Interfacial Self-Assembly and Oriented Attachment in the Family of PbX \((X = S, Se, Te)\) Nanocrystals

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ABSTRACT: The realization of materials with new optoelectronic properties draws much scientific attention toward the field of nanocrystal superstructures. Low-dimensional superstructures created by interfacial assembly and oriented attachment of PbSe nanocrystals are a striking example because theory showed that PbSe sheets with a honeycomb geometry possess non-trivial flat bands and Dirac cones in the valence and conduction bands. Here, we report on the formation of one-dimensional linear and zigzag structures and two-dimensional \((2D)\) square and honeycomb structures for the entire lead chalcogenide family: PbX \((X = S, Se, Te)\). We observe that PbTe, with a lower bulk melting temperature and enthalpy of formation than those of PbSe, shows a higher nanocrystal surface reactivity, such that the surface must be passivated and the reaction conditions moderated to obtain reasonably ordered superstructures. The present findings constitute a step forward in the realization of a larger family of atomically coherent \(2D\) superstructures with variable IV–VI and II–VI compositions and with electronic properties dictated by the nanogeometry.

INTRODUCTION

Nanocrystals (NCs) are currently being extensively studied by the scientific community because of their unique size-tunable properties caused by their nanoscale dimensions. Colloidal NCs also form the basis of solid materials, in which the properties are dictated by the interactions between the individual NC building blocks. When NCs with their original organic capping ligands are directly used in colloidal crystallization, the interaction between the NCs is weak and the electronic conductivity is low. Applications in photovoltaics and electronics therefore necessitated the development of ligand exchange chemistry that improves the electronic coupling between the NCs.

Almost 3 decades ago, it was found that crystal growth does not always strictly proceed via monomer-by-monomer addition. For example, NC nuclei can form larger crystallites by directly fusing together by a process called oriented attachment. Oriented attachment implies that two identical crystal facets face each other and rearrange some of their constituent atoms such that a neck grows between them. In this way, the crystallites fuse in such a neat manner that the resulting structure is singly crystalline.

More recently, it was reported that, with PbSe NCs, oriented attachment could be employed to create two-dimensional \((2D)\) superstructures (SSs) in which the NC building blocks are atomically connected to each other and are therefore also electronically coupled. Moreover, it was found that the oriented attachment of PbSe NCs could be combined with interfacial self-assembly. In this way, low-dimensional SSs with a linear, square, or honeycomb geometry can be created. These systems show long-range periodicity at the nm scale (i.e., the geometry) and strict atomic crystallinity over a few NC units. Tight-binding calculations predict that this nanoscale ordering gives rise to truly novel band structures and hence properties that cannot be derived from the individual building blocks. Although the exact mechanism of formation of such \(2D\) SSs is not yet fully understood, the first steps toward unraveling their chemistry and physical chemistry have just been reported.

In the present study, the preparation by interfacial self-assembly of four low-dimensional SSs, namely, lines, squares, zigzags, and honeycombs, is reported for NCs from the entire lead chalcogenide family: PbS, PbSe, and PbTe (PbX). Successful synthesis of these SSs with different members of the PbX family opens the pathway to further tailoring SS properties toward specific ends. By also employing cation exchange as a post-treatment, the synthesis of, for example, wide-bandgap SSs of CdX compounds or SSs with strong spin–orbit coupling (e.g., HgX compounds) might become possible. We remark that all PbX NCs have a rock salt crystal structure, a
similar truncated cubic shape, and Pb-oleate ligands. However, the PbX compounds differ in their bulk lattice properties, such as melting temperature and enthalpy of formation. We, therefore, endeavored into a comparative study of the reaction conditions and compared the SSs that have been formed.

**EXPERIMENTAL METHODS**

**Nanocrystal Synthesis.** All PbX NCs in this study have been prepared via adaptations of the hot injection method. PbS, PbSe, and PbTe NCs have respectively been produced according to Abel et al., Steckel et al., and Urban et al. Furthermore, the PbTe particles were capped with additional chloride ligands according to Woo et al. to slow down their intrinsically fast attachment; more discussion will be given in the Results and Discussion section. See Supporting Information 1.1 for the full experimental conditions of the NC syntheses.

**Nanocrystal Analysis.** All NCs were analyzed by transmission electron microscopy (TEM) using FEI TECNAI 10/12 and near-infrared (NIR) spectroscopy (Perkin Elmer, Lambda 950 UV/VIS/IR absorption spectrophotometer) to determine their size, monodispersity, and/or concentration. Although sizing curves for each of the PbX NCs have been published in the literature, the ways these sizing curves were established vary for each member in the PbX family. To have a better comparable estimate of the size of the NCs, the TEM images were analyzed in the ImageJ program by performing a background subtraction and particle detection.

To determine the concentration of the PbX NCs, NIR spectroscopy was used. However, no such procedure exists in the literature for PbTe NCs. Therefore, the procedure for concentration determination of PbSe NCs was also used for PbTe NCs. This procedure proved to work well enough for obtaining good and comparable results with the oriented attachment procedures. These concentrations were used to calculate the experimental surface area per NC (= inverse NC surface density) by converting this number to nm$^2$/NC with the dilution factors and the surface area of the substrate.

**Superstructure Assembly via Oriented Attachment.** All PbX SSs in this study have been prepared via adaptations of the oriented attachment method described by Evers et al. and Boneschanscher et al. In a nitrogen-purged glovebox, a dilute PbX NC suspension in an apolar liquid is dropcasted onto an ethylene glycol substrate. Ethylene glycol is chosen as a liquid substrate because it is a sink for Pb(oleate) moieties, and in this way is important in the desorption of the oleate ligands from the {100} facets. After the solvent is completely evaporated, a sample is scooped with a TEM grid and analyzed by TEM. The surface area per NC and bonds per NC values in resulting SSs were manually obtained. See Supporting Information 1.2 for more experimental details on the SS assembly.

**RESULTS AND DISCUSSION**

**Size, Shape, and Surface Facets of Nanocrystals in the Lead Chalcogenide Family.** Figure 1 displays TEM images of the PbX NCs that were synthesized and used for the assembly of the SSs through oriented attachment. Using automated particle detection, the NC sizes were determined from these TEM images assuming a spherical particle shape (see Experimental Methods for more details). It was found that the particle sizes for the PbS, PbSe, and PbTe NCs are, respectively, 5.2 ± 0.6 nm (sample size: 124), 5.5 ± 0.5 nm (sample size: 465), and 4.8 ± 0.5 nm (sample size: 2254). These three sizes are sufficiently close, such that a comparative study of the influence of the surface chemistry on SS formation is possible. Furthermore, for each PbX compound, several NC suspensions were used and the results were reproducible enough to be able to indicate and discuss meaningful differences between the three PbX compounds.

All PbX NCs were synthesized with a capping layer of Pb-oleate ligands that stabilizes the NC colloidal dispersions and passivates the NC surfaces, mostly the {111} crystal facets. The PbTe NCs were capped with additional Cl-ligands, which had a profound effect on their stability in ambient air, as was already found for PbS NCs. Also, the chloride ligands slightly reduced their reactivity during the oriented attachment procedure, which was usually necessary to obtain well-ordered PbTe SSs. As oleate ligands are very strongly bound to the Pb{111} facets, we expect that the Cl-ions are only attached to surface Pb of the {100} and {110} facets.

All PbX NCs possess the rock salt crystal structure. Their shape can be well described by a cube, which is strongly truncated in the {111} directions and some studies also suggest some cantillation in the {110} directions. This exposes the {100} and {111} (and possibly {110}) facets on the NC’s surface and gives especially the small (<10 nm) particles the appearance of a sphere when observed by TEM, as can be seen in Figure 1.

We remark that the magnitude of the surface energy of the bare {100} facets is considerably lower than that of the bare {110} and {111} facets. This is in line with recent findings of...
Peters et al. showing that oleate and Pb-oleate moieties are weakly bound to the \{100\} facets.24

All oriented attachment in the present study occurs at the \{100\} facets, which can be seen as a checkboard of lead and chalcogenide atoms. As a result, all NC bond angles are approximately 90 or 180°. This coincides well with the literature on oriented attachment of PbSe NCs at liquid interfaces.10,14,32 PbS and PbSe NCs have been observed to attach only with other facets under reaction conditions that resemble those of the NC synthesis.8,33

Comparison of the Reactivity and Superstructure Assembly Conditions for the Lead Chalcogenides. Figure 2 shows an overview of models, TEM images, and selected area electron diffraction (SAED) patterns of the formed SSs: one-dimensional (1D) linear and zigzag SSs and 2D square and honeycomb SSs were observed for each PbX. The most comparable reaction conditions under which these SSs have been synthesized are listed in Table 1. It might be hard to see in Figure 2 that the NCs have actually performed oriented attachment. Figure S4 shows a close-up image in which each of

![Image of Figure 2](image-url)
the PbX NCs is clearly attached. This proves that the NCs have
the propensity to perform oriented attachment.

When comparing the three members of the PbX family, it
was found that each formed SSs under mostly similar reaction
conditions: all on an ethylene glycol substrate, all with a
reaction time on the order of 1 h, all dispersed in a volatile
apolar solvent, all with a size of ±5 nm NCs, and all with an
area of a few tens of nm²/NC (i.e., inverse NC density). This
can be explained by the similar properties of materials in the
PbX family. NCs of the three compounds all have the rock salt
crystal structure and a very similar shape.

The strong similarities in reaction conditions aside, the
temperature, NC passivating ligands, and oleic acid concentrations
vary slightly among PbS, PbSe, and PbTe. This was
done to compensate for the fact that under reaction conditions
ideal for creating PbSe SSs, some PbS NC batches performed
only oriented attachment at a slightly increased temperature
that speeds up the reaction. In contrast, some PbTe NC
batches would perform uncontrolled agglomeration under ideal
PbSe attachment conditions. An image of such suboptimal
attachment is presented in Figure S5. To prevent this, the PbTe
NCs had to be capped with additional chloride ligands and
oleic acid was added to the substrate. These measures have
been proven to inhibit NC surface oxidation and moderate the
process of oriented attachment, respectively.10,21

These observations are indicative of a higher surface
reactivity of the PbTe NCs and a lower reactivity of the PbS
tones, compared to that of PbSe NCs. This follows the trend of
a decrease in the binding energy of the PbX lattice from PbS to
PbTe, which is reflected in the bulk melting temperature of the
materials, 1113, 1078, and 924 °C respectively, and their
formation enthalpies, −100.4, −102.9, and −70.7 kJ/mol.34
Moreover, PbTe NCs are exceptionally prone to surface
deterioration, exemplified in their enhanced propensity for
surface oxidation.15 More evidence that the NC surface
reactivity follows the trend PbS < PbSe < PbTe will be
presented below in the section on neck formation between the
NCs.

**Honeycomb and Zigzag Superstructures.** The scientific
literature on experimental realization of the honeycomb NC
SSs is limited9,11 despite the extensive theoretical studies
published predicting interesting non-trivial optoelectronic
properties due to the honeycomb geometry.15,37-39 This is
probably due to the fact that the honeycombs are much harder
to make with an appreciable yield and reproducibility than the
other SSs. In this article, the synthesis of small domains of
epitaxially connected NCs with the silicene honeycomb
geometry is reported for all three PbX compound NCs. The
domain size and reproducibility are most pronounced in the
case of PbSe.

The TEM images and SAED data acquired on the
honeycomb SSs are similar for all PbXs, as can been seen in
Figure 2i-1. Each NC in the honeycomb SS has a (111)
crystallographic direction up and is atomically connected to up
to three NCs. Not directly visible in these images, but already
established in the literature, is that the NCs in these SSs are
arranged in a quasi-bilayer also called the silicene structure.11
This bilayer structure is depicted in perspective view in Figure
4b.

The zigzag SSs, displayed in Figure 2m-p, have so far not
been described in the literature. An unattached PbS NC
superlattice very reminiscent of the zigzag SS has been reported
by Novák et al.40 Cho et al. have also described zigzagging SSs
made by oriented attachment of PbSe NCs,41 however, the latter
SSs clearly differ from the ones presented in the present study.
as those are made from much larger, octahedrally shaped NCs. Moreover, those SSs are attached in their \langle 111 \rangle crystallographic directions in contrast to the \langle 100 \rangle attachment that is observed in this study.

A more thorough geometrical analysis will be provided for the zigzag SSs as these can sometimes appear as linear SSs when observed by TEM, for example the zigzags displayed in Figure S2n. In Figure 3 the 1D SSs are further analyzed by Fourier transformation and SAED. (We remark that for PbTe NCs, Figure 2p, our analysis of the SSs being zigzags is thus far based on the TEM images only, as SAED data could not be obtained.) Particularly, SAED can differentiate well between the two SSs, as the \langle 110 \rangle up orientation of NCs in zigzags allows for reflections from their \{111\} planes to be visible in their SAED patterns. In contrast, lines are oriented \langle 100 \rangle up, so \{111\} planes are not at their Bragg angle with the incoming electron beam and thus their reflections are not visible in their SAED patterns. These differences in the SAED pattern can be seen in Figure 3c-f.

Furthermore, TEM images of zigzags show lighter and darker regions within each line of zigzagging NCs. By Fourier transforming the images of the SSs, it follows that zigzags are periodic at the length scale one would expect for two NCs connected through their \{100\} facets in a 90° angle out of the image plane. In contrast, linear structures show the periodicity at the NC scale. On adding up these two observations, we conclude that zigzag SSs are shaped as illustrated in Figure 4a,c: the NCs are ordered in a zigzag fashion and form a quasi-bilayer in the image plane. The NCs in zigzags are sometimes attached to each other in the image plane and most likely also in their zigzagging directions. In this respect, zigzag SSs can be seen as 1D sections of the honeycomb SSs, as was also the case for linear SSs with respect to squares.

We remark that some images of the zigzag SS deviate from the idealized schematics in the present article. In reality, honeycomb and zigzag structures are more like the extremes of a continuous span of possible structures. Very dense regions of NCs, such as can be seen in Figure S2n and S2p, match the presented zigzag structure perfectly. Intermediate density patches look more wiggly in the image plane, as can be seen in Figure 2n,o. In low-density regions, those wiggles coherently break open into a honeycomb structure.

Even though the NC ordering between honeycombs and zigzags appears to be rather fluid, the NC orientation in them is not. This is clearly visible in the accompanying SAED patterns. All NCs in a honeycomb have a \{111\} facet pointing up and all NCs in a zigzag have a \{110\} facet pointing up. This is the reason we made a clear distinction between the two structures. We remark that in the silicene honeycomb SSs each NC is attached via three \{100\} facets, one more than in the zigzag structure, reducing the overall surface energy.

These observations make it tempting to speculate that both SSs originate from a common pre-phase but more in situ research on the formation of these SSs should be performed to verify such a statement.

Mechanistic Aspects of Interfacial Nanocrystal Self-Assembly. NC Adsorption and Assembly at the Toluene/Air Interface. A striking observation on the samples is that SSs never overlap. Even when looking at larger sample patches, such as those displayed in Figure S3, NC densities fluctuate but the SS domains do not overlap. This observation of non-overlapping SSs is most peculiar for the lines, examples of which can be seen in Figure 2n–p and Figures S1n–p, S2n–p.
and S3. This is in contrast with the results of Cho et al., where oriented attachment presumably takes place in the bulk solution (i.e., without a liquid substrate and under reaction conditions reminiscent of PbX NC synthesis).

This indicates that all SSs discussed in the present study are formed at the liquid/gas interface, as was already proven for the square SSs in ref 15. For square PbSe SSs, it was found that the NCs adsorb to the toluene/air interface with a random orientation first. After 30 min, the toluene is (almost) evaporated and the NCs form a single hexagonal layer at the liquid/gas interface. Over the course of a few minutes, the NC layer starts to contract and slowly reforms itself to a square geometry; during this transformation, the NCs gradually orient their \{100\} facets toward each other. Finally, the NCs attach via their \{100\} facets. From the non-overlapping SS domains, it can safely be concluded that linear, square, zigzag, and honeycomb structures also originate all from an adsorbed NC (sub)monolayer at the interface.

Formed of Superstructure Domains. By further analyzing the geometry of the formed SSs in Figure S2, it was found that the NC density and the amount of bonds per NC can deviate strongly from those in the “geometrically perfect” models in Figure 2a,e,i,m. The deviations in NC density can be attributed to the relatively broad NC size distribution (±10% by TEM). Deviations in the amount of bonds per NC can be attributed to exhaustion of mobile surface atoms needed to form crystalline necks; the NCs preferably form robust necks with a few neighbors instead of weaker necks with all of them.

The observation of rather extended domains of one type of SS despite fluctuations in defining parameters (i.e., NC density and bonds/NC) indicates that once a given SS has been nucleated under the right conditions its further growth is quite robust. This aspect resembles classic monomer-by-monomer crystal growth of atomic or molecular building blocks.

Can We Understand the Concomitant Formation of Multiple Superstructures? Although the NC density for each SS fluctuates per domain, it does generally follow the geometrically predicted trend for bare PbX NCs: lines < squares < honeycombs < zigzags. Furthermore, on a microscopic scale, NC density fluctuations reminiscent of patterns caused by solvent flow have often been observed. These variations in the NC density at the liquid/air interface may arise from irregular flows during the evaporation of the toluene; see Supporting Information 3 for more details. This might indicate that local fluctuations in the density of NCs at the toluene/air interface are important in the type of SS that is formed. We remark that due to time limitations this comparative study has to be performed with still considerable rates of solvent evaporation. This may result in local gradients of temperature, NC density, etc., which limits the domain size and quality of the SSs. A limited-case study under ultra-slow nearly reversible process conditions is under way.

Figure S3a and S3b, respectively, show examples of the observation that domains of line and square SSs and domains of zigzag and honeycomb SSs often form nearby each other or even interlace each other. This indicates that the formation of these sets of SSs has a common origin and that the local NC density on the liquid/air interface finally decides between linear and square structures or between zigzag and honeycomb structures, respectively.

In fact, squares can simply be formed by sideways attachment of line strands and also zigzag and honeycomb SSs are very close in geometry. This is illustrated in Figure 4: a honeycomb structure results when tilting zigzag strands by 35°, shifting them by the length of less than a NC, and then connecting them together. Local NC surface density during SS formation therefore seems the most defining difference between the squares and lines, as well as between honeycombs and zigzags.

However, why square and honeycomb SSs formed concomitantly and can be observed on the same TEM grid is not very clear. It could indicate that the free energy of the pre-attached phases of these SSs (i.e., a 2D NC superlattice attached to the toluene/air interface) is similar. Soligno et al. have recently studied the effect of the toluene surface tension on the orientation of the NCs at the toluene surface and found that in most cases the energy for adsorption with the \{100\} axis upright (square SSs) or the \{111\} axis upright (honeycomb SSs) is similar.

Formation of One-Dimensional Superstructures. Both the line and zigzag SSs clearly show a preference for attachment...
Propagating in one direction, whereas orthogonal binding sites are seemingly fully available. In both SSs, the NCs attach via their \{100\} facets but their direction of propagation differs: lines propagate in a \langle 100 \rangle direction and zigzags in a \langle 110 \rangle direction. Presumably, attaching \{100\} NC facets such that a corner or T-split in the 1D SSs is formed should be just as favorable as attaching them in a linear fashion, but this is apparently in contrast with linear structures consisting of many NC units. The propensity of NCs to preferentially form 1D SSs is hard to rationalize at the moment.

Finally, we would like to remark that 1D SSs often contain far more bends, kinks, or wiggles along their direction of propagation than those in 2D SSs, examples of which can clearly be seen in Figures 2f,h,o and 3b,e. This jitter in morphology is probably caused by the fact that oriented attachment is not a reversible process; the first attachment of two NC cores will lock them together, even if their connection is not perfect. The interfacial NC self-assembly prior to attachment is reversible. During the formation of 2D SSs, the NCs are in a stronger self-assembled scaffold, causing the 2D SSs to be less prone to irregularities in the final attachment. In fact, Savitzky et al. have shown that a scaffold of NC SSs increases the long-range ordering in overlaying SSs.12

Mechanistic Aspects of Neck Formation. General Aspects. The last step in the formation process of the PbX SSs is oriented attachment of the NCs. We remark that it is essential for the formation of highly periodic SSs that the self-assembly and oriented attachment processes are separated in time. This was indeed observed for the square formation.15

The oriented attachment of the NCs happens through a process called necking. Necking implies that atoms from the two attaching crystallites solidify into a bridge between two opposing similar crystal facets, \{100\} facets in the present study.6 This follows from the fact that in the SSs the center-to-center distance is always larger than the original size of the NCs.11 Note that the process of necking requires vast atomic motion of the atoms in crystallites, as multiple layers of material have to solidify between two attaching NCs. This process is most likely a rearrangement of surface atoms, finally resulting in a more extended single crystal.

We present a tentative model for a step-by-step necking process in Figure 5. Initially, a couple of atoms "click" together by random thermal motion and thereby form the nucleus of a first connection. (b, c) Atoms at the NC corner sites are expected to be the most labile as they have the lowest coordination number. Therefore, they will be the most mobile surface atoms at the NC surface, so they will find atoms from the other NC first by random thermal motion and click to form a first connection. (d, e) Site of the first click forms an ideal nucleus for other labile surface atoms to find a more stable position with a higher coordination number. Finally, these surface atoms start to "cascade into the NC" bordering area. (f) After thorough surface reconstructions, a neck is formed between the two NCs.

![Figure 5. Model images of how PbX NCs are presumed to perform oriented attachment through a “click and cascade” necking model.](image-url)
Of course, Figure 5 depicts a highly idealized image of NC attachment projected in two dimensions, which in reality must be more complex and occurs in three dimensions. Both high-resolution transmission electron microscopy observations and modeling studies show that the surface atoms of PbX NCs are at non-crystallographic positions because of surface reconstructions or random thermal motion. Still, the general idea of the proposed model holds even then. Atoms from the “cloud” of loosely bound surface atoms meet and form a nucleus for further neck growth.

Comparison of Neck Formation in the PbX Family. Although the SSs formed by oriented attachment of PbX NCs showed mostly similarities in geometry, some subtle differences can be identified upon closer scrutiny. The observed differences are increasing disorder in attachment, thicker neck formation, and preferential 2D SS formation, all with increasing atomic weight of the anions, i.e., PbS < PbSe < PbTe.

The first two differences can best be discussed together as both are related to the neck formation process itself. First, when comparing Figure 2n−p, it can be seen that the lines formed by PbTe NCs are less straight than those formed by PbS and PbSe. Second, neighboring PbTe NCs in a SS generally formed thicker necks between each other; two examples of this thicker necking can be seen in Figure S2d and S2l.

Both these observations can be explained by a weaker binding of the surface atoms to the NC core. Particularly, the Pb-oleate moieties at the {100} facets are expected to be highly mobile as these do not have to stabilize the underlying surface facet, such as ligands bound to a {111} facet. In this way, the ligands at {100} facets can easily move out of the way and let the NCs attach faster. A faster attachment makes reversible reconstructions more difficult. Hence, this results into less nicely ordered SSs, as observed in the more wiggly PbTe lines.

Also, weaker binding of the ligands allows for a more rigorous reformation of the structure’s surface toward a thermodynamic minimum, which is bulk PbX. Thicker necks between NCs, as we observe for PbTe, is the closest to the bulk geometry that the system can come by reordering the surface moieties.

The last observed difference in SS formation between the PbXs is that PbS NCs showed a preference for forming 1D SSs, whereas PbTe showed a preference for forming 2D SSs. The 1D SSs need at least two bonds to form, whereas the 2D SSs need at least three. Therefore, it seems likely that more reactive species would prefer forming 2D SSs instead of 1D ones.

As was already discussed above, the slight optimizations of the reaction conditions also show a trend that coincides well with the binding energy in the different PbX lattices, as reflected in their bulk melting temperatures and formation enthalpies. The subtle differences in the neck formation corroborate that the surface reactivity trend is indeed PbS < PbSe < PbTe.

CONCLUSIONS

In this study, a synthetic self-assembly route toward four (quasi) 2D SSs, namely, squares, honeycombs, zigzags, and lines, from PbX NCs is described in detail. Their common features but also their differences are highlighted. The geometry of the SSs made with different PbXs shows mostly similarities, which coincides well with the fact that their constituent NCs all have the rock salt crystal structure and Pb-oleate capping ligands, leading to similar colloidal behavior and a similar surface chemistry. Therefore, also the reaction conditions under which the SSs formed are comparable. It was deduced that all of these SSs form at a liquid/gas interface. The surface reactivity of the NC cores increases slightly when going from PbS to PbSe and greatly when going from PbSe to PbTe, which coincides well with their bulk melting temperatures and enthalpies of formation. Finally, a click and cascade model of PbX oriented attachment was proposed that explains neck formation as a process to remove solvent molecules from the area between two attaching NCs.

Full reproducibility and comparability of the reaction conditions toward these SSs could not be reached because the exclusive formation of a single kind of SS requires very fine tuning of the nanoscopic NC density at the liquid/air interface during the experiment, but this is hampered by surface liquid flow during the solvent evaporation. Future research should focus on homogenizing the NC density throughout the experiment and on further exploring the parameter space in which the SSs are formed to allow quantitative research into the microscopic parameters (NC, ligand, and surfactant concentrations) for finding fully reproducible parameters toward each of the desired PbX NC SSs.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.8b01876.

Full experimental methods for NC synthesis and SS assembly, SSs with corresponding SAED patterns, effects of solvent flow on SS assembly, additional images showing close-ups of linear attachment of PbX NCs, and an image of oriented attachment with PbTe NCs, which have not been extra passivated (PDF)

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C.v.O., J.L.P., S.A.P.v.R., and M.S. performed the experiments. The manuscript was written by C.v.O., M.A.v.H., and D.V. supervised the project. All authors have given approval to the final version of the manuscript.

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Notes

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The PyMOL Molecular Graphics System, Version 1.8 Schrödinger, LLC was used to generate 3D nanocrystal images.

ABBREVIATIONS

NC, nanocrystal; 1D, one-dimensional; 2D, two-dimensional; SS, superstructure; PbX, lead chalcogenide (S, Se, and Te); TEM, transmission electron microscopy; SAED, selected area electron diffraction

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