Stacks of a Hidden Treasure: on the Self-Assemble of Perovskite Nanoplates in Organic Solvents


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Abstract

In recent years, perovskite nanocrystal superlattices have been reported with collective optical and electronic quantum phenomena. Regarding perovskite nanoplates, their superlattices can be easily observed on electron microscopy grids, for example, and they too present ensemble optical response. However, little is known on the self-assemble and optical properties of the perovskite nanoplates superlattices in solvents. Here, we report a simple strategy to induce the formation of these nanoplates stacks (1D superlattices) in suspension in different organic solvents. We investigate the influence of concentration and viscosity on their formation. For that purpose, we combined wide- and small-angle X-ray scattering and scanning transmission electron microscopy to evaluate CsPbBr₃ and CsPbI₃ perovskite nanoplates with different thickness distributions. We found that, in hexane, the concentration threshold for the formation of the aggregated stacks is rather high and approximately 80 mg/mL. In contrast, in decane, dodecane, and hexadecane, we observe a much easier formation of these stacks: the higher is the viscosity, the easier is the stacking of the nanoplates. We, then, discuss the impact of the proximity of the perovskite nanoplates in their colloidal stacks or solid superlattices in terms of Föster resonant energy transfer. We predict an efficiency higher than 50% in the energy transfer even in a low photoluminescence quantum yield scenario for both perovskite compositions.

Introduction

Metal halide perovskite semiconductors and their nanoscale derivatives have attracted enormous attention from the scientific community, both in terms of fundamental and applied science. This notoriety is due to their outstanding electronic and optical properties such as direct bandgap with high optical absorption near the band edge, high PLQY of their
nanocrystals, balanced ambivalent charge mobility, easy processing and synthesis, and low cost. The basic structure of a metal halide perovskite is ABX₃, where A is a monovalent cation (organic or inorganic), B is a divalent cation (normally Sn²⁺ and Pb²⁺), and X is a halide (Cl, Br, or I). Regarding metal halide perovskite nanocrystals, the most notorious composition is CsPbX₃ due to its impressive photoluminescence properties. These nanocrystals present bright emissions, covering the entire visible spectrum by simply tailoring their halide composition or changing their dimensionality.

As for any other nanomaterial, the variety of morphologies in which perovskite nanocrystals can be synthesized offers a rich toolset for superlattice and collective quantum phenomena investigations. For instance, in the work of Rainò et al., the authors reported a superfluorescence from a superlattice of perovskite nanocubes. Later, Mattiotti and colleagues developed a theoretical model accounting for thermal effects and structural disorder on the radiative decay rate of the superfluorescence, complementing the findings of Rainò et al. Conversely, perovskite nanoplates (PNPls) are a rich platform for the design of superlattices and for the study of collective optical phenomena. In the work of Jagielski et al., for instance, the authors explain an enhancement of the PL quantum yield in superlattices of PNPls (compared to their PLQY in suspension) by an aggregation-induced emission effect. In this avenue, perovskite superlattices are an abundant field of research opportunities. However, very little is known on their self-assemble in colloidal suspensions in organic solvents.

Examples of the stacking of nanoplates (NPls) in colloidal suspensions have been reported for CdSe. These stacks can be considered as 1D superlattices with colloidal stability, and changes in the optical properties of the NPls also occur upon aggregation. For instance, in the work of Tessier et al., the authors showed an enhancement of the exciton-phonon coupling, evidenced by a side band in the emission spectrum, due to the formation of stacks of CdSe NPls. In a different work, Guzelturk et al. reported nearly 100% efficient Förster resonant energy transfer (FRET) within the stacks of CdSe NPls. The stacking resulted in a strong reduction of the PLQY, which the authors attributed to trapping of excitons in small-bandgap, non-emissive NPls. A last example is the work of VanOrman et al., where the authors use CdSe NPls as a triplet sensitizer in a molecular up-conversion system based on triplet-triplet annihilation. The authors argue that, when there is aggregation of the NPls, the up-conversion dynamics is compromised. While several examples are found for cadmium chalcogenides, little is known about the optical implications of stacks of PNPls in suspension. In addition, the common use of ethanol as an antisolvent as means to induce the stacking cannot be applied to PNPls, given the sensitivity of these materials to most polar antisolvents. Therefore, a method to induce the self-assemble of PNPls into stacks in colloidal suspensions is of great importance to enable the investigation of fundamental properties of these materials and further develop their applications.

In this work we report an effective strategy to induce the aggregation of PNPls into their 1D superlattices in organic solvents and discuss the impact of these stacks in FRET. A
powerful way to investigate these colloidal superlattices is the use of small-angle X-ray scattering (SAXS), and several reports have demonstrated its analytical power and the uniqueness of the insights it provides.\textsuperscript{14,21,27–30} Thus, we probed the suspensions of PNPls with CsPbBr\textsubscript{3} and CsPbI\textsubscript{3} compositions in different solvents and conditions using SAXS. We chose a set of different solvents with different viscosities such as hexane, decane, dodecane, and hexadecane. We found that, by increasing the viscosity of the solvents, we increase the aggregation of the NPls: the increase in viscosity leads to a lowering of the diffusion of the NPls, favoring the formation of stacks. The aggregated stacks of PNPls present good colloidal stability. Also, we show that the concentration threshold for the aggregation in hexane is somewhere close to 80 mg/mL, while in all other solvents the stacking occurs much more favorably. We, then, calculated the Föster distance, R\textsubscript{0}, using the absorption cross-section of the PNPls. We predict an efficiency of FRET of more than 50%, even in the worst scenario of low PLQY of the donor species for both CsPbBr\textsubscript{3} and CsPbI\textsubscript{3} compositions.

Results

Material Synthesis and Characterization

We synthesized the nanoplates with different compositions and different temperatures, following a protocol previously reported by our group.\textsuperscript{31} Briefly, lead acetate and cesium carbonate are dissolved in 1-octadecene, oleic acid, and oleylamine, and a second solution of SnX\textsubscript{4} (X = Br or I) is prepared separately in the same mixture of solvents. The SnX\textsubscript{4} solution

![Figure 1](image.png)

**Figure 1.** a) Absorption and PL spectra of CsPbBr\textsubscript{3} and CsPbI\textsubscript{3} samples synthesized at different temperatures, showing excitonic resonances relative to their thickness; b) HAADF-STEM images of the four samples in (a), showing their aggregation motif according to their morphology; and c) schematic representation of the superlattice of two representative samples with some metrics taken from the FFT of their respective STEM images.
(halide precursor) is swiftly injected into the lead/cesium precursor in the desired temperature to yield PNPls. The two compositions we chose for this work were CsPbBr₃ and CsPbI₃ PNPls, both synthesized at 110 °C and 170 ºC. For simplicity, these samples will be referred to as Br-110, Br-170, I-110, and I-170 hereafter.

**Figure 1a** shows the absorption and emission spectra of all the samples with the respective picture of a quartz cuvette containing their hexane suspensions under UV light. The intense excitonic resonance in the absorption implies in strong quantum confinement effect along of the thickness of the PNPls. The position of the excitonic resonance is directly related to the number of octahedron layers (n) in each PNPl: in the case of the CsPbBr₃ compositions, we have well defined n = 2 (λ_{exc} = 425 nm – Br-110)²⁰ and n = 3 (λ_{exc} = 454 nm – Br-170)²¹ excitonic maxima in the absorption spectra. For CsPbI₃ compositions, the I-110 sample shows predominantly n = 3 excitonic absorption (λ_{exc} = 587 nm), while I-170 shows a mixture of larger particles together with the n = 3 excitonic resonance.³¹ Regarding the PL spectra, the samples synthesized at 110 ºC show more intense emissions from the main excitonic state: n = 2 for Br-110 (λ_{max} = 439 nm) and n = 3 for I-110 (λ_{max} = 606 nm). The latter also shows a shoulder of n = 4 emission. The samples synthesized at 170 ºC show a mixture of emission bands, reflecting the broader thickness distribution in these samples; the emissions come from nanoplates with n ≥ 3.

The absorption and PL features of the PNPls can be directly related to the HAADF-STEM images in **Figure 1b**. The sample Br-110 is a network of thin (possibly n = 2 ~1.18 nm thick)³² nanowires. For convenience, when we use the generic term “perovskite nanoplates” and the acronyms “PNPls” or “NPls”, we also refer to the Br-110 sample. The sample Br-170 is comprised of nanoplates with well-defined sizes that self-assemble into stacks organized in columns laterally aligned. Similarly, the I-110 sample also shows stacks of nanoplates, much smaller than those observed in the Br-170, with random orientation. At last, the sample I-170 shows a rough size distribution in all dimensions, with nanocrystals varying from nanoplates to nanorods. This behavior can be explained by a size defocusing that widens the size distribution in the case of CsPbI₃ perovskite nanocrystals after a few seconds of reaction.³³

Except in the case of I-170 sample, we could take some superlattice parameters of the PNPls using the HAADF-STEM images. A fast Fourier transform (FFT) of the images in **Figure 1b** revealed patterns in the reciprocal space that are proportional to the distance between the nanoplates and, in the case of Br-170, between the columns of the stacks. These measurements are shown in **Figure S1a** to S1f, and a schematic representation of their structure is shown in **Figure 1c**. For all the samples, regardless of the composition, the distance between particles is very similar, about 5 nm. However, the Br-110 sample shows a range of distances from ~4.6 to ~7 nm (**Figure S1f**), reflecting the fluctuation of distances observed in **Figure 1b** where the nanowires are not perfectly parallel to each other. To estimate the thickness of the PNPls, we evaluated the contrast scale along segments of NPls for the three samples, Br-110, Br-170, and I-110 (**Figure S2a**). The profile peaks (**Figure
were fitted with gaussian functions, and their FWHM were used as the thickness of the NPls. The parameters of the fits are shown in Table S1. Considering an orthorhombic \textit{Pnma} crystal structure with the thickness of a single Pb-Br slab of 0.59 nm for CsPbBr$_3$ and an orthorhombic \textit{Pbnm} crystal structure with the thickness of a single Pb-I slab of 0.64 nm for CsPbI$_3$, the resulting thickness for all the samples corresponds to approximately four octahedron layers ($n = 4$). This thickness is slightly overestimated because it does not reflect the absorption and PL spectra from Figure 1a. Subtracting the thickness from the interparticle distances found in the FFT images, we calculated an average length of the bilayer of oleylammonium cations to be $\sim 2.8$ nm, which is consistent to the work of Bekenstein \textit{et al.} and contrasting with some previous reports where this distance is reported to be $\sim 3.5$ nm. However, since the thickness of the NPls is overestimated, this value must be in between 2.8 and 3.5 nm.

The morphology of the NPls were further evaluated by the form factor modeling from SAXS measurements in two sample-to-detector distances: 3.8 and 0.3 m. A parallelepiped form factor included in Irina macros for IgorPro® software was used for the modeling of the NPls. To more details on data reduction and modeling form factor, see Methods section. To perform the analysis, we used the parameters from the STEM images and the absorption spectra as starting points. For instance, for Br-170, which is a quite regular sample in terms of size distribution, we chose the mean thickness to be 1.77 nm ($n = 3$) with a standard deviation of 0.33 (the variation of a single octahedron layer). We also chose the largest size of the nanoplate to be about 11 nm (estimated from the distance between the columns – Figure 1c). The model fits the data very well, and the resulting fit is shown in Figure 2a (gray curve). The parameters from the fit are summarized in Table 1 and, for Br-170 sample, the parameters are in excellent agreement with the STEM images. For the Br-110 sample, we started with a thickness of 2 layers (1.18 nm) and allowed the length to be much larger. Although the model fits the scattering data well (Figure 2b), the correlation between SAXS and STEM results (Table 1 and Table S1) is not trivial. One observation is noteworthy: the size we measure from the STEM images is apparently not the thickness of the nanowires, but the B-side (defined in Table 1). Evidence for that is the low contrast presented by the nanowires in the transmission mode of electron microscopy (Figure S3), suggesting that the thickness direction is perpendicular to the plane of the TEM grid. Also, although slightly overestimated, the thickness found from the SAXS modeling agrees with a $n = 2$ nanowire, presenting the optical properties from Figure 1a, and the B-side extracted is consistent to the
thickness measurement from the STEM images. Thus, SAXS and STEM data for Br-110 also present reasonable agreement.

For the samples I-170 and I-110, the same modeling strategy was adopted, yielding satisfactory fits with realistic size parameters (Figure 2c and 2d). The inset 3D drawings in each panel in Figure 2 were created using a 1:1 Å/mm ratio of the parameters in Table 1, and then resized by the same factor to fit within the figures. Therefore, these insets represent the relative aspect ratio and mean sizes extracted from the modeling. By simple eye inspection, we can verify in the insets the general characteristics of the PNPls observed in the STEM images. SAXS data also show that lower synthesis temperature yields narrower thickness/size distributions, reflected by the smaller standard deviation from these samples resulted from the models. It is also noteworthy the presence of the diffraction of {101} crystallographic planes of perovskites at Q ≈ 1 Å⁻¹ for all samples.

Table 1. Extracted parameters from the scattering curves of 20 mg/mL samples in hexane using a parallelepiped form factor

<table>
<thead>
<tr>
<th>Sample</th>
<th>A side (nm)</th>
<th>B side (nm)</th>
<th>C side (nm)</th>
<th>A std. deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br-170</td>
<td>1.80</td>
<td>5.62</td>
<td>11.01</td>
<td>0.33</td>
</tr>
<tr>
<td>Br-110</td>
<td>1.74</td>
<td>4.38</td>
<td>28.58</td>
<td>0.05</td>
</tr>
</tbody>
</table>
To verify the crystalline phase of the materials, we collected WAXS images from the same suspensions we measured SAXS from Figure 2a to 2d. The WAXS data (Figure 2e) agrees with the orthorhombic crystalline phase of perovskites and present some insights on the growth directions of the nanoplates. While in the SAXS curves we observe the diffractions of \{101\} planes, in the WAXS data, we observe the diffractions from the \{202\} and beyond. In Figure 2e, the diffractions whose Miller indexes are (040) and (202) are convoluted for all the samples. Interestingly, however, when the sample thickness is decreased (e.g., from I-170 to I-110 samples), the (202) diffraction loses intensity, suggesting that its respective crystallographic planes are parallel to the thickness of the nanoplates. On the contrary, the (040) diffraction remains with similar intensity even in the thinner nanoplates, suggesting that its respective crystallographic planes are perpendicular to the thickness of the nanoplates and, therefore, do not lose intensity upon thickness reduction. This observation can be explained in terms of the distance correlation in WAXS: the more crystallographic planes are present in a certain direction, the better will be the distance correlation for the diffraction, increasing the intensity of the signal and decreasing the FWHM of the peaks. To illustrate our analysis, a schematic representation of a nanoplate and its growth directions is shown in Figure S4.

**Solid State Superlattices of the Perovskite Nanoplates**

We now turn our attention to the self-assemble properties of the PNPls. To evaluate the formation of stacks in the nanoplates’ suspensions, we first collected SAXS data from the solid samples, forcing them to assemble into their superlattices. Briefly, we filled 1.5-mm borosilicate capillaries with 80 mg/mL PNPls suspensions. Then, we dried the hexane under reduced pressure with the help of a desiccator. This process allows the nanoplates to self-assemble into their stacks, and so we could have a reference for the analysis in suspension. **Figure 3** shows the curves of these solid samples.
In Figure 3, the samples Br-170 and I-110 show a very well-defined stacking pattern, while Br-110 showed a mixture of phases. The I-170 sample does not show any evidence of an organized superlattice. To extract the parameters from these scattering curves, we fitted the peaks with Lorentzian functions, and, for the background, we used a sum of different spheric populations only to match the curve (no physical meaning). An example of the fitting is shown in Figure S5, and the parameters extracted from all samples are summarized in Table 2. The family of peaks enumerated from 1 to 3 is consistent with Bragg reflections of a lamellar crystal structure resulting from the stacking of the nanoplates. Interestingly, the sample Br-170 shows an additional scattering feature between 0.03 and 0.06 Å⁻¹ that is the reflection from the space between columns of stacks (average of 14 nm), just like in the FFT of the STEM image in Figure S1. The reflection is broad because this distance varies with the lateral size of the nanoplates. Furthermore, the I-110 sample does not show this broad feature in low Q values, even in the dry sample. This lack of signal in this region suggests that the stacks of these nanoplates are randomly oriented, confirming what we
observed in its STEM image of Figure 1b. The reason for this lack of column alignment might be the higher variability of the B- and C-side in this sample compared to its Br-170 analogue.

Table 2. Extracted parameters from the scattering curves of the solid samples using Lorentzian functions for the diffractions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( d_1 ) (Å)</th>
<th>( d_l ) (nm)</th>
<th>( d_{1'} ) (Å)</th>
<th>( d_{1'} ) (nm)</th>
<th>( \sqrt{1} ) (Å)</th>
<th>( d_3 ) (Å)</th>
<th>( 2 ) (Å(^{-1}))</th>
<th>( 2' ) (Å(^{-1}))</th>
<th>( \sqrt{3} ) (Å(^{-1}))</th>
<th>( 3 ) (Å(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br-110</td>
<td>0.122</td>
<td>5.15</td>
<td>0.130</td>
<td>4.81</td>
<td>0.113</td>
<td>5.51</td>
<td>0.240</td>
<td>0.259</td>
<td>0.198</td>
<td>0.482</td>
</tr>
<tr>
<td>Br-170</td>
<td>0.123</td>
<td>5.09</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.246</td>
<td>-</td>
<td>-</td>
<td>0.493</td>
</tr>
<tr>
<td>I-110</td>
<td>0.122</td>
<td>5.15</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.244</td>
<td>-</td>
<td>-</td>
<td>0.487</td>
</tr>
</tbody>
</table>

\( d_l \) = crystallographic spacing corresponding to the peak i

The sample Br-110 shows different features in addition to the diffractions from the lamellar phases observed in its counterparts. First, we can distinguish two different lamellar structures in this sample with slightly different particle distances: \( d_1 = 5.15 \) and \( d_{1'} = 4.81 \) nm (Table 2). The peaks of the second lamellar phase are marked with a prime for clarity (1’ and 2’). The distinction of the peak 1 is difficulted by the convolution of 3 diffractions in this region (Figure S6). Nonetheless, the existence of two close related lamellar phase is consistent with the difference between the thickness (A-side) and the B-side in this sample (Table 1). Coexisting with the two lamellar phases, we can also assign an extra crystalline phase of the nanowires. The peaks at 0.113 Å\(^{-1}\) \((\sqrt{1})\) and 0.198 Å\(^{-1}\) \((\sqrt{3})\) present relative positions with the relation \( \sqrt{1} : \sqrt{3} \), which can be related to a pseudo-hexagonal lattice where \( a = b\sqrt{3} \) (a, b = lattice constants). Lastly, the sample I-170 does not show any crystallographic arrangement due to the irregular morphology of the nanoplates. However, the large size of the particles in this sample allows the acquisition of an intense [101] diffraction of the perovskite crystalline structure. In close agreement to the WAXS discussion above, this diffraction loses intensity when decreasing the thickness of the nanoplates (see curves I-170 and I-110 in Figure 3).

Just by analyzing 1D-SAXS curves in Figure 3, one loses orientation information when integrating and reducing the detector images, and one of these samples presents some preferential orientation. It is the case of the Br-110 sample that seems to present a gravitational effect, causing the nanowires to orient vertically relative to the X-ray beam. This effect generates higher-intensity signals along the \( Q_y \) axis of the diffraction discs, as depicted in Figure S7.

1D Superlattices of the Perovskite Nanoplates in Organic Solvents

With the parameters extracted from these solid samples, we were able to assess the self-assemble properties of the PNPIs while in suspension in hydrocarbon solvents. Hexane is a commonly used solvent because it disperses very well nanoparticles with large ligands such as oleylammonium or oleic acid. It is exactly this property that makes the self-assemble of PNPIs into stacks difficult in this solvent. For this study, we chose the Br-170 and I-110 samples due to their intuitive lamellar assembly.
Figure 4 shows an initial survey of these PNPs suspended in hexane, varying their concentrations from 1 to 80 mg/mL. As we can observe in Figure 4a and 4b, neither the Br-170, nor the I-110 samples, show any signal of stacking in suspension in hexane in the concentration window we chose (note that the SAXS curves from the solid samples are presented for comparison). Even the most concentrated samples did not show any evidence of stacking. This result reaffirms the great solvation ability of hexane for oleylammonium-capped PNPs. This observation is also of critical importance to the interpretation of FRET phenomenon in more diluted suspensions, since it suggests that, in those cases, the NPs are far from one another, and FRET is less probable.31,40

To further evaluate these hexane suspensions, we varied the temperature of the 80-mg/mL samples from 30 to 5 °C, and we performed a hysteresis test, raising back the temperature from 5 to 30 °C with the same intervals. The resulting curves are shown in Figure 4c and 4d. Again, no obvious stacking signal could be observed in these scattering curves upon decreasing the temperature; however, a careful look in Figure 4c (I-110 sample), in the curves from 5 to 30 °C (middle to bottom), reveals discrete undulations between 0.1 and 0.3 Å⁻¹. These undulations suggest that lower temperatures induce the formation of a small number of small aggregates in this sample. To confirm this hypothesis, we compared the hexane suspensions with three other solvents: decane, dodecane, and hexadecane.

The higher viscosity (η) of these solvents decreases the diffusion of the particles, lowering their kinetic energy; if the kinetic energy is not high enough to overcome attractive van der Waals forces, then aggregation will occur.41 The additional solvents present viscosity values as follows: decane (η = 0.85 mPa s), dodecane (η = 1.36 mPa s), and hexadecane (η = 3.96

![Figure 4](image-url)

**Figure 4.** 1D-SAXS curves with different concentrations of a) I-110 hexane suspensions and b) Br-170 hexane suspensions; c – d) 1D-SAXS curves of the respective samples with 80 mg/mL varying the temperature from 30 to 5 °C. Both experiments do not present any obvious aggregation signal of the nanoplates in hexane suspensions.
We, then, prepared 80-mg/mL Br-170 samples with all the solvents, including hexane ($\eta = 0.29$ mPa s), and probed their scattering pattern in the same conditions of the previous experiment in room temperature. The scattering curves are displayed in Figure 5.

**Figure 5** shows a smooth increase in the aggregation of the NPls into their stacks with increasing viscosity of the solvents. Furthermore, with this experiment, we could demonstrate that, for both I-110 and Br-170 samples, the undulations between 0.1 and 0.3 Å$^{-1}$ are indeed the beginning of the stacking of the nanoplates. Therefore, the threshold for this stacking in hexane is about 80 mg/mL, which is a rather high concentration for nanocrystalline colloidal suspensions. We hypothesize that this stacking in liquids must occur in equilibrium: depending on the solvent, there is a mean size of the stacks, and the nanoplates from the extremes must go on and off the surface with a certain exchange rate. In addition, since the viscosity in inversely proportional to temperature, the solubility of the aggregates must increase in higher temperatures. Interestingly, these stacks show remarkable colloidal stability; i.e., upon concentration saturation, they do not precipitate over time. **Figure S8**

![Figure 5](image-url)

**Figure 5.** 1D-SAXS curves with suspensions in different organic solvents for the CsPbBr$_3$ synthesized at 170 °C sample. The concentration of the suspensions is 80 mg/mL. The curves show a smooth increase of the aggregation of the nanoplates with increasing viscosity of the solvents.
shows curves of a Br-170 hexadecane suspension collected along seven hours, and the scattering signals from the stacking present similar intensity and width.

**Implications in Föster Resonant Energy Transfer**

The proximity of the PNPls in their stacks, both in solid state or in liquids, will influence on their charge carriers and exciton dynamics. For instance, we can use the insights gained by our experiments to discuss the effectiveness of FRET in those systems. For this purpose, we considered a donor acceptor system comprised of a \( n = 2 \) nanoplate (donor) and an \( n = 3 \) nanoplate (acceptor) for CsPbBr\(_3\). We, then, calculated the molar extinction coefficient at 3.1 eV for the acceptor species using its absorption cross-section (see Supplementary Text for details). With this information, we could estimate the Föster distance, \( R_0 \), which is the distance where the FRET efficiency is 50% (Equation 1).

\[
R_0^6 = \frac{9000(\ln10)k^2\phi_f}{128\pi^5Nn^4} \int_0^{\infty} F_D(\lambda)\varepsilon_R(\lambda)\lambda^4 d\lambda \quad \text{Equation 1}
\]

Where \( N \) corresponds to the Avogadro’s number, \( K^2 \) is the orientation factor regarding the transition vectors of the donor PL and acceptor absorption, \( \phi_f \) is the PLQY of the donor in the absence of acceptor, \( n \) is the refractive index of the solution, \( F_D(\lambda) \) is the normalized fluorescence spectrum of the donor, \( \varepsilon_R(\lambda) \) is the molar absorption coefficient of the acceptor (L.mol\(^{-1}\).cm\(^{-1}\)), and \( \lambda \) is the wavelength (nm) in which the \( \varepsilon_R \) was determined.\(^{46,47}\)

In Figure 6a, we show the overlapping spectra between donor PL and acceptor absorption, as well as the respective overlap integral (gray). To estimate \( R_0 \), we considered a range of possible PLQY values for the donor and the approximation of isotropic conditions for the transition vectors, which is expressed by \( K^2 = 2/3 \).\(^{47,48}\) We also considered the values for \( R_0 \) when \( k^2 = 1 \); i.e., parallel orientation of the transition vectors. A summary of the estimated \( R_0 \) for different values of PLQY is shown in Table 3.
Table 3. Estimated $R_0$ values for CsPbBr$_3$ and CsPbI$_3$ donor-acceptor systems considering different orientation regimes – $k^2 = 2/3$ and $k^2 = 1$

<table>
<thead>
<tr>
<th>Donor</th>
<th>Acceptor</th>
<th>$J / \text{L mol}^{-1} \text{cm}^{-1} \text{nm}^4$</th>
<th>$\Phi_f / \text{.}$</th>
<th>$^{2/3}R_0 / \text{nm}$</th>
<th>$^4R_0 / \text{nm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsPbBr$_3n = 2$</td>
<td>CsPbBr$_3n = 3$</td>
<td>$5.7 \times 10^{16}$</td>
<td>0.05</td>
<td>5.6</td>
<td>6.4</td>
</tr>
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<td>CsPbBr$_3n = 3$</td>
<td>$5.7 \times 10^{16}$</td>
<td>0.10</td>
<td>6.3</td>
<td>7.2</td>
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<td>$5.7 \times 10^{16}$</td>
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<td>7.7</td>
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<td>CsPbBr$_3n = 2$</td>
<td>CsPbBr$_3n = 3$</td>
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<td>CsPbI$_3n = 3$</td>
<td>CsPbI$_3n = 3$</td>
<td>$1.8 \times 10^{17}$</td>
<td>0.05</td>
<td>5.2</td>
<td>5.9</td>
</tr>
<tr>
<td>CsPbI$_3n = 3$</td>
<td>CsPbI$_3n = 3$</td>
<td>$1.8 \times 10^{17}$</td>
<td>0.10</td>
<td>6.8</td>
<td>7.7</td>
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<tr>
<td>CsPbI$_3n = 3$</td>
<td>CsPbI$_3n = 3$</td>
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<td>CsPbI$_3n = 3$</td>
<td>$1.8 \times 10^{17}$</td>
<td>0.20</td>
<td>8.5</td>
<td>9.8</td>
</tr>
</tbody>
</table>

$k^2R_0$ denotes the values of $R_0$ for the respective $k^2$

Considering the distance between nanoplates in their stacks determined by SAXS ($r \sim 5.2 \text{ nm}$), we can infer from Table 3 that, even in a low PLQY scenario (5%), the FRET efficiency is 52% for CsPbBr$_3$ system (Efficiency $= R_0^{-5}/(r^6 + R_0^6)$), considering isotropic conditions. Now, if we consider parallel orientations ($k^2 = 1$), the efficiency reaches 55%, which is not a significant difference. The same analysis was performed for CsPbI$_3$ composition, but the energy transfer was considered in a system where both donor and acceptor are the nanoplates with $n = 3$ (homo-FRET). The absorption, PL, and overlapping integral between the spectra is shown in Figure 6b. Because the PLQY is probably higher for $n = 3$ CsPbI$_3$ nanoplates compared to $n = 2$ CsPbBr$_3$ analogue, we considered the values of $R_0$ with PLQY of at least 10%. Therefore, in the case of CsPbI$_3$ system, the FRET efficiency is calculated to be 57% in isotropic conditions and 60% in parallel orientation, considering the same distance ($r \sim 5.2 \text{ nm}$) of the nanoplates’ stacks. Methods to improve the PLQY of these nanoplates can increase further the efficiency of FRET in their superlattices and aggregates. Nonetheless, FRET formalism relies on some approximations that we must consider for these systems.
Förster formalism has two important approximations: the ideal dipole approximation (IDA) and the isotropic condition approximation. In the first the electronic coupling between donor and acceptor is considered as a dipole-dipole coupling, and this approximation may fail depending on the distance and orientation factors. The second considers randomly oriented transition vectors of donor and acceptors (solution systems). 47,48 Both approximations are interconnected, as we discuss herein. For a randomly oriented, isotropic donor-acceptor system (i.e., $k^2 = 2/3$), the IDA fails in distances < 2 nm. However, when the donor-acceptor system present restricted relative mobility, the distance in which the IDA fails can be higher than 5 nm, posing strong limitations in FRET experiments in these systems. 50 The isotropic approximation is a rough approximation when applied to the stacks of the nanoplates since their transition dipoles of the excitonic states present both in plane and out-of-plane orientations. 51 While the in-plane dipole-dipole coupling is still adequate for the IDA, the perpendicular, out-of-plane/in-plane coupling will result in $k^2 = 0$ (thus the coulombic coupling is also zero). 50 Therefore, in the FRET formalism, the electronic coupling is null for the perpendicular orientation of the transition dipoles, while from a more accurate quantum-mechanical description, this coupling is non-zero. 50,52

In addition to the observation above, it is important to consider the influence of the dimensionality and geometry of the acceptor on the distance dependence for FRET. For instance, in the work of Hernández-Martínez et. al., the authors predicted a dependence proportional to $1/d^4$ for the energy transfer between two quantum-wells (QWs), which is the case of PNPls. 53 This prediction is supported by the work of Murphy et al., where the authors find this same distance dependence for a nanoparticle (donor)/quantum-well (acceptor) system. 54 This less sensitive distance dependence improves the energy transfer rate between nanoplates (Equation 2), especially in their aggregated stacks.

$$\frac{1}{\tau_{DA}} = \frac{1}{\tau_D} \left( \frac{R_0}{r} \right)^6$$

Equation 2

Where $1/\tau_{DA}$ is the FRET rate and $1/\tau_D$ is the recombination rate of the donor in the absence of the acceptor. This equation shows the dependence of the FRET rate with the interparticle distance.

In alignment with all these considerations, the work of Singldinger et al. shows evidence of energy transfer from $n = 2$ to $n = 3$ CsPbBr$_3$ PNPls, reaching up to 69% efficiency. 55 Interestingly, the most efficient energy transfer regime was achieved with a sample with twenty times more acceptors then donors (A:D = 20), which suggests an effect of efficiency enhancement through a scaffold of acceptors around a common donor. 58 Therefore, in an overall perspective, the efficiency reported by the authors is consistent to our discussion and conclusions in this work.
Discussion

With the information acquired by SAXS, we could undoubtedly observe the stacking of PNPls in organic solvents suspensions and the influence of the viscosity of these liquids in their aggregated stacks. The use of this solvents is a convenient strategy to induce the aggregation of the PNPls into their superlattices stacks without the use of antisolvents. These findings allowed us to discuss and make predictions on the efficiency of Föster resonant energy transfer in these systems. We also demonstrated the power of SAXS and WAXS techniques, combined with STEM, to elucidate important structural aspects of colloidal suspensions and superlattices of perovskite nanoplates, both in solid state and in solvents. For instance, we used size and morphology information acquired from STEM as starting points to model the SAXS curves of the PNPls; this modeling provided reliable and unique information on the thickness and size of the nanoplates, placing SAXS as a non-destructive alternative to probe perovskite nanocrystals in general.

In future works, to be published elsewhere, it is important to expand the choice of solvents and evaluate the behavior of the nanoplates in each of them. Clearly, the threshold concentration for aggregation changes for different solvents, and it is desirable to find the critical concentration for aggregation in each of them. Also, the influence of temperature is an important measurement to evaluate the dynamics of these aggregates and how it influences their formation. In addition, those colloidally stable stacks of PNPls provide a reliable system for fundamental optical research such as resonant energy transfer, phonon-driven processes, and complex heterogeneous energy/charge transfer systems such as in the work of VanOrman et al.24

As a final remark, our findings deepen the understanding on perovskite nanoplates self-assemble properties and allow for the rational development of these systems and their applications. Some synthesis protocols for PNPls yield nearly monodisperse nanoplates with a specific thickness.49,55 This is important for the design of their superlattices or even superlattices with perovskite nanocrystals with different morphologies. At last, a critical aspect for the further development of these materials is the stability of their superlattices, which remains a challenge and limits their practical applications into optoelectronic devices.41,56

Methods

Synthesis of the Perovskite Nanoplates

Precursor of SnX₄ (X = Br and I): 907 mg of SnBr₄ (2.0 mmol) is loaded in a 50-mL flask with 10 mL of 1-octadecene (ODE), 5 mL of oleic acid, and 5 mL of oleylamine. The mixture is then heated to 100 °C under reduced pressure for at least 1 h. The procedure is
important to remove the water and oxygen from the precursor. The same procedure is followed to prepare the iodide precursor with SnI₄ (1296 mg – 2.0 mmol).

**Precursor of Cs and Pb-oleate:** 75 mg of Cs₂CO₃ (0.46 mmol of Cs⁺) and 790 mg of lead acetate trihydrate [Pb(OAc)₂·3H₂O] (2.0 mmol) are dissolved in 5 mL of oleic acid. The mixture is heated to 100 °C for at least 1 h under reduced pressure to remove water and residual acetic acid from the reaction. The resulting Cs- and Pb-oleate are then used as necessary.

**Synthesis of Perovskite Nanoplates:** 1 mL of the Cs/Pb precursor was dissolved in 4.5 mL of ODE and 0.5 mL of oleylamine. The mixture is heated to 110 °C under reduced pressure for at least 1 h. After this time, the mixture is kept in the temperature of the reaction (in the case of this work, 110 and 170 °C), and 2 mL of the SnX₄ precursor solution is swiftly injected into the Cs/Pb solution. The SnX₄ precursor is pre-heated to 100 °C under reduced pressure before the injection. In the case of CsPbI₃ PNPs, the reaction is quenched immediately after the injection with an ice/water bath. In the case of CsPbBr₃ PNPs, the reaction is quenched after 30 s after the injection with ice/water bath. To precipitate the product from the synthesis of CsPbI₃ at 110 °C by centrifugation (see next section), an addition 0.5 mL of oleic acid was added to the Cs/Pb precursor solution. With the original synthesis, very little or almost no precipitate is formed upon centrifugation.

**Purification of the Perovskite Nanoplates:** to purify these materials we cannot make use of antisolvents because nanoplates are sensitive to even mildly polar solvents. We, thus, centrifuge the crude solution after the completion of the reaction at 13,500 rpm for 10 minutes. A pellet of material is deposited on the bottom of the tube after the centrifuge step. The supernatant is discarded, the global yield is measured, and the pellet is resuspended in anhydrous hexane to give a ~20 mg/mL suspension. This hexane suspension is then kept in a fridge at 5 °C overnight. For CsPbI₃, a new centrifuge step is necessary to precipitate some remaining insoluble materials. For the second centrifuge, though, the supernatant is kept and the solid on the bottom of the centrifuge tube is discarded (*note that it will change the initial concentration*). The supernatant is then filtered in a hydrophobic syringe filter with 22-µm pore. The filtered suspensions are kept refrigerated and sealed under N₂ atmosphere until their use.

**Scanning Transmission Electron Microscopy (TEM):** the electron microscopy of the perovskite nanoplates was performed in a TEM-Titan Cubed Themis (FEI company) equipment. The images were acquired with 300 kV in High-Angular Annular Dark Field mode (HAADF-STEM). The samples were prepared in a holey carbon coated TEM copper grid. To prepare the samples, we dripped 3 µL of a 1 mg/mL of the perovskite nanoplates suspensions in hexane and allowed it to dry in the ambient. The grids were loaded into the equipment and remained under reduced pressure overnight. To remove the excess of organic compounds, a 20-minute beam shower was performed in a large area of the grid to avoid excessive beam damage.
Wide- and Small-Angle X-ray Scattering (WAXS and SAXS): X-ray scattering experiments were carried out in a Xenocs Xeuss 2.0 equipment in two sample-to-detector distances: 0.3 and 3.8 m. The X-ray source was a GeniX 3D with a copper target with photon energy of ~8 keV ($\lambda = 1.5419$ Å). The detectors used were a Dectris Pilatus 300 k for SAXS and Dectris Pilatus 100 k for WAXS (WAXS detector was at 36° with respect to the X-ray beam). The colloidal suspensions of the perovskite nanplates (with several concentrations) were loaded in 1.5-mm borosilicate capillaries, as well as their dry samples. To prepare the dry samples, we filled the capillaries with 80 mg/mL hexane suspensions, placed them inside a desiccator with the help of a rack, and dried the solvent under reduced pressure for at least an hour. All the measurements were performed in ambient atmosphere with controlled temperature and humidity. The background for the samples was collected using their neat solvent in a capillary. The calibration of the distances for the 2D scattering curves was performed using silver behenate as a standard. We calibrated and reduced the data (radial integration of the 2D scattering image to obtain a scattering curve) using the Nika$^{57}$ macros for IgorPro® software. To obtain the scattering curves from Figure 2 (I(q) vs q), we merged the curves from the two sample-to-detector distances and subtracted the respective backgrounds. To model the scattering curves, we used a parallelepiped form factor included in Irina$^{38}$ package for IgorPro software.

UV-visible absorption spectroscopy: Absorption spectroscopy was performed in a Carry 60 UV-Vis Agilent Technologies spectrophotometer, using a 10-mm quartz cuvette. All the spectra were collected using ~0.2 mg/mL hexane suspensions of the perovskite nanplates. A neat cuvette with neat hexane was used as a background.

Photoluminescence spectroscopy: measurements were performed in an Ocean Optics QEPro spectrofluorometer with and 365 nm LED as an excitation light source directly on the quartz cuvettes containing the hexane suspension of the perovskite nanplates.

References

14. Guzelturk, B., Erdem, O., Olutas, M., Kelestemur, Y. & Demir, H. V. Stacking in...


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