

METHODS

Chemicals. The following reagents were used to prepare CsPbX₃ nanocrystals: caesium carbonate (Cs₂CO₃, Aldrich, 99.9%), 1-octadecene (ODE, Sigma-Aldrich, 90%), oleic acid (OA, Sigma-Aldrich, 90%), oleylamine (OAm, Acros Organics, 80%–90%), lead chloride (PbCl₂, ABCR, 99.999%), lead bromide (PbBr₂, ABCR, 98%), lead iodide (PbI₂, ABCR, 99.999%), *n*-trioctylphosphine (TOP, Strem, 97%), hexane (Sigma-Aldrich, ≥95%) and toluene (Fisher Scientific, HPLC grade).

Synthesis. The CsPbX₃ (X = Cl, Br or I) and CsPbBr₂Cl nanocrystals were synthesized by fast reaction between Cs-oleate and PbX₂ in the presence of OA and OAm (and TOP in the case of CsPbCl₃ and CsPbBr₂Cl nanocrystals). First, the Cs-oleate was prepared by loading Cs₂CO₃ (0.407 g) into a 50-ml 3-neck flask along with ODE (20 ml) and OA (1.25 ml). The mixture was dried under vacuum for 1 h at 120 °C and then switched to N₂. Because Cs-oleate precipitates out of ODE at room temperature, it must be pre-heated to 100 °C before injection. The ODE, OA and OAm were pre-dried before use by degassing under vacuum at 120 °C for 1 h. For the nanocrystal-forming reaction, 0.376 mmol PbX₂ (X = Cl, Br or I), dried OA (3 ml for PbCl₂, 1 ml for PbBr₂ or 1.5 ml for PbI₂), dried OAm (3 ml for PbCl₂, 1 ml for PbBr₂ or 1.5 ml for PbI₂) and dried ODE (5 ml) were combined in a 25-ml 3-neck flask. For CsPbCl₃, TOP (1 ml) was also added. The mixture was then degassed for 10 min under vacuum at 120 °C, and the flask was filled with N₂ and heated to 200 °C. Cs-oleate (0.8 ml from the stock solution prepared as described above) was injected swiftly when 200 °C was reached. After 10 s the reaction was stopped by cooling the reaction system with a water bath. The solution was centrifuged (4 min, 13,750g) and the supernatant discarded. Hexane (0.3 ml) was added to the precipitate to disperse the nanocrystals and the mixture was then centrifuged again. The precipitate obtained was re-dispersed in 3 ml toluene and centrifuged (2 min, 2,200g). The supernatant was separated from the precipitate, filtered and used for our investigations. For CsPbBr₂Cl, 0.094 mmol PbCl₂, 0.282 mmol PbBr₂, dried OA (1.5 ml), dried OAm (1.5 ml), TOP (1 ml) and dried ODE (5 ml) were loaded into a 25-ml 3-neck flask and the same protocol was followed.

Sample preparation. For single-nanocrystal spectroscopy, the colloidal dispersions from the above syntheses were diluted to nanomolar concentrations in solutions of 3-wt% polystyrene in toluene. This dispersion was then spin-casted at 5,000 r.p.m. onto intrinsic crystalline Si wafers with a 3-μm-thick thermal-oxide layer. For ensemble measurements, the undiluted nanocrystal dispersions were drop-casted on glass substrates. For photoluminescence quantum-yield measurements, 0.1 ml of the colloidal dispersion was mixed with 0.1 ml of a 5-wt% solution of poly(methyl methacrylate) (PMMA, molecular weight of 495,000) in toluene.

Optical characterization. All optical measurements of single nanocrystals were performed in a self-built micro-photoluminescence (μ-PL) set-up. The samples were mounted on xyz nano-positioning stages inside an evacuated liquid-helium flow cryostat and cooled down to a targeted temperature of 5 K (see Fig. 3 caption). Single nanocrystals were excited by means of a fibre-coupled excitation laser at an energy of 3.06 eV with a repetition rate of 40 MHz and a pulse duration of 50 ps. The excitation beam was sent through a linear polarizer and a short-wavelength-pass filter before being directed towards the sample by a dichroic beam splitter. Typical power densities used to excite single nanocrystals were 2–120 W cm⁻². Assuming an absorption cross section³¹ of 8×10^{-14} cm², these power densities yield 0.0057–0.34 excitons per nanocrystal per pulse³². For both excitation and detection, a long-working-distance 100× microscope objective with a numerical aperture of 0.7 was used. The nearly Gaussian excitation spot had a $1/e^2$ diameter of 1.4 μm. The emission was filtered using a long-pass filter and dispersed by a 0.75-m monochromator with a grating of 1,800 lines mm⁻¹ before detection with a back-illuminated, cooled charge-coupled device camera. For polarization-dependent measurements, a liquid-crystal retarder was used to compensate for retardation effects in the set-up. For photoluminescence lifetime and time-tagged time-resolved (TTTR3) single-photon-counting measurements, we filtered the emission with a suitable tunable bandpass filter either to measure only the excitonic photoluminescence decay or to correlate excitonic and trionic emission

intensities and decay times with a time-correlated single-photon-counting system with nominal time resolution of 30 ps.

Ensemble measurements were performed in an exchange-gas cryostat at 5 K. Here, the samples were excited with a frequency-doubled Ti:sapphire femtosecond pulsed laser with a repetition rate of 80 MHz at 3.1 eV. Optical power densities were below 3 W cm⁻². The emitted light was dispersed by a grating of 150 lines per mm within a 300-mm-focal-length spectrograph and detected by a streak camera with 2-ps resolution. Absolute photoluminescence quantum-yield measurements at room temperature were performed on a Quantaurus QY (C11347-11, Hamamatsu).

Band-structure calculations. Figure 1b and Extended Data Fig. 1 show calculated band structures for CsPbBr₃, CsPbCl₃ and CsPbI₃. We assume that these materials exist in the cubic perovskite structure with a lattice constant of 5.865 Å, 5.610 Å and 6.238 Å, respectively³³. The electronic structure of these crystals was determined using the Vienna *Ab-initio* Simulation Package (VASP)^{34–36} with projector-augmented wavefunctions³⁷. Our initial calculations used the PBEsol³⁸ generalized gradient approximation, and included spin–orbit coupling. We used an energy cut-off of 400 eV and a Γ -centred *k*-point grid of $6 \times 6 \times 6$, which yield 40 *k*-points in the irreducible Brillouin zone.

As expected, standard density functional theory (DFT) underestimates the bandgap in these materials substantially. Accordingly, we used a modified version of the Heyd–Scuseria–Ernzerhof ‘HSE06’ hybrid functional³⁹, which mixes exact Hartree–Fock exchange with conventional DFT. We initially started with 25% mixing, and planned to adjust the mixing to match the observed bandgap. However, this was not possible, even with 45% Hartree–Fock in the calculation for CsPbBr₃. This initial mixing produced a bandgap of 1.4 eV, far smaller than the experimentally determined gap of 2.8 eV. Rather than using even higher mixing, or even a full-scale Hartree–Fock calculation, we instead added a scissors operator to adjust the bandgap to the experimental result. We found that the electron and hole masses were nearly unchanged with Hartree–Fock mixing, leading us to believe that this technique still provides the correct physics. Further confirmation was provided by conducting *G₀W₀* calculations (also with VASP) on top of the PBE results. For this approach, we used a plane-wave energy cut-off of 600 eV, a 150-eV energy cut-off for the response functions, 1,894 unoccupied states, spin–orbit coupling, and ‘GW’ pseudopotentials including all semi-core electrons. Although these calculations yielded bandgaps that were in closer agreement with the experiments (1.96 eV for CsPbI₃, 2.36 eV for CsPbBr₃ and 3.27 eV for CsPbCl₃), other aspects of the band structure remained virtually unchanged.

Data availability. All data generated or analysed during this study are included in the published article (and its Supplementary Information).

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