### Electronic Supplementary Information

# Fine Structure of Excitons and Electron-Hole Exchange Energy in Polymorphic CsPbBr<sub>3</sub> Single Nanocrystals

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## I Chemical synthesis of CsPbBr<sub>3</sub> nanocrystals (NCs)

### I.1 Chemicals

Lead (II) bromide (PbBr<sub>2</sub>, > 98 %, Aldrich), lead (II) iodide (PbI<sub>2</sub>, 99 %, Aldrich), caesium carbonate (Cs<sub>2</sub>CO<sub>3</sub>, 99 %, Aldrich), lead (II) acetate trihydrate (Pb(CH<sub>3</sub>COO)<sub>2</sub>.3H<sub>2</sub>O, 99 %, Aldrich), oleic acid (OA, 90 %, Aldrich), 1-octadecene (ODE, 90 %, Aldrich), oleylamine (OLA, 80-90 %, Acros Organics), methylacetate (CH<sub>3</sub>COOCH<sub>3</sub>, 99 %, Merck-Schuchardt).

### I.2 Caesium Oleate precursor

In a three-neck 100 mL flask, 0.8 g of  $Cs_2CO_3$  are mixed with 2.5 mL of OA and 30 mL of ODE. The flask is degassed under vacuum for the next 30 minutes at 110 °C. The atmosphere is then switched to Ar and the temperature is either kept at 110 °C or raised to 200 °C for 10 minutes. At this point the caesium salt is fully dissolved. The temperature is cooled down below 110 °C and the flask is further degassed for 10 minutes. The obtained gel is used as stock solution.

### I.3 CsPbBr<sub>3</sub> nanocrystals synthesis

In a three-neck flask, we introduced 147 mg of PbBr<sub>2</sub> with 10 mL of ODE and degassed the solution for 30 minutes at 110 °C. Then we inject 0.5 mL of OA and 0.5 mL of OLA into this degassed reaction mixture. The atmosphere is switched to Ar and the temperature is raised to 180 °C. We then quickly inject 0.8 mL of caesium oleate. The reaction color turns yellow greenish immediately. We let the reaction occur for 30 seconds and use fresh air to cool the flask. The obtained solution is centrifuged at 6000 rpm for 5 minutes. The supernatant is discarded and the obtained pellet is redispersed in 2 to 3 mL of hexane.

## II Spectroscopic data

### II.1 Sample 2 characterization



Fig. S. 1: TEM image (a) and size distribution deduced from TEM image analysis (b), for nanoparticles synthetized at 110 °C, and used to prepare sample 2 (see main text). The scale bar in panel (a) corresponds to 50 nm.

#### **II.2** Temperature dependence of optical absorption and luminescence



Fig. S. 2: Temperature dependence of the absorption (solid line) and photoluminescence (PL) (dashed line) of sample 1 (synthesis at 180  $^{\circ}$ C).



Fig. S. 3: Evolution of both absorption and emission peak positions (sample 1) with temperature; index 1 is for the lowest energy absorption peak (1S exciton) and index 2 refers to the structure appearing as a shoulder at higher energy (2S exciton). Data follow a linear fit in good approximation. Linear coefficients (inset) are given for each peak with their respective dispersion in brackets. In typical semiconductors, the temperature dependence of the band gap is fixed by two different contributions: the thermal expansion, which is the weaker contribution, and the electron-phonon coupling contribution. Huang and Lambrecht have calculated that the bandgap of perovskite materials decreases with the lattice constant [1] and this is explained by the fact that the gap energy is controlled by the Pb s to Br p covalent antibonding interaction which governs the valence band width. Then, the temperature diminishing, the lattice constant reduces and leads to an upper-energy shift of the valence band that pushes up its maximum, thus decreasing the energy gap. The experimental shifts of figure S. 2 have been fitted with the Varshni relation, [2] which gives the temperature dependence of the energy gap of bulk semiconductors. In our case, fits lead to very low values of the Debye temperature (that is not reported here) and quasi-linear dependences are obtained; the slope values (inset) are in good agreement with previous results in CsPbBr<sub>3</sub> [3].



Fig. S. 4: Temperature dependence of the absorption (solid line) and emission (dashed line) of sample 2 (synthesis achieved at 110  $^{\circ}$ C).

#### II.3 Transition energies and energy spacings in excitonic fine structures: summary

Peak energy

(eV)

2.4752

2.4761

2.4923

2.4931

2.4685

2.4694

2.5186

2.5195

2.4931

2.4942

2.4816

2.4823

2.4613

2.4624

2.4812

2.4826

2.4668

2.4680

Linewidth

(meV)

0.9

0.6

0.4

0.4

1.0

0.5

0.4

0.3

0.5

0.4

0.3

0.3

0.8

0.9

0.8 0.9

0.5

0.4

Statistics:

	Energy peak (eV)	Linewidth (meV)	Energy spacing (meV)
	2.4733	0.4	
	2.4737	0.2	0.4
	2.4746	0.5	0.9
	2,4694	0.4	
	2.4701	0.2	0.7
	2.4710	0.4	0.9
	2.4975	0.4	
Energy spacing	2.4979	0.5	0.4
(meV)	2.4985	0.4	0.6
, <i>,</i>	2.4955	0.2	
0.9	2.4959	0.3	0.4
	2.4963	0.3	0.4
0.8	2.4969	0.2	
	2.4972	0.2	0.3
0.9	2.4974	0.2	0.2
	2.4743	0.7	
0.9	2.4750	0.2	0.7
0.5	2.4756	0.5	0.6
1.1	2.4780	0.4	
	2.4784	0.4	0.4
0.7	2.4789	0.3	0.5
	2.4863	0.3	
1.1	2.4868	0.2	0.5
	2.4872	0.3	0.4
1.4	2.4635	0.3	
	2.4641	0.2	0.6
1.2	2.4647	0.2	0.6
1.2	2.5095	0.2	
$1.0\pm0.2$ meV	2.5098	0.2	0.3
	2.5102	0.2	0.4
	2.4566	0.5	
	2.4572	0.4	0.6
	2.4577	0.5	0.5
	Statistics: - Energy spacing be $\overline{E_{3+}^X - E_{3-}^X} = 0.55 \pm 0$ - Energy difference:	tween the two higher 0.20 meV. $\overline{\left(\frac{E_{3+}^X + E_{3-}^X}{D}\right) - F} = 0.7$	r energy lines: 75 + 0.22 meV

Table S. 1: Energy, linewidth and energy spacings, characterizing, at 5 K, experimentally evidenced doublets and triplets.



Fig. S. 5: Experimental X-Ray diffractogram of CsPbBr<sub>3</sub> nanocrystals (NCs) synthetized at 180 °C (blue line) and computed diffractogram of CsPbBr<sub>3</sub> orthorhombic structure (black line) and CsPbBr<sub>3</sub> cubic structure (red line).



#### II.5 Luminescence traces

Fig. S. 6: Typical traces of two single NC emissions: the fine structure is composed either by a triplet (upper panels) either by a doublet (lower panels). Dashed lines indicate the positions in time of cross sections that are represented on the right side of the figure. In our experiments, spectral jumps are observed that may shift the lines by an amount equal to their linewidths.



Fig. S. 7: Left panel: Emission spectrum corresponding to a low-energy exciton  $(|Z\rangle)$  state of a triplet) recombination; the red solid line is a Lorentzian fit. Right panel: time-resolved emission of the  $|Z\rangle$  state whose emission is shown in left panel. At  $\approx 5$  K the decay looks monoexponential (given the instrumental dynamics); a lifetime of  $\approx 80$  ps is obtained from the fit (red solid line). The experiment was carried out using a streak camera (C5680 model from Hamamatsu incorporating a M5675 synchroscan unit) synchronized with the pulse train of a frequency doubled picosecond Ti:Sapphire laser operating at 82 MHz. Note that a decay with similar characteristic constant is found at 5 K for the higher energy  $|X\rangle$  state. The highest energy line ( $|Y\rangle$  state in the text) could not be addressed due to its much lower intensity. Extended temperature dependent time-resolved studies are still required to gain insights into the relaxation mechanisms and determine position in energy of the optically inactive state (see, for instance, reference 35 of main text for detailed investigation of bright state - dark state coupling in simple three levels system based model).

### III Theoretical support: Fine structure of band edge excitons in CsPbBr<sub>3</sub>

#### III.1 Band structure

The following analysis is built on the base of analytical developments that can be found in reference 4 with an approach that goes beyond the basic monoelectronic band picture. The exciton fine structure is described in a Frenkel picture for an uniaxial system (as shown already for 2D and 3D halide perovskites in references 5 to 7). By comparison to classical semiconductors, the band ordering in lead-halide perovskites is reversed with a direct band gap at R point for the cubic reference structure [8-12]. The conduction band is dominated by a giant spin-orbit coupling (SOC) characterized by the constant  $\Delta > 0$  (notation  $\Delta_{SO}$  is used in the main text). The CsPbBr<sub>3</sub> system can exist in the cubic, tetragonal and orthorhombic phases with a transition from the orthorhombic to the tetragonal phase around 88 °C when increasing temperature. The cubic phase was found stable at higher temperature (>130 °C). In the orthorhombic and tetragonal structures direct band gap transitions are at the  $\Gamma$  point.

We start from the analytic solutions for the tetragonal phase where we use the  $|J, J_z\rangle^e$  basis; we note  $E_V$  the energy of the valence band maximum whereas  $E_A$ ,  $E_B$  and  $E_C$  are the bottom energies of the different conduction bands [4, 7]. The value of  $E_B$  is fixed at zero as in [7], and we note T < 0 the additional tetragonal crystal field term with respect to the totally symmetric cubic case (T = 0). In the tetragonal phase, the scheme of levels is then as follows:

$$J = 3/2 \quad \begin{cases} j_z = \pm 1/2 & E_c \\ j_z = \pm 3/2 & E_B \\ J = 1/2 & j_z = \pm 1/2 & E_A \\ & VB & E_v \\ \end{cases} \quad E_I \quad E$$

The band energies at the  $\Gamma$  point are

$$E_A = -\frac{1}{2}(T+\Delta) - \frac{1}{2}\sqrt{\Delta^2 + T^2 - \frac{2}{3}T\Delta}$$
(1)

with eigenvectors

$$|1/2, 1/2\rangle^e = \cos\theta |Y_1^1\downarrow\rangle - \sin\theta |Y_1^0\uparrow\rangle \text{ and } |1/2, -1/2\rangle^e = \cos\theta |Y_1^{-1}\uparrow\rangle - \sin\theta |Y_1^0\downarrow\rangle , \qquad (2)$$

$$E_B = 0 \tag{3}$$

with eigenvectors

$$|3/2, 3/2\rangle^e = |Y_1^1\uparrow\rangle \text{ and } |3/2, -3/2\rangle^e = |Y_1^{-1}\downarrow\rangle ,$$

$$(4)$$

and 
$$E_C = -\frac{1}{2}(T+\Delta) + \frac{1}{2}\sqrt{\Delta^2 + T^2 - \frac{2}{3}T\Delta}$$
 (5)

with eigenvectors

$$|3/2, 1/2\rangle^e = \sin\theta |Y_1^1\downarrow\rangle + \cos\theta |Y_1^0\uparrow\rangle \text{ and } |3/2, -1/2\rangle^e = \sin\theta |Y_1^{-1}\uparrow\rangle + \cos\theta |Y_1^0\downarrow\rangle , \tag{6}$$

where

$$\tan(2\theta) = \frac{2\sqrt{2}\Delta}{\Delta - 3T} \quad (\text{with } 0 < \theta < \pi/2) \text{ and } Y_1^{\pm 1} = \frac{\mp (X \pm iY)}{\sqrt{2}}, \ Y_1^0 = Z.$$
(7)

 $|X\downarrow\rangle, |X\uparrow\rangle, |Y\downarrow\rangle, |Y\downarrow\rangle, |Y\uparrow\rangle, |Z\downarrow\rangle$  and  $|Z\uparrow\rangle$  are the Bloch functions related to the Pb p-orbitals [12].

Note that  $E_A$ ,  $E_B = 0$  and  $E_C$  are energies relative to  $E_B$  while  $E_I$ ,  $E_{II}$  and  $E_{III}$  of the main text refer to the band-to-band transitions (from valence band). We of course have  $E_{III} - E_I = E_C - E_A$  and  $E_{II} - E_I = E_B - E_A$ .

As shown in [4], when introducing the additional crystal field term  $\epsilon$  to account for the symmetry lowering in

the orthorhombic structure, the same reduced Hamiltonian is obtained within the  $|1/2, -1/2\rangle^e$ ,  $|3/2, -1/2\rangle^e$ ,  $|3/2, 3/2\rangle^e$  and  $|1/2, 1/2\rangle^e$ ,  $|3/2, 1/2\rangle^e$ ,  $|3/2, -3/2\rangle^e$  subspaces:

$$\mathbf{H^{Ortho}} = \begin{bmatrix} E_A & 0 & -\epsilon \cos \theta \\ 0 & E_C & -\epsilon \sin \theta \\ -\epsilon \cos \theta & -\epsilon \sin \theta & E_B = 0 \end{bmatrix} .$$
(8)

Considering  $\epsilon$  as a small energetic perturbation by comparison to the relevant energy differences, the first-order corrections for the eigenvectors as well as the second-order energy corrections can be obtained (the first-order energy corrections being zero here).

To the first order in  $\epsilon$ , in the basis  $\{|1/2, \pm 1/2\rangle^e, |3/2, \pm 1/2\rangle^e, |3/2, \mp 3/2\rangle^e\}$ , the new eigenvectors associated to the lowest  $E'_A$  eigenenergy reads:

$$|SO^{\pm}\rangle^{e} = |1/2, \pm 1/2\rangle^{e} - \frac{\epsilon \cos \theta}{E_{A} - E_{B}} |3/2, \mp 3/2\rangle^{e} , \qquad (9)$$

where the coefficient  $\epsilon \cos \theta / (E_A - E_B)$  (that quantifies the perturbation) is a crucial ingredient whose amplitude will determine the exciton fine structure splitting (see below). For energy second-order corrections, we obtain:

$$\Delta E_A = \frac{\epsilon^2 \cos^2 \theta}{E_A - E_B},\tag{10}$$

$$\Delta E_B = \epsilon^2 \left( \frac{\cos^2 \theta}{E_B - E_A} + \frac{\sin^2 \theta}{E_B - E_C} \right),\tag{11}$$

$$\Delta E_C = \frac{\epsilon^2 \sin^2 \theta}{E_C - E_B} \,. \tag{12}$$

The energy third-order corrections are exactly zero. A graph representing each variation  $\Delta E vs |\epsilon|$  when appropriate values of  $\theta$  and  $E_{A,B,C}$  are used, is presented at the end of the section (once each parameter is known); the estimation of the actual  $\Delta Es$  reveals in particular the validity of the perturbation approach.

Following the development in [4], we write the lowest conduction band states (namely the spin-orbit split-off states) that tend towards  $|1/2, \pm 1/2\rangle^e$  in the limit  $\epsilon \to 0$  in the Bloch states basis:

$$\begin{cases} |SO^{+}\rangle^{e} = -\alpha |X \downarrow\rangle - \beta |iY \downarrow\rangle + \gamma |Z \uparrow\rangle \\ |SO^{-}\rangle^{e} = +\alpha |X \uparrow\rangle - \beta |iY \uparrow\rangle + \gamma |Z \downarrow\rangle. \end{cases}$$
(13)

Using equation (9) we find, after a change of basis:

$$\alpha = \frac{\cos\theta}{\sqrt{2}} \left( 1 + \frac{\epsilon}{E_A - E_B} \right), \ \beta = \frac{\cos\theta}{\sqrt{2}} \left( 1 - \frac{\epsilon}{E_A - E_B} \right), \ \gamma = -\sin\theta, \tag{14}$$

with (as  $E_B$  is taken as the origin of energy):

$$E_A - E_B = E_A - 0 = -\left[\frac{1}{2}(T + \Delta) + \frac{1}{2}\sqrt{\Delta^2 + T^2 - \frac{2}{3}T\Delta}\right].$$
 (15)

#### III.2 Complementary remark about the determination of $\Delta$ and T parameters

We associate the three peaks located at 2.33 eV, 3.44 eV and 3.68 eV denoted I, II and III in the absorption spectrum of sample 1 (Figure 1c in main text), to optical transitions between bands A, B and C. For consistency reasons, several comments should be made:

- First the calculation proposed by Yu [7] applies only for a pure tetragonal phase (with uniaxial symmetry) whereas it is likely that two structures coexist in our samples (see below and main text). It is indeed now well documented that a second order phase transition from the tetragonal to the orthorhombic structure arises around 88 °C - by decreasing temperature - while the tetragonal phase exists up to 130 °C [13, 14]. XRD measurements point to the orthorhombic structure being the majority (see Figure S. 5), but micro-photoluminescence studies indeed evidence the presence of both structures, the tetragonal NCs being

probably stabilized by fast cooling applied to the mixture during the synthesis. Calculations presented in the previous paragraph show that the position in energy of the A, B and C bands are very slightly impacted by the further lowering of symmetry that characterizes the transition from the tetragonal phase to the orthorhombic one. The modification of the crystal field acts as a perturbation, and leads to second-order corrections of the  $E_i$  energies (i = A, B, C) which are in the meV range (see Figure S. 9). To sum up, as far as the determination of T and  $\Delta$  are concerned, there is nearly no incidence in considering the absorption spectrum as resulting from one particular phase or a mixing.

- Second, excitonic corrections are neglected in the treatment, and the experimental transitions are identified with the band-to-band transitions. As T and  $\Delta$  are extracted from energy differences, only variations in binding energy of excitons I, II and III may play a role. A manner to estimate the effect of those variations is to map the T and  $\Delta$  values with respect to the  $E_i$  energies (i=I, II, III).

By considering an upper excursion  $u(E) = \pm 10$  meV for each  $E_i$  (that already represents  $\approx 25$  % of the binding energy), one obtains weak dispersions on T and  $\Delta$  values, which can be written as an uncertainty. Our measurements provide (with  $E_B$  set to zero)  $E_A = -1.11$  eV and  $E_C = 0.24$  eV, leading to the central values:  $\Delta = 1.20$  eV and T = -0.34 eV. Taking into account u(E) finally leads to:

$$\Delta = 1.20 \pm 0.06 \text{ eV}$$
 and  $T = -0.34 \pm 0.05 \text{ eV}$ .

#### III.3 Exciton structure

#### III.3.1 Bulk excitonic structure [4]

#### A. Tetragonal crystalline structure: observation of spectral doublets

The Coulomb interaction between an electron from the spin-orbit split-off conduction band and a hole from the valence band leads to the stabilization of a new excitation (exciton) which energy is lowered compared to the corresponding band-to-band transition. The coulombic interaction shows through the Coulomb and exchange integrals that are noted  $U_b$  and  $J_b$ . In the tetragonal symmetry, the fine structure consists of a dark optical state and two bright components.

As  $\cos^2 \theta > 2 \sin^2 \theta$  (this inequality holds because  $\Delta > 0$  and T < 0), the optically active lower energy state has an energy  $E_2^X = 2J_b \sin^2 \theta - U_b$  (<sup>X</sup> is for exciton) relative to the gap energy  $E_I$ ; its emission is polarized along the **c** axis of the unit cell. The optically active, higher energy state, has an energy  $E_3^X = J_b \cos^2 \theta - U_b$  relative to the gap energy  $E_I$ ; it is two-fold degenerate and associated emission is polarized along the **a** and **b** axes. A doublet in emission is thus expected. The energy separation between the observable components then reads:

$$\Delta E^{doublet} = E_3^X - E_2^X = J_b (1 - 3\sin^2 \theta) \,. \tag{16}$$

#### B. Orthorhombic crystalline structure

The excitonic fine manifold is composed of four non-degenerate states, the lowest one being optically inactive. The bright-states energies are expressed in terms of the  $\alpha$ ,  $\beta$  and  $\gamma$  coefficients (see equation (14)) and read:

$$E_{\alpha} = 2J_b \alpha^2 - U_b \text{ emission polarized along } X, \tag{17}$$

$$E_{\beta} = 2J_b\beta^2 - U_b \text{ emission polarized along } Y, \tag{18}$$

$$E_{\gamma} = 2J_b\gamma^2 - U_b$$
 emission polarized along  $Z \equiv \mathbf{c}$ . (19)

Those energies are relative to the gap energy  $E_I + \Delta E_A$ . The orthorhombic crystal field thus leads to the splitting of the higher energy state of energy  $E_3^X$  in the tetragonal structure. They correspond to the levels labeled  $\alpha$  and  $\beta$  in the previous equations, however the sign of  $\epsilon$  remains unknown so that the absolute value of their energy difference has to be considered. For the sake of clarity and in order to establish a connection between the tetragonal and orthorhombic excitonic structures, we adopt the notation  $E_{3+}^X$  and  $E_{3-}^X$  for the new energies of the split states, with  $E_{3+}^X > E_{3-}^X$  (see figure S. 8). From equations (17) and (18) we thus find:

 $E_{3+}^X - E_{3-}^X = 4J_b \frac{|\epsilon|\cos^2\theta}{E_B - E_A}.$  (20)



Fig. S. 8: Energy labeling used in the text. Note that the diagrams are positioned arbitrarily with  $E_2^X = E_{\gamma}$ .

The correction to this expression is of order  $\epsilon^3$ . Remarking that, neglecting a second-order term in  $\epsilon/(E_A - E_B)$ , the distance in energy

$$\Delta E' = \overline{E}_3 - E_\gamma = J_b (1 - 3\sin^2 \theta), \tag{21}$$

where  $\overline{E}_3 = (E_{3+}^X + E_{3-}^X)/2$ , it is possible to reach the value of the exchange energy in the orthorhombic system. Then the absolute value,  $|\epsilon|$ , can be retrieved from equation (20).

#### III.3.2 Excitonic structure with cubic confinement

#### A. General considerations

In the framework of the effective mass approximation, the confined band-edge exciton wavefunctions are a product of the envelope function and the following Bloch functions [4]:

$$\frac{1}{\sqrt{2}} \left( |1/2^{h}, 1/2^{e}\rangle \mp |-1/2^{h}, -1/2^{e}\rangle \right), \ |-1/2^{h}, 1/2^{e}\rangle, \ |1/2^{h}, -1/2^{e}\rangle, \text{ for tetragonal symmetry, (22)}$$
$$\frac{1}{\sqrt{2}} \left( |1/2^{h}, SO^{+}\rangle \mp |-1/2^{h}, SO^{-}\rangle \right), \ \frac{1}{\sqrt{2}} \left( |-1/2^{h}, SO^{+}\rangle \mp |1/2^{h}, SO^{-}\rangle \right), \text{ for orthorhombic crystals}$$
(23)

The envelope function for the electron (hole) in strong confinement regime is the solution of the following equation:

$$\left[\frac{-\hbar^2}{2m_{e(h)}}\nabla^2 + V^{e(h)}(\overrightarrow{r}_{e(h)})\right]\phi^{e(h)}(\overrightarrow{r}_{e(h)}) = E^{e(h)}\phi^{e(h)}(\overrightarrow{r}_{e(h)}),\tag{24}$$

with

$$V^{e(h)}(\overrightarrow{r}_{e(h)}) = \begin{cases} 0 \text{ inside the cube of side } d \\ \infty \text{ outside the cube.} \end{cases}$$
(25)

If the origin of the coordinates is placed at the center of the cube, the envelope function reads:

$$\phi_{n_1,n_2,n_3}^{e(h)} = \left(\frac{2}{d}\right)^{3/2} \cos\left(\frac{n_1 \pi x_1}{d}\right) \cos\left(\frac{n_2 \pi x_2}{d}\right) \cos\left(\frac{n_3 \pi x_3}{d}\right). \tag{26}$$

For the lowest confined exciton,  $n_1 = 1$ ,  $n_2 = 1$ ,  $n_3 = 1$  and the confinement energy is

$$E_{1,1,1} = \frac{3\hbar^2 \pi^2}{2m_{e(b)}^* d^2}.$$
(27)

When compared to the bulk situation, all band-edge excitonic transitions will thus be increased by the amount  $E_{1,1,1}$ .

We also expect that Coulomb energy and electron-hole exchange energy are enhanced by confinement and more precisely are a function of the size, d. Nevertheless, the exciton electronic structure should not be very much affected by confinement if the NC shape does not impose a new symmetry to the electronic structure. This allows to use formulae (16), (20) and (21) where we replace  $J_b$  (and  $U_b$ ) by J (and U respectively) which are now characteristic of the confined system.

#### B. Determination of the electron-hole exchange energy and crystal field term

- **a.** For the tetragonal case,  $\Delta = 1.20 \pm 0.06$  eV and  $T = -0.34 \pm 0.05$  eV (see paragraph above) lead to  $\sin^2 \theta = 0.23$ . From the mean value  $\Delta E^{doublet} = 1.0 \pm 0.2$  meV and neglecting the uncertainty on the  $\theta$  value, we finally extract  $J = 3.2 \pm 0.6$  meV in tetragonal NCs.
- **b.** For the orthorhombic case, our measurements provide  $\Delta E' = 0.75 \pm 0.22$  meV as well as  $E_{3+}^X E_{3-}^X = 0.55 \pm 0.20$  meV, that lead to  $J = 2.4 \pm 0.7$  meV and to a value  $|\epsilon| = 0.08 \pm 0.04$  eV. The dark state is then expected at  $2J\gamma^2 \approx 1.1$  meV below the lowest bright state in orthorhombic NCs. Similar value is found in the tetragonal structure, where their energy separation is  $2J \sin^2 \theta \approx 1.5$  meV.

Finally, the figure S. 9 shows the variations, as a function of  $|\epsilon|$ , of the second-order corrections that affect the tetragonal band energies. For  $|\epsilon| \approx 0.08$  eV they are all in the meV range, so that the values of T and  $\Delta$  are not affected by the actual nature of the NCs phase probed in absorption. We also have  $|\epsilon| \cos \theta \ll E_B - E_A$  and  $|\epsilon| \sin \theta \ll E_C - E_B$ ; in this context, the perturbation approach which is the base for our developments is mathematically justified.



Fig. S. 9: Variations with  $|\epsilon|$  of the band-edge energies in the orthorhombic crystal. The variations are obtained through a second-order perturbation calculation with respect to  $\epsilon$ . The vertical dashed line marks the value  $|\epsilon| \approx 0.08$  eV determined from experimental values of the transitions (extracted from the absorption spectrum). Corresponding energy variations are  $\Delta E_A \approx -4.4$  meV,  $\Delta E_B \approx -1.7$  meV and  $\Delta E_C \approx +6.0$  meV.

### **IV** Useful references for Supporting Information

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