The dark exciton ground state promotes photon-pair emission in individual perovskite nanocrystals

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Cesium lead halide perovskites exhibit outstanding optical and electronic properties for a wide range of applications in optoelectronics and for light-emitting devices. Yet, the physics of the band-edge exciton, whose recombination is at the origin of the photoluminescence, is not elucidated. Here, we unveil the exciton fine structure of individual cesium lead iodide perovskite nanocrystals and demonstrate that it is governed by the electron-hole exchange interaction and nanocrystal shape anisotropy. The lowest-energy exciton state is a long-lived dark singlet state, which promotes the creation of biexcitons at low temperatures and thus correlated photon pairs. These bright quantum emitters in the near-infrared have a photon statistics that can readily be tuned from bunching to antibunching, using magnetic or thermal coupling between dark and bright exciton sublevels.
Recent advances in the colloidal synthesis of strongly emitting perovskite nanocrystals (NCs) open up new opportunities for the fabrication of tunable light sources based on the composition and quantum size effect tuning, such as light-emitting diodes and lasers, and for the exploration of their potential use as quantum light sources. The knowledge of the band-edge exciton fine structure in perovskites and the ability to tailor it with NC composition, morphology, or external fields are of prime importance for the development of efficient single-photon sources or sources of entangled photons for quantum information processes, and for applications in optoelectronics and spin-based technologies. Yet, the bright or dark character of the ground exciton in perovskites is the subject of continuing debate. The band-edge exciton of perovskites is formed with a hole (h) in an S-like state with angular momentum \( J_h = 1/2 \) and an electron (e) in a spin-orbit split-off state with angular momentum \( J_e = 1/2 \). The resulting four-fold degenerate exciton level is split by the e-\(-h\)-on-hole exchange interaction into a dark ground singlet state \( (J = 0) \) and a bright triplet \( (J = 1) \). At liquid helium temperatures, single cesium lead halide (CsPbX₃) perovskite NCs display a bright photoluminescence (PL) with a spectral structure similar to the bright triplet structure in perovskites and the ability to fine-tune it with NC composition, morphology, or external fields, as demonstrated in a recent study. The exciton fine structure in these NCs with a mean size slightly larger than twice the exciton Bohr radius \( a_0 = 4.6 \) nm in CsPbI₃, measured by using a home-built scanning confocal microscope operating at cryogenic temperatures, and using a polystyrene matrix and weakly excited at a laser wavelength of 561 nm (see “Methods” section for details). Their emission energy centered on 1.77 eV (Fig. 1a) is red-shifted with respect to the room temperature value, due to a displacement of the valence band energy with lattice contraction. At low temperature (~4 K), thermal dephasing is reduced and the PL spectra of single NCs present sharp peaks attributed to the zero-phonon emission lines (ZPLs) resulting from the recombination of the charge complexes formed in the NC, as exemplified in the typical spectral trail displayed in Fig. 1d. This trail shows an emission switch of a NC from its neutral state, displaying ZPLs labeled X for the exciton and XX for the biexciton, to its charged state characterized by a single ZPL labeled X*. As shown in Fig. 1e, integrating the spectra gives greater details of the fine structure of these charge complexes, as well as the longitudinal optical (LO) phonon replicas of the ZPLs. The exciton fine structure is revealed both through the biexciton-to-exciton transitions and through the bright exciton recombinations. Merging the biexcitonic transition multiplet XX onto the excitonic one X (see inset of Fig. 1e) shows evidence for a perfect match in their spectral structures and allows a straightforward correspondence of the transition lines (see also Supplementary Fig. 1). As exemplified in Fig. 2 and Supplementary Fig. 2, this spectroscopic study reveals one-line, two-line, or three-line PL spectra in proportions of ~5%, 30%, and ~65%, respectively. Within a resolution of ~120 μeV, these spectral structures result from a subtle interplay of crystal structure and shape anisotropy effects. For instance, assuming a cubic symmetry of the NC crystal structure (resp. shape), shape (resp. crystal structure) anisotropy governs the number of bright levels: Single-line, two-line, and three-line spectra will be, respectively, assigned to cubic, tetragonal, and orthorhombic anisotropy of the NC shape (resp. crystal structure).

Exciton fine structure and signature of the dark singlet. The spectral signature of the dark singlet exciton is evidenced under the application of an external magnetic field, as demonstrated in Fig. 2 (see other examples in Supplementary Fig. 2). Regardless of the triplet structure, a new emission line indeed emerges from the LO-phonon sidebands, a few meV below the bright triplet, as a signature of magnetic brightening of a low-lying dark exciton state in these inorganic lead halide perovskites. Despite this level ordering, perovskite NCs display an intense luminescence at low temperature because of an extremely reduced bright-to-dark phonon-assisted relaxation, a remarkable property of these materials as compared to more conventional III–V or II–VI semiconductors. Indeed, spin relaxation processes involving polar acoustic phonons related to piezoelectricity are absent, and carrier–phonon interactions via deformation potentials are reduced in these structurally soft semiconductors with strong lattice anharmonicity affecting the optical modes. The structure of the optical phonon modes of the CsPbI₃ NCs is detailed in Supplementary Fig. 3 and compared with that of CsPbBr₃ NCs. It shows evidence that the bright-to-dark relaxation remains inhibited even when the bright-dark splitting coincides with the phonon modes. The fact that phonons do not carry angular momentum likely explains why the bright-to-dark relaxation is inhibited in perovskites. Indeed, it requires Raman-like phonon processes involving two-phonon modes whose energy difference matches the bright-dark splitting (2,3,3) (see Fig. 2d and Supplementary Fig. 4). Interestingly, a direct signature of extremely slow phonon relaxation within the bright sublevels is the equality in relative weights between the corresponding XX and X triplet components (see Fig. 1e and Supplementary Fig. 1). It proves that the relaxation is slower than the exciton recombination, whose lifetime is on the nanosecond time scale. This points to a...
negligible Rashba-like spin–orbit coupling\textsuperscript{35–37} that would allow one-phonon bright-to-dark relaxation in these materials.

We have studied the exciton fine structure of tens of individual NCs and find a clear increase of the bright triplet splittings (up to \(~1\) meV) and the bright-dark splittings (up to \(~5\) meV) with the exciton recombination energy, as shown in Fig.\textsuperscript{3a, b} and Supplementary Fig.\textsuperscript{5}. The trend of such a correlation also shows up for the bright triplet splittings of CsPbBr\textsubscript{3} NCs (see Supplementary Fig.\textsuperscript{6}) and CsPbBr\textsubscript{2}Cl NCs\textsuperscript{20}. These results demonstrate that fine structure splittings are dominated by the exchange interaction under the combined effects of quantum confinement and screening of the electron–hole interaction. Indeed, the contribution of the Rashba effect to the bright state splittings has been predicted to decrease with increasing NC sizes\textsuperscript{38}, which points to a reduced contribution of this effect in cesium lead halide perovskite NCs. In order to reproduce these results, we have calculated the exchange interaction for cuboid shaped NCs with a cubic crystal phase in the weak quantum confinement regime, using a variational approach based on an effective mass model for the monoionic states (Supplementary Note 1). Figure\textsuperscript{3c} shows the results obtained in the case of a tetragonal NC shape, where the bright sublevels form a doublet comprising a non-degenerate sublevel (Z state) defined by the NC elongation axis and a two-fold degenerate sublevel (X and Y states). Their splitting increases with the NC aspect ratio (see also Supplementary Fig.\textsuperscript{7}), and their ordering becomes reversed when the NC shape switches from flattened to elongated. This is illustrated in Fig.\textsuperscript{3d}, where the PL spectra of two nearly tetragonal NCs with different aspect ratios are presented (NCs with sides \(L_x/C > L_y > L_z\) for the left spectrum, and \(L_y > L_x \approx L_z\) for the right spectrum). Importantly, our observations are in contradiction with the assumption of a Rashba effect that would always place the bright Z level below the twofold degenerate X–Y level\textsuperscript{23}. This is also the case in CsPbBr\textsubscript{3} NCs, as shown in Supplementary Fig.\textsuperscript{6}. Finally, we find that the evolution of the calculated bright-dark splitting as a function of the exciton
The weakest value is obtained for FAPbI\textsubscript{3} perovskites. It is consistent with spectroscopic studies of weakly confined single FAPbI\textsubscript{3} NCs, which present a narrow exciton fine structure within a few hundred \textmu eV that could not be resolved under a magnetic field of 7 T\textsuperscript{15}. CsPbBr\textsubscript{3} perovskites display the largest bulk exchange interaction, explaining why the distributions of bright triplet splittings measured in CsPbBr\textsubscript{3} NCs\textsuperscript{15,18,20} are larger than those of FAPbBr\textsubscript{3} and CsPbI\textsubscript{3} NCs. Despite spectroscopic investigations on different CsPbBr\textsubscript{3} NCs with different sizes, shapes, and surface ligands, we could not observe magnetic brightening of the dark state with magnetic fields up to 7 T\textsuperscript{15} for different exciton confinement regimes (NCs with sizes \textasciitilde 4 to \textasciitilde 20 nm) and different surface ligands. Since magnetic brightening is inversely proportional to the square of the bright-dark splitting, it is likely negligible at such fields due to a large offset between the dark ground singlet state and the bright triplet in these NCs. This picture is supported by the onset of a long-time component in the PL decay of ensembles of CsPbBr\textsubscript{3} NCs at fields higher than 10 T\textsuperscript{40}, as an indirect signature of a low-lying long-lived sublevel\textsuperscript{11}.

**Exciton optical coherence lifetime.** Due to their bright PL in the near-infrared and sharp ZPLs at low temperature, single CsPbI\textsubscript{3} NCs are attractive solid-state emitters for a potential use as quantum light sources. In particular, sources that deliver single indistinguishable photons on demand are required for a number of quantum information processing schemes\textsuperscript{7}. Such photons stem from the ZPL when its spectral linewidth $1/\pi T_2$ reaches its fundamental lower bound $1/(2\pi T_1)$, where $T_2$ is the optical coherence lifetime of the emission and $T_1$ the emitting state lifetime. Time-resolved photon-correlation Fourier spectroscopy has provided a coherence lifetime $T_2 \sim 80$ ps for individual CsPbBr\textsubscript{3} NCs\textsuperscript{46}. However, time-resolved approaches without spectral filtering fail at identifying the charge complexes at the origin of the emission. For CsPbI\textsubscript{3} NCs, a similar coherence lifetime has been extracted from first-order PL correlation measurements\textsuperscript{42}. In these early investigations, the excess energy between absorption and emitted photons may induce spectral diffusion of the transition energy\textsuperscript{31}. We thus measure the ultimate limit of the optical coherence lifetime of perovskite NCs through resonant excitation on their excitonic ZPLs. Resonant excitation spectra are recorded by scanning a single-mode laser across one of the fine structure ZPLs, while collecting the fraction of PL emitted on the LO phonon replicas, as shown in Fig. 4a. A narrow Lorentzian ZPL is presented in Fig. 4b with a homogeneous linewidth as narrow as \textasciitilde 5 GHz FWHM, corresponding to an optical coherence time $T_2 \sim 64$ ps. This value is still short in comparison with the exciton lifetime $T_1 \sim 1$ ns measured on the same NC (see Fig. 4c). A possible origin of ZPL broadening is fast-spectral diffusion induced by fluctuations of the local electric field and dielectric screening, as a result of charge noise produced by charge displacements at the surface of the NCs or in its local environment. These processes are likely the same as those responsible for slow spectral diffusion accompanied by variations of the exciton fine-structure splittings. As shown in Supplementary Fig. 8, the fine-structure splittings increase with the exciton recombination energy, which suggests that the spectral jumps take their origin in fluctuations of the dielectric confinement that affects both the transition energy and the electron–hole exchange interaction. Despite these homogeneous broadening mechanisms, our high-resolution PL excitation method provides a precious tool to investigate subtle lifts of degeneracy in the exciton fine structure, that would be buried within the spectral resolution of the PL spectra. In further investigations, such variations of the exciton fine structure should be correlated with the 3D characterization of the NCs morphology.

**Tuning the photon statistics of single NCs.** We now study the statistics of the photons emitted by individual CsPbI\textsubscript{3} NCs, using recombination energy (Fig. 3e) is in quantitative agreement with the experimental results when taking into account the effect of dielectric confinement on the exchange interaction. More quantitative comparison between theory and experiment, in particular the assignment of non-degenerate bright triplet ZPLs to the levels X, Y, and Z, would require refined models that take into account crystal phase and shape anisotropies\textsuperscript{39} together with the knowledge of the low-temperature crystal structure, 3D shape, orientation, and dielectric environment of each NC.

In order to predict the offset of the dark ground state in the fine structure of lead halide perovskites, we have calculated the exchange interaction in bulk perovskites with various compositions and plotted them as a function of their exciton Bohr radius in Fig. 3f. The weakest value is obtained for FAPbI\textsubscript{3} perovskites. It is consistent with spectroscopic studies of weakly confined single FAPbI\textsubscript{3} NCs, which present a narrow exciton fine structure within a few
a Hanbury Brown and Twiss coincidence setup to measure the histograms of time delays between consecutive photon pairs. A striking feature is the strong bunching observed at low temperatures with the PL signal formed by all emission lines, as exemplified in Fig. 5a. We attribute this behavior to the exciton-shelving role played by the long-lived ground exciton state, which favors the generation of bieexcitons in the NCs, followed by bieexciton to bright-exciton-correlated photon pairs. The photon bunching character weakens when the temperature is raised. This results from thermal mixing between bright and dark states, which shortens the effective lifetime of the dark state. As this lifetime approaches its limit given by the bright exciton lifetime, photon bunching turns to antibunching (see Fig. 5a and Supplementary Figs. 4, 9) with a zero-delay autocorrelation function set by the bieexciton radiative yield. This behavior is well reproduced with simulated autocorrelation functions (Fig. 5b) deduced from the solutions of rate equations in a simple four-level model including the zero-exciton ground level, thermally mixed bright and dark exciton sublevels and a bieexciton level (see Supplementary Note 2). To further support the role of the dark state on the photon statistics, we have studied the evolution of the autocorrelation function with magnetic fields. Clearly, magnetic coupling of dark and bright states leads to shortening of the long component of the PL decay and to weakening of the photon bunching, as shown in Fig. 5c, which presents a ground exciton sublevel located a few meV below the lowest bright state. Strong photon bunching is observed for single CdSe NCs at liquid helium temperatures and weak intensities. However, the transition from bunching to antibunching occurs at much lower temperatures than for perovskites, as soon as the thermal energy approaches the dark-exciton energy matches the bright-dark splitting, while in perovskites, this transition is observed for single CdSe NCs at liquid helium temperatures and weak intensities. However, the transition from bunching to antibunching occurs at much lower temperatures than for perovskites, as soon as the thermal energy approaches the dark-exciton level.

In order to generalize the picture of a long-lived ground state promoting photon pairs in quantum dots, we have performed similar experiments on CdSe core–shell NCs (see Supplementary Fig. 13), which present a ground “dark” exciton sublevel located a few meV below the lowest bright state. Strong photon bunching is observed for single CdSe NCs at liquid helium temperatures and weak intensities. However, the transition from bunching to antibunching occurs at much lower temperatures than for perovskites, as soon as the thermal energy approaches the dark-bright splitting. Indeed, thermalization between fine structure sublevels is mediated in these NCs by one acoustic phonon whose energy matches the bright-dark splitting, while in perovskites...
Lorentzian response function is shown in gray. The red curve is an exponential decay of a single NC, for an average number of exciton per pulse. As shown in Fig. 5d, one can foresee important developments motivated by the promising prospects of these materials as classical or quantum light sources. The next investigations will aim at reducing the dephasing rate and spectral diffusion in these materials and improve the indistinguishability character of the emitted photons, with the application of strong local electric fields that stabilize the charge distributions in the NC, or further surface passivation with suitable ligands or the growth of inorganic shells. In general, photon pairs emitted by conventional quantum dots undergo various entanglement-degrading effects such as band mixing, exciton spin-flip processes and fine structure splitting, which drastically reduce their degree of entanglement. With a view to achieving ideal sources of entangled photons, perovskite NCs exhibit pure electron and hole bands, extremely slow spin-flip relaxation and, for a fraction of them, degenerate bright triplet emission.

Methods

Preparation of cesium-oleate precursor. In a 100 mL three-necked round-bottom flask a mixture of 0.5 g Cs₂CO₃, 2 mL OA, and 50 mL ODE is dried at 120 °C for 2 h under vacuum, followed by purging with nitrogen for 30 min. The reaction is finished when the Cs₂CO₃ powder dissolves completely to give a clear solution. The prepared solution of cesium oleate in ODE (0.06 M) is used as cesium precursor and stored under nitrogen atmosphere.

Synthesis of colloidal CsPbI₃ NCs. In a 100 mL three-necked round-bottom flask, 200 mg PbI₂ (0.43 mmol) are suspended in ODE (10 mL). The reaction mixture is degassed at 100 °C under vacuum for 3 h. Subsequently, 1 mL OA, 1 mL OAm, and 1 mL TOP are added under nitrogen atmosphere. The reaction temperature is increased to 175 °C and preheated (~70 °C) Cs-oleate solution (1.6 mL, 0.06 M) is swiftly injected to the reaction flask. In 10 s the reaction mixture is cooled by a water-ice bath.

Purification of CsPbI₃ NCs. Purification of the synthesized NCs is conducted in a glovebox under inert atmosphere. In order to remove the excess of ligands, 35 mL anhydrous MeOAc are added to the crude solution, then centrifuged at 12,100 rpm for 1 min (20,130 x g; centrifuge: Eppendorf 5810R). The supernatant is discarded and the precipitate is dissolved in ~5 mL anhydrous hexane. The resulting solution is centrifuged at 4000 rpm for 10 min and the precipitate is discarded. The obtained solution of CsPbI₃ NCs (supernatant) is used for further studies.

Single NC spectroscopy. The NCs in hexane are kept under Ar atmosphere for further analysis. For measurements on single NCs at cryogenic temperatures, a dilute solution of CsPbI₃ NCs is mixed with a 2 wt% polystyrene solution and spin-coated onto a clean sapphire coverslip with a rotation speed of 2000 rpm. A home-built scanning confocal microscope based on a 0.95 numerical aperture objective is placed in a cryostat and used to image single NCs by raster scanning the sample. For the acquisition of PL spectra, the NCs are excited at 561 nm with a cw laser.
A single-mode tunable Ti:Sa laser is used, together with a resolution of ~120 µeV using a grating of 1800 lines/mm. For tuning, a Twiss setup is used to build the start-stop coincidence histograms. Filtering of the exciton ZPLs, showing photon antibunching. Each histogram is surmounted by the corresponding fitting scheme. Left panel: Histogram recorded in a cross-correlation configuration, selecting the exciton ZPLs on one channel of the correlation setup and the biexciton ZPLs on the other. The asymmetry of the histogram is a signature of ordered biexciton-exciton–zero exciton photon cascades. Right panel: Histogram recorded with high-pass filtering of the exciton ZPLs, showing photon antibunching.

**Data availability**

All relevant data that support our experimental findings are available from the corresponding author upon reasonable request.

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**Author contributions**

A.S., M.L.B., and M.V.K. prepared the samples and performed the ensemble characterization. P.T. and L.H. performed the optical experiments. P.T., L.H., J.-B.T., and B.L. analyzed and interpreted the data. L.B. and Y.L. performed the experiments on CdSe NCs. J.E. developed the model of exchange interaction for the exciton fine structure. P.T., L.H., J.E. and B.L. wrote the manuscript with inputs from all authors. B.L. supervised the project.

**Competing interests**

The authors declare no competing interests.

**Additional information**

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