

PEROVSKITE NANOCRYSTALS

Shedding light on dark excitons

A magnetic-field-dependent spectroscopy study on single perovskite nanocrystals reveals the spectral signatures of an exciton dark state below the bright triplet states.

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Lead halide perovskites (LHPs) form an emerging class of materials with promising opto-electronic properties for solar cells, lighting, displays and other applications¹. The optical properties for nanocrystalline LHPs are similar to those of chalcogenide semiconductor quantum dots (QDs) and yet markedly different in certain aspects. Recently, an unexpected new difference was reported: inversion in the order of the two lowest exciton states by the Rashba effect². The lowest excited state in LHP nanocrystals (NCs) was reported not to be the dark exciton state (as in all chalcogenide QDs) but the bright exciton state. Writing in *Nature Materials*, Brahim Lounis and colleagues³ present convincing evidence based on single-NC

spectroscopy that in fact there is no inversion. Their findings reveal that the dark exciton state is lower in energy than the bright state in perovskite NCs.

Perovskites form a well-known class of materials with a crystal structure consisting of a cubic close packing of large anions and large cations with smaller cations occupying octahedral holes (Fig. 1a). Owing to the strong recent focus on lead halide perovskites, the general name for the perovskite crystal structure is now often used as label for LHPs, either all inorganic (large cation is Cs⁺) or hybrid organic–inorganic — with, for example, formamidinium (FA, CH(NH₂)₂⁺) as the large cation. LHP NCs are not new. In the 1990s quantum confinement was reported

in CsPbCl₃ and CsPbBr₃ NCs embedded in solid CsCl or CsBr, but these early papers went largely unnoticed⁴. The more recent discovery of a facile colloidal synthesis method for CsPbX₃ (X = Cl, Br, I) NCs with high quantum yield and colour-tunable visible emission marks the beginning of intense research on the optical properties and applications of a wide variety of LHP NCs⁵.

Different from chalcogenide QDs, colour tuning in LHP NCs is realized by changing the chemical composition (not by size variation). LHPs also show an unusual defect tolerance that enables high efficiencies in spite of surface defects¹. Recently a surprising additional difference between QDs and LHP NCs was reported².

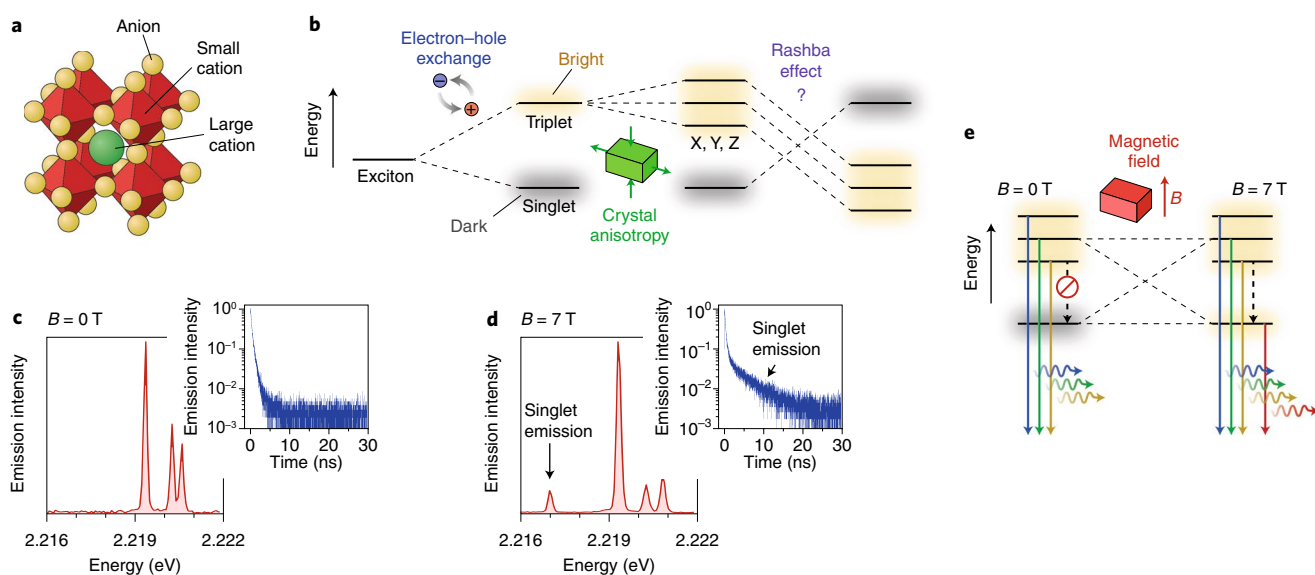


Fig. 1 | Exciton fine structure of perovskite nanocrystals. **a**, Unit cell of the perovskite crystal structure. **b**, Theoretical exciton fine structure of LHP NCs. Electron–hole exchange interaction splits the fourfold degenerate lowest-energy exciton in a triplet at higher energy and a singlet state at lower energy. The triplet exciton is ‘bright’, meaning that radiative recombination is electric-dipole allowed, whereas the singlet exciton is ‘dark’. Anisotropy of the unit cell or nanocrystal shape further splits the triplet into up to three states. Finally, the Rashba effect — due to a structural asymmetry — has been proposed to invert the order of triplet and singlet states. **c**, Emission spectrum of an individual LHP NC at $T = 4$ K in the absence of a magnetic field, showing three triplet emission lines. Inset: corresponding photoluminescence decay curve, showing fast sub-nanosecond emission. **d**, Emission spectrum of the same LHP NC with magnetic field, showing an additional singlet emission line at lower energy. Inset: corresponding photoluminescence decay curve, showing a 4-ns component due to the partially allowed singlet emission. **e**, Explanation for the magnetic-field-dependent observations. At zero magnetic field, non-radiative relaxation from the higher-energy triplet states to the lower-energy singlet is very inefficient, resulting in nearly pure triplet emission. A magnetic field admixes triplet character into the singlet state inducing triplet–singlet relaxation and making the singlet state brighter. Credit: Adapted from ref. ³, SNL (**c,d**)

In chalcogenide QDs the lowest exciton level is a dark state and slow (microsecond) emission occurs at cryogenic temperatures from this state. In contrast, LHP NCs show extremely fast sub-nanosecond emission at 4 K. At these low temperatures only emission from the lowest exciton state is expected (assuming Boltzmann equilibrium). To rationalize the observation of bright state emission an inversion of the dark and bright state by the Rashba effect was proposed² (Fig. 1b). Still, doubt remained as measurements on single NCs in magnetic fields and ensembles of LHP NCs showed signatures of a 'normal' exciton structure with a lower-energy dark state. As an alternative explanation inhibited bright–dark state relaxation was proposed to explain efficient bright state emission at 4 K.

Confocal fluorescence microscopy measurements for single FAPbBr₃ perovskite NCs by the Lounis team now seem to settle the debate. Their measurements show changes in the exciton emission and decay dynamics upon increasing a magnetic field from 0 to 7 T that can only be explained by an exciton dark state situated below the bright state. Turning on the magnetic field induces an extra redshifted peak in the emission spectrum and a slow exciton emission decay component (Fig. 1c,d). Both observations indicate a lower-energy dark state. The absence of dark-state emission at 0 T can be understood by inhibited bright–dark state relaxation, resulting in almost exclusively bright state emission (Fig. 1e, left). The lower-energy dark exciton is simply not reached as radiative decay from the bright state is much faster than relaxation to the dark state. Increasing the

magnetic field induces coupling between the dark and bright state that enables bright–dark state relaxation and emission from the dark state appears (Fig. 1e, right). The polarization behaviour and magnetic-field dependence of the bright and dark exciton emission and decay rate are carefully analysed and modelled and provide a consistent picture. The dark–bright state splitting is much larger than the acoustic phonon energy but smaller than the optical phonon energy. The lack of resonant phonons combined with weak electron–phonon coupling explains the inhibition of bright–dark state relaxation at 4 K.

The findings by Lounis and colleagues have limited implications for 'popular' applications of LHP NCs such as light emitting devices. Lamps and displays operate above room temperature where the order of the bright and dark states is not relevant as their splitting is a few meV, far below the thermal energy at room temperature. The population of the dark and bright states is thus independent of their order. However, in more exotic future areas these insights are highly relevant. For quantum-light applications the extremely fast single-photon emission of LHP NCs at 4 K is very advantageous⁶. LHP NCs with sub-nanosecond bright exciton decay can serve as efficient single-photon sources operating at GHz repetition rates. Here it is crucial to know whether or not there is a lower energy dark state that can interfere. With a lower energy dark state, on/off blinking behaviour might occur with off periods of ~10–100 ns (dark-state lifetime), analogous to blinking of single dye molecules after intersystem crossing

to the dark spin-forbidden state. For a fundamental understanding the findings are important as the influence of the Rashba effect in LHPs is unclear and under debate⁷. The results reported by Lounis and colleagues provide an important step forward in resolving the issue on bright–dark state splitting but also encourage further experiments. In earlier work these researchers reported similar experiments on CsPbBr₃ LHP NCs (in contrast to the FAPbBr₃ NCs studied here) but could not find evidence for a lower energy dark state⁸. Future work, including blinking and photon correlation experiments at 4 K, on single inorganic and hybrid LHP NCs, will provide insight in bright–dark state emission and relaxation processes in various LHP NCs, providing a more complete understanding of the energy level structure and low-temperature emission properties for this class of materials. □

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MECHANOBIOLOGY

Platelet mechanosensing axis revealed

An intermediate affinity state of integrin $\alpha_{IIb}\beta_3$ has been identified to be a key player in platelet mechanosignalling.

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Platelets are small (2 to 3 μm in diameter), anucleated blood cells that play an essential role in haemostasis, thrombosis and blood coagulation¹. Platelets normally circulate while inactivated. When vascular damage occurs, the luminal endothelial layer of the blood vessel is disrupted, resulting in exposure of subendothelial matrix components, such as collagen and

fibronectin. The blood plasma protein von Willebrand factor (VWF) can adhere immediately to exposed collagen under high shear flow. Platelets can also attach to subendothelial collagen via the receptor glycoprotein VI (GPVI) and to immobilized VWF through receptor complex glycoprotein (GP) Ib-IX. The attached platelets then undergo a robust activation process,

including a drastic change in shape from a smooth, flattened disc to a spiny sphere, and also become much more adhesive. This activation process causes platelets to attach firmly onto the subendothelial matrix. Activated platelets also adhere to one another, mediated by the interaction between platelet surface receptor $\alpha_{IIb}\beta_3$ and fibrinogen, a multivalent plasma protein