Quantum Size Effect in Organometal Halide Perovskite Nanoplatelets

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Supporting Information

ABSTRACT: Organometal halide perovskites have recently emerged displaying a huge potential for not only photovoltaic, but also light emitting applications. Exploiting the optical properties of specifically tailored perovskite nanocrystals could greatly enhance the efficiency and functionality of applications based on this material. In this study, we investigate the quantum size effect in colloidal organometal halide perovskite nanoplatelets. By tuning the ratio of the organic cations used, we can control the thickness and consequently the photoluminescence emission of the platelets. Quantum mechanical calculations match well with the experimental values. We find that not only do the properties of the perovskite, but also those of the organic ligands play an important role. Stacking of nanoplatelets leads to the formation of minibands, further shifting the bandgap energies. In addition, we find a large exciton binding energy of up to several hundreds of meV for nanoplatelets thinner than three unit cells, partially counteracting the blueshift induced by quantum confinement. Understanding of the quantum size effects in perovskite nanoplatelets and the ability to tune them provide an additional method with which to manipulate the optical properties of organometal halide perovskites.

KEYWORDS: Perovskite, nanoplatelets, quantum size effect, photoluminescence

Organometal halide perovskites have been studied since the 1970s, but only in the last 5 years has the vast potential of this material come to light. The combination of excellent optical and electronic properties enables the use of this material not only for photovoltaic applications, but also in light-emitting devices. In general, perovskites possess an ABX3 crystal structure, with the cation B, typically lead or tin, in the center of an octahedron formed by six halide (X) ions and an organic cation A, most commonly methylammonium (MA), located between these octahedra. Varying the constituent ions and creation of mixtures offer a possibility of fine-tuning the properties of the material. Recently, the fabrication of colloidal perovskite nanocrystals of lower dimensionality has been reported. One of these structures is the quasi-two-dimensional nanoplatelet. Layered perovskites have been investigated since the late 1980s, but only recently have the experimental techniques become available to probe these structures at the nanometer scale. These nanoplatelets have an increased exciton binding energy, reduced fluorescence decay times, and enhanced absorption cross-sections with respect to the bulk as well as a notable optical nonlinearity. This makes nanoplatelets especially interesting for not only light-emitting applications, but also for biosensors and as photo detectors. A recent study on perovskite nanoplatelets showed a strong blueshift in the photoluminescence (PL) signal, which was attributed to quantum confinement in the strongly confined nanostructures. The synthesis method used was similar to that used for fabrication of layered perovskite structures, namely by use of an organic ammonium cation with an alkyl chain of varying lengths. However, while the older studies mainly only used a single organic cation with a longer chain, resulting in macrocrystals of the layered material, the more recent studies producing nanostructured perovskites used a mixture of a long organic molecule, for example, octylammonium (OA) and the shorter MA. The idea behind this approach is the size of the longer cation, which cannot be incorporated into the perovskite crystal structure. Instead it binds to the perovskite with the alkyl chain sticking outward.

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and arrests crystal growth in that dimension, leading to nanocrystal formation. However, the exact function of the large cation on the crystal formation and especially on the quantum size effects in these nanostructures is still not fully understood. Here, we investigate the quantum size effect in organometal halide perovskite nanoplatelets by varying the ratio of the larger OA to OA+MA. We find that as the content of OA in the precursor suspension is increased, the thickness of the produced nanoplatelets is reduced, resulting in an increasing quantum size effect quantified by optical spectroscopy. In the limiting case of using only OA, a perovskite nanoplatelet is formed only a single PbBr$_6$ octahedron thick, similar to studies on layered perovskite macrocrystals. Quantum-mechanical calculations yield a strong agreement with experimentally determined values of the optical bandgap of the nanoplatelets. This shows the complete extent of the quantum size effect in organometal halide nanoplatelets and should help to specifically engineer perovskite nanoparticles with desired optical properties.

The synthesis of organometal bromide perovskite nanocrystals was carried out by a modification of the method reported by Schmidt et al. (Figure 1a). Octylammonium bromide (OABr) and methylammonium bromide (MABr) were prepared by addition of HBr to octylamine and to a solution of methylamine in ethanol, respectively. The acid was added in slight molar excess (1.1:1.0 ratio) to procure full protonation of the precursor amine. The crystallization of the ammonium salts was completed in a rotary evaporator. Stock solutions of PbBr$_2$, OABr, and MABr were prepared in dimethylformamide (DMF). The reagents were then mixed and diluted in DMF in due proportions to obtain a series of precursor solutions with fixed total concentration of PbBr$_2$ (0.05 M) and ammonium ions (0.05 M), but a varying fraction of OABr. All solutions were prepared at 80 °C to attain full solubilization. To induce crystallization of the desired product, the precursor solution was added dropwise into toluene under vigorous stirring (20 mL of toluene for every mL of precursor solution). The resulting precipitates were centrifuged and dispersed in neat toluene using mild sonication and stirring. Three full washing cycles with toluene were carried out for each sample. Under ambient light, the suspensions have a yellowish color, typical of the bromide perovskites, with an opacity that decreases with increasing OA fraction (Figure 1b).

Suspensions were produced with OA fractions in steps of 20% from 0% to 60% and in steps of 10% from 60% to 100%. To confirm the observed nanostructures were actually perovskites, we performed X-ray powder diffraction (XRD) measurements. The solvent was evaporated, and the resulting powders were fixed between two Kapton foils. Scattering from the nanocrystals of the pure methylammonium lead bromide (MAPbBr$_3$) revealed peaks that could be ascribed to lattice planes from a cubic crystal structure with a lattice constant of 5.93 Å, characteristic of the bulk perovskite (Figure 2a). These peaks were prevalent for all samples up to and including a content of 80% OA, indicating that the observed structures in all of these cases were indeed perovskites (see Supporting Information, Figure S1). In the 100% OA sample many additional peaks appeared. A comparison with XRD measurements of pure PbBr$_2$ showed that this sample consisted of a mixture of perovskite and the precursor material.

Transmission electron microscopy (TEM) images of the resulting perovskites were acquired to investigate their...
geometry. In Figure 2, panel b, an image of the perovskite in the 20% OA sample is shown. The perovskites here formed rectangular structures, which SEM images revealed to be cubes (Figure 2c) with size dimensions on the order of several hundred nanometers. In comparison, the perovskite structures in the 80% OA sample appeared distinctly different (Figure 2d). While they possessed similar lateral dimensions, the far weaker contrast in some of the nanostructures indicates that these nanostructures were actually very thin nanoplatelets, in agreement with earlier reports.21,29 The platelets were not separated but instead stacked on top of each other, which can also be seen by the varying contrast in the image. We used several methods to estimate the thickness of these nanoplatelets. Scanning electron microscopy (SEM) images on tilted samples confirmed that the nanostructures were in fact nanoplatelets (Figure 2e). TEM measurements additionally revealed structures appearing to be nanoplatelets aligned perpendicularly to the substrate. These have dimensions of only a few nanometers, with the thinnest observed to be only 1.5 nm thick (see Supporting Information, Figure S2).

Figure 2. (a) XRD scattering spectrum of the 80% OA sample. The scattering peaks coincide with the lattice planes of a cubic perovskite with a 5.93 Å lattice constant. (b) TEM and (c) SEM image of nanostructures found in the 20% OA sample. (d) TEM and (e) SEM image of nanostructures found in the 80% OA sample. The scale bar in all images corresponds to 200 nm.

Figure 3. (a) TEM images of the nanostructures found in the OA/MA perovskite suspensions. (b) Photographs of the perovskite suspensions under UV light. (c) PL and UV–vis spectra of perovskite films prepared from the aforementioned suspensions.

TEM images of the platelets produced for each fraction of OA show a decreasing contrast with increasing OA content (Figure 3a). In the case of 90% OA or 100% OA, the contrast for single platelets is very low, strongly suggesting that they are only a couple of nanometers thick at the most. Further support for this came from XRD measurements on the perovskite suspensions. The measurements revealed a relative decrease of Bragg intensities with increasing OA content, see Supporting Information, Figure S3. This effect can be explained by a reduced platelet thickness if the peak multiplicity and resolution function of the powder geometry are taken into account.

Decreasing the thickness of the nanoplatelets down to the size of the exciton Bohr radius should lead to quantum size effects and a consequent blueshift of their absorption onset and fluorescence.24,30 To investigate this, we imaged the perovskite suspensions excited only with UV light (Figure 3b). All of the suspensions showed bright fluorescence, with the exception of the 0% and 100% OA suspensions, which did not fluoresce as strongly. We experimentally determined the quantum efficiencies of all perovskite suspensions, with the maximum yield of over 30% obtained from the 70% OA sample. The efficiency drops off both for higher and lower OA content, with the 0% OA and 100% OA having quite low efficiencies (cf. Supporting Information description and Table S1). More importantly, however, the perceived color of the suspensions changed gradually from green (0% OA) via blue–green (70% OA) to
blue (90% OA) and violet (100% OA). To quantify these observations, UV−vis and photoluminescence (PL) spectroscopy were performed on perovskite films created by dropcasting the suspensions onto quartz substrates (Figure 3c). The 0% OA sample, effectively pure MAPbBr$_3$, showed a steep absorption onset around 528 nm, close to values reported for this bulk perovskite.$^{31}$ As the concentration of OA was increased, the absorption blueshifted very slightly up to a concentration of 60% OA. In this sample, additional higher energy peaks appeared at 463 and 446 nm. At 80% OA content, the absorption onset shifted by over 30 nm, and the absorption peak at 446 nm greatly increased in intensity. For the 90% and 100% OA samples, the absorption onset continued shifting to shorter wavelengths with additional features appearing at shorter wavelengths.

PL spectroscopy revealed a similar picture. A single peak was present in the 0% OA sample centered at 519 nm, also close to values reported for the bulk perovskite. This peak shifted continuously to shorter wavelengths with increasing OA content. For the 60% OA sample, the peak was blueshifted by 15 nm with respect to the 0% OA sample, and a long tail toward shorter wavelengths appeared. At 70% OA, this tail grew in intensity, and an additional shoulder became visible at 482 nm. The shape of the PL spectrum of the 80% OA sample continued with this trend, with a maximum value at 469 nm and additional peaks present at 490 and 454 nm. The shape of the PL spectra of the 90% and 100% OA samples again showed only one peak, at 454 and 427 nm, respectively, with longer tails on the longer wavelength side.

To understand the optically obtained spectra, we must consider the perovskite structure. The thickness of the nanoplatelets is always a multiple of a single perovskite layer, comprising a sheet of corner-sharing PbBr$_6$ octahedra, with the octylammonium ligand forming a layer around the nanoplatelet (Figure 1). This leads to discrete energy levels for the thinnest perovskite sheets. These can be seen in the PL spectra, with the shortest wavelength peaks occurring at 427, 454, 469, 482, and 490 nm. While the spectra of the 100% OA and 90% OA samples only comprised one peak, the spectra of the 60−80% OA samples comprised multiple peaks at the same spectral positions but with a varying intensity ratio. To ascribe the PL emissions to platelets of a specific thickness, we must revisit the 100% OA sample, which does not contain any MA. Thus, the perovskite platelets observed here are unlikely to be anything but one unit cell thick, and thus the PL emission at 427 nm should originate from the $n = 1$ platelet. Consequently, we ascribe the remaining PL peaks in order of increasing wavelength to nanoplatelets with $n = 2, 3, 4$, and 5, respectively, in agreement with previous reports on layered perovskites.$^{32−34}$ The energy gap between the PL maxima decreases as the thickness of the layers increases due to the decreasing degree of quantum confinement. This further supports the peak assignment made previously.

Quantum confinement in semiconductor nanostructures is generally calculated using the effective mass approximation. There are two regimes of importance, depending on the size of the nanostructure, $d$, and the exciton Bohr radius, $a_B$. For $d \gg a_B$ an excited electron and hole pair bind together, forming an exciton. The energy shift due to exciton confinement is low and can be calculated by using the reduced mass of the exciton. For $a_B \gg d$, also known as the strong confinement regime, the electron and hole need to be viewed as separate particles and their respective confinement energies calculated individually.$^{35}$

For lower dimensional bromide perovskite, we calculate the excitonic Bohr radius to be 1.36 nm, which is in between the thickness of the $n = 2$ and $n = 3$ nanoplatelets (see Supporting Information for details). Consequently, we consider the platelets with $n = 1$ and $n = 2$ to be in the strong confinement regime and platelets with $n \geq 3$ to be in the weak confinement regime. Values for the effective masses of the electron and hole ($m_e^\text{QW}$ and $m_h^\text{QW}$, respectively) were taken from literature.$^{37}$ and the optical bandgap ($E^\text{QW}$) was estimated from the results of the UV−vis measurements shown earlier (see Figure 3c).

As a first approximation, we employed the simple infinite quantum well (Figure 4a), which strongly overestimates the quantization energy with respect to the experimentally determined values (Figure 4b). A reason for this is the oversimplification of the perovskite nanoplatelet. Our approach assumes a quantum well with an infinite confinement energy outside of the perovskite layer. While the ligands surrounding the perovskite will have a strong confinement energy, it will not be infinite. Thus, we revised the model by taking into account the ligands surrounding the perovskite (Figure 4a, two-step infinite QW). A potential was adapted from values in literature$^{38}$ and the ligands were estimated to be 10 Å in length. For the masses in the ligands, we chose to use the free electron mass, as suggested in literature.$^{39,40}$ These calculations reproduced the values of the $n = 4, 5$ nanoplatelets but still overestimated the energies of the thinner platelets. An additional effect so far has not been taken into account and stems from the fact that in the perovskite films the platelets...
were not separate but were stacked together. The electron and hole wave functions, which extend outside of the platelets, can thus hybridize with those from neighboring platelets, leading to the formation of minibands.\textsuperscript{41} In the limit of an infinitely long stack of platelets, we obtain the one-band effective-mass Kronig–Penney model.\textsuperscript{41,42} With this, the separate dispersion relations for the electron and hole can be written as

\[ \cos(kL) \cosh(\alpha L^2) + \frac{1}{2} \left( \eta - \frac{1}{\eta} \right) \sinh(kL) \sinh(\alpha L^2) = \cos(\delta) \]

with

\[ k = \sqrt{\frac{2m_{\text{eff}} E_{x(h)}}{\hbar^2}} \]

\[ \alpha = \sqrt{\frac{2m_{B}^2 (V_{CB(VB)} - E_{x(h)})}{\hbar^2}} \]

\[ \eta = \frac{a_{\text{eff}}^B}{k m_{B}^E} \frac{q}{\alpha} \]

and the quantization energies of the electron and hole \( E_{x(h)} \), the width of the quantum well and barrier \( L_{QW}^2 \) and \( B^2 \), respectively, the effective masses of the electron and the hole in the quantum well, \( m_{\text{eff}} \), and in the ligand barrier, \( m_{B} \), and a real parameter \( \delta \) equal to \( q(L_{QW} + B^2) \), where \( q = \left( 2 \alpha \right) = \left( \frac{1}{\alpha} \right) \). \( L \) is length of the lattice, and \( n \in \mathbb{Z} \). The modified band gap energy is given by the following formula:

\[ E_g = E_g^{3D} + E_{x} + E_{h} \]

We chose a barrier width of 15 Å to account for the probability that the OA ligands surrounding the nanoplatelets will intercalate to some extent during stacking. This resulted in a further decrease of the calculated values, and the bandgap energies of the \( n = 3, 4 \) S platelets were reproduced well. Stacking of nanoplatelets could possibly explain the gradual blueshift of the PL peaks observed at lower OA concentrations.

While the remaining deviation from the experimentally obtained values for the \( n = 2 \) platelet only amounts to 170 meV, for the \( n = 1 \) nanoplatelet it is considerably larger, approximately 600 meV. This remaining discrepancy is most likely due to the large exciton binding energies common in thin 2D semiconductor structures.\textsuperscript{43–45} These energies result from the fact that in bulk perovskite, which has a large dielectric constant, the Coulomb interaction between the electron and hole is strongly screened, reducing the binding energy. As the thickness of the platelets decreases, more and more of the electric field lines between the charge carriers are outside of the perovskite where the dielectric constant is significantly lower. This reduces the screening, and in the case of only a single perovskite layer, the screening becomes minimal, greatly enhancing the exciton binding energy.

To quantitatively describe this effect we have calculated \( E_x \), the exciton binding energy, separately in weak and strong confinement regimes\textsuperscript{36} and included this into the Kronig–Penney model to obtain the transition energy of the exciton:

\[ E_x = E_g^{3D} + E_x + E_h - E_x^X \]

For weak confinement, when \( L_{QW} \gg a_0 \), the exciton binding energy is assumed to be close to the effective Rydberg energy of the three-dimensional exciton.\textsuperscript{37} In the case of strong confinement, when \( L_{QW} \ll a_0 \), we have used an expression derived by R. Guseinov (see Supporting Information for details on the calculations).\textsuperscript{46} This allowed us to reproduce the experimental value for \( n = 2 \) platelet exactly and that of the \( n = 1 \) nanoplatelet with a deviation of 140 meV (Figure 4b), which can be seen as reasonable as discussed in the following paragraph.

In our calculations, we have approximated the conduction band of the perovskite as parabolic. However, the conduction band is actually anisotropic, which has a noticeable impact for relatively thin wells.\textsuperscript{37} The in-plane curvature of the dispersion relation at the bottom of the subband gives different values of the effective mass than calculated as in the bulk. The electron effective mass becomes a function of confinement energy depending rather strongly on the width of the quantum well.\textsuperscript{37} The nonparabolicity could be the source of the remaining small mismatch between the experimental and calculated values. Unfortunately, many parameters are necessary to calculate not only the nonparabolicity correction itself \( E_{\text{corr}}^{np} \), but also the transition energy of the exciton, \( E_x \). Specifically the dielectric constants of the quantum well and the barrier as well as the effective masses in the barrier and the Luttinger valence parameters in both regions are not known.\textsuperscript{12,37} Thus, any \( E_{\text{corr}}^{np} \) cannot produce reliable values and is thus not included in the presented model. Other methods employing, for example, a standard density functional theory, especially when spin–orbit coupling is neglected in calculations, also do not fully reproduce the band structure of halide perovskites and would thus offer no improvement on the approach employed here.\textsuperscript{48}

Finally, we would like to report an interesting observation that was made during TEM measurements. In some cases, along with the nanoplatelets, we could observe quasi-spherical structures, roughly 6 nm in size (see Supporting Information, Figure S4). These resembled the nanoparticles observed in previous studies.\textsuperscript{16,19,20,21} The quasi-spherical nanoparticles were always seen in conjunction with a rectangular background, arranged quite regularly. Furthermore, on some areas of the TEM grids, the nanoplatelets could be observed to transform, yielding these nanocrystals. Upon further exposure to the electron beam, these nanocrystals actually shrank in size until they vanished altogether. Previous studies have also reported this effect, although the nature of the particles was unknown.\textsuperscript{16,21} High-resolution TEM showed these structures to be highly crystalline, and lattice parameters could be extracted from the observed fringes. While these could originate from MAPbBr\(_3\), it could not be excluded that they stemmed from PbBr\(_2\). Additionally, some particles were shown to consist of metallic Pb (cf. Supporting Information, Figure S5). Energy-dispersive X-ray spectroscopy (EDX) on many of the quasi-spherical nanoparticles revealed a molar content of Pb to Br between 1:1.3 and 1:0.75 (see Supporting Information, Figure S6). This result suggests that these crystals were actually not perovskites but were rather composed of a mixture of PbBr\(_2\), pure Pb, and potentially other phases. EDX measurements performed on thin rectangular structures revealed a ratio of Pb to Br of approximately 1:2.8. This latter measurement was difficult to perform, as the transformation of the nanostructures partially occurred during the measurement. For bulk perovskite, the expected ratio is 1:3, and for layered perovskites, this value increases with decreasing thickness, up to 1:4. Therefore, while our obtained values are not as high as this, this is most likely due to a degradation of the nanostructure during the measurement. These results suggest that the quasi-spherical nanoparticles observed by electron microscopy were not
perovskite nanocrystals but rather a degradation product of perovskite nanoplatelets created by the focused electron beam. Consequently, this supports the argument that the synthesis method used here and in previous studies generally leads to the formation of 2D perovskite nanoplatelets instead of nanostructures with other dimensionalities.

In conclusion, we have investigated quantum size effects in two-dimensional organometal halide perovskite nanoplatelets. By controlling the ratio of the organic cations used in the synthesis, we were able to obtain nanoplatelets of varying thickness. As the fraction of the large organic ion OA was increased, the thickness of the platelets shrank until only one single octahedral layer was left. From optical spectroscopy measurements, we were able to determine the energetic bandgaps for perovskite nanoplatelets of incremental thickness. Calculations modeling the quantum size effects were performed and yielded good overlap with the experimental values. We found that both the ligand and the degree of stacking of the individual platelets play an important role in determining their optical properties. We concluded that for nanoplatelets with $n \leq 2$, the exciton binding energy becomes extremely large, on the order of several hundred meV, partially counteracting the blueshift occurring due to quantum confinement. Additionally, we determined that the quasi-spherical nanocrystals observed in our and previous studies were most likely not initially present in the suspensions but were caused by degradation of the nanoplatelets under strong electron beams and laser illumination. These findings will help to utilize perovskite nanostructures in applications ranging from sensing to photodetectors and most importantly light-emitting applications. By understanding the nature of the quantum size effects in perovskite nanostructures, new synthesis methods could be developed to obtain nanostructures with desired optical and even electrical properties.

**ASSOCIATED CONTENT**

**Supporting Information**
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.5b02985.

XRD scattering of perovskite nanoplatelet powders; HRTEM images of investigated nanostructures; EDX measurements and corresponding HRTEM images of analyzed nanostructures; Bragg intensities from powder diffraction experiments; details on XRD measurements, PL quantum yield measurements, and calculations (PDF)

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**Author Contributions**
J.A.S. and Y.T. contributed equally to this work. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Notes**
The authors declare no competing financial interest.

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**ABBREVIATIONS**

MA, methylammonium; OA, octylammonium; OABr, octylammonium bromide; MABr, methylammonium bromide; DMF, dimethylformamide; TEM, transmission electron microscopy; SEM, scanning electron microscopy; PL, photoluminescence; EDX, energy-dispersive X-ray spectroscopy

**REFERENCES**

Supporting Information

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Figure S1. XRD scattering spectra of perovskite powders with varying octylammonium (OA) content and of PbBr$_2$. 
Figure S2. TEM images of CH3NH3PbBr3 perovskite nanoplatelets. (a) A dropcasted sample of OA 60% comprising quasi-2D nanoplatelets. The nanoplatelets stack together as seen by the dark contrast. Some platelets appear to be standing on their sides, enabling an estimate of their thickness (b-d).
Figure S3. The Bragg intensities I_{HKL} from powder diffraction experiments for different OA concentrations (data points), normalized to the respective (100) intensity. The solid lines are a guide to the eye; they indicate the reduction in intensity with increasing OA concentration.

Table S1. Quantum yield of perovskite suspensions depending on OA content.

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Figure S4. TEM image of perovskite structures showing quasi-spherical nanostructures aligned with a rectangular nanoplatelet.

Figure S5. a) HRTEM image of quasi-spherical nanocrystals. (b) High magnification image of one nanocrystal and (c) FFT analysis of its observed lattice planes. The distances and angles match those of metallic lead.
Figure S6: HRTEM images and corresponding EDX spectra for different observed nanostructures.
**X-ray Powder Diffraction Bragg Intensities**

The integrated diffracted intensity $I_{\text{int}}$ from a small parallelepiped crystallite scales with the number of unit cells $N$, i.e. it does not depend on the particular shape of the crystallite as long as the number of scatterers in the beam remains the same. If, however, one dimension of the crystallite is very small along the (100) direction, the measured intensity per resolution element is strongly reduced, since at some point the instrumental resolution does not cover the whole peak. Due to the orientational averaging in a powder experiment, the effect is strongest for reflections which have no in-plane peaks. For example, the (111) reflection has a multiplicity of 8, and all peaks are out of the platelet surface. Thus, the (111) intensity would be very sensitive to platelet thickness; unfortunately the (111) peak is always very weak due to the unit cell form factor. However, the effect can also be seen for the rather strong (210) peak, which has a multiplicity of 24; 8 reflections in the platelet surface and 16 out of plane. Thus, an intensity reduction of up to 2/3 with respect the original intensity due to reduced platelet thickness is possible. The (200) reflection, on the other hand, has a multiplicity of 6, with 4 reflection in the platelet plane, and 2 reflections out of the plane. In turn, the measured intensity should drop at the most by 1/3 for thin platelets. Our data confirms this trend nicely, i.e. we see a strong reduction of the (210) peak intensity but only a very weak reduction of the (200) peak intensity with increasing OA concentration. Here, for simplicity, we have normalized to the (100) intensity.

**Calculations**

1) Calculating the exciton Bohr radius

The Bohr radius of the three-dimensional exciton is defined as:

$$a_B = \frac{\varepsilon m_o}{\varepsilon_o \mu} a_H,$$

where $\varepsilon_o$ and $\varepsilon$ are the dielectric constants of vacuum and the material, $\mu$ and $m_o$ are the effective masses of the exciton ($\mu = \frac{1}{m_e} + \frac{1}{m_h}$) and the free electron, and $a_H$ is the Bohr radius.\(^1,2\)

2) Calculating the exciton binding energy

The transition energy of the exciton is defined as the difference between the lowest transition energies evaluated without and with the Coulomb coupling between the electron and the hole:

$$E_X = E^{3D}_B + E_e + E_h - E^X_B$$

The exciton binding energy $E^X_B$ needs to be calculated separately in the weak and strong confinement regimes.\(^2,3\)

a) weak confinement regime:
In the weak confinement regime, when \( L_{QW} \gg a_B \) with the quantum well width \( L_{QW} \), the exciton binding energy is given by the well-known equation describing the effective Rydberg energy of the three-dimensional exciton:

\[
E_b^X = \left( \frac{\varepsilon}{\varepsilon_o} \right)^2 \frac{\mu}{m_o} R_H,
\]

where \( R_H \) is the Rydberg constant. For these calculations, \( m_e^{QW} = 0.23 m_o \), \( m_h^{QW} = 0.29 m_o \), \( \varepsilon = 3.29 \varepsilon_o \) were considered. \(^4\) \(^5\)

b) strong confinement regime:

In the case of the strong confinement regime, when \( L_{QW} \ll a_B \), the exciton binding energy is calculated according to a formula taken from Ref. [4]:

\[
E_b^X = -\frac{e^2}{\varepsilon_{QW} L_{QW}} \left( \ln \left( \frac{8 \varepsilon_{QW} L^B}{\varepsilon_{QW} a_B^{'}} \right) - 2 C + 2 \gamma_0 \right),
\]

where \( \varepsilon_{QW}, \varepsilon^B \) are dielectric constants for the quantum well and barrier respectively, \( L^B \) is the width of the ligand barrier, \( C \) is Euler’s constant, \( a_B^{'}, \varepsilon \) is the effective radius of exciton, and \( \gamma \) is an eigenvalue which does not depend on the parameters of the problem. Both dielectric constants were taken from Ref. [5] as \( \varepsilon_{QW} = \varepsilon = 3.29 \varepsilon_o \) and \( \varepsilon^B = 1.84 \varepsilon_o \).

**Methods**

**UV-vis, PL**

UV-vis absorption was measured with a Varian Carry 5000 UV-vis-NIR spectrometer. For photoluminescence (PL) measurements the samples were excited with a monochromated Xe-lamp. PL spectra were taken with a Fluorolog-3 FL3-22 (Horiba Jobin Yvon GmbH) spectrometer equipped with a water-cooled R928 PMT photomultiplier tube mounted at a 90° angle. Relative quantum yield measurements were taken using a coumarin 6 dye as a reference and exciting at 365 nm. All measurements were performed on perovskite suspensions, for the quantum yield measurements the suspensions were diluted to prevent self-quenching and reabsorption.

**TEM, SEM, HRTEM, EDX**

The morphology of the samples was investigated using a JEOL JEM-1011 TEM operating at an accelerating voltage of 80-100 kV. For SEM measurements, a Gemini Ultra Plus field emission scanning electron microscope with a nominal resolution of \( \sim 2 \) nm (Zeiss, Germany) was used. The images were collected by the in-lens detector
at an electron accelerating voltage of 0.5 kV and a working distance of 1 mm. High-resolution images in TEM mode were recorded with a Titan 80-300 at an accelerating voltage of 300 kV. For elemental analysis with this instrument, energy dispersive X-ray (EDX) analysis was performed with a Si(Li) detector. Samples for S/TEM and EDX were prepared by drop casting about 20µl of the sample on a copper grid covered with a holey carbon film.

XRD

The X-ray setup has a microfocus X-ray source with Mo target (Xenocs) with corresponding 2D multilayer mirror (Genix3D). It provides a highly collimated beam with less than 0.2 mrad divergence in vertical and horizontal direction; the wavelength is 0.71 Å. The collimation path of the setup is 84 cm long; two scatterless slits suppress parasitic scattering. The sample to detector distance is typically 32 cm, the precise distance and other geometrical factors are calibrated with a lanthanum hexaboride standard sample for each setting. The detector (Pilatus 100k, 1mm sensor, Dectris) has a quantum efficiency of 76%. The beam diameter is around 1mm and the flux at the sample is typically $3.3 \times 10^6$ photons/s. The detector is mounted on a x-z-stage and two images are stitched together to increase the q-range which covers values up to 5 Å$^{-1}$ ($2\theta = 34^\circ$).

We measured powder samples which were fixed between two 25 µm thick Kapton foils with magnets. The recorded powder rings were transformed to 2$\theta$ angles via radial integration with the Igor Pro software plugin Nika.  

REFERENCES