

Figure 2 | Characterization of fast radiative lifetimes in CsPbX₃ nanocrystals. a, Photoluminescence decays (open circles) measured from single CsPbI₃ (L = 14 nm), CsPbBr₃ (L = 11 nm) and CsPbBr₂Cl (L=14 nm) perovskite nanocrystals. By fitting the data with an exponential decay function (red lines), radiative decays of 0.85 ns, 0.38 ns and 0.18 ns were obtained for CsPbI₃, CsPbBr₃ and CsPbBr₂Cl perovskite nanocrystals, respectively. b, Calculated radiative lifetimes of the bright triplet exciton versus transition energy for CsPbX3 nanocrystals with X = Cl, Br or I. The theoretical results (circles) are divided into three size regimes (labels on individual points give the edge lengths, L, of the cubeshaped nanocrystals): strong (orange), intermediate (blue) and weak (green) exciton confinement. These values are compared with measured photoluminescence decays from individual perovskite nanocrystals (squares; sizes of the CsPbI₃, CsPbBr₃ and CsPbBr₂Cl crystals as in a). A data point for an ensemble of CsPbCl₃ nanocrystals ($\dot{L} = 10 \text{ nm}$) is also shown. Measured values are consistent with calculations in the intermediate confinement regime, which include electron-hole

a self-consistent model for CsPbX_3 nanocrystals be obtained, as we describe below.

The Rashba coefficient was estimated from low-temperature photo-luminescence spectra (see below). If the effective Rashba field is parallel to one of the orthorhombic symmetry axes of the nanocrystal (see Supplementary Information section 1 for details and other cases), then the bright triplet exciton ($J\!=\!1$) is split into three non-degenerate sublevels

$$\begin{split} |\Psi_{x}\rangle &= \frac{1}{\sqrt{2}} [|\uparrow\rangle_{e}|\uparrow\rangle_{h} - |\downarrow\rangle_{e}|\downarrow\rangle_{h}] \\ |\Psi_{z}\rangle &= |\Psi_{1,0}\rangle \\ |\Psi_{y}\rangle &= \frac{1}{\sqrt{2}} [|\uparrow\rangle_{e}|\uparrow\rangle_{h} + |\downarrow\rangle_{e}|\downarrow\rangle_{h}] \end{split} \tag{4}$$

which lie below the dark singlet (Fig. 1c). The triplet states represent three linear dipoles polarized along the orthorhombic symmetry axes (x, y, z). Transitions from these three sublevels have the same oscillator

correlations. c, d, Detected photon counts (left panels) versus time from individual CsPbI₃ (c) and CsPbBr₃ (d) nanocrystals (sizes as in a). Traces show 'A-type' blinking from the nanocrystals²⁵. These data can be analysed to separate contributions to the photoluminescence decay from exciton and trion emission (right panels). The targeted temperature in all experiments was 5 K, but may be higher (10-20 K; see Fig. 3). e, Calculated distribution of the z component of the electric field normalized to the applied field (along the z direction) at infinite distance, E_z^z/E_∞^z . This quantity is plotted versus position z across the centre line of spherical (dashed lines) or cube-shaped (solid lines) nanocrystals for various ratios of the dielectric constant inside (ε_{in}) and outside (ε_{out}) the nanocrystals (see legend). The field inside the nanocrystal is essentially always lower for the cube than for the sphere. Upper inset, calculated two-dimensional distribution of E_z^z/E_∞^z inside a cube-shaped nanocrystals plotted on the x-z mid-plane for $\varepsilon_{\rm in}/\varepsilon_{\rm out}=6$. Lower inset, calculated ratio $\tau_{\rm ex}^{\rm sphere}/\tau_{\rm ex}^{\rm cube}$ of radiative decay times for spherical and cubical nanocrystals with the same volume versus $\varepsilon_{\rm in}/\varepsilon_{\rm out}$ for strong (blue) and weak (red) confinement.

strength. Moreover, in cube-shaped nanocrystals, these states still emit as linear dipoles despite the inhomogeneous field (Supplementary Information sections 1 and 3).

The radiative lifetime of the triplet exciton $\tau_{\rm ex}$ is evaluated from

$$\frac{1}{\tau_{\rm ex}} = \frac{4\omega n E_{\rm p}}{9 \times 137 m_0 c^2} I_{\parallel}^2 \tag{5}$$

with ω the angular transition frequency, n the refractive index of the surrounding medium, m_0 the free-electron mass, c the speed of light, $E_{\rm p}=2P^2/m_0$ the Kane energy (Extended Data Fig. 7) and P the Kane parameter²². I_{\parallel} is an overlap integral that includes the envelope functions of the electron and hole and the field-averaged transition-dipole moment (Supplementary Information section 3).

In Fig. 2b we present the $\tau_{\rm ex}$ calculated for CsPbX₃ nanocrystals (circles). The results can be divided into three regimes, depending on the size of the nanocrystal. When the nanocrystal is smaller than the Bohr radius of the exciton $a_{\rm B}$ (strong exciton confinement,