Figure 1 | Crystal and electronic structure for CsPbBr₃ perovskite. a, Orthorhombic crystal structure of $CsPbBr_3$ (*Pnma* space group, unit cell shown as a frame), which differs from the idealized cubic perovskite by an octahedral tilting. **b**, Calculated band structure of cubic $CsPbBr_3$ perovskite. The inset shows the first Brillouin zone of the cubic crystal lattice. The electronic bandgap is indicated in the band structure at the R point. The valence (conduction) band maximum (minimum) has R_6^+ (R_6^-) symmetry. **c**, The expected fine structure of the band-edge exciton considering short-range electron–hole exchange (middle) and then including the Rashba effect (right) under orthorhombic symmetry. The latter splits the exciton into three bright states with transition dipoles oriented along the orthorhombic symmetry axes (labelled *x*, *y* and *z*) and a higher-energy dark state (labelled 'd'). The energetic order of the three lowest sublevels is determined by the orthorhombic distortion. The orthorhombic unit cell (bottom) and the resulting sublevel order is shown for $CsPbBr_3$. **d**, Transmission electron micrograph of an individual $CsPbBr_3$ nanocrystal with an edge length of $L = 14$ nm.

where each $|\Psi_{J,J_z}\rangle$ is labelled with J_z, the *z* projection of **J**. The probability of light emission due to electron–hole recombination from these excitons can then be calculated (Supplementary Information section 1). We find a probability of zero for $|\Psi_{0,0}\rangle$ and of non-zero for $|\Psi_{1,J_z=0,\pm1}\rangle$, indicating a dark singlet and a bright triplet.

These selection rules are confirmed by group theory. At the R point, the band-edge electron and hole states transform as irreducible representations R_6^- and R_6^+, respectively (with the superscript denoting parity)[23]. Exchange then splits the exciton into a dark singlet (R_1^-) and a bright triplet (R_4^-); see Supplementary Information section 2 and Supplementary Table 3.

Detailed calculations (see Supplementary Information section 1) reveal the energetic order of these levels. If only short-range exchange is included, then the singlet lies below the triplet (Fig. 1c). However, CsPbX₃ perovskites should also exhibit a large Rashba effect[5]. This occurs in semiconductors with strong spin–orbit coupling and an inversion asymmetry. For the closely related hybrid organic–inorganic perovskites, the impact of this effect on photovoltaic and spintronic devices has been discussed extensively[6–9]. Although the cause of the inversion asymmetry (cation positional instabilities[24] or surface effects[9]) remains unknown, the Rashba effect should alter the fine structure. Indeed, the bright triplet exciton can be lowered below the dark singlet exciton.

To examine this possibility, we studied colloidal nanocrystals of CsPbX₃ (Methods). Compared to bulk crystals, nanocrystals enable the additional effect of system size to be investigated. Such particles are roughly cube-shaped with edge lengths of $L = 8$–15 nm (Fig. 1d). Before these nanocrystals were introduced[11], all technologically relevant semiconductor nanocrystals exhibited slow, sub-microsecond radiative lifetimes at cryogenic temperatures, owing to the lowest exciton being dark[4]. By contrast, CsPbX₃ nanocrystals emit about 1,000 times faster (with sub-nanosecond lifetimes)[12]. In Fig. 2a we show photoluminescence decays for individual CsPbI₃, CsPbBr₃ and CsPbBr₂Cl nanocrystals at cryogenic temperatures. The decay times are 0.85 ns, 0.38 ns and 0.18 ns, respectively, decreasing with increasing emission energy. The photoluminescence quantum yield for the fastest

of these samples, the CsPbBr₂Cl nanocrystals ($L = 14 \pm 1$ nm; throughout we quote the mean value and standard deviation from several measurements), was measured to be near unity (88% ± 14%) at 5 K (Extended Data Fig. 2), which indicates that these decay times can be related directly to radiative lifetimes. In Fig. 2b we present a larger set of decay times (squares) for individual CsPbI₃, CsPbBr₃ and CsPbBr₂Cl nanocrystals. All are much shorter than those reported for CdSe, CdS, CdTe, InAs, InSb, InP, PbSe, PbS and PbTe nanocrystals[13–16], consistent with the lowest exciton being the bright triplet.

However, fast decays could also indicate emission from trions (charged excitons). Trions are optically active, but suffer from rapid non-radiative Auger recombination. They should therefore exhibit quicker but weaker decays than excitons. In our single-nanocrystal experiments discussed above, trion contributions are reduced by spectral filtering (Extended Data Fig. 3). However, to test the role of trions explicitly, we analysed the photon stream from individual nanocrystals without filtering (Fig. 2c, d, left). The correlation of emission intensity with lifetime allows the strong exciton and weak trion contributions to be separated (Fig. 2c, d, right)[25]. We confirm fast exciton lifetimes for CsPbI₃ and CsPbBr₃ nanocrystals of 1.2 ns and 0.4 ns, respectively, consistent with ensemble measurements (Extended Data Fig. 4).

To compare with theory, we calculated radiative lifetimes for perovskite nanocrystals within the effective-mass model. In addition to the wavefunctions in equations (2) and (3), exciton confinement within the nanocrystal must be included via envelope functions for the electron and hole. If CsPbX₃ nanocrystals were spherical, excitonic lifetimes could be calculated using previously described methods (Supplementary Information section 3). However, for cubes, the electric field of a photon not only changes across the boundary of the nanocrystal, owing to dielectric screening (as in spherical nanocrystals), but also becomes inhomogeneous (Fig. 2e, Extended Data Figs 5, 6). We included this inhomogeneity, along with the Rashba effect and the orthorhombic lattice distortion in CsPbX₃ nanocrystals in our calculations[26]. For simplicity, we assumed the nanocrystals were cube-shaped. Only when the Rashba effect was included could