_{R,yz}^{x,h})^2 + (\tilde{\alpha}_{R,xz}^{y,h})^2 \right] \\
& - \frac{2m_h m_e}{M} (A_R^c - A_R^r) \\
& \times \left[ \left( \tilde{\alpha}_{R,xy}^{z,e} \tilde{\alpha}_{R,xy}^{z,h} + \tilde{\alpha}_{R,xz}^{y,e} \tilde{\alpha}_{R,xz}^{y,h} \right) \sigma_x^e \sigma_x^h + \left( \tilde{\alpha}_{R,yz}^{x,e} \tilde{\alpha}_{R,yz}^{x,h} + \tilde{\alpha}_{R,yx}^{z,e} \tilde{\alpha}_{R,yx}^{z,h} \right) \sigma_y^e \sigma_y^h \right. \\
& + \left( \tilde{\alpha}_{R,zx}^{y,e} \tilde{\alpha}_{R,zx}^{y,h} + \tilde{\alpha}_{R,zy}^{x,e} \tilde{\alpha}_{R,zy}^{x,h} \right) \sigma_z^e \sigma_z^h - \tilde{\alpha}_{R,xz}^{y,e} \tilde{\alpha}_{R,yz}^{x,h} \sigma_x^e \sigma_y^h - \tilde{\alpha}_{R,yz}^{x,e} \tilde{\alpha}_{R,xz}^{y,h} \sigma_y^e \sigma_x^h - \tilde{\alpha}_{R,xy}^{z,e} \tilde{\alpha}_{R,yx}^{z,h} \sigma_x^e \sigma_z^h \\
& \left. - \tilde{\alpha}_{R,zy}^{x,e} \tilde{\alpha}_{R,zy}^{x,h} \sigma_z^e \sigma_x^h - \tilde{\alpha}_{R,zx}^{y,e} \tilde{\alpha}_{R,yx}^{z,h} \sigma_z^e \sigma_y^h - \tilde{\alpha}_{R,yx}^{z,e} \tilde{\alpha}_{R,zx}^{y,h} \sigma_y^e \sigma_z^h \right], \quad (\text{S22})
\end{aligned}$$

where,  $\tilde{\alpha}_{R,ij}^{z,e;h} = \alpha_{R,ij}^{z,e;h} n_z$ ,  $\tilde{\alpha}_{R,ij}^{y,e;h} = \alpha_{R,ij}^{y,e;h} n_y$ ,  $\tilde{\alpha}_{R,ij}^{x,e;h} = \alpha_{R,ij}^{x,e;h} n_x$ ,  $A_R^c = 128/(27\pi^2)$ , and  $A_R^r = (64/81\sqrt{3})^2$ . The terms proportional to  $A_R^c$  and  $A_R^r$  come from the intermediate states connected with the exciton center-of-mass motion and the relative motion of the electron and hole, respectively. The third term in Eq. (S22) consists of spin-spin coupling terms and has the same form as the effective spin-dependent electron-hole exchange Hamiltonian. Such terms determine the fine structure of the band-edge exciton. One can see that the contributions of the center-of-mass motion and the relative motion of the exciton have different signs and result in a different level order. However, because  $A_R^c > A_R^r$  it is the center-of-mass motion that determines the level order of the exciton.

The fine structure of the exciton is thus defined by the following matrix:

$$\hat{H} = -(A_R^c - A_R^r) \frac{2m_e m_h}{M} \times
\begin{pmatrix}
|\uparrow\uparrow\rangle & |\uparrow\downarrow\rangle & |\downarrow\uparrow\rangle & |\downarrow\downarrow\rangle \\
\left( \begin{array}{cccc}
\tilde{\alpha}_{R,zy}^{x,e} \tilde{\alpha}_{R,zy}^{x,h} + \tilde{\alpha}_{R,zx}^{y,e} \tilde{\alpha}_{R,zx}^{y,h} & -\tilde{\alpha}_{R,zy}^{x,e} \tilde{\alpha}_{R,xy}^{z,h} + i\tilde{\alpha}_{R,zx}^{y,e} \tilde{\alpha}_{R,yx}^{z,h} & -\tilde{\alpha}_{R,xy}^{z,e} \tilde{\alpha}_{R,zy}^{x,h} + i\tilde{\alpha}_{R,yx}^{z,e} \tilde{\alpha}_{R,zx}^{y,h} & M_{14} \\
-\tilde{\alpha}_{R,zy}^{x,e} \tilde{\alpha}_{R,xy}^{z,h} - i\tilde{\alpha}_{R,zx}^{y,e} \tilde{\alpha}_{R,yx}^{z,h} & -\tilde{\alpha}_{R,zy}^{x,e} \tilde{\alpha}_{R,zy}^{x,h} - \tilde{\alpha}_{R,zx}^{y,e} \tilde{\alpha}_{R,zx}^{y,h} & M_{23} & \tilde{\alpha}_{R,xy}^{z,e} \tilde{\alpha}_{R,zy}^{x,h} - i\tilde{\alpha}_{R,yx}^{z,e} \tilde{\alpha}_{R,zx}^{y,h} \\
-\tilde{\alpha}_{R,xy}^{z,e} \tilde{\alpha}_{R,zy}^{x,h} - i\tilde{\alpha}_{R,yx}^{z,e} \tilde{\alpha}_{R,zx}^{y,h} & M_{32} & -\tilde{\alpha}_{R,zy}^{x,e} \tilde{\alpha}_{R,zy}^{x,h} - \tilde{\alpha}_{R,zx}^{y,e} \tilde{\alpha}_{R,zx}^{y,h} & \tilde{\alpha}_{R,zy}^{x,e} \tilde{\alpha}_{R,xy}^{z,h} - i\tilde{\alpha}_{R,zx}^{y,e} \tilde{\alpha}_{R,yx}^{z,h} \\
M_{41} & \tilde{\alpha}_{R,xy}^{z,e} \tilde{\alpha}_{R,zy}^{x,h} + i\tilde{\alpha}_{R,yx}^{z,e} \tilde{\alpha}_{R,zx}^{y,h} & \tilde{\alpha}_{R,zy}^{x,e} \tilde{\alpha}_{R,xy}^{z,h} + i\tilde{\alpha}_{R,zx}^{y,e} \tilde{\alpha}_{R,yx}^{z,h} & \tilde{\alpha}_{R,zy}^{x,e} \tilde{\alpha}_{R,zy}^{x,h} + \tilde{\alpha}_{R,zx}^{y,e} \tilde{\alpha}_{R,zx}^{y,h}
\end{array} \right), \quad (\text{S23})
\end{pmatrix}$$

where:

$$\begin{aligned}
M_{14} = M_{41}^* &= \tilde{\alpha}_{R,xy}^{z,e} \tilde{\alpha}_{R,xy}^{z,h} - \tilde{\alpha}_{R,yx}^{z,e} \tilde{\alpha}_{R,yx}^{z,h} + (\tilde{\alpha}_{R,xz}^{y,e} + i\tilde{\alpha}_{R,yz}^{x,e})(\tilde{\alpha}_{R,xz}^{y,h} + i\tilde{\alpha}_{R,yz}^{x,h}), \\
M_{23} = M_{32}^* &= \tilde{\alpha}_{R,xy}^{z,e} \tilde{\alpha}_{R,xy}^{z,h} + \tilde{\alpha}_{R,yx}^{z,e} \tilde{\alpha}_{R,yx}^{z,h} + (\tilde{\alpha}_{R,xz}^{y,e} + i\tilde{\alpha}_{R,yz}^{x,e})(\tilde{\alpha}_{R,xz}^{y,h} - i\tilde{\alpha}_{R,yz}^{x,h}).
\end{aligned} \quad (\text{S24})$$

The exciton fine structure can be found analytically from Eq. (S23) in the case when the Rashba anisotropy axis  $\mathbf{n}$  is aligned along one symmetry axis of the nanocrystal ( $n_x =$

$n_y = 0$ , and  $|n_z| = 1$ ). In this case, the energy level structure and the level polarization can be written:

Energy	Polarization
$\epsilon_d = \alpha_{R,xy}^{z,e} \alpha_{R,xy}^{z,h} + \alpha_{R,yx}^{z,e} \alpha_{R,yx}^{z,h}$	dark = $ d\rangle$
$\epsilon_x = \alpha_{R,xy}^{z,e} \alpha_{R,xy}^{z,h} - \alpha_{R,yx}^{z,e} \alpha_{R,yx}^{z,h}$	$ x\rangle$
$\epsilon_y = -\alpha_{R,xy}^{z,e} \alpha_{R,xy}^{z,h} + \alpha_{R,yx}^{z,e} \alpha_{R,yx}^{z,h}$	$ y\rangle$
$\epsilon_z = -\alpha_{R,xy}^{z,e} \alpha_{R,xy}^{z,h} - \alpha_{R,yx}^{z,e} \alpha_{R,yx}^{z,h}$	$ z\rangle$ ,

(S25)

where the energy is in units of  $(A_R^e - A_R^r)(2m_e m_h / M)$ . As a result, if the Rashba coefficient for both the electron,  $\alpha_{R,jk}^{i,e}$ , and hole,  $\alpha_{R,jk}^{i,h}$ , have the same sign, the upper exciton state is the dark exciton, and the lowest of the three optically active states is polarized along the anisotropy direction  $z$ . Generally, the two intermediate levels are split and have  $x$  and  $y$  polarization. When the electron and hole Rashba coefficients have the same sign, this means that the conduction band minimum and the valence band maximum have the same angular-momentum texture. That is, the angular-momentum helicity at the band extrema is the same [S25, S26]. Indeed, such co-helical textures have been found for certain distortions of the hybrid metal halide perovskite MAPbI<sub>3</sub> using first-principles calculations [S26]. In perovskite nanocrystals with cubic lattice symmetry, the Rashba coefficients can in principle be estimated using expressions derived from third-order perturbation theory within an extended Kane model [S27]. If only the near-band coupling (coupling between the conduction and valence bands) is taken into account, the Rashba coefficients for the electron and the hole would have opposite signs and therefore opposite angular-momentum textures. However, they can take on the same sign if coupling to remote bands is accounted for in quasi-degenerate (Lowdin) perturbation theory [S27]. This is consistent with the tight-binding models of refs. S25 and S26 where it has been shown that the relative helicity of the two bands in MAPbI<sub>3</sub> is controlled by the values of the  $sp$  and  $pp$  hopping parameters and the octahedral distortions of the Pb and the halogen atoms.

However, in the case when  $\alpha_{R,xy}^{z,e} = \alpha_{R,yx}^{z,e}$  and  $\alpha_{R,xy}^{z,h} = \alpha_{R,yx}^{z,h}$ , which occurs in nanocrystals with two equivalent symmetry axes, the  $x$  and  $y$  lines become degenerate and create a circularly polarized doublet, with polarization  $x \pm iy$ . The eigenvalues from Eq. (S25) are reduced to  $\epsilon_x = \epsilon_y = 0$  and  $\epsilon_z = -\epsilon_d$ . This level structure we believe was observed recently [S16]. The Rashba splitting between the two bright excitons in that case is described as

$$2m_e m_h (A_R^c - A_R^r) \epsilon_d / M.$$

Another analytical expression for the exciton fine structure can be found for the case when  $n_z = 0$  and  $n_x, n_y \neq 0$ . Diagonalization of the matrix described by Eq. (S23) gives energy levels, again in units of  $2m_e m_h (A_R^c - A_R^r) \epsilon_d / M$ , which can be written as:

$$\begin{aligned} \epsilon_1 &= \tilde{\alpha}_{R,zy}^{x,e} \tilde{\alpha}_{R,zy}^{x,h} + \tilde{\alpha}_{R,zx}^{y,e} \tilde{\alpha}_{R,zx}^{y,h} + Q, \\ \epsilon_2 &= \tilde{\alpha}_{R,zy}^{x,e} \tilde{\alpha}_{R,zy}^{x,h} + \tilde{\alpha}_{R,zx}^{y,e} \tilde{\alpha}_{R,zx}^{y,h} - Q, \\ \epsilon_3 &= -\tilde{\alpha}_{R,zy}^{x,e} \tilde{\alpha}_{R,zy}^{x,h} - \tilde{\alpha}_{R,zx}^{y,e} \tilde{\alpha}_{R,zx}^{y,h} + Q, \\ \epsilon_4 &= -\tilde{\alpha}_{R,zy}^{x,e} \tilde{\alpha}_{R,zy}^{x,h} - \tilde{\alpha}_{R,zx}^{y,e} \tilde{\alpha}_{R,zx}^{y,h} - Q, \end{aligned} \quad (\text{S26})$$

where  $Q = \sqrt{[(\tilde{\alpha}_{R,xz}^{y,e})^2 + (\tilde{\alpha}_{R,yz}^{x,e})^2][(\tilde{\alpha}_{R,xz}^{y,h})^2 + (\tilde{\alpha}_{R,yz}^{x,h})^2]}$ . The corresponding eigenstates can be written up to a normalization constant as:

$$\begin{aligned} |\psi_1\rangle &= \frac{i(\tilde{\alpha}_{R,xz}^{y,e} \tilde{\alpha}_{R,xz}^{y,h} + \tilde{\alpha}_{R,yz}^{x,e} \tilde{\alpha}_{R,yz}^{x,h} + Q)}{-\tilde{\alpha}_{R,yz}^{x,e} \tilde{\alpha}_{R,yz}^{x,h} + \tilde{\alpha}_{R,xz}^{y,e} \tilde{\alpha}_{R,xz}^{y,h}} |d\rangle + |z\rangle, \\ |\psi_2\rangle &= \frac{i(-\tilde{\alpha}_{R,xz}^{y,e} \tilde{\alpha}_{R,xz}^{y,h} - \tilde{\alpha}_{R,yz}^{x,e} \tilde{\alpha}_{R,yz}^{x,h} + Q)}{\tilde{\alpha}_{R,yz}^{x,e} \tilde{\alpha}_{R,yz}^{x,h} - \tilde{\alpha}_{R,xz}^{y,e} \tilde{\alpha}_{R,xz}^{y,h}} |d\rangle + |z\rangle, \\ |\psi_3\rangle &= \frac{-\tilde{\alpha}_{R,xz}^{y,e} \tilde{\alpha}_{R,xz}^{y,h} + \tilde{\alpha}_{R,yz}^{x,e} \tilde{\alpha}_{R,yz}^{x,h} - Q}{\tilde{\alpha}_{R,yz}^{x,e} \tilde{\alpha}_{R,yz}^{x,h} + \tilde{\alpha}_{R,xz}^{y,e} \tilde{\alpha}_{R,xz}^{y,h}} |x\rangle + |y\rangle, \\ |\psi_4\rangle &= \frac{-\tilde{\alpha}_{R,xz}^{y,e} \tilde{\alpha}_{R,xz}^{y,h} + \tilde{\alpha}_{R,yz}^{x,e} \tilde{\alpha}_{R,yz}^{x,h} + Q}{\tilde{\alpha}_{R,yz}^{x,e} \tilde{\alpha}_{R,yz}^{x,h} + \tilde{\alpha}_{R,xz}^{y,e} \tilde{\alpha}_{R,xz}^{y,h}} |x\rangle + |y\rangle. \end{aligned} \quad (\text{S27})$$

In this configuration, in which the Rashba asymmetry direction  $\mathbf{n}$  contains components along two nanocrystal symmetry axes, that is,  $\mathbf{n}$  lies in a mirror plane, the dark exciton is activated. It is easy to show that the directions of the dipoles of the former bright states remain orthogonal to each other, despite that their dipole orientations have been changed. The only non-orthogonal pair of dipoles here correspond to  $|\psi_1\rangle$  and  $|\psi_2\rangle$ , but they both are polarized along the same  $z$  direction.

Going further, we can consider a general orientation of the Rashba asymmetry axis. In that case, we have not yet found a closed-form solution to the expressions above. Nevertheless, it is clear that, for a general asymmetry direction  $\mathbf{n}$ , the dark state mixes with each of the bright states, creating a higher-order coupling between each state via the “dark” intermediate state. This results in the orthogonality of the dipoles being weakly broken. Numerical calculations have been performed that confirm this.

The results above can be understood in the context of group theory. If the Rashba asymmetry direction  $\mathbf{n}$  is parallel to any one symmetry axis of the orthorhombic nanocrystal,

the symmetry is reduced to  $C_{2v}$ . In that case, the dark state remains dipole inactive and the three bright states are split into mutually orthogonal, linearly polarized dipoles. But if the Rashba asymmetry also has a component along either of the other two axes, the symmetry is reduced further to  $C_s$  for which no dark state exists. Finally, for a general Rashba asymmetry direction, with components along all three nanocrystal symmetry axes, the symmetry is reduced to  $C_1$  for which all exciton states are coupled and as a result all dipole components are present for every state. These considerations are further discussed in Section S2.

### F. Rashba coefficient in inorganic perovskite nanocrystals

From the results from the previous subsection, Section S1.E, we now estimate the Rashba coefficients necessary to explain our experimental exciton fine-structure splittings, which are  $\sim 1$  meV. Specifically, we can exploit Eq. (S25). For simplicity, we assume that all Rashba coefficients for the electron and hole are equal to each other,  $\alpha_{R,jk}^{i,e} = \alpha_{R,jk}^{i,h} = \bar{\alpha}$  for any  $i$ ,  $j$ , and  $k$ , and that their effective masses are equal:  $m_e = m_h = M/2$ . The Rashba energy  $E_R = \bar{\alpha}^2 m_e / 2$  can then be found as

$$4E_R \times (A_R^c - A_R^r) \approx 1 \text{ meV}. \quad (\text{S28})$$

This gives  $E_R \approx 0.92$  meV. For comparison, in organic perovskites it was found to be 13 meV [S25]. It is more appropriate, however, to compare the Rashba coefficient  $\alpha_R$  rather than the Rashba energy between different materials, because the Rashba coefficient does not depend on the effective mass. Using  $m_e = 0.13$  for CsPbBr<sub>3</sub> from Table S1, we obtain for the traditional definition of the Rashba coefficient  $\alpha_R = \bar{\alpha} \hbar = 0.38$  eVÅ. For comparison, the measured value for InSb/InAsSb quantum wells is  $\alpha_R = 0.14$  eVÅ [S28]; in InGaAs/InP quantum wells,  $\alpha_R = 0.065$  eVÅ [S29], and in InAs quantum wells,  $\alpha_R = 0.22$  eVÅ [S30]. In organic–inorganic hybrid perovskites,  $\alpha_R$  is much larger due to their ferroelectricity:  $\alpha_R = 7 \pm 1$  eVÅ in ortho-CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub>; while  $\alpha_R = 11 \pm 4$  eVÅ in cubic-CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> [S31]. The value of  $\alpha_R$  we estimate from the experimental data is quite reasonable in comparison with other semiconductors. This leads us to conclude that the Rashba effect indeed is responsible for the observed exciton fine structure in the CsPbX<sub>3</sub> perovskite nanocrystals.

### G. The role of Fröhlich polarons in metal halide perovskite nanocrystals

It has been proposed that Fröhlich polarons (also known as large polarons) may play a role in the transport physics of hybrid organic–inorganic lead halide perovskites [S32]. Thus, one might question what role large polarons might play in the fine structure discussed in this work. However, large polarons do not contribute significantly to the exciton physics of the metal halide perovskites examined here. Such polar phonons interact with the total charge distribution of both the electron and hole. In our metal halide perovskites, the electron and hole effective masses are almost equal. Consequently, the wavefunctions of the electron and hole in the exciton are practically identical. Due to the resulting local charge neutrality within the exciton, the interaction between the exciton and polar phonons is negligible.

### S2. SYMMETRY ANALYSIS OF THE EXCITON FINE-STRUCTURE

Here we consider the point-group symmetry and irreducible representations appropriate for describing the band-edge excitons of quasi-cubic perovskite nanocrystals. Table S3 below shows how degeneracies and selection rules are modified as we descend in symmetry from cubic ( $O_h$ ) to tetragonal ( $D_{4h}$ ) or orthorhombic ( $D_{2h}$ ) due to lattice or shape distortions. Note that in the table, the irreducible representation labels are given for the nanocrystal point group rather than the bulk space group. For each of these “parent” point groups, we also show the symmetry breaking effect of a Rashba asymmetry for different orientations  $\mathbf{n}$  of the asymmetry axis. The groupings for each parent group ( $O_h$ ,  $D_{4h}$ , and  $D_{2h}$ ) are separated by double vertical lines in Table S3. Optical selection rules for exciton transitions are shown in Table S3 by writing the allowed transition-dipole components for each exciton irreducible representation as  $x, y, z$  for linear polarized dipoles or  $\sigma_{\pm}$  for circular polarization. In constructing the table, we utilized the irreducible representation labels, and the character and multiplication tables of KDWS [S3].

The results summarized in the table show that the cubic perovskite band-edge exciton fine structure consists of a threefold degenerate (triplet) bright state split from a singlet dark state. As the nanocrystal symmetry is reduced by unit-cell or shape distortions the bright triplet is expected to split. For the tetragonal phase  $D_{4h}$ , the triplet splits into a singlet linearly polarized along the axis of symmetry and a doublet circularly polarized in the

plane perpendicular to the symmetry axis. An orthorhombic distortion of  $D_{2h}$  symmetry will split the bright triplet into three non-degenerate states each linearly polarized along the orthorhombic symmetry axes as follows:  $\Gamma_4^-(\sigma_+, \sigma_-, z) \rightarrow \Gamma_2^-(y) + \Gamma_3^-(z) + \Gamma_4^-(x)$ .

The addition of a Rashba asymmetry further breaks the symmetry of the nanocrystal beyond the shape or lattice distortions just discussed. A Rashba asymmetry directed along the  $z$ -axis breaks the symmetry of cubic ( $O_h$ ) and tetragonal ( $D_{4h}$ ) nanocrystals to  $C_{4v}$ , characterized by a dark singlet, a bright doublet and a linearly polarized singlet. The effect of a Rashba asymmetry along the  $z$  axis of an orthorhombic nanocrystal takes the symmetry from  $D_{2h}$  to  $C_{2v}$ , maintaining the dark state and three linearly polarized, orthogonal bright excitons. However, if the Rashba asymmetry is directed off the principle axis, the symmetry reduces to  $C_s$  in the case that the asymmetry is oriented within a mirror plane of the nanocrystal, and to  $C_1$  otherwise. In both cases, the dark exciton state is mixed with the bright excitons. In the case of symmetry  $C_s$ , the Rashba asymmetry further mixes two of the bright excitons; in the lowest symmetry case, all bright excitons are mixed and the orthogonality of the dipoles is broken, at least in principle. Calculations show, however, that this mixing is a second-order effect and the resulting non-orthogonality of the dipoles is expected to be weak.

Note that in Table S3, where relevant, the  $z$ -axis is taken as the principle axis unless otherwise specified as a superscript on the group symbol. The  $x, y$  axes are then the axes associated with other symmetry elements such as  $C_2$  rotations where they exist. When a Rashba asymmetry is oriented along a particular direction that creates a mirror plane, this mirror plane is given as a superscript on the point-group symbol. For example,  $C_s^{\sigma_{xz}}$  denotes the  $C_s$  point group defined with a mirror plane  $\sigma_{xz}$  containing the  $z$  and  $x$  axes.



TABLE S3. Descent of symmetry for band-edge excitons in quasi-cubic perovskite nanocrystals: Point group  $O_h$  and its subgroups. Rashba fields are described in the table in terms of an asymmetry direction  $\mathbf{n} = n_x\hat{x} + n_y\hat{y} + n_z\hat{z}$  as in Section S1.E. See text for explanation.

$O_h$	$C_{4v}$ ( $O_h$ $+n_z\hat{z}$ )	$D_{4h}$	$C_{4v}^z$ ( $D_{4h}$ $+n_z\hat{z}$ )	$C_{2v}^x$ ( $D_{4h}$ $+n_x\hat{x}$ )	$C_s^{\sigma_{xz}}$ ( $C_{4v}$ $+n_x\hat{x}$ )	$D_{2h}$	$C_{2v}$ ( $D_{2h}$ $+n_z\hat{z}$ )	$C_s^{\sigma_{xz}}$ ( $C_{2v}^z$ $+n_x\hat{x}$ )	$C_1$ ( $C_s^{\sigma_{xz}}$ $+n_y\hat{y}$ )
$\Gamma_1^-$ (d)	$\Gamma_2$ (d)	$\Gamma_1^-$ (d)	$\Gamma_2$ (d)	$\Gamma_3$ (d) $\Gamma_1$ (x)	$\Gamma_2$ (y) $\Gamma_1$ (x, z)	$\Gamma_1^-$ (d)	$\Gamma_3$ (d) $\Gamma_4^-$ (x)	$\Gamma_2$ (y) $\Gamma_2$ (x)	$\Gamma_1$ (x,y,z) $\Gamma_1$ (x,y,z)
$\Gamma_4^-$ (z, $\sigma_{\pm}$ )	$\Gamma_5$ ( $\sigma_{\pm}$ ) $\Gamma_1$ (z)	$\Gamma_5^-$ ( $\sigma_{\pm}$ ) $\Gamma_2^-$ (z)	$\Gamma_5$ ( $\sigma_{\pm}$ ) $\Gamma_1$ (z)	$\Gamma_2$ (y) $\Gamma_4$ (z)	$\Gamma_2$ (y) $\Gamma_1$ (z, x)	$\Gamma_2^-$ (y) $\Gamma_3^-$ (z)	$\Gamma_4$ (y) $\Gamma_1$ (z)	$\Gamma_2$ (y) $\Gamma_1$ (z, x)	$\Gamma_1$ (x,y,z) $\Gamma_1$ (x,y,z)

### S3. CALCULATION OF EXCITON AND TRION RADIATIVE LIFETIMES

#### A. Radiative lifetime of excitons in cube-shaped nanocrystals

The probability of optical excitation of, or recombination from, any exciton state  $|\Psi^{ex}\rangle$  is proportional to the square of the matrix element of the operator  $\mathbf{e}\hat{\mathbf{p}}$  between that state and the vacuum state, where  $\mathbf{e}$  is the polarization vector of the emitted or absorbed light, and  $\hat{\mathbf{p}}$  is the momentum operator. In cube-shaped nanocrystals, the calculation of these matrix elements is complicated by the fact that the electric field of a photon inside the nanocrystal not only changes its value from outside due to dielectric screening, as in spherical nanocrystals, but it also becomes inhomogeneous.

As we discussed in Section S1.E, the triplet state in perovskite nanocrystals with orthorhombic symmetry is always split into three orthogonal dipoles with the same oscillator transition strength. Therefore, let us consider the optical transition to the triplet exciton state with  $J_z = 0$ , which has a linear  $z$  dipole. The square of this matrix element can be written:

$$|\langle 0 | [\mathbf{e}^z(\mathbf{r})/E_{\infty}^z] \cdot \hat{\mathbf{p}} | \Psi_{1,0}^{ex} \rangle|^2 = \frac{2}{3} P^2 I_{\parallel}^2, \quad (\text{S29})$$

where  $I_{\parallel} = \int d^3r e_z^z(\mathbf{r}) v(\mathbf{r}, \mathbf{r}) / E_{\infty}^z$ , and  $e_z^z(\mathbf{r})$  is the  $z$  component of the electric field of the light in the nanocrystal created by a photon with an electric field  $E_{\infty}^z$ , which is linearly polarized along  $z$  and defined at infinite distance from the nanocrystal. The inhomogeneous distributions of the electric field in the cube-shaped nanocrystals created by the external

homogeneous electric field is calculated in the next subsection, Section S3.B, for various ratios of dielectric constants and are shown in Fig. 2e of the main text. Due to the even parity of the electron and hole envelope functions participating in the band-edge optical transitions  $I_{\perp} = \int d^3r e_x^z(\mathbf{r})v(\mathbf{r}, \mathbf{r})/E_{\infty}^z = \int d^3r e_y^z(\mathbf{r})v(\mathbf{r}, \mathbf{r})/E_{\infty}^z = 0$ . This analysis shows that despite the inhomogeneous distribution of the photon electric field in the cube-shaped nanocrystals, the linearly polarized dipoles of each sublevel of the triplet only emit or absorb photons having a nonzero electric-field projection on the respective dipole orientation. In short, the linearly polarized dipoles emit linearly polarized light.

Substituting the matrix elements from Eq. (S29) into the expression for the radiative decay rate from ref. S33 we find the radiative lifetime of the triplet exciton  $\tau_{ex}$ :

$$\frac{1}{\tau_{ex}} = \frac{4e^2\omega n}{3\hbar m_0^2 c^3} |\langle 0 | [\mathbf{e}(\mathbf{r})/E_{\infty}^z] \hat{\mathbf{p}} | \Psi_{1,0}^{ex} \rangle|^2 = \frac{4\omega n E_p}{9 \cdot 137 m_0 c^2} I_{\parallel}^2, \quad (\text{S30})$$

where  $\omega$  is the transition (angular) frequency,  $n$  is the refractive index of the surrounding media,  $m_0$  is the free-electron mass,  $c$  is the speed of light in vacuum, and  $E_p = 2P^2/m_0$  is the Kane energy. The calculated radiative lifetimes in perovskite nanocrystals can be directly compared with experimental results at low temperature because the experimental data are not obscured by contributions of a low-energy dark exciton. The largest uncertainty in the radiative lifetime defined by Eq. (S30) is connected to the uncertainty in the high-frequency dielectric constant,  $\epsilon_{in}$ , for the perovskites, which together with  $\epsilon_{out} = n^2$  determines the depolarization of the photon electric field in the nanocrystals.

Using Eq. (S30) we have calculated the radiative lifetimes in CsPbX<sub>3</sub> (X=I, Br, and Cl) nanocrystals and their optical-transition energies. These are plotted in Fig. 2b in the main text. In these calculations, we used the energy-band parameters and dielectric constants from Table S1 and a refractive index of  $n = 1.6$  for the surrounding medium, which yields  $\epsilon_{out} = n^2$ . Calculations were conducted for the three nanocrystal size regimes: (i) strong spatial confinement when the nanocrystal size  $L$  is smaller than the exciton Bohr radius  $a_B$ , (ii) weak spatial confinement when  $L \gg a_B$ , and (iii) intermediate confinement when  $L \sim a_B$ . The discussion of these three cases is presented further in Section S3.C.

## B. Calculation of the interior electric field in cube-shaped nanocrystals

We consider the inhomogeneous electric field inside a cube-shaped nanocrystal, modeled as a dielectric cube. The field is induced by an arbitrarily oriented electric field that is homogeneous at a large distance from the cube. Such a field can always be decomposed into three components created independently by the three projections of this remote electric field along the cube axes. In Fig. 2e in the main text, we show the distribution of the normalized  $z$  component of the electric-field magnitude,  $E_z^z/E_\infty^z$ , in the cross-section passing through the middle of the cube, created by a homogeneous external electric field,  $\mathbf{E}_\infty^z \parallel \mathbf{z}$ , calculated for several ratios of internal  $\epsilon_{in}$  to external  $\epsilon_{out}$  dielectric constants. We describe here the approach followed to compute it.

The generalized Gauss's law states that the total electric flux through any closed surface in space of any shape drawn in an electric field is proportional to the total electric charge enclosed by the surface. The differential expression of this law, obtained via the divergence theorem, represents the local conservation of charge in the form of the well known partial differential equation (PDE)

$$\nabla \cdot (\epsilon \mathbf{E}) = \rho_v, \quad (\text{S31})$$

where  $\epsilon$  and  $\rho_v$  represent the electric permittivity (dielectric constant) of the medium and the electric charge density, respectively. In the context of electrostatics, the electric field is computed as the negative gradient of the electric potential scalar field  $\phi$ , which, together with the charge conservation Eq. (S31), yields

$$\nabla \cdot (\epsilon \nabla \phi) = -\rho_v, \quad (\text{S32})$$

which is Poisson's equation for the electric potential. This PDE is discretized and solved numerically using the finite element method (FEM). It is applied for a computational domain that involves a rectangular electrode capacitor configuration where the upper electrode is set to  $\phi = 1 \text{ V}$  and the bottom one is grounded at  $\phi = 0 \text{ V}$ .

The proper distance between the capacitor plates in relation to the size of the embedded dielectric cube was determined by performing successive FEM analyses at various distances such that the far-field difference among all solutions remained less than 1% for various values of the dielectric constants. The distribution of both the electric potential and the electric-field magnitude along the  $z$ -axis line that coincides with the intersection of the  $zx$

and  $zy$  planes as it extends between the two electrodes of the capacitor assembly is shown in Extended Data Fig. 5 for the final selected configuration.

Contour plots of the normalized electric-field magnitude,  $E_z^z/E_\infty^z$ , as a function of the ratio  $\epsilon_{in}/\epsilon_{out}$  are displayed in Extended Data Fig. 6a-d. This figure shows that as the  $\epsilon_{in}/\epsilon_{out}$  ratio increases (from 4 to 6, 8, and 10, respectively), the overall magnitude of  $E_z^z/E_\infty^z$  decreases. It should also be noted that the perturbations of the contours near the corners are artifacts of the interpolation resolution utilized by the software employed to construct them.

A contour plot of the normalized electric-field component  $E_z^z/E_\infty^z$  on the  $xz$  mid-plane for  $\epsilon_{in}/\epsilon_{out}$  of 6 is shown in Fig. 2e in the main text. By symmetry this is also valid for the  $yz$  mid-plane. Contours for the normalized electric-field component  $E_x^z/E_\infty^z$  for the  $xz$  mid-plane are shown in Extended Data Fig. 6e for the case of  $\epsilon_{in}/\epsilon_{out} = 9$ . Note that the  $E_y^z/E_\infty^z$  distribution on the  $yz$  mid-plane is identical to Extended Data Fig. 6e.

### C. The exciton-photon coupling strength in cube-shaped nanocrystals

The coupling strength between the exciton dipole and the inhomogeneous electric field of a photon in a cube-shaped nanocrystal is controlled by the square of the integral  $I_{\parallel}$  [see Eq.(S29)]:

$$I_{\parallel} = \int d^3r e_z^z(\mathbf{r}) v(\mathbf{r}, \mathbf{r}) / E_\infty^z. \quad (\text{S33})$$

In the strong-confinement regime, when the exciton Bohr radius  $a_B$  is larger than the nanocrystal size  $L$ , then  $v(\mathbf{r}, \mathbf{r}) = |\Phi_{\text{gr}}^c(\mathbf{r})|^2$ . The ground-state wavefunctions of electrons or holes can be written as  $\Phi_{\text{gr}}^c(x, y, z) = (2/L)^{3/2} \cos(\pi x/L) \cos(\pi y/L) \cos(\pi z/L)$ , where  $L$  is the cube edge length. Introducing dimensionless variables  $\tilde{x} = x/L$ ,  $\tilde{y} = y/L$ , and  $\tilde{z} = z/L$ , we can rewrite  $I_{\parallel}$  in dimensionless form:

$$I_{\parallel}^{\text{strong}} = 8 \int_{-0.5}^{0.5} d\tilde{x} \int_{-0.5}^{0.5} d\tilde{y} \int_{-0.5}^{0.5} d\tilde{z} [e_z^z(\tilde{x}, \tilde{y}, \tilde{z}) / E_\infty^z] \cos^2(\pi\tilde{x}) \cos^2(\pi\tilde{y}) \cos^2(\pi\tilde{z}). \quad (\text{S34})$$

This expression was used in Eq. (S30) to calculate the radiative lifetimes of CsPbX<sub>3</sub> (X=I, Br, and Cl) nanocrystals with  $L = 6$  and  $7$  nm,  $L = 5$  and  $6$  nm, and  $L = 4$  and  $5$  nm, respectively. The energy of the optical transition in this limit is well described by  $\hbar\omega = E_g + (3\hbar^2\pi^2/2\mu L^2) - 3.05e^2/\epsilon_{in}L$ , where  $E_g$  is the bulk energy gap of the perovskite

and  $\mu = (1/m_e + 1/m_h)^{-1}$  is the reduced effective mass of the exciton. We used the energy-band parameters of the perovskites from Table S1.

In the weak-confinement regime, when  $L \gg a_B$ , the exciton wavefunction can be written as a product of the relative motion of the electron and hole  $\phi(\mathbf{r}_e - \mathbf{r}_h)$  and the exciton center-of-mass motion confined in the nanocrystal,  $\Phi_{\text{gr}}^c(\mathbf{R})$ , where  $\mathbf{R} = (m_e \mathbf{r}_e + m_h \mathbf{r}_h)/M$  and  $M = m_e + m_h$  is the exciton effective mass [S9]:  $v(\mathbf{r}_e, \mathbf{r}_h) = \phi(\mathbf{r}_e - \mathbf{r}_h)\Phi_{\text{gr}}^c(\mathbf{R})$ . In the weak-confinement regime it is more convenient to directly calculate  $I_{\parallel}^2$ :

$$(I_{\parallel}^{\text{weak}})^2 = \frac{8}{\pi} \frac{V}{a_B^3} \left| \int_{-0.5}^{0.5} d\tilde{x} \int_{-0.5}^{0.5} d\tilde{y} \int_{-0.5}^{0.5} d\tilde{z} \frac{e_z^z(\tilde{x}, \tilde{y}, \tilde{z})}{E_{\infty}^z} \cos(\pi\tilde{x}) \cos(\pi\tilde{y}) \cos(\pi\tilde{z}) \right|^2, \quad (\text{S35})$$

where  $V = L^3$  is the volume of the cube-shaped nanocrystal. One can see that under weak confinement, the ratio  $V/a_B^3$  in  $I_{\parallel}^2$  dramatically shortens the radiative decay times of the exciton in Eq.(S30) due to its giant oscillator transition strength [S34]. The energy of the optical transitions in the weak-confinement regime is described as  $\hbar\omega = E_g - E_B + 3\hbar^2\pi^2/2ML^2$ , where  $E_B = e^4\mu/(2\hbar^2\epsilon_{\text{in}}^2) = \hbar^2/(2\mu a_B^2)$  is the exciton binding energy.

Figure 2b in the main text shows the results of the calculations of the exciton radiative lifetime in perovskite nanocrystals with  $L = 17$  to 25 nm. One can see that the lifetime is strongly reduced, becoming shorter than 100 ps in CsPbBr<sub>3</sub> and CsPbCl<sub>3</sub> nanocrystals. Further, one can see in Fig. 2b that the experimentally measured decay times are in between the lifetimes predicted for strong ( $L \ll a_B$ ) and weak ( $L \gg a_B$ ) confinement. This is because the correlation of the electron and hole motion in nanocrystals, which shortens the radiative decay time, can already be seen in nanocrystals with intermediate size  $L \geq a_B$ . To demonstrate this, we studied the energy of the confined excitons in nanocrystals with  $L \geq a_B$  using a one-parameter ansatz function:

$$v(\mathbf{r}_e, \mathbf{r}_h) = C e^{-\beta|\mathbf{r}_e - \mathbf{r}_h|} \Phi_{\text{gr}}^c(\mathbf{r}_e) \Phi_{\text{gr}}^c(\mathbf{r}_h), \quad (\text{S36})$$

where  $\beta$  is a variational parameter and  $C$  is a normalization constant determined by the condition  $\int d^3r_e d^3r_h v^2(\mathbf{r}_e, \mathbf{r}_h) = 1$ . Using the results of these calculations (see the next subsection, Section S3.D) we show in Fig. 2b in the main text the exciton radiative lifetimes of CsPbX<sub>3</sub> nanocrystals (X=I, Br, and Cl) with  $L = 6$  to 16 nm,  $L = 5$  to 16 nm, and  $L = 4$  to 16 nm, respectively.

### D. Variational calculation for the intermediate-confinement regime

In the variational approach we calculate the expectation value of the two-particle Hamiltonian in a cube with edge length  $L$  and minimize this with respect to the variational parameter  $\beta$ . The Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{\hbar^2}{2m_h}\nabla_h^2 - \frac{e^2}{\epsilon_{in}|\mathbf{r}_e - \mathbf{r}_h|}. \quad (\text{S37})$$

Introducing the dimensionless variables  $\tilde{\mathbf{r}}_e = \mathbf{r}_e/L$ ,  $\tilde{\mathbf{r}}_h = \mathbf{r}_h/L$ , and the dimensionless parameter  $b = \beta L$ , the expectation value  $\langle v|\hat{H}|v\rangle$  reduces to the calculation of three dimensionless integrals. The first integral describes the average kinetic energy:

$$I_1(b) = \int_{-1/2}^{1/2} d^3\tilde{r}_1 \int_{-1/2}^{1/2} d^3\tilde{r}_2 e^{-b|\tilde{\mathbf{r}}_1 - \tilde{\mathbf{r}}_2|} \tilde{\Phi}_{\text{gr}}^c(\tilde{\mathbf{r}}_1) \tilde{\Phi}_{\text{gr}}^c(\tilde{\mathbf{r}}_2) \nabla_{\tilde{\mathbf{r}}_1}^2 e^{-b|\tilde{\mathbf{r}}_1 - \tilde{\mathbf{r}}_2|} \tilde{\Phi}_{\text{gr}}^c(\tilde{\mathbf{r}}_1) \tilde{\Phi}_{\text{gr}}^c(\tilde{\mathbf{r}}_2), \quad (\text{S38})$$

where  $\tilde{\Phi}_{\text{gr}}^c(\tilde{x}, \tilde{y}, \tilde{z}) = \cos(\pi\tilde{x})\cos(\pi\tilde{y})\cos(\pi\tilde{z})$ . The second integral describes the average Coulomb interaction:

$$I_2(b) = \int_{-1/2}^{1/2} d^3\tilde{r}_1 \int_{-1/2}^{1/2} d^3\tilde{r}_2 \frac{1}{|\tilde{\mathbf{r}}_1 - \tilde{\mathbf{r}}_2|} \left( e^{-b|\tilde{\mathbf{r}}_1 - \tilde{\mathbf{r}}_2|} \tilde{\Phi}_{\text{gr}}^c(\tilde{\mathbf{r}}_1) \tilde{\Phi}_{\text{gr}}^c(\tilde{\mathbf{r}}_2) \right)^2. \quad (\text{S39})$$

Finally, the third integral determines the normalization constant  $C$ :

$$I_3(b) = \int_{-1/2}^{1/2} d^3\tilde{r}_1 \int_{-1/2}^{1/2} d^3\tilde{r}_2 \left( e^{-b|\tilde{\mathbf{r}}_1 - \tilde{\mathbf{r}}_2|} \tilde{\Phi}_{\text{gr}}^c(\tilde{\mathbf{r}}_1) \tilde{\Phi}_{\text{gr}}^c(\tilde{\mathbf{r}}_2) \right)^2. \quad (\text{S40})$$

The normalization constant is connected with this integral as  $C = L^{-3}/\sqrt{I_3(b)}$ .

Using the integrals defined in Eqs. (S38), (S39), and (S40), we can rewrite the expectation value of the Hamiltonian as,

$$\langle \Psi(b)|H|\Psi(b)\rangle = -\frac{\hbar^2}{m_e L^2} \left[ \frac{1}{2} \left( 1 + \frac{m_e}{m_h} \right) \frac{I_1(b)}{I_3(b)} + \frac{L}{a_e} \frac{I_2(b)}{I_3(b)} \right], \quad (\text{S41})$$

where  $a_e$  is the electron Bohr radius:  $a_e = \epsilon_{in}\hbar^2/(m_e e^2)$ . We find the dependence of all three integrals on  $b$  using Monte-Carlo integration and determine the value of  $b$  that minimizes the energy for a range of the ratios  $L/a_e$ . The results of these calculations are shown in Extended Data Fig. 8a.

Now we can calculate  $I_{\parallel}$ , which is defined as

$$I_{\parallel} = \int d^3r [e_z^z(\mathbf{r})/E_{\infty}^z] v(\mathbf{r}, \mathbf{r}). \quad (\text{S42})$$

Using the ansatz function definition in Eq.(S36) and the relation of the normalization constant  $C$  with  $I_3(b)$ , we can directly connect  $I_{\parallel}^{inter}$  in the intermediate-confinement regime with the corresponding result in the strong-confinement limit,  $I_{\parallel}^{strong}$ , defined in Eq.(S34):

$$I_{\parallel}^{inter}(\epsilon_{in}/\epsilon_{out}, b) = \frac{1}{8\sqrt{I_3(b)}} I_{\parallel}^{str}(\epsilon_{in}/\epsilon_{out}) . \quad (\text{S43})$$

The radiative lifetime is proportional to  $I_{\parallel}^2$ . To describe the dependence of the radiative lifetime on the nanocrystal size,  $L$ , we plot the dependence  $|I_{\parallel}^{inter}/I_{\parallel}^{strong}|^2$  as a function  $L/a_e$  in Extended Data Fig. 8b.

### E. Radiative lifetime in spherical nanocrystals

It is interesting to compare the radiative lifetimes obtained for spherical and cube-shaped nanocrystals. In spherical nanocrystals, the electric field of the photon is homogeneous and the ratio  $\mathbf{e}(\mathbf{r}_e)/E_{\infty}$  at each point  $\mathbf{r}$  of the nanocrystal is equal to the depolarization factor  $\mathcal{D} = 3\epsilon_{out}/(2\epsilon_{out} + \epsilon_{in})$ . Substituting this ratio into Eq. (S30) we find the radiative lifetime of the triplet exciton  $\tau_{ex}$  in spherical nanocrystals:

$$\frac{1}{\tau_{ex}} = \frac{4\omega n E_p}{9 \cdot 137 m_0 c^2} \mathcal{D}^2 K, \quad (\text{S44})$$

where  $K = |\int d^3r v(\mathbf{r}, \mathbf{r})|^2$  is the overlap integral squared.

The radiative lifetime defined in Eq. (S44) depends strongly on the nanocrystal radius  $a$  via the size dependence of the overlap integral  $K$ . In small nanocrystals that are in the strong-confinement regime ( $a < a_B$ ), the photoluminescence is determined by the optical transitions between the ground quantum confinement levels of the electrons and holes [S9]. In this case, the exciton wavefunction  $v(\mathbf{r}, \mathbf{r}) = \Phi_{gr}^2(\mathbf{r})$  is the product of the two identical wavefunctions  $\Phi_{gr}^s(\mathbf{r}) = \sqrt{1/2\pi a} \sin(\pi r/a)/r$  for the electron and hole ground states resulting in  $K = 1$  independent of size. The radiative lifetime in Eq.(S44) also weakly depends on nanocrystal size via the size dependence of the transition frequency,  $1/\tau_{ex} \propto \omega$ .

In the weak-confinement regime, when the nanocrystal radius  $a \gg a_B$ , shortening of the radiative lifetime is expected at low temperatures due to the giant oscillator transition strength of the exciton localized in the nanocrystal [S34]. As discussed in Section S3.C, the exciton wavefunction can then be written as a product of the relative motion of the electron and hole  $\phi(\mathbf{r}_e - \mathbf{r}_h)$  and the exciton center-of-mass motion confined in the nanocrystal.

For spherical nanocrystals, the latter is  $\Phi_{\text{gr}}^s(\mathbf{R})$  yielding:  $v(\mathbf{r}_e, \mathbf{r}_h) = \phi(\mathbf{r}_e - \mathbf{r}_h)\Phi_{\text{gr}}^s(\mathbf{R})$ . Substituting this wavefunction into the overlap integral gives [S9]:  $K = (8/\pi^2)(a/a_B)^3$ . The resulting dramatic increase of  $K$  is due to the correlation of the electron and hole motion, increasing the oscillator transition strength and shortening of the radiative lifetime. This shortening can already be observed in nanocrystals with radius  $a \geq a_B$ .

The ratio of the exciton radiative lifetime in spherical and cube-shaped nanocrystals that have the same volume is equal to  $I_{\parallel}^2/K\mathcal{D}^2$ . The result of this comparison is shown in the inset of Fig. 2e in the main text for nanocrystals in the strong- and the weak-confinement regimes. One can see that the exciton radiative lifetime in spherical nanocrystals is always shorter than in cube-shaped nanocrystals of the same volume. This is because the electric field of the photon in spherical nanocrystals is larger than the average field in cube-shaped nanocrystals.

## F. Trion radiative lifetime and polarization

The electron spin is not conserved during optical transitions in perovskite nanocrystals. As a result the trion optical transition rate is given by summing over the two possible radiative transitions the trion can undergo. The rate is the same for both positive and negative trions. Using the notation introduced in the main text, we can write for the positive trion in the strong-confinement regime:

$$\frac{1}{\tau_{\text{trion}}} = \frac{4e^2\omega n}{3\hbar m_0^2 c^3} (|\langle \Psi_{\uparrow}^e | [e_z^z(\mathbf{r}_e)/E_{\infty}^z] \hat{p}_z | \Psi_{\uparrow}^h \rangle|^2 + |\langle \Psi_{\uparrow}^e | e_x^x(\mathbf{r}_e)/E_{\infty}^x \hat{p}_x | \Psi_{\downarrow}^h \rangle|^2 + |\langle \Psi_{\uparrow}^e | e_y^y(\mathbf{r}_e)/E_{\infty}^y \hat{p}_y | \Psi_{\downarrow}^h \rangle|^2) . \quad (\text{S45})$$

The three matrix elements in Eq.(S45) describe transitions that are accomplished by emission of photons with three different orthogonal polarizations. All these matrix elements are equal to each other, and as a result, the trion photoluminescence is not polarized. This can be confirmed by symmetry analysis. For nanocrystals of cubic symmetry (point group  $O_h$ ), electrons and holes have symmetry  $\Gamma_6^{\mp}$ , respectively, and are two-fold degenerate. Therefore, a positive/negative trion has symmetry  $\Gamma_6^{\mp}$  and is also two-fold degenerate, since  $\Gamma_6^+ \times \Gamma_6^- \times \Gamma_6^{\pm} = \Gamma_6^{\mp}$ . Moreover, optical decay from a trion state to a single-carrier state is allowed for all polarizations: The x, y, and z components of the dipole operator all transform as  $\Gamma_4^-$ , and  $\Gamma_6^{\mp} \times \Gamma_4^-$  contains  $\Gamma_6^{\pm}$ . Furthermore, the matrix elements are equal for the x, y, and z components by symmetry.



For nanocrystals with orthorhombic symmetry we arrive at similar conclusions: Electrons and holes have symmetry  $\Gamma_5^\mp$  respectively; the positive/negative trion has symmetry  $\Gamma_5^\mp$  since  $\Gamma_5^+ \times \Gamma_5^- \times \Gamma_5^\pm = \Gamma_5^\mp$ . Again, dipole transitions are allowed for all polarizations since  $x$ ,  $y$ , and  $z$  transform as  $\Gamma_4^-$ ,  $\Gamma_2^-$ , and  $\Gamma_3^-$ , respectively, and  $\Gamma_5^\mp \times \Gamma_n^- = \Gamma_5^\pm$  for  $n = 2, 3$ , or  $4$ . Given that the initial and final states involved in these transitions are twofold degenerate, it is also clear by symmetry that the trion emission has no fine structure.

Expressing the matrix elements via  $I_{\parallel}$ , we obtain for the trion lifetime

$$\frac{1}{\tau_{\text{trion}}} = \frac{2\omega n E_p}{3 \cdot 137 m_0 c^2} (I_{\parallel}^{\text{str}})^2. \quad (\text{S46})$$

Comparison of this expression with the exciton radiative lifetime in the strong-confinement regime from Eq. (S30) shows that trion lifetime is shorter:  $\tau_{\text{trion}} = (2/3)\tau_{ex}$ .

In Fig. 2b in the main text we show the experimental decay times measured in perovskite nanocrystals via single-nanocrystal experiments. The photoluminescence traces shown in Fig. 2c,d demonstrate A-type blinking [S35], during which the drops in photoluminescence intensity are correlated with shortening of the decay time. The intermittency of the photoluminescence intensity and the decay time is connected with switching between trion and exciton emission as a result of nanocrystal charging. As a result Fig. 2 provides direct information on the exciton radiative lifetime. The radiative decay time of the trion is 1.5 times faster than that of the exciton. The  $\sim 2.5$ -fold drop in photoluminescence intensity suggests however that for these nanocrystals, non-radiative Auger recombination significantly contributes to the decay, further shortening the trion lifetime.

Another indicator to distinguish between exciton transitions and those from trions is their polarization dependence. According to Fig. 3a-c, we observe that excitonic transitions exhibit typical dipolar emission with a high degree of linear polarization. In Extended Data Fig. 3a we plot the spectrum of a single CsPbBr<sub>2</sub>Cl nanocrystal that exhibits two emission peaks at 2.5158 and 2.5175 eV and an additional trion-emission peak that is red-shifted by approximately 16 meV. For measuring the polarization, we analyzed the emitted intensity of both exciton peaks and the trion peak as function of the linear polarizer angle in front of the spectrograph, which can be seen in Extended Data Fig. 3b. Both exciton peaks, depicted in blue and red, show again typical dipolar emission along different axes of polarization, which are indicated by the blue and red straight lines. The trion peak is essentially unpolarized, in agreement with theory.

#### S4. RELATIVE INTENSITIES OF PHOTOLUMINESCENCE FROM THREE ORTHOGONAL DIPOLES AND THEIR POLARIZATION PROPERTIES

The relative intensity of the photoluminescence created by three orthogonal emitting dipoles polarized along the  $\mathbf{x}$ ,  $\mathbf{y}$ , and  $\mathbf{z}$  axes and its polarization properties depend on the observation direction. The probability of emitting light for each of the dipoles is proportional to  $\propto |\mathbf{e} \cdot \mathbf{x}|^2$ ,  $\propto |\mathbf{e} \cdot \mathbf{y}|^2$ , and  $\propto |\mathbf{e} \cdot \mathbf{z}|^2$ , where the polarization unit vector  $\mathbf{e}$  is perpendicular to the light-propagation direction. To calculate these dependences we denote the light-propagation direction by the unit vector  $\mathbf{u}$  with components given by

$$\begin{aligned} u_x &= \sin \theta \cos \phi, \\ u_y &= \sin \theta \sin \phi, \\ u_z &= \cos \theta, \end{aligned} \quad (\text{S47})$$

where  $\theta, \phi$  are the standard polar angles. We then form a light polarization unit vector  $\mathbf{e}$  in the plane perpendicular to  $\mathbf{u}$  by

$$\mathbf{e} = (0, -u_z, u_y) / \sqrt{u_z^2 + u_y^2}. \quad (\text{S48})$$

Finally, we gradually rotate the vector  $\mathbf{e}$  around  $\mathbf{u}$  and calculate the scalar products of the form  $\propto |\mathbf{e} \cdot \mathbf{x}|^2$ ,  $\propto |\mathbf{e} \cdot \mathbf{y}|^2$ ,  $\propto |\mathbf{e} \cdot \mathbf{z}|^2$  at each angle. Each one of these scalar products represents the probability that the corresponding dipole will emit light in the direction  $\mathbf{u}$  with linear polarization  $\mathbf{e}$ .

The rotation of  $\mathbf{e}$  around  $\mathbf{u}$  is performed using the following transformation

$$\begin{pmatrix} e_x \\ e_y \\ e_z \end{pmatrix} \rightarrow \begin{pmatrix} Cs + u_x^2(1 - Cs) & u_x u_y(1 - Cs) - u_z Si & u_x u_z(1 - Cs) + u_y Si \\ u_y u_x(1 - Cs) + u_z Si & Cs + u_y^2(1 - Cs) & u_y u_z(1 - Cs) - u_x Si \\ u_z u_x(1 - Cs) - u_y Si & u_z u_y(1 - Cs) + u_x Si & Cs + u_z^2(1 - Cs) \end{pmatrix} \begin{pmatrix} e_x \\ e_y \\ e_z \end{pmatrix}, \quad (\text{S49})$$

where  $Cs = \cos \alpha$ ,  $Si = \sin \alpha$ , and  $\alpha$  is a rotation angle. In fact, our calculations directly simulate the measurements performed by placing a linear polarizer perpendicular to a certain direction with respect to the emitting dipoles, and recording the intensity of the transmitted light as a function of the polarizer angle for each of the dipoles.

To obtain the total photoluminescence intensity emitted in the direction  $\mathbf{u}$  for each of the lines, we integrate  $|\mathbf{e} \cdot \mathbf{x}|^2$ ,  $|\mathbf{e} \cdot \mathbf{y}|^2$ , and  $|\mathbf{e} \cdot \mathbf{z}|^2$  over all polar angles  $\alpha$ . In Extended Data Fig.

11 we provide several examples of the angular dependence of the emission probability in the plane perpendicular to the light-propagation direction and the relative photoluminescence intensity which can be observed from three orthogonal emitting dipoles, for four different directions. The calculations were conducted for: (i) a high temperature,  $T$ , that results in equal occupation of all three exciton levels (Extended Data Fig. 11a-d) and (ii) a temperature  $T$  that provides thermal energy that is comparable to the fine-structure splitting,  $kT = \Delta_1 = \Delta_2$  (Extended Data Fig. 11e-h).

One can see in Extended Data Fig. 11a-d that two dipoles contribute for any observation direction. The one photoluminescence line can be observed only if the upper exciton sublevels are unoccupied (compare photoluminescence spectra in panels a and b with the ones in panels e and f). The relative photoluminescence intensities of two lines whose polarizations are perpendicular to each other allows us to measure the relative population of the exciton spin sublevels and therefore the effective temperature (compare panels b and f). One can also see that at high temperature when all exciton sublevels are populated the detected photoluminescence intensity of the upper energy line can be larger than that of the lower energy line (compare panels d and h).

Extended Data Fig. 11 shows photoluminescence intensity peaks and their polarization calculated for cube-shaped nanocrystals. In perovskite nanostructures with orthorhombic symmetry the triplet exciton state is always split into three orthogonal dipoles. As a result, the polarization curves should look very similar to the curves shown in the insets of Extended Data Fig. 11. The intensity of photoluminescence emitted by each of these dipoles can be very sensitive to the nanocrystal shape, due to the different screening of the photon electric field by the different facets of nanocrystals with non-cube shapes. The fluctuation of the nanocrystal shape could also affect the radiative decay time of the nanocrystals.

Varying the observation directions, we can describe the photoluminescence polarization curves measured in individual-nanocrystal experiments (compare insets in Fig. 3a-c and Fig. 3d-f in the main text) and determine the observation direction. To describe these photoluminescence polarization curves, we assumed a Boltzmann occupation of the exciton spin sublevels. Using this assumption, we fit the experimental data with a temperature of 11.5 K for the inset of Fig. 3b in the main text and 20 K for the inset of Fig. 3c. Potential reasons for the slightly elevated temperatures extracted from the fit (instead of the targeted 5 K) include: (i) non-perfect thermal contact between the sample holder (where

the temperature of 5K was measured) and the nanocrystals embedded in the polymer film and (ii) mild local heating due to the laser illumination. We note, however, that with only two fitting parameters (temperature and nanocrystal orientation) and our assumption of cube-shaped nanocrystals, good fits to the experimental data could be obtained.

### S5. EMISSION FROM $\text{CsPbX}_3$ VERSUS CDSE NANOCRYSTALS AT ROOM TEMPERATURE

Because the exciton splittings predicted in this work are on a meV scale, a remaining question is why  $\text{CsPbX}_3$  perovskite nanocrystals emit  $\sim 20\times$  faster than other conventional nanocrystals at room temperature. Under these conditions, one would expect all exciton sublevels (bright and dark) to be thermally populated. However, the bright triplet still has significant impact on the photoluminescence behavior at room temperature. For example, we can compare the exciton fine structure in  $\text{CsPbX}_3$  perovskite and CdSe nanocrystals. The latter is well described in ref. S36. There, the band-edge  $1S_{3/2}1S_e$  exciton, which consists of 8 electron-hole states, is described. Because 6 of these combine into three doubly degenerate states, we are left with 5 sublevels labeled by the  $z$ -projection of the total exciton angular momentum,  $J_z = \pm 2, \pm 1, 0, \pm 1, 0$ . The lowest sublevel ( $J_z = \pm 2$ ) is dark. The next sublevel (the lower  $J_z = \pm 1$ ) is within  $k_b T$  of the ground-state dark exciton, where  $k_b$  is the Boltzmann constant and  $T$  is temperature. Consequently, this sublevel is significantly populated at room temperature. However, it is only poorly dipole active. Thus, it is a weak transition. The next sublevel is completely dark ( $J_z = 0$ ). Finally, the remaining levels ( $J_z = \pm 1, 0$ ) are strongly dipole active. But these lie well above the ground-state dark exciton in energy. In small CdSe nanocrystals, they are typically split by more than  $k_b T$  at room temperature. Moreover, for a complete description we must also include the dark  $1P_{3/2}1S_e$  exciton, which consists of 8 states. These are sufficiently close in energy to the  $1S_{3/2}1S_e$  exciton [S37, S38] that they can be thermally populated at room temperature. When all of the above complications are considered, the result is slower emission. Even in the high-temperature limit, in which all of these sublevels are equally populated, the effective radiative lifetime in CdSe is  $\sim (16/3)\tau_0^{\text{CdSe}}$  where  $\tau_0^{\text{CdSe}}$  is the radiative lifetime for the upper bright state.

In contrast, the situation in  $\text{CsPbX}_3$  perovskite nanocrystals is quite different. Not only

does it help that the lowest sublevel is bright rather than dark, but also the lowest three sublevels belong to the triplet state. Because the triplet state is inherently bright in this system, each of these sublevels carries the full oscillator transition strength. Furthermore, in the perovskites the electron and hole masses (see Table S1) are nearly identical. Due to the smaller hole effective mass in the perovskites in comparison to CdSe, dark excitons derived from excited hole states are frozen out at room temperature for even large nanocrystals. For example, for CsPbBr<sub>3</sub>, this occurs for radii below 7 nm. As a result, the band-edge fine structure in CsPbX<sub>3</sub> perovskite nanocrystals consists of 4 electron-hole pair states, 3 of which are bright, and only 1 of which is dark. Hence, in the case of equal thermal population, the effective radiative lifetime in a perovskite nanocrystal is  $(4/3)\tau_0$  where  $\tau_0$  is the bright-state radiative lifetime. This is extremely favorable compared to CdSe nanocrystals, where only 3 of the 16 thermally occupied electron-hole pair states associated with the band edge  $1S_{3/2}1S_e$  and  $1P_{3/2}1S_e$  states are strongly dipole active. Moreover, the 3 bright states in CdSe lie well above the lowest level in energy.

In addition to the above effects, several other factors contribute to the faster emission in CsPbX<sub>3</sub> perovskite nanocrystals. For larger particles, like the perovskite nanocrystals studied here, the phenomenon of giant oscillator transition strength plays a role. We note, however, that even in small CsPbX<sub>3</sub> perovskite nanocrystals, where this phenomenon would not contribute, we would still expect an enhancement of the radiative rate for several reasons. First, CsPbX<sub>3</sub> perovskites have a smaller value of the high-frequency dielectric constant in comparison with more conventional nanocrystal systems ( $\sim 4.5$  in CsPbX<sub>3</sub> versus 6.3 in CdSe). This increases the dielectric depolarization factor [see Eq. (S44)]. Second, the CsPbX<sub>3</sub> perovskites have a larger Kane energy in comparison to more conventional nanocrystals systems ( $E_p \sim 40$  eV versus  $\sim 17.5$  eV in CdSe). As Eq. (5) in the main text shows, the radiative lifetime is inversely proportional to the Kane energy parameter.

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