



Figure 3 | Fine structure of the bright triplet exciton for CsPbBr₂Cl nanocrystals. **a–c**, Photoluminescence spectra (points) of individual nanocrystals ($L = 14 \pm 1$ nm) that exhibit a single peak (**a**), two peaks (**b**) and three (**c**) peaks. Single- and multi-Lorentzian-function fits are displayed as solid lines (grey lines are the cumulative fits). The targeted temperature was 5 K; however, the quantitative fits of the relative peak intensities, based on a Boltzmann distribution (Supplementary Information section 4), required higher temperatures (10–20 K). This may indicate a warmer sample temperature due to imperfect thermal contact and/or laser heating. Alternatively, deviations from a Boltzmann distribution may be present. The insets show the polarization of each of the spectral features. For the spectra, a linear polarizer was placed in the

detection path. The angle of this polarizer was adjusted so that the relative intensity of the features in the spectra matched the polarization dependence in the insets. **d–f**, Simulated spectra and polarizations for nanocrystal orientations that match the experimental results in **a–c**; see Supplementary Information section 4 for details. Each panel lists the required observation direction relative to the orthorhombic unit-cell axes. **g**, Experimental statistics for the observation of single-, two- and three-peak spectra from individual nanocrystals with $L = 7.5$ –14 nm (51 spectra with 35 splittings in total). **h**, **i**, Experimental fine-structure splittings measured for the two- (**h**) and three-peak (**i**) spectra. The average splitting $\bar{\Delta}$ in each case is provided.

orange circles), the predicted radiative lifetime decreases from 2 ns to 1 ns with increasing emission energy. For large nanocrystals in the opposite limit (weak exciton confinement, green circles), the lifetime should be even shorter because weakly confined excitons exhibit larger oscillator strengths²⁷. In this size regime ($L \approx 15$ –25 nm), the calculated lifetimes decrease below 100 ps for CsPbBr₃ and CsPbCl₃ nanocubes. The lifetime would be decreased further in spheres of the same volume (Fig. 2e, lower inset).

The measured photoluminescence decays in Fig. 2b (squares) lie between those predicted for strong and weak confinement. Because the size of the nanocrystals and a_B are comparable, the electron and hole motion is correlated. If this effect is taken into account (intermediate exciton confinement, blue circles), then calculations for $L \approx 4$ –16 nm (Supplementary Information section 3, Extended Data Fig. 8) agree well with the experiment.

The order of exciton levels used above depends on the values and relative signs of the Rashba coefficients for the electron and hole. If they have the same sign, then the angular-momentum texture (that is, how the orientation of the angular momentum varies with wavevector) exhibits the same helicity at the valence-band maximum and conduction-band minimum⁷. Optical transitions between these bands are allowed when the helicity is preserved (owing to their s and p symmetry, respectively.) Thus, for this case, the lowest exciton sublevel should be bright; see Supplementary Information section 1.E for details. A similar situation exists in transition-metal dichalcogenide monolayers²⁸.

We estimated the values of the Rashba coefficients from photoluminescence spectra of individual nanocrystals, which reveal the fine structure directly. Our nanocrystals exhibit one, two or three peaks, all with near-linear polarization (Fig. 3a–c, Extended Data Figs 9, 10). This is consistent with the three non-degenerate exciton sublevels in equation (4) under orthorhombic symmetry, which should emit as orthogonal linear dipoles. For simplicity, we assume that the electron and hole Rashba coefficients are equal. The value (0.38 eV Å) required to fit the observed splittings (about 1 meV) is reasonable, lying between those for conventional III–V quantum wells and organic–inorganic perovskites (see Supplementary Information section 1.F). We note that for nanocrystals with tetragonal symmetry, $|\Psi_x\rangle$ and $|\Psi_y\rangle$ in equation (4) remain degenerate (Supplementary Information section 1.E), which explains recently observed two-peak spectra from individual CsPbBr₃ nanocrystals²⁹.

Emitting dipoles that are perpendicular (parallel) to the observation direction should show strong (no) emission. Thus, the intensity from each bright triplet sublevel is explained by both its thermal population and the orientation of the nanocrystal. Single-line spectra (Fig. 3a) arise when the two upper sublevels are unpopulated. Strong linear polarization from this single line (Fig. 3a, inset) supports this interpretation. If the sublevel splitting in this nanocrystal were instead spectrally unresolved, then the line would be unpolarized. From the expected three orthogonal dipoles, we calculated the relative intensity of the photoluminescence peaks and their polarization for arbitrary observation directions (Supplementary Information section 4, Extended Data Fig. 11). We then determined