LETTER

Bright triplet excitons in caesium lead halide perovskites

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Nanostructured semiconductors emit light from electronic states known as excitons[1]. For organic materials, Hund's rules[2] state that the lowest-energy exciton is a poorly emitting triplet state. For inorganic semiconductors, similar rules[3] predict an analogue of this triplet state known as the 'dark exciton'[4]. Because dark excitons release photons slowly, hindering emission from inorganic nanostructures, materials that disobey these rules have been sought. However, despite considerable experimental and theoretical efforts, no inorganic semiconductors have been identified in which the lowest exciton is bright. Here we show that the lowest exciton in caesium lead halide perovskites (CsPbX₃, with X = Cl, Br or I) involves a highly emissive triplet state. We first use an effective-mass model and group theory to demonstrate the possibility of such a state existing, which can occur when the strong spin–orbit coupling in the conduction band of a perovskite is combined with the Rashba effect[5–10]. We then apply our model to CsPbX₃ nanocrystals[11], and measure size- and composition-dependent fluorescence at the single-nanocrystal level. The bright triplet character of the lowest exciton explains the anomalous photon-emission rates of these materials, which emit about 20 and 1,000 times faster[12] than any other semiconductor nanocrystal at room[13–16] and cryogenic[4] temperatures, respectively. The existence of this bright triplet exciton is further confirmed by analysis of the fine structure in low-temperature fluorescence spectra. For semiconductor nanocrystals, which are already used in lighting[17], lasers[18] and displays[19], these excitons could lead to materials with brighter emission. More generally, our results provide criteria for identifying other semiconductors that exhibit bright excitons, with potential implications for optoelectronic devices.

An exciton involves an electron in the conduction band that is bound Coulombically to a hole in the valence band. Its energy depends in part on the spin configuration of these two charge carriers. In organic semiconductors, the lowest-energy exciton is a triplet state in which these two carriers have parallel spins. For the electron and hole to recombine and emit light, one spin must flip simultaneously with the release of the photon to satisfy the Pauli exclusion principle. Because this coordinated process is unlikely, triplet excitons are poorly emitting.

In addition to spin, the exciton energy depends on the atomic orbitals that constitute the conduction and valence bands. In many inorganic semiconductors, the orbital motion and spin of the carriers are strongly coupled. Spin is no longer conserved, and the total angular momentum of the electron and hole (J_e and J_h) must be considered. Further, the exchange interaction mixes these momenta so that only the total exciton momentum $J = J_e + J_h$ is conserved. Owing to these and other effects, each exciton state is split into several energy sublevels, known

as fine structure. Studies on various materials have found that the lowest-energy sublevel is 'dark', meaning that optical transitions to the ground state are dipole-forbidden. Emission, if it occurs, is very slow. For example, in CdSe, recombination of the lowest exciton requires a change of two units of angular momentum[4]. Because the photon carries one unit, light cannot be emitted unless another unit is dissipated simultaneously, another unlikely process. The lowest excitons in all known inorganic semiconductors behave similarly, leading to the common belief that such states must be dark.

We show that this belief is incorrect by examining CsPbX₃ (X = Cl, Br or I) perovskites. Crystals of these perovskites comprise corner-sharing PbX₆ octahedra with Cs⁺ ions filling the voids in between (Fig. 1a). We first approximate the lattice as cubic and calculate band structures (Methods) for CsPbBr₃ (Fig. 1b), CsPbCl₃ and CsPbI₃ (Extended Data Fig. 1). The bandgap occurs at the R point in the Brillouin zone, near which the valence and conduction bands are well described within the effective-mass model (see Supplementary Table 1). The top of the valence band arises from a mixture of Pb 6s and Br 4p atomic orbitals, with an overall s symmetry[20,21]. Thus, including spin, the hole can occupy one of two s-like Bloch states with $J_h = 1/2$: $|\uparrow\rangle_h = |S\rangle|\uparrow\rangle$ or $|\downarrow\rangle_h = |S\rangle|\downarrow\rangle$, using standard notation[22]. The conduction band consists of Pb 6p orbitals, leading to three possible orthogonal spatial components for the Bloch function[20,21]: $|X\rangle$, $|Y\rangle$ or $|Z\rangle$. Because of strong spin–orbit coupling, these components are mixed with spin to obtain a doubly degenerate $J_e = 1/2$ state for the electron at the bottom of the conduction band:

$$|\Uparrow\rangle_e = -\frac{1}{\sqrt{3}}[(|X\rangle + i|Y\rangle)|\downarrow\rangle + |Z\rangle|\uparrow\rangle]$$
$$|\Downarrow\rangle_e = \frac{1}{\sqrt{3}}[|Z\rangle|\downarrow\rangle - (|X\rangle - i|Y\rangle)|\uparrow\rangle] \tag{1}$$

When the momentum of the electron and hole states are then combined, the exciton splits as a result of electron–hole exchange into a $J = 0$ singlet state

$$|\Psi_{0,0}\rangle = \frac{1}{\sqrt{2}}[|\Downarrow\rangle_e|\uparrow\rangle_h - |\Uparrow\rangle_e|\downarrow\rangle_h] \tag{2}$$

and a threefold degenerate $J = 1$ triplet state

$$|\Psi_{1,-1}\rangle = |\Downarrow\rangle_e|\downarrow\rangle_h$$
$$|\Psi_{1,0}\rangle = \frac{1}{\sqrt{2}}[|\Downarrow\rangle_e|\uparrow\rangle_h + |\Uparrow\rangle_e|\downarrow\rangle_h] \tag{3}$$
$$|\Psi_{1,+1}\rangle = |\Uparrow\rangle_e|\uparrow\rangle_h$$