Intense Dark Exciton Emission from Strongly Quantum Confined CsPbBr$_3$ Nanocrystals

Daniel Rossi$^1$, Xiaohan Liu$^3$, Yangjin Lee$^{1,5}$, Mohit Khurana$^3$, Joseph Puthenpurayil$^2$, Kwanpyo Kim$^{1,5}$, Alexey Akimov$^{3,6,7}$, Jinwoo Cheon$^{1,4,*}$ and Dong Hee Son$^{2,1,*}$

$^1$Center for Nanomedicine, Institute for Basic Science (IBS), Seoul 03722, Republic of Korea
$^2$Department of Chemistry, Texas A&M University, College Station, Texas, 777843, USA
$^3$Department of Physics, Texas A&M University, College Station, Texas, 777843, USA
$^4$Department of Chemistry, Yonsei University, Seoul 03722, Republic of Korea
$^5$Department of Physics, Yonsei University, Seoul 03722, Republic of Korea
$^6$Russian Quantum Center, Skolkovo, Moscow, 143025, Russia
$^7$PN Lebedev Institute RAS, Moscow, 119991, Russia

*Correspondence to:
E-mail: dhson@chem.tamu.edu
E-mail: jcheon@yonsei.ac.kr
Abstract

Dark ground state exciton in semiconductor nanocrystals has been a subject of much interest due to its long lifetime attractive for applications requiring long-lived electronic or spin states. Significant effort has been made recently to explore and access the dark exciton level in metal halide perovskite nanocrystals, which are emerging as a superior source of photons and charges compared to other existing semiconductor nanocrystals.(1-6) However, the direct observation of long-lived photoluminescence from dark exciton has remained elusive in metal halide perovskite nanocrystals. Here, we report the observation of the intense emission from dark ground state exciton with 1-10 µs lifetime in strongly quantum confined CsPbBr$_3$ nanocrystals, which contrasts the behavior of weakly confined system explored so far. The study in CsPbBr$_3$ nanocrystals with varying degree of confinement has revealed the crucial role of quantum confinement in enhancing the bright-dark exciton level splitting which is important for accessing the dark exciton. Our work demonstrates the future potential of strongly quantum-confined perovskite nanocrystals as a new platform to utilize dark excitons.
Main

Metal halide perovskite (MHP) nanocrystals (NCs) have gained explosive interest as a superior source of photons and charge carriers compared to many other semiconductor NCs. The integration of MHP NCs into the technological applications, such as solar cells and light emitting devices, has driven intensive research on characterization and structural control of the energetics, relaxation dynamics, and transport properties of excitons. (6-12) Recently, the exciton fine structure of MHP NCs has become a subject of much interest, in particular on the level ordering of the bright and dark exciton and access to the dark exciton with potential use for applications such as quantum information processing.

In most semiconductor NCs, the lowest energy exciton is an optically inactive state located typically less than a few meV below the bright exciton level. At sufficiently low temperatures with thermal energy (kT) smaller than the bright-dark energy splitting (ΔE_{BD}), the dark exciton dominates the photoluminescence (PL). (13-16) Recently, the reversal of the bright and dark exciton level ordering was reported in weakly quantum-confined cesium lead halide (CsPbX₃) NCs, based on the observation of only fast-decaying bright exciton PL in single-particle studies at cryogenic temperatures. (1) On the other hand, a study in FAPbBr₃ NCs under magnetic field reported the signature of a dark exciton ~2.5 meV below the bright exciton, where the application of magnetic field brightened up the dark exciton that was otherwise not observable in the PL spectra. (2) Another study in CsPbCl₃ NCs also argued for the dark ground state exciton from the observation of the weak but longer-lived decay component in the lower-temperature PL kinetics, while the dark exciton could not be spectrally resolved from bright exciton. (3) In both cases however, the intensities of the PL attributed to the dark exciton were much smaller than that from the bright exciton. Because of the domination of the bright exciton PL even at cryogenic temperatures, and the absence of the direct measurement of the dark exciton decay dynamics, the dynamics of bright-dark level transition and dark exciton decay as well as accurate estimation of ΔE_{BD} in MHP NCs still remain elusive.

Here, we report the direct observation of intense μs-lived PL from dark excitons with ΔE_{BD} up to 24 meV in CsPbBr₃ NCs with strong quantum confinement. In contrast to the weakly confined MHP NCs in the earlier studies, the low temperature PL from strongly confined CsPbBr₃ NCs of varying dimensionalities, i.e., quantum dots (QDs), nanowires (NWs) and nanoplatelets (NPLs), were dominated by dark exciton PL with lifetime (τ_D) in the range of 1-10 μs. Time-dependent PL spectra of the NC ensemble at cryogenic temperatures showed well-resolved bright and dark exciton PL directly revealing ΔE_{BD} and τ_D in the spectra. ΔE_{BD} in strongly confined CsPbBr₃ NCs is an order of magnitude larger than in weakly confined CsPbBr₃ NCs, indicating the confinement-enhanced ΔE_{BD} by the stronger electron-hole exchange energy, consistent with recent theoretical prediction. (17) The results from this study demonstrate the potential of strongly quantum confined MHP NCs as the platform to utilize dark excitons, taking advantage of the large confinement-enhanced ΔE_{BD} combined with their superb properties as the source of photons and charges.

Figure 1 shows the electron microscopy images, absorption spectra (solid lines), and PL spectra (dashed lines) of weakly confined NCs and strongly confined QDs, NWs, and NPLs of CsPbBr₃. The size of the NCs in the quantum confined dimension (indicated in Figure 1) in the QDs, NWs, and NPLs is much smaller than twice the exciton Bohr radius of CsPbBr₃ (2a_B = 7 nm) imposing strong quantum confinement in varying dimensionality. (5) The weakly confined NCs were prepared following the procedure reported by Protesescu et al. (5) QDs, NWs, and NPLs were synthesized following the methods developed by Dong et al. which can control the size and
morphology precisely with high ensemble uniformity, as reflected in the microscopy images and the optical spectra showing the well-defined features of strongly confined excitons.\(^{(18, 19)}\) For the optical measurements, all the samples were passivated with dimethyl-dioctadecyl-ammonium bromide (DDAB) via ligand exchange for improved stability and PL quantum yield in polystyrene (PS) matrix used to disperse the NCs for PL measurements. Detailed descriptions of the synthesis and measurement methods are in the supplementary information.

Figure 1: Electron microscopy images (a-d), and optical spectra (e-h) of weakly confined NCs, and strongly confined QDs, NWs, and NPLs (left to right). The cartoon depicting the NC morphology and the size are indicated in each panel. Solid and dashed lines in the spectra are for the absorption and photoluminescence respectively. (a-c) are TEM images and (d) is STEM image.

Figure 2 shows the time-dependent PL spectra (a-d), spectrally integrated PL decay dynamics (e-h) and steady state PL spectra (i-l) following above bandgap excitation at 5K for the four CsPbBr\(_3\) NC samples shown in Figure 1. While the PL spectra at 300K exhibits a single well-defined PL feature which decays on the several ns time scale for all samples, (Figure S1-S5), at 5K the PL shows very different spectral and dynamic features. In the weakly confined CsPbBr\(_3\) NCs, a single PL peak with ~500 ps decay time is observed (Figure 2a, e, i), consistent with the results from earlier studies.\(^{(1, 4)}\) Because of the bright and fast-decaying PL on the sub-ns time scale, the earlier studies concluded that the dark exciton state in CsPbBr\(_3\) NCs is higher in energy than the bright exciton.\(^{(1)}\) This is opposite to most other semiconductor NCs exhibiting long-lived dark exciton PL at cryogenic temperatures as the lower energy dark exciton gains more population with decreasing temperatures.\(^{(13, 14)}\)

In contrast, all three strongly confined NCs (QDs, NWs and NPLs) exhibit two different PL peaks with decay time constants that differ by many orders of magnitude (Figure 2 b-d). Time gating the PL spectra near 0 ps and 0.5 \(\mu\)s readily reveals the two different PL peaks separated by 17-24 meV as shown to the right of Figure 2b-d. The fast and slow decay components (\(\tau_{\text{fast}}\), \(\tau_{\text{slow}}\)) of the PL decay kinetics in Figure 2 f-h are associated with the higher-energy and lower-energy PL peaks respectively. Fitting the steady state PL spectra (Figure 2 j-l) with the two PL peaks indicates that the lower-energy PL constitutes ~70 % of the total photons emitted at 5K in these NCs.
Figure 2: Time-dependent PL spectra (a-d), normalized spectrally integrated PL decay dynamics (e-h), and steady state PL spectra (i-l) of four different CsPbBr$_3$ NCs measured at 5K. The data are for weakly confined NCs, QDs, NWs, and NPLs from top to bottom. The two spectra shown next to panels b-d are the time-gated PL spectra taken near 0 ps (blue) and 0.5 $\mu$s (red).

Table 1: Parameters extracted from the PL decay data at 5K. $\Delta E_{BD}$ and $\tau_D$ were extracted directly from the time-dependent PL spectra and PL decay kinetics. The fraction of dark exciton PL from total PL was obtained by fitting of the steady state PL spectra. $\tau_B$ and $\tau_{BD}$ were estimated from the analysis of the steady state PL intensity and $\tau_{fast}$. Accurate $\tau_{fast}$ was obtained from short-time window PL decay kinetics data (Figure S8) that provide higher time resolution as detailed in supplementary information.

| Sample | $\Delta E_{BD}$ (meV) | $\tau_{slow} = \tau_D$ ($\mu$s) | $\tau_{fast}$ (ps) | $\tau_B$ (ps) | $\tau_{BD}$ (ps) | $I_D/I_{tot}$ (%) |
|--------|------------------------|-------------------------------|-----------------|-------------|---------------|-----------------|
| QD     | 17                      | 10                            | 387             | 1600        | 510           | 76              |
| NW     | 19                      | 0.85                          | 44              | 160         | 62            | 68              |
| NPL    | 24                      | 1.2                           | 37              | 124         | 54            | 73              |
We assign the higher-energy and lower-energy PL peaks to the bright and dark excitons respectively, as will be discussed in detail shortly. Table 1 summarizes the separation between the two PL peaks in Figure 2b-d, representing ΔE_{BD}, the time constants $\tau_{\text{fast}}$ and $\tau_{\text{slow}}$ of the time-dependent PL intensity, and the fraction of photons from the dark exciton determined from the fitting of the steady state PL spectra. Since the bright and dark exciton PL are spectrally well separated and ΔE_{BD} is 50-70 times larger than $kT$ at 5K, thermal excitation from the dark to bright exciton states is suppressed, and $\tau_{\text{slow}}$ can reliably be taken as the dark exciton lifetime $\tau_D$. On the other hand, $\tau_{\text{fast}}$ reflects the decay of the bright exciton population via radiative and nonradiative relaxation combined with phonon-assisted transition from the bright to the dark exciton. The estimation of the bright exciton lifetime ($\tau_B$) and the time constant for the bright-to-dark transition ($\tau_{\text{BD}}$) has been made from the analysis of the relative intensities of the bright and dark exciton PL at 5K, as described in detail in the supplementary information.

In Table 1, $\tau_B$ is longer than $\tau_{\text{BD}}$ for all the samples, showing qualitatively the same trend as many other colloidal semiconductor QDs.(20) $\tau_B$ of QDs (1.6 ns) is significantly longer than in weakly confined NCs (~500 ps), which is consistent with the calculated bright exciton lifetime of strongly confined CsPbBr$_3$ QDs from recent study.(1) Interestingly, $\tau_B$ of NWs and NPLs are nearly an order of magnitude shorter than in QDs. The faster $\tau_B$ in NWs and NPLs compared with QDs is reminiscent of the enhanced exciton recombination rate observed in other 1D and 2D confined semiconductors, reflecting the larger exciton binding energies and enhanced electron-hole correlations, although a more systematic study is needed for better understanding. (1, 21) Despite the relatively short $\tau_B$ of NWs (160 ps) and NPLs (124 ps), the PL is predominantly from dark exciton below ~20 K (Figure S2-S5). The stark contrast of in the PL dynamics at cryogenic temperatures between the weakly and strongly confined NCs is mainly due to the large increase of ΔE_{BD} from the confinement enhanced exchange coupling in conjunction with the rapid transition from bright to dark exciton state. The confinement enhancement of ΔE_{BD} is further corroborated by the comparison of the time-dependent PL spectra from QDs and NPLs with varying quantum confinement at 5K, which shows the smaller ΔE_{BD} for the weaker confinement. (Figure S6-S7).

The assignment of the lower-energy PL observed in QDs, NWs, and NPLs to the dark exciton has been made for the reasons discussed below, however other processes that can produce a PL peak redshifted from the bright exciton PL in MHP NCs must be considered. Self-trapped exciton, phonon replica, and defect emission have been discussed previously as the origin of redshifted PL observed in several MHP materials, both in bulk and nanocrystalline forms.(22-26) In addition, trion emission and interparticle excimer-like emission have been discussed as the origin of certain PL features redshifted from the exciton PL in CdSe NPLs, although such observations have not been reported for MHP NCs yet.(27, 28) These alternative explanations can be ruled out in our study by examining the difference in the spectral characteristics of the PL, such as the linewidth, lifetime, the magnitude of redshift from the bright exciton, and the dependence of the lifetime on external magnetic field.

Self-trapped exciton has been discussed extensively to explain a broad PL feature redshifted from the exciton PL observed in some MHP NCs, especially prominent under slight sub-gap excitation condition.(22) PL from the self-trapped NCs typically has a much larger spectral linewidth and Stokes shift than the exciton PL due to the larger lattice displacement associated with these transitions. In CsPbBr$_3$ NCs, the PL from self-trapped exciton was observed ~100 meV redshifted from the exciton PL, with three times broader linewidth, and a lifetime of ~170 ns, very different from the lower-energy PL observed in the strongly confined CsPbBr$_3$ NCs of this study.
Furthermore, the disappearance of the self-trapped exciton PL with above-bandgap excitation further rules out self-trapped exciton as the origin for the μs-lived lower-energy PL observed in our study. Similarly, phonon overtones are observed in the low-temperature PL spectra for all semiconductors. The first phonon overtone will appear as a PL sideband redshifted by one optical phonon energy, with an intensity proportional to the exciton-phonon coupling. While $\Delta E_{BD}$ in this study is similar in the order of magnitude to the optical phonon energy of bulk CsPbBr$_3$, the large disparity between the lifetimes of the two PL peaks by many orders of magnitude immediately dismisses this possibility.

A redshifted PL feature with similar spectral linewidth to the exciton PL is commonly observed in the low-temperature PL spectra of CdSe NPLs. While its origin is still debated, two recent works suggested it may result from the excimer-like emission from stacked NPLs or trion emission.(27, 28) Considering that we observed the redshifted PL universally in all strongly quantum confined NCs of different dimensionality (QDs, NPLs, NWs), the excimer-like emission observed in CdSe NPLs is not likely to explain our observation in MHP NCs. Furthermore, the independence of the PL lifetime on the magnetic field from these two origins contrasts with the strongly magnetic field-dependent lifetime of the slow-decay component in the PL shown in Figure 3, further ruling out these two options.

**Figure 3**: Magnetic field-dependent PL decay dynamics of CsPbBr$_3$ NPLs at liquid helium temperature. Only the slow-decay component of the PL from CsPbBr$_3$ NPLs is plotted.

Figure 3 shows the dependence of the slow-decay component of the PL from CsPbBr$_3$ NPLs under 0T, 4T, and 8T magnetic field at liquid helium temperature. The lifetime shortens with increasing magnetic field, consistent with the description of the dark and bright exciton levels mixed by the magnetic field. The similar magnetic field dependence of the dark exciton lifetime was observed in recent studies on single FAPbBr$_3$ NCs and Mn-doped CsPbCl$_3$ NC ensembles.(2, 3) For self-trapped exciton, defect emission, trion emission and excimer-like emission, the dependence of the PL lifetime on the magnetic field is not expected, as has been experimentally confirmed in several studies.(27, 28) In addition to the discussion above, the dependence of the PL lifetime on the magnetic field provides strong support for the assignment of the μs-lived lower-energy PL to the dark exciton.
Figure 4: Temperature dependence of $\tau_{\text{fast}}$ and $\tau_{\text{slow}}$ from weakly confined NCs, QDs, NWs and NPLs (a-d). For weakly confined NCs, only one time constant is plotted from single exponential fit of the PL decay kinetics data.

Figure 4 compares the temperature dependence of $\tau_{\text{fast}}$ and $\tau_{\text{slow}}$ from the strongly confined QDs, NWs and NPLs with the PL decay time of weakly confined NCs in the temperature range of 5-100 K. For the weakly confined NCs (Figure 4a), the exciton PL decay kinetics are nearly single exponential, similar to the earlier observation, although a slight departure from single exponential decay is observed between 5-50 K. (Figure S1) In contrast, the strongly confined NCs show clearly biexponential decay in the entire 5-100 K temperature range, characterized by $\tau_{\text{fast}}$ and $\tau_{\text{slow}}$, which vary strongly with the temperature (Figure 4 b-d). The temperature dependence of $\tau_{\text{fast}}$ and $\tau_{\text{slow}}$ is understood in the context of a commonly used three-level kinetic model describing the relaxation of the bright and dark exciton states separated by $\Delta E_{\text{BD}}$. In this model, the temperature-dependent competition among the radiative recombinations and the reversible dark-bright state transition gives rise to the temperature dependence of the time constants as explained in detail in supplementary information. For QDs, the temperature-dependent $\tau_{\text{fast}}$ and $\tau_{\text{slow}}$ in Figure 4b are accurately reproduced with the three-level model using $\Delta E_{\text{BD}}$, $\tau_{\text{B}}$, $\tau_{\text{D}}$, and $\tau_{\text{BD}}$ in Table 1, determined from the PL spectra and decay dynamics at 5K, as nonadjustable parameters. (Figure S10) For NWs and NPLs, the three-level kinetic model with the nonadjustable $\Delta E_{\text{BD}}$, $\tau_{\text{B}}$, $\tau_{\text{D}}$, and $\tau_{\text{BD}}$ values in Table 1 shows a little larger discrepancy between the measured and modeled $\tau_{\text{fast}}$, while the model fits $\tau_{\text{slow}}$ very well. The larger discrepancy in $\tau_{\text{fast}}$ is possibly due to the involvement of an additional nonradiative decay channel of the bright exciton that exhibits more complex temperature dependence than QDs in the 5-100 K range, as can be hinted from the larger and more complex variation of the total PL intensity of NWs and NPLs compared to the QDs. (Figure S9) Nevertheless, the overall temperature dependence of $\tau_{\text{slow}}$ and $\tau_{\text{fast}}$ are fully consistent with the dark ground state exciton thermally equilibrated with the bright exciton level. This model serves not only to demonstrate the differences in dynamics between the weakly confined NCs and strongly confined QDs, NWs, and NPLs, but also highlights the importance of the large enhancement of $\Delta E_{\text{BD}}$ by the quantum confinement, resulting in the dominance of the long-lived dark exciton in the low temperature PL. This discovery opens an exciting possibility to take advantage of the superior photonic properties of strongly confined MHPs in numerous applications utilizing long live states, including lasing, sensing and quantum information processing.
References:

1. M. A. Becker, R. Vaxenburg, G. Nedelcu, P. C. Sercel, A. Shabaev, M. J. Mehl, J. G. Michopoulos, S. G. Lambrakos, N. Bernstein, J. L. Lyons, T. Stöferle, R. F. Mahrt, M. V. Kovalenko, D. J. Norris, G. Raino, A. L. Efros, Bright triplet excitons in caesium lead halide perovskites. Nature 553, 189-193 (2018).

2. P. Tamarat, M. I. Bodnarchuk, J.-B. Trebbia, R. Erni, M. V. Kovalenko, J. Even, B. Lounis, The ground exciton state of formamidinium lead bromide perovskite nanocrystals is a singlet dark state. Nat. Mater. 18, 717-724 (2019).

3. K. Xu, J. F. Vliem, A. Meijerink, Long-lived dark exciton emission in Mn-Doped CsPbCl₃ perovskite nanocrystals. J. Phys. Chem. C 123, 979-984 (2019).

4. G. Raino, G. Nedelcu, L. Protesescu, M. I. Bodnarchuk, M. V. Kovalenko, R. F. Mahrt, T. Stöferle, Single cesium lead halide perovskite nanocrystals at low temperature: fast single-photon emission, reduced blinking, and exciton fine structure. ACS Nano 10, 2485-2490 (2016).

5. L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, A. Walsh, M. V. Kovalenko, Nanocrystals of cesium lead halide perovskites (CsPbX₃, X = Cl, Br, and I): novel optoelectronic materials showing bright emission with wide color gamut. Nano Lett. 15, 3692-3696 (2015).

6. F. Hu, H. Zhang, C. Sun, C. Yin, B. Lv, C. Zhang, W. W. Yu, X. Wang, Y. Zhang, M. Xiao, Superior optical properties of perovskite nanocrystals as single photon emitters. ACS Nano 9, 12410-12416 (2015).

7. S. Yakunin, L. Protesescu, F. Krieg, M. I. Bodnarchuk, G. Nedelcu, M. Hummer, G. De Luca, M. Fiebig, W. Heiss, M. V. Kovalenko, Low-threshold amplified spontaneous emission and lasing from colloidal nanocrystals of caesium lead halide perovskites. Nat. Commun. 6, 8056 (2015).

8. K. Wu, G. Liang, Q. Shang, Y. Ren, D. Kong, T. Lian, Ultrafast interfacial electron and hole transfer from CsPbBr₃ perovskite quantum dots. J. Am. Chem. Soc. 137, 12792-12795 (2015).

9. G. Nedelcu, L. Protesescu, S. Yakunin, M. I. Bodnarchuk, M. J. Groenendijk, M. V. Kovalenko, Fast anion-exchange in highly luminescent nanocrystals of cesium lead halide perovskites (CsPbX₃, X = Cl, Br, I). Nano Lett. 15, 5635-5640 (2015).

10. H. Utzat, W. Sun, A. E. K. Kaplan, F. Krieg, M. Ginterseder, B. Spokoyny, N. D. Klein, K. E. Shulenberger, C. F. Perkinson, M. V. Kovalenko, M. G. Bawendi, Coherent single-photon emission from colloidal lead halide perovskite quantum dots. Science 363, 1068-1072 (2019).

11. S. D. Stranks, G. E. Eperon, G. Grancini, C. Menelaou, M. J. P. Alcocer, T. Leijtens, L. M. Herz, A. Petrozza, H. J. Snaith, Electron-hole diffusion lengths exceeding 1 micrometer in an organometal trihalide perovskite absorber. Science 342, 341-344 (2013).

12. L. Dou, Y. Yang, J. You, Z. Hong, W.-H. Chang, G. Li, Y. Yang, Solution-processed hybrid perovskite photodetectors with high detectivity. Nat. Commun. 5, 5404 (2014).

13. M. Nirmal, D. J. Norris, M. Kuno, M. G. Bawendi, A. L. Efros, M. Rosen, Observation of the "dark exciton" in CdSe quantum dots. Phys. Rev. Lett. 75, 3728-3731 (1995).

14. M. S. Gaponenko, A. A. Lutich, N. A. Tolstik, A. A. Onushchenko, A. M. Malyshevich, E. P. Petrov, K. V. Yumashev, Temperature-dependent photoluminescence of PbS quantum dots in glass: Evidence of exciton state splitting and carrier trapping. Phys. Rev. B 82, 125320-125329 (2010).

15. X.-X. Zhang, Y. You, S. Y. F. Zhao, T. F. Heinz, Experimental evidence for dark excitons in monolayer WSe₂. Phys. Rev. Lett. 115, 257403-257409 (2015).

16. Z. Li, T. Wang, C. Jin, Z. Lu, Z. Lian, Y. Meng, M. Blei, S. Gao, T. Taniguchi, K. Watanabe, T. Ren, S. Tongay, L. Yang, D. Smirnov, T. Cao, S.-F. Shi, Emerging photoluminescence from the dark-exciton phonon replica in monolayer WSe₂. Nat. Commun. 10, 2469 (2019).

17. P. C. Sercel, J. L. Lyons, D. Wickramaratne, R. Vaxenburg, N. Bernstein, A. L. Efros, Exciton fine structure in perovskite nanocrystals. Nano Lett. 19, 4068-4077 (2019).

18. Y. Dong, T. Qiao, D. Kim, D. Parobek, D. Rossi, D. H. Son, Precise control of quantum confinement in cesium lead halide perovskite quantum dots via thermodynamic equilibrium. Nano Lett. 18, 3716-3722 (2018).

19. Y. Dong, T. Qiao, D. Kim, D. Rossi, S. J. Ahn, D. H. Son, Controlling anisotropy of quantum-confined CsPbBr₃ nanocrystals by combined use of equilibrium and kinetic anisotropy. Chem. Mater. 31, 5655-5662 (2019).

20. O. Labeau, P. Tamarat, B. Lounis, Temperature dependence of the luminescence lifetime of single CdSeZnS quantum dots. Phys. Rev. Lett. 90, 257404-257408 (2003).
21. M. D. Tessier, C. Javaux, I. Maksimovic, V. Loriette, B. Dubertret, Spectroscopy of single CdSe nanoplatelets. *ACS Nano* 6, 6751-6758 (2012).
22. X. Ma, F. Pan, H. Li, P. Shen, C. Ma, L. Zhang, H. Niu, Y. Zhu, S. Xu, H. Ye, Mechanism of single-photon upconversion photoluminescence in all-inorganic perovskite nanocrystals: the role of self-trapped excitons. *J. Phys. Chem. Lett.* 10, 5989-5996 (2019).
23. X. Lao, Z. Yang, Z. Su, Z. Wang, H. Ye, M. Wang, X. Yao, S. Xu, Luminescence and thermal behaviors of free and trapped excitons in cesium lead halide perovskite nanosheets. *Nanoscale* 10, 9949-9956 (2018).
24. C. M. Iaru, J. J. Geuchies, P. M. Koenraad, D. Vanmaekelbergh, A. Y. Silov, Strong carrier–phonon coupling in lead halide perovskite nanocrystals. *ACS Nano* 11, 11024-11030 (2017).
25. X. Wu, M. T. Trinh, D. Niesner, H. Zhu, Z. Norman, J. S. Owen, O. Yaffe, B. J. Kudisch, X. Y. Zhu, Trap states in lead iodide perovskites. *J. Am. Chem. Soc.* 137, 2089-2096 (2015).
26. M. Fu, P. Tamarat, J.-B. Trebbia, M. I. Bodnarchuk, M. V. Kovalenko, J. Even, B. Lounis, Unraveling exciton–phonon coupling in individual FAPbI$_3$ nanocrystals emitting near-infrared single photons. *Nat. Commun.* 9, 3318 (2018).
27. B. T. Diroll, W. Cho, I. Coropeanu, S. M. Harvey, A. Brumberg, N. Holtgrewe, S. A. Crooker, M. R. Wasielewski, V. B. Prakapenka, D. V. Talapin, R. D. Schaller, Semiconductor nanoplatelet excimers. *Nano Lett.* 18, 6948-6953 (2018).
28. E. V. Shornikova, D. R. Yakovlev, L. Biadala, S. A. Crooker, V. V. Belykh, M. V. Kochiev, A. Kuntzmann, M. Nasilowski, B. Dubertret, M. Bayer, Negatively charged excitons in CdSe nanoplatelets. *Nano Lett.*, (2020).
Methods:

Materials

Materials: Cesium Carbonate (Cs$_2$CO$_3$, 99.995%, Trace Metal Basis, Sigma Aldrich), Lead Bromide (PbBr$_2$, 99.999%, Trace Metal Basis, Sigma Aldrich), Zinc Bromide (ZnBr$_2$, 99.999%, Trace Metal Basis, Sigma Aldrich), Cobalt Bromide (CoBr$_2$, 99%, Sigma Aldrich), Copper Bromide (CuBr$_2$, 99%, Sigma Aldrich), Oleylamine (OAm, 70%, Technical Grade, Sigma Aldrich), Oleic Acid (OA, 90%, Technical Grade, Sigma Aldrich), Octadecene (ODE, 90%, Technical Grade, Sigma Aldrich), Polystyrene (Sigma Aldrich, 192,000 average molecular weight).

Preparation of CsPbBr$_3$ Nanocrystals

Preparation of Cs Precursor Solution
All NC samples were prepared using the same Cs$_2$CO$_3$ precursor solution. 250 mg Cs$_2$CO$_3$, 1 mL OA, 7 mL ODE were loaded into a 50 mL three neck flask and vacuumed on a Schlenk line for 10 minutes at room temperature. The flask was refilled with Ar gas and heated to 150 °C. The solution was held at 150 °C until use.

Preparation of CsPbBr$_3$ weakly confined nanocrystals (NCs)
CsPbBr$_3$ NCs were prepared following the methods Protesescu et al. $(1)$ Typically 70 mg PbBr$_2$, 5 mL ODE, 0.5 mL OA, and 0.5 mL OAm were loaded into a three neck flask and vacuumed on a Schlenk line at room temperature for 10 minutes. The solution was heated to 110 °C under vacuum and the flask was refilled with Ar gas. The solution as heated to 200 °C and held for 5 minutes. 0.4 mL of Cs precursor was injected into the reaction mixture and the reaction was quenched in an ice bath. The resulting NC suspension was centrifuged at 7000 rpm for 10 minutes and the supernatant was discarded. The precipitate NCs were dispersed in hexane and the solution was centrifuged at 17000RPM for 10 minutes. The supernatant was collected and stored under Ar at 4 °C until use.

Preparation of CsPbBr$_3$ strongly confined quantum dots (QDs)
Strongly confined CsPbBr$_3$ QDs (4nm) were prepared via methods recently developed by Dong et al. $(2)$ In a glove box, 600 mg ZnBr$_2$, 250 mg PbBr$_2$, 8 mL ODE, 4 mL OA and 4 mL OAm were loaded into a 25 mL 3 neck flask and transferred to a Schlenk line where they were vacuumed at 100 °C for 20 minutes. The solution was cooled to 80 °C and 1.2 mL Cs precursor solution was injected. The reaction proceeds for 90 seconds and was cooled in an ice bath. The resulting suspension was centrifuged at 7000 rpm for 10 minutes and the supernatant collected. The collected solution was allowed to sit for up to 24 hours and centrifuged whenever a significant amount of salt had precipitated. Once the solution remains clear, 1.5 the volume of acetone was added to precipitate the QDs. The QDs were dissolved in a minimum volume hexane and precipitated with methyl acetate. The resulting QDs were stored in hexane under Ar at 4 °C until use.

Preparation of CsPbBr$_3$ nanowires (NWs) and nanoplatelets (NPLs)
NWs and NPLs were prepared via methods recently developed by Dong et al. For 2 nm-thick NWs, 120 mg CoBr₂, 65 mg PbBr₂, 5 mL ODE, 3 mL OA, and 3 mL OAm were loaded into a 25 mL three neck flask and vacuumed at room temperature for 10 minutes. For 2 nm-thick NPLs, 400 mg CuBr₂, 100 mg ZnBr₂, 65 mg PbBr₂, 5 mL ODE, 3 mL OA, and 3 mL OAm were loaded into a 25 mL three neck flask and vacuumed at room temperature for 10 minutes. In both cases, the solution was vacuumed at 100 °C for 10 minutes then returned to Ar gas atmosphere. The solution was heated to 200 °C and held for 5 minutes to dissolve all the salt. The solution were cooled to room temperature (20-30 °C). 0.4 mL Cs precursor was cooled to room temperature in a syringe and injected into the solution and the solution as transferred to a centrifuge tube. 1.5 X the volume of acetone was added carefully so as not to directly mix the acetone and the precursor solution. The container was shaken vigorously to initiate the reaction and allowed to react for 2 minutes. The resulting suspension was centrifuged at 7000 rpm for 10 minutes. The supernatant was discarded, the particles were dissolved in 1 mL hexane and centrifuged at 3000 rpm for 5 minutes to remove salts. The supernatant was collected and the particles were precipitated with 2 mL methyl acetate and centrifuged at 7000 rpm for 10 minutes. The supernatant was discarded and the particles were dissolved in 2 mL hexane and centrifuged at 17000 rpm for 10 minutes, the supernatant collected and stored under Ar gas at 4 °C until used.

Ligand exchange of CsPbBr₃ NCs with dimethyl-dioctadecyl-ammonium bromide (DDAB)
10 µl NC stock solution was dried and dissolved in 200 µl toluene. ~10 µl of 0.05 M DDAB solution in toluene was added and the solution was stirred. The PL intensity was monitored until it reached maximum (the amount of DDAB can be adjusted batch to batch to reach maximum QY), the particles were precipitated with methyl acetate and centrifuged at 1700 rpm. The resulting nanocrystals were dispersed in 1% PS/toluene solution.

Preparation of NC film on sapphire substrate for temperature-dependent PL measurement
DDAB-passivated NCs were initially dispersed in 1% PS-toluene solution. PS polymer was used as the matrix to disperse the NCs in the dried film of NCs on the substrate. The concentration of NCs were adjusted such that the absorbance in 1 cm cell is approximately 5 near 400 nm. The solution was drop cast on a sapphire substrate and dried in a vacuum chamber for 30 minutes.

Sample Characterization

Temperature-dependent photoluminescence measurements
NC film on a sapphire substrate were loaded into an open cycle cryostat (Oxford Instruments Microstat-HE), coupled to an inverted microscope (Nikon Ti-e), to record the photoluminescence in the temperature range of 5-300K. Excitation was provided with either 405 nm pulsed diode laser (Hamamatsu) with pulse width of 45 ps or frequency doubled Ti:Sapphire laser (One-Five Origami) producing 800 nm pulses with pulse width of 200fs. The intensity of excitation light was maintained below 0.2 W/cm² to minimize the heating of the sample by light absorption at cryogenic temperatures.

Photoluminescence (PL) was collected using a 50X objective with a long working distance (15 mm) and sent to the imaging spectrograph EMCCD (Andor, iXon) for steady-state PL measurement. For time resolved measurements, the PL was coupled to an imaging spectrograph
to spectrally disperse the PL onto a Hamamatsu streak camera (C14831). Since the time resolution of the PL spectra depends on the total time window of the acquisition in the streak camera, several different time windows (1 ns, 20 ns, 100 ns, 2 µs and 20 µs) were used to cover the necessary time window to observe the dark exciton PL and obtain sufficient time resolution for the fast component of PL decay dynamics.

Frequency doubled Ti:Sapphire laser was used for <20 ns time window on the streak camera, which gives maximum time resolution of ~20 ps. For all other measurements with >20 ns time window, pulsed diode laser that provides more flexible control of repetition rate was used as the excitation source.

**Magnetic field-dependent dark exciton PL lifetime measurements**
For the measurement of magnetic field-dependent PL lifetime, the sample film on a sapphire substrate was mounted in a magneto optical cryostat oriented in Faraday geometry (Cryostat J2205). The NC sample was excited with 405 nm, 150 ns excitation pulses produced at the repetition rate of 200 kHz using a CW laser and acousto-optic modulator. Time-resolved photoluminescence was collected by time-correlated single photon counting (PicoHarp 300) with an avalanche photodiode. 150 ns pulse width was sufficient to measure the PL decay dynamics of dark exciton with 1-10 µs lifetime.

**Transmission Electron Microscope Measurements**
TEM and STEM images were obtained with a double Cs-aberration corrected JEOL ARM-200F operated at 200 kV.

**Methods References:**

1. L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, A. Walsh, M. V. Kovalenko, Nanocrystals of cesium lead halide perovskites (CsPbX3, X = Cl, Br, and I): novel optoelectronic materials showing bright emission with wide color gamut. *Nano Lett.* **15**, 3692-3696 (2015).
2. Y. Dong, T. Qiao, D. Kim, D. Parobek, D. Rossi, D. H. Son, Precise control of quantum confinement in cesium lead halide perovskite quantum dots via thermodynamic equilibrium. *Nano Lett.* **18**, 3716-3722 (2018).
3. Y. Dong, T. Qiao, D. Kim, D. Rossi, S. J. Ahn, D. H. Son, Controlling anisotropy of quantum-confined CsPbBr3 nanocrystals by combined use of equilibrium and kinetic anisotropy. *Chem. Mat.* **31**, 5655-5662 (2019).
**Funding:** DHS and AA acknowledge the National Science Foundation (CHE-1836538) for financial support. JC acknowledges Institute for Basic Science (IBS-R026-D1) for financial support.

**Author contributions:** DHS conceived the idea for the study. DR synthesized the materials and performed the low temperature streak measurements. XL and MK performed the low temperature magnetic field measurements under the supervision of AA. YL performed the TEM measurement under the supervision of KK and JC. DR and DHS wrote the manuscript. All authors discussed the results and commented on the manuscript. DHS and JC supervised the project.

**Competing interests:** None declared.

**Materials and Correspondence:** Correspondence should be addressed to Dong Hee Son and Jinwoo Cheon.

**Data and materials availability:** All (other) data needed to evaluate the conclusions in the paper are present in the paper or the supplementary information.
Supplementary Information

Intense Dark Exciton Emission from Strongly Quantum Confined CsPbBr$_3$ Nanocrystals

Daniel Rossi$^1$, Xiaohan Liu$^3$, Yangjin Lee$^{1,5}$, Mohit Khurana$^3$, Joseph Puthenpurayil$^2$, Kwanpyo Kim$^{1,5}$, Alexey Akimov$^{3,6,7}$, Jinwoo Cheon$^{1,4,*}$ and Dong Hee Son$^{2,1,*}$

$^1$Center for Nanomedicine, Institute for Basic Science (IBS), Seoul 03722, Republic of Korea
$^2$Department of Chemistry, Texas A&M University, College Station, Texas, 777843, USA
$^3$Department of Physics, Texas A&M University, College Station, Texas, 777843, USA
$^4$Department of Chemistry, Yonsei University, Seoul 03722, Republic of Korea
$^5$Department of Physics, Yonsei University, Seoul 03722, Republic of Korea
$^6$Russian Quantum Center, Skolkovo, Moscow, 143025, Russia
$^7$PN Lebedev Institute RAS, Moscow, 119991, Russia

*Correspondence to:
E-mail: dhson@chem.tamu.edu
E-mail: jcheon@yonsei.ac.kr
List of Supplementary information:

S1. Temperature Dependent PL dynamics (Figure S1-S5)
S2 Effects of Quantum Confinement on ΔE_{BD} (Figure S6-S7)
S3. Estimation of τ_B and τ_{BD} from the Steady State PL Spectra (Figure S8-S9)
S4. Three-Level Kinetic Model and Temperature-Dependent τ_{fast} and τ_{slow} (Figure S10)
S1. Temperature Dependent PL dynamics of different CsPbBr$_3$ NCs (Figure S1-S5)

**Figure S1:** Temperature-dependent PL spectra and PL decay dynamics of the weakly confined CsPbBr$_3$ NCs (10 nm size). Time-dependent PL spectra (a-f), time averaged PL spectra (g-l), and the spectrally averaged PL decay dynamics (m-r).
Figure S2: Temperature-dependent PL spectra and PL decay dynamics of the strongly confined CsPbBr$_3$ QDs (4 nm size). Time-dependent PL spectra (a-f), time-gated PL spectra separating the spectra from the short (blue) and long (red) component of the decay (g-l), and the spectrally averaged PL decay kinetics (m-r).
Figure S3: Temperature-dependent PL spectra and PL decay dynamics of the strongly confined CsPbBr₃ NWs (2 nm thick). Time-dependent PL spectra (a-f), time-gated PL spectra separating the spectra from the short (blue) and long (red) component of the decay (g-l), and the spectrally averaged PL decay kinetics (m-r).
Figure S4: Temperature-dependent PL spectra and PL decay dynamics of the strongly confined CsPbBr$_3$ NPLs (2 nm-thick). Time-dependent PL spectra (a-f), steady state PL spectra(g-l), and the spectrally averaged PL decay dynamics (m-r). The data shown in n-q were obtained using 150 ns-long excitation pulse, which shows artifactual signal at first early times.
Figure S5: Temperature-dependent steady state PL spectra of the strongly confined CsPbBr$_3$ NWs (a-f) and NPLs (g-l).
S2. Size-dependence of \( \Delta E_{BD} \) in Strongly Confined QDs and NPLs (Figure S6-S7)

**Figure S6:** Comparison of the time-dependent PL spectra (a,b) and time-gated PL spectra (c, d) of two sizes (4nm and 5nm) QDs at 5K. The size of the QDs are indicated next to each panel. Time gating was done near 0 ns and 10 ns to separate the bright and dark exciton PL spectra.

**Figure S7:** Comparison of the time-dependent PL spectra (a,b) and time-gated PL spectra (c, d) of the strongly confined NPLs of two different thicknesses at 5K. The thickness of the NPLs are indicated next to each panel. Time gating was done near 0 ns and 10 ns to separate the bright and dark exciton PL spectra.
S3. Estimation of $\tau_B$ and $\tau_{BD}$ from the Steady State PL Spectra (Figure S8-S9)

Time constants for the relaxation of bright exciton ($\tau_B$) and transition from bright to dark exciton ($\tau_{BD}$) were estimated from the steady state PL spectra (Figure 2) and the fast-decay kinetics data obtained from streak camera on narrow time window (Figure S8) at 5K. We extract accurate $\tau_{fast}$ values listed in Table 1 from Figure S8.

Figure S8: PL decay dynamics from the QD (a,b), NW (c,d), and NPL (e,f) measured with a streak camera with narrow time window. Instrument response is sufficiently fast (~20 ps for 1 ns window) to reliably extract $\tau_{fast}$. The top row shows the time-resolved PL spectra and the bottom row shows the spectrally integrated PL decay kinetics with the long decay component subtracted.

At 5K, the fast-decay dynamics represent the sum of the relaxation of the bright exciton and transfer from bright to dark exciton level if dark exciton relaxation is sufficiently slow compared to all other processes. (See S4 for details of derivation)

\[
\frac{1}{\tau_B} + \frac{1}{\tau_{BD}} = \frac{1}{\tau_{fast}} \quad \text{(Eq. S1)}
\]

Because $\Delta E_{BD} >> kT$ at 5K, thermal excitation from bright to dark state can be ignored. We can take the ratio of the PL intensities from bright ($I_B$) and dark ($I_D$) exciton in steady state PL spectra at 5K as the branching ratio for bright exciton relaxation and bright-to-dark transition under the following two assumptions: (i) The time scale for cooling from the initially excited level to the bandedge bright exciton level is much shorter than $\tau_B$ and $\tau_{BD}$, (ii) nonradiative decay of bright and dark exciton is not significant at 5 K.

\[
\frac{\tau_B}{\tau_{BD}} = \frac{I_D}{I_B} \quad \text{(Eq. S2)}
\]

Assumption (i) is reasonable since the time scale for cooling of hot exciton reported is typically sub ps in perovskite nanocrystals. Assumption (ii) is less straightforward, but we assume it is approximately valid considering the near-maximum PL intensity at 5 K as shown in Figure S9.

Sample calculation of $\tau_B$ and $\tau_{BD}$ for NPLs:
Since the bright and dark excitons PL are spectrally well separated, we can obtain $\frac{I_D}{I_B}$ accurately from the fitting of the steady state PL shown in Figure 2.

For the NPL sample, $\frac{I_D}{I_B} = 2.3$, therefore $\tau_B = 2.3\tau_{BD}$.

$1/\tau_B + 1/\tau_{BD} = 1/\tau_{fast} = \frac{1}{38\, ps}$ from Figure S8 (f).

From the two equations above, we obtain $\tau_{BD} = 54\, ps$ and $\tau_B = 124\, ps$.

**Figure S9:** Normalized temperature dependent integrated intensities from the weekly confined NC, and strongly confined QD, NW, and NPL films used in the main text(a-d).
S4. Three-Level Kinetic Model and Temperature-Dependent $\tau_{\text{fast}}$ and $\tau_{\text{slow}}$ (Figure S10)

It is common to model the kinetics of the bright and dark exciton after a three-level system with two emitting states (bright and dark) with lifetime $\tau_B$ and $\tau_D$ separated in energy by $\Delta E_{BD}$. Transition between these two states occurs via absorption or emission of a phonon with rates $\gamma_{DB} = \gamma_0 N_B$, and $\gamma_{BD} = \gamma_0 (N_B + 1)$, where $\gamma_0$ is the zero temperature bright-to-dark transition rate and $N_B$ is the phonon occupation number. We can model the time dependent population dynamics of the bright ($P_B$) and dark ($P_D$) state as follows.

\[
\frac{dP_B}{dt} = -(\Gamma_B + \gamma_0 (N_B + 1))P_B + \gamma_0 N_B P_D \quad \text{(Eq. S3)}
\]

\[
\frac{dP_D}{dt} = -(\Gamma_D + \gamma_0 N_B)P_D + \gamma_0 (N_B + 1)P_B \quad \text{(Eq. S4)}
\]

Where $\Gamma_B = \frac{1}{\tau_B}$, $\Gamma_D = \frac{1}{\tau_D}$, $\gamma_0 (N_B + 1) = \frac{1}{\tau_{BD}}$, $\gamma_0 N_B = \frac{1}{\tau_{BD}}$, and $N_B = \frac{1}{(\exp(\Delta E_{BD}/kT) - 1)}$ at temperature $T$.

Solving Eq. S3 and S4 with initial condition of $P_B(t=0) = 1$, $P_D(t=0) = 0$, we get the biexponential decay for both $P_B(t)$ and $P_D(t)$ with the two temperature dependent rate constants $\Gamma_{\text{slow}}(T) = 1/\tau_{\text{slow}}(T)$ and $\Gamma_{\text{fast}}(T) = 1/\tau_{\text{fast}}(T)$ expressed as follows.

\[
\Gamma_{(\text{fast}(+), \text{slow}(-))}(T) = \frac{1}{2} \left( \Gamma_B + \Gamma_D + \gamma_0 + 2N_B\gamma_0 \pm \sqrt{(\Gamma_B - \Gamma_D + \gamma_0)^2 + 4N_B\gamma_0^2(N_B + 1)} \right) \quad \text{(Eq. S5)}
\]

At 5 K, $N_B \approx 0$. Under the condition $\Gamma_D \ll \Gamma_B$ and $\gamma_0$, we obtained the following two equations.

\[
\Gamma_{\text{slow}}(5K) \approx \frac{1}{2} \left( \Gamma_B + \Gamma_D + \gamma_0 - \sqrt{(\Gamma_B - \Gamma_D + \gamma_0)^2} \right) = \Gamma_D = \frac{1}{\tau_D} \quad \text{(Eq. S6)}
\]

\[
\Gamma_{\text{fast}}(5K) \approx \frac{1}{2} \left( \Gamma_B + \Gamma_D + \gamma_0 + \sqrt{(\Gamma_B - \Gamma_D + \gamma_0)^2} \right) = \Gamma_B + \gamma_0 = \frac{1}{\tau_B} + \frac{1}{\tau_{BD}} \quad \text{(Eq. S7)}
\]
Therefore, $\Gamma_D$, $\Gamma_B$ and $\gamma_0$ can be experimentally determined from PL decay kinetics at 5K and $\Gamma_{slow}(T)$ and $\Gamma_{fast}(T)$ can be obtained from Eq. S5 using these parameters.

Figure S10 (a-c) shows the comparison of the experimental PL decay dynamics at 5K and the calculated time-dependent PL intensity, $I(t)$, at 5K obtained using Eq. S3, S4 and S8 with the nonadjustable parameters in Table 1. The time-dependent bright and dark exciton populations are converted to the time dependent PL intensity, $I(t)$, using Eq. S8:

$$I(t) = \Phi_B \Gamma_B P_B(t) + \Phi_D \Gamma_D P_D(t) \quad \text{(Eq. S8)}$$

$\Phi_B$ and $\Phi_D$ are the bright and dark exciton quantum yield (assumed to be the same). Figure S10 (d-f) shows the comparison of the result from Eq. S5 with the experimentally measured temperature dependent $\tau_{slow}$ and $\tau_{fast}$ for strongly confined QDs, NWs and NPLs. The model fits the experimental data for QDs well. On the other hand, the model overestimates $\tau_{fast}$ of NWs and NPLs, suggesting the presence of an additional thermally activated decay pathway of bright exciton consistent with the more complicated change in relative PL QY for the NWs and NPLs as shown in Figure S9.

**Figure S10:** (a-c) Comparison of experimental (blue) and calculated (black) time-dependent PL intensity for QDs (a), NWs (b) and NPLs (c). (d-f) Comparison of experimental (markers) and calculated (black curves) $\tau_{slow}$ and $\tau_{fast}$ as a function of temperature for QDs (d), NWs (e) and NPLs (f).
1. M. Nirmal, D. J. Norris, M. Kuno, M. G. Bawendi, A. L. Efros, M. Rosen, Observation of the "dark exciton" in CdSe quantum dots. *Phys. Rev. Lett.* 75, 3728-3731 (1995).