Shape-Directed Co-Assembly of Lead Halide Perovskite Nanocubes with Dielectric Nanodisks into Binary Nanocrystal Superlattices

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ABSTRACT: Self-assembly of colloidal nanocrystals (NCs) holds great promise in the multiscale engineering of solid-state materials, whereby atomically engineered NC building blocks are arranged into long-range ordered structures—superlattices (SLs)—with synergistic physical and chemical properties. Thus far, the reports have by far focused on single-component and binary systems of spherical NCs, yielding SLs isostructural with the known atomic lattices. Far greater structural space, beyond the realm of known lattices, is anticipated from combining NCs of various shapes. Here, we report on the co-assembly of steric-stabilized CsPbBr₃ nanocubes (5.3 nm) with disk-shaped LaF₃ NCs (9.2−28.4 nm in diameter, 1.6 nm in thickness) into binary SLs, yielding six columnar structures with AB, AB₂, AB₄, and AB₆ stoichiometry, not observed before and in our reference experiments with NC systems comprising spheres and disks. This striking effect of the cubic shape is rationalized herein using packing-density calculations.

KEYWORDS: colloidal nanocrystals, nanocrystal shape, self-assembly, binary superlattice, electron microscopy, lead halide perovskites, superfluorescence

Inorganic nanocrystals (NCs) bridge the gap between bulk solids and atoms or molecules due to their size- and morphology-dependent properties, such as optical, plasmonic, and magnetic properties.¹² Self-assembly of NCs into long-range ordered superlattices (SLs), comprising one or more kinds of NCs, holds great promise for creating metamaterials with functionalities, which arise from the addition or synergy of the properties of individual building blocks (i.e., electronic, plasmonic or magnetic coupling, etc.).³⁵ Collective properties could be tunable through the interparticle distance, relative NC orientation, and interparticle medium, as it was demonstrated for band-like charge transport in SLs of semiconductor NCs,³−⁷ dipolar interactions in arrays of magnetic NCs,⁸−¹⁰ or near-field couplings in SLs of plasmonic NCs.¹¹−¹³ Although dozens of periodic and quasicrystalline SL structures were reported for binary mixtures of spherical NCs, examples of multicomponent SLs comprising nonspherical NCs were reported only for mixtures of spherical NCs with triangular nanoplates,¹⁴ nanorods,¹⁵ octapods¹⁶ and nanocubes,¹⁷ rhombic nanoplates with tripodal nanoplates,¹⁸

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Figure 1. (a) Ligand deformation in NC SLs comprising sphere–sphere (left), disk–cube edge (middle), and cube edge–cube edge (right) contacts. According to the OTM model, ligand bending affords smaller interparticle separation for anisotropic NCs interacting through sharp contacts. (b) Packing analysis of columnar AB₂(II)-type structures with nanodisks as A-component and spherical NCs (dashed line) or cubic NCs (solid line) as B-component, within the hard particle approximation, except for an indicated OTM branch. The black arrow indicates the size ratio at which the structure was observed experimentally; the black dashed line marks the limit of the close-packed hexagonal disk lattice. (c) Visualization of contacts between NCs in AB₂(II)-type SL according to hard particle and OTM models; lighter blue and gray regions denote the ligand shells around inorganic cores. (d) Didodecyldimethylammonium is the shortest ligand (1.71 nm) that still renders CsPbBr₃ NCs colloidaly robust. Smaller ligand size reduces the structural softness of these NCs and maintains an effective cubic shape.

nanodisks with nanorods, and nanocubes with triangular nanoplates. To this end, a range of shape-engineered and size-uniform NCs are synthetically accessible as building blocks for SLs; for instance, rod-shaped or polyhedral metallic NCs, faceted lanthanide fluoride nanoplates, rod- and prism-shaped lanthanide-doped fluoride NCs, diverse Cd chalcogenide morphologies (nanotetrahedra, nanorods, nanoplatelets), and lead halide perovskite nanocubes. NC self-assembly into SLs is driven by both energetic interactions and entropic contributions.

The former include dipole–dipole, Coulombic, magnetic, and van der Waals forces between inorganic cores and capping ligands, whereas relevant entropic factors comprise free volume entropy gain, depletion attraction interactions, and entropy associated with ligand configurations. In the case of entropy-driven crystallization of binary mixtures of spheres, the binary SLs of NaCl-, AlB₂-, and NaZn₁₃-type are known for hard-sphere systems of micrometer-sized colloidal beads characterized by only a steep steric repulsion term in their interparticle potential, as they maximize the packing fraction (η) at a given size ratio (γ = d₈/d₆ ≤ 1), exceeding that of single-component densest lattices of spheres (face-centered cubic or hexagonal closed packed; fcc and hcp). Much smaller spherical NCs (3–20 nm) stabilized by flexible hydrocarbon ligand chains depart from such purely hard-sphere behavior and yield more than 20 different binary SL structures isostructural with known atomic lattices. Most of these SLs are of much lower packing density if the latter is estimated, assuming the unaltered and uniform thickness of the surface ligand shell. Note that the packing density in this context is the volume fraction occupied by the NC core and ligand shell. Much higher packing densities can be estimated, thereby rationalizing the observation of such structural diversity, taking into account deformability of the ligand shell. Specifically, hydrocarbon chains of the ligands can bend away from the axis of contact between NCs (Figure 1a) in a structure-specific manner, as captured by the recently introduced orbifold topological model (OTM). OTM-corrected packing densities agree well with the experimental observations. Sharper NC shapes will favor the formation of vortices by ligand bending in specific mutual geometries of two kinds of NCs upon the “sharp contacts” between these NCs (Figure 1a), thereby favoring denser structures. Hence, the possibilities for obtaining NC SLs are anticipated to be gigantic for multicomponent assemblies of nonspherical NCs. In this context, we have recently reported on the co-assembly of cubic CsPbBr₃ NCs (8.6 nm) and larger spherical NCs (NaGdF₄·Fe₂O₃) into perovskite ABO₃-type binary SLs (with cubes occupying B and O sites). Emergence of ligand vortices on cube vertices (Figure 1a) densifies the lattice and hence explains the high propensity for crystallizing in an ABO₃-type SL within a broad γ-range and also the uniformity of this specific SL-type in all-sphere mixtures. Notably, CsPbBr₃ NCs, besides being of great interest for their compelling luminescent properties, represent a rare, if not a single, example of sub-10 nm NCs with a nontruncated, sharp cubic shape.

A further avenue for mesoscale assembly of nanocubes is to combine them with nonspherical NCs, since the anisotropic or even complementary shape of the second component can further promote long-range positional and orientational order of both constituent building blocks. Toward this end, we have targeted assemblies with LaF₃ nanodisks, owing to their well-defined, ensemble-uniform morphology and facile and reproducible synthetic tuning of their dimensions (~1.6 nm in thickness, 6.5–28.4 nm in diameter), as well as proven utility as building blocks in NC assembly (see columnar assemblies with nanorods in ref 19). We note that there exist no reports on successful co-assembly of nanodisks and spherical NCs, and also our trials have not led to such assemblies, which we
rationalize by comparatively low packing densities for various disk-sphere SL structures. On the contrary, CsPbBr3 nanocubes combined with LaF3 nanodisks yield a variety of columnar (periodic intermixing in two dimensions) and structurally three-dimensional SLs. An overarching effect of switching from spheres to cubes of the same size, namely, an increase in space-filling, is illustrated in Figure 1b by plotting hard-particle packing densities for one observed columnar structure [in the following termed as AB2(II)]. We further assessed the effect of ligand deformability upon the approach between the cube edge and a rim of a disk (Figure 1c). In particular, for the case of an AB2(II) structure that is observed at $\gamma = 0.430$, an OTM calculation suggests considerable densification upon ligand bending ($\eta = 0.915$ vs $\eta = 0.878$), exceeding the density values for hexagonal columnar packing of disks as a separate competing phase ($\eta = 0.907$).

Overall, we report the formation of six columnar SLs by combining 5.3 nm CsPbBr3 nanocubes with LaF3 nanodisks (9.2–28.4 nm in diameter). In these structures, stacked face-to-face disks and cubes form pillars, which assemble into twodimensional long-range ordered, periodic lattices. Transmission electron microscopy (TEM) and selected area electron diffraction (ED) characterization reveal that nanocubes in AB(I)-, AB3(I)-, and AB2(II)-type SLs lose orientational freedom and are aligned in one direction, whereas in AB2- and AB3-type SLs, cubes may have different orientations. Closely related are binary lamellar SLs, with chains of stacked cubes and disks lying flat with the substrate surface. In the mixtures of 8.6 nm CsPbBr3 NCs and comparably sized LaF3 nanodisks (6.5–12.5 nm), we observe a range of highly dense SL structures, wherein disks and cubes alternate in each of the three dimensions. Peculiarly, one lattice site can be occupied by several nanodisks. These findings indicate that a vast structural diversity of long-range ordered mesostructures is at reach through entropy-driven crystallization when two (or more) kinds of nonspherical, shape-engineered NC building blocks are employed.

Photoluminescence studies of lamellar and ReO3-type SLs, employing large 8.6 nm CsPbBr3 NCs, reveal collective emission properties at cryogenic temperatures. In particular, excitation at high fluences gives rise to a drastic superradiant acceleration of the radiative rates, along with ringing behavior in the time-resolved traces—signatures of superfluorescence (SF).

**RESULTS AND DISCUSSION**

Monodisperse oleate-capped LaF3 nanodisks of various sizes, namely, 6.5, 9.0, 9.2, 12.5, 13.3, 16.6, 18.5, 21.0, 26.5, and 28.4 nm in diameter (all being ~1.6 nm in thickness), were synthesized by thermal decomposition of lanthanum trifluoroacetate in a high-boiling solvent in the presence of long-chain capping ligands. These nanodisks readily stack in a face-to-face manner, lying both flat and perpendicular to the substrate, forming, respectively, hexagonal close-packed columnar or lamellar structures (see TEM characterization in Figure S1). A wide-angle ED pattern from a columnar assembly shows intense (110) and (300) reflections, in agreement with the trigonal crystal structure and basal surface termination by (001) lattice planes. In ED, due to a small electron wavelength,
structure of CsPbBr3 NCs is treated as pseudocubic with six simplicity of the ED analysis and peak assignment, the terminated by two {010} and four {101} planes. For exhibit an orthorhombic Pnma axis parallel to the electron beam (Figure S1). CsPbBr3 NCs monolayer indicate the alignment of cubes with the [001] zone localization. Narrow arcs in a wide-angle ED from an ordered schematic in Figure 1d and Figure S2 for optical characterization. Narrow arcs in a wide-angle ED from an ordered monolayer indicate the alignment of cubes with the [001] zone axis parallel to the electron beam (Figure S1). CsPbBr3 NCs exhibit an orthorhombic Pnma structure with six facets terminated by two {010} and four {101} planes. For simplicity of the ED analysis and peak assignment, the structure of CsPbBr3 NCs is treated as pseudocubic with six facets terminated by {100} pseudocubic planes, as the d-spacing between {010} and between {101} planes of the orthorhombic structure are very similar. Self-assembly experiments were carried out utilizing the slow solvent evaporation method over a tilted substrate with the use of octane or toluene as a solvent; see the Experimental Section for the NC synthesis and assembly details. Co-assembly of 5.3 nm cubes with nanodisks yielded six binary columnar structures [two AB, two AB2, AB4, and AB6 Figures S3–S6, domain areas up to 15 μm2 for AB(I), 0.5 μm2 for AB(II), 2 μm2 for AB2(I), 1 μm2 for AB2(II), 0.8 μm2 for AB6, 4 μm2 for AB4] depending on NC size and concentration ratios. The 5.3 nm CsPbBr3 NCs with 12.5, 13.3, 16.6, and 18.5 nm LaF3 nanodisks (γ = 0.430, 0.408, 0.337, and 0.306) form an AB(I)-type lattice. Therein, stacks of nanodisks oriented vertically to the substrate form a simple square columnar lattice with p4mm plane group symmetry (see also ref S3), while pillars of nanocubes fill the interstitial sites, as confirmed by TEM, high-angle annular dark-field scanning TEM (HAADF-STEM, wherein heavy-element containing CsPbBr3 NCs have higher contrast), and energy-dispersive X-ray spectroscopy (EDX-STEM) elemental maps (Figures 2a–e and S7a–e). With 26.5 nm nanodisks (γ = 0.221), centered rectangular AB2(I)-type binary SL with a c2mm symmetry forms, in which each void between the four nanodisk columns is occupied by two pillars of nanocubes, in agreement with EDX-STEM maps (Figures 2f–j and S7h–j). Similarly to AB2(I)-type SL comprising disks and rods, there are also two possible configurations owing to the different alignment of four nanocube sets around each nanodisk column: one with four sets aligned in the same directions and hence D2h point group symmetry and another one with a 79° angle between two sets of nanocubes, possessing C2v symmetry (Figure 2g,h). The presence of both configurations within one domain induces twin boundaries (Figure S7i) and indicates a minor difference in their formation energies.19,54 Wide-angle ED patterns of AB(I) and AB2(I) domains (Figure S7i,j) display four weak and broad arcs corresponding to (200) reflections of the CsPbBr3 nanocubes (contrary to continuous rings originating from randomly rotated LaF3 disks) which implies the vast prevalence of nanocube face–nanodisk contacts (Figure 2c,h) over nanocube edge–nanodisk contacts. The absence of (111) reflections from perovskite and LaF3 may indicate the alignment of their [011] zone axis with the out-of-plane z-direction of the SL. A higher degree of orientational coherence, evident from distinct peaks in the ED pattern, is observed in AB(I)-type SLs assembled from larger cubes and disks maintaining a similar size ratio (8.6 nm CsPbBr3 nanocubes, 26.5 nm LaF3 nanodisks, γ = 0.335, Figure S7f,g) and can be attributed to a sharper shape of these larger cubes because of their reduced softness.55

Another AB2(II)-type, centered rectangular lattice with AB2 stoichiometry and c2mm symmetry forms when combining 5.3 nm cubes with 12.5 nm disks (γ = 0.430, Figure 3). In this

Figure 3. Columnar AB2(II)-type binary SL assembled from 5.3 nm CsPbBr3 NCs and 12.5 nm LaF3 nanodisks. (a) TEM image and (b) HAADF-STEM images with outlined unit cell. (c) Structural models (showing D2h and C2v configurations), (d) TEM image of nonagonally assembled SL domain. (e) Low-magnification TEM image along with (bottom inset) small-angle ED and (f) wide-angle ED patterns measured from the area shown as an upper inset in e.
structure, the parent hexagonal close-packed disk lattice expands in one direction due to the inclusion of cubes into each interstitial site (at 0.121 < γ < 0.707, Figures 3c and S3e–i). Each disk column is surrounded by two disk and six cube pillars; each cube orients its two faces and one edge to three neighboring disks, as illustrated in Figure 3c, in agreement with the ED pattern of a single SL domain (Figure 3f). As with the AB₃(I) structure, the different relative positioning of eight adjacent NCs around one disk leads to twin boundaries between two possible configurations (Figure 3c): the dominant one with neighboring disks separated from both sides by three nearest cubes (D₃h symmetry) and the second one with four (from one side) and two (from another side) cubes between two adjacent disks and about a 140° angle (C₃v symmetry with mirror plane intersecting the disks). The presence of nine adjacent nanodisk columns belonging to Cs₃, moieties may lead to a nonagonal flower-like assembly (Figure 3d).

Increasing the concentration of 5.3 nm CsPbBr₃ NCs relative to the same nanodisks (γ = 0.430) favors the formation of an AB₄-type SL (Figures 4 and S8a–c). Such a lattice has not been reported or predicted for binary mixtures of disks or for combinations of disks with spheres or other shapes. In this structure, columns of nanodisks which form a simple hexagonal lattice are uniformly surrounded by nanocubes. The columns of cubes, however, are not resolvable, which precludes the exact determination of their vertical stacking. Following the analysis of the intensity distribution in HAADF-STEM images (Figure 4c), a plausible stacking of AB₃ layers is such that they are shifted by 60° above one another (Figure 4d). This would yield the observed intensity maxima originating from cubes in the middle of the lines connecting adjacent disks and in the center of the triangles from neighboring disks. Having all of these sites occupied by one layer of cubes is physically infeasible and would result in an AB₄-type SL with resolvable pillars of cubes.

Hexagonal AB₆-type SL with 12 distinct pillars of nanocubes, dedecagonally arranged around columns of nanodisks, was obtained with 21.0 and 28.4 nm LaF₃ NCs (γ = 0.273 and 0.207, Figures 5 and S8d–g). Continuous rings in wide-angle ED patterns (Figures 5c and S8c,f) originating from CsPbBr₃ lattice planes agree with the diversity of in-plane orientations of cubes in the AB₆-type and AB₇-type SLs, while hexagonal arcs from LaF₃ imply slight hexagonal faceting of nanodisks. Nanodisks of 9.2 nm with 5.3 nm CsPbBr₃ NCs (γ = 0.555) form a centered rectangular AB(II)-type lattice where sets of two columns of cubes fill interstitial sites formed by six columns of contacting disks (Figures 6 and S4d–g). Here, the translational order is distorted by a different alignment of nanocube sets: parallel or at an angle of about 102°.

In order to rationalize the outcome of crystallization by controlling the size ratio, we analyzed packing densities of the observed structures depending on the effective size ratio defined as γ = lᵣ/d₄ ≤ 1, where lᵣ (effective cube edge length) and d₄ (effective disk diameter) are treated within the hard-particle model. Assuming the preferable orientation of nanocubes (corroborated with ED data), the results are presented in Figure 7a and discussed in Supplementary Note 1. At magic size ratios [γ = 0.272 for AB₃(I), 0.289 for AB₆, 0.414 for AB(1), 0.545 for AB(II), 0.561 for AB₇(II)], the columns of disks still retain the close packing (direct contact), while cubes are large enough to fill the space in between tightly (without rattling). In the vicinity of these size ratios, the packing densities of the structures are close to or exceed the value for the hexagonal close-packed lattice of disk columns (η = 0.907), thus explaining their formability. The experimental lattice parameters (from the analysis of TEM data) generally agree with the calculated values, with a typical divergence of ca. 0.5
layers can be rotationally aligned in a nonparallel yet regular ill-crystalline, columnar packing, owing to its in-plane disorder and unit cell is outlined. The lattice can be considered as liquid a shows a perspective and top view of the AB(II) structure; the Figure 6. Centered rectangular columnar binary AB(II)-type SL assembled from 5.3 nm CsPbBr3 NCs and 9.2 nm LaF3 nanodisks. (a, b) TEM images at different magnifications. (c) And the inset in a shows a perspective and top view of the AB(II) structure; the nm (see Table S2 and Supplementary Note 1 for details). Our trials to obtain these columnar structures from the mixtures of nanodisks and spherical NCs have not been successful (Figure S9). The results can be explained by low packing densities (Figure 7b) of the structures comprising columns of spheres which occupy only 2/3 of the space within the pillar projection, unlike columns of cubes, rods, or disks which fully occupy the space and form columnar structures with larger disks as shown in this work and ref 19. Larger 8.6 nm CsPbBr3 nanocubes do not assemble with nanodisks into columnar SLs. Instead, extended lamellar architectures obtained from the systems of rhombic and tripodal nanoplates,18 nanoplates and nanospheres,56 nanodisks and nanorods,16 the smectic liquid crystalline lamellar structure consists of alternating one-dimensional strings of nanodisks and nanocubes stacked face-to-face and lying on the substrate. Nanodisk strings of the next layer stand above the nanocube strings of the previous layer, emulating a columnar AB(I)-type structure. Interestingly, the strings in different layers can be rotationally aligned in a nonparallel yet regular manner (see Figure S10 for the structure formed from 5.3 nm CsPbBr3 and 18.5 nm LaF3). The distance between two cube chains within the same layer (l ≈ 31.0 nm, see Figure 8b) corresponds to the sum of cube edge length and nanodisk diameter (l + dL = 30.7 nm), in agreement with the cube face−disk edge contacts in the AB(I)-type lamellar SL. The orientational coherence of nanocubes and nanodisks was further confirmed by ED, wherein the presence of (002) LaF3 reflection indicates vertical orientation of nanodisks with flat facets pointing along the string direction (Figure 8c). The topology of binary domains was visualized by scanning electron microscopy (SEM, Figure 8f) and atomic force microscopy (AFM, Figure 8g–i), revealing alternating chains of stacked disks and cubes. Extended long-range ordered binary lamellar SL domains (domain areas up to 30 μm²) of different types can be obtained from the mixture of 5.3 nm CsPbBr3 and 6.5 nm LaF3 NCs (Figure 9). Template matching and averaging of a homogeneous area of the HAADF-STEM image results in the image with an improved signal-to-noise ratio (Figure 9b). The observed images can originate from an A2B-type structure (Figure 9c) in which chains of cubes are surrounded by six chains of disks. The interdisk separation of about 2.9 nm indicates that face-to-face contacts within stacks of disks are preserved, while the top view of the model still resembles “interdigitated” columns of disks observed in TEM as a result of the out-of-plane shift of adjacent disk chains also shifted in-plane. The proposed ordering is also in agreement with the distance between neighboring cubes’ projections (l ≈ 13.0 nm); the sum of disk diameter and half of the cube face diagonal is 13.3 nm.

Combining disks and cubes of similar size gives rise to vastly different SL structural space—structures with noncolumnar but three-dimensional intermixing and periodicity. For instance, 8.6 nm CsPbBr3 nanocubes combined with 12.5 nm nanodisks yield a lattice that can be described as a NaCl type, in which clusters of three disks occupy individual lattice sites in the fcc sublattice (Figure 10a–d). The ED pattern comprises horizontally oriented disks [see (110) and (300) rings from yellow disks, Figure 10c] and two sets of vertically oriented nanodisks with faces aligned along with two in-plane SL directions [(002) and (111) reflections, red and green disks]. The orientation of cubes is locked with faces pointing...
along with three $<100>_{\text{SL}}$ directions. TEM images also suggest self-substitutional point defects,\textsuperscript{57} seen as several neighboring lattice sites occupied by stacks of disks.

Another observed and very distinct SL motif is a structure which can be described as a ReO$_3$-type SL (Figures 10e−h, S11d−f), and its appearance is favored when the disk diameter is further reduced to about equal to the edge of the cube (9 nm vs 8.6 nm; 12.5 nm disks are too large to form an ordered three-dimensional ReO$_3$-type structure, see Figures 10e,f and S11a−c). Nanocubes reside in the primitive positions of the unit cell (forming simple cubic packing), whereas disks interlayer the cubes in a face-to-face manner in all three dimensions (O sites in the ReO$_3$ lattice). ED confirms the orientations of cubes and disks within the lattice as depicted in the inset in Figure 10g. Similar packing, driven by the strong face-to-face interactions, has been reported for LaF$_3$ triangular plates sandwiched between PbTe cubes.\textsuperscript{20}

With the smallest LaF$_3$ disks (6.5 nm), the space-filling in the ReO$_3$ lattice is compromised. Additional voids that emerge in the ReO$_3$-lattice can be occupied by the additional disks (Figures 10i,j and S11g-i). Alternatively, another three-dimensional structure emerges, featuring both single disks and their pairs (Figure 10k,l). CsPbBr$_3$ cubes form columns, in which cubes are interlayered with single disks \[\text{contributing to}\]
Figure 9. Lamellar binary SL self-assembled from 5.3 nm CsPbBr3 nanocubes and 6.5 nm LaF3 nanodisks. (a) Low-magnification TEM image showing a large single SL domain. (b) HAADF-STEM image; inset is the image obtained by template-matching analysis of the corresponding HAADF-STEM image. (c) Perspective and top views of A,B-type SL structure that are in agreement with TEM images.

Figure 10. Binary SLs self-assembled from 8.6 nm CsPbBr3 nanocubes and LaF3 nanodisks. (a) SEM and (inset) low-magnification TEM images, (b) TEM image with the corresponding (inset) small-angle ED and (c) wide-angle ED patterns, (d) HAADF-STEM image of a NaCl-type SL self-assembled with 12.5 nm nanodisks; model of a NaCl-type SL unit cell assuming preferable orientation of NCs is shown as an inset. (e) TEM image of a ReO3-type monolayer binary domain comprising 12.5 nm LaF3 NCs along with (f) the corresponding wide-angle ED pattern. (g) TEM image and (h) the respective wide-angle ED pattern of a ReO3-type binary domain assembled from 9.0 nm LaF3 NCs; structural model of ReO3-type unit cell and the SL projection are depicted as an inset in g. Small-angle ED pattern is shown as an inset in h. (i) TEM image of a binary ReO3-type related SL domain assembled from 6.5 nm LaF3 nanodisks, along with (j) wide-angle and (j, inset) small-angle ED patterns. The upper inset in i is a TEM image of a thin SL domain, and the structural model of a unit cell and SL projection is depicted as a lower inset in i. (k) TEM images taken at different magnifications of a columnar binary SL domain assembled from 6.5 nm LaF3 nanodisks, along with (i) the corresponding wide-angle ED pattern. The NCs that contribute to particular wide-angle ED reflections are depicted in corresponding colors in insets (c, f, j, l).

(110) and (300) rings in wide-angle ED) in the vertical direction. Pairs of disks occupy single lattice sites, and these sites form columns as well, in which the in-plane orientation of disks alternates. The top-view onto the resulting structure reveals a checkerboard lattice formed by both NC components. Lamellar and ReO3-type SLs, employing large 8.6 nm CsPbBr3 NCs, can be assembled as large and phase-pure domains on Si3N4 grids. The use of such transparent dielectric support membranes instead of carbon films was previously found as decisive for the observation of SF from thin-film SLs.
comprising perovskite NCs. Lamellar and ReO$_3$-type SLs feature a high volume fraction of CsPbBr$_3$ NCs of 0.136 (concentration $2.1 \times 10^5$ NCs/μm$^3$) and 0.188 (concentration $2.9 \times 10^5$ NCs/μm$^3$), respectively. These values are close to the volume fraction obtained in ABO$_3$ SLs, which were shown to exhibit SF, and a factor of 2 higher than for NaCl-type SLs, which could not be driven into the SF regime. In the ReO$_3$-type SL, the occurrence of SF is manifested by the appearance of a red-shifted emission band (of about 30 meV), while in the lamellar-type SL, the SF is almost resonant to the excitonic emission (Figure 11a,c). In both cases, a continuous shortening of the radiative lifetimes down to a few tens of picoseconds has been observed by increasing the excitation fluences (Figure 11b,d). These results further suggest that the number of coherently coupled dipoles (oscillators) per volume is pivotal for the radiative lifetime speed-up, in addition to low energetic disorder, the mutual alignment among the dipoles, and a long coherence time.

As recently predicted by theoretical calculations based on non-Hermitian radiative Hamiltonians for simple cubic packing

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**Figure 11.** Optical properties of binary SLs at cryogenic temperature (6 K). (a) Emission spectrum of ReO$_3$-type SLs employing 8.6 nm CsPbBr$_3$ NCs and 9 nm LaF$_3$ disks (on Si$_3$N$_4$ membranes), featuring, at high excitation fluences, two emission bands separated by ca. 28 meV. (b) Time-resolved emission traces at low (10 μJ cm$^{-2}$), medium (40 μJ cm$^{-2}$), and high (320 μJ cm$^{-2}$) excitation fluences. Shortening of the radiative lifetime and ringing behavior, typical of SF, are observed. The emission spectrum and the time-resolved photoluminescence traces obtained for lamellar SLs (on Si$_3$N$_4$ membranes) are reported in c and d. In this case, characteristic SF emission features can be observed that are almost resonant with the NC excitonic emission. (e) Emission spectrum of lamellar SLs employing small 5.3 nm CsPbBr$_3$ NCs (on carbon membranes). (f) A red-shifted band attributed to incoherently coupled NC emission is observed with typical 80 to 100 meV splitting.
of CsPbBr₃ nanocubes, smaller NCs should yield stronger coupling and stronger superradiant emission rate enhancement and overall a more facile emergence of SF as compared to larger NCs. Thus far, our studies with such densely packed SLs of 5.3 nm NCs (unpublished) and with ABO₃-type SLs comprising these small NCs have not yielded spectroscopic features of SF. Here, we extended the search for SF to lamellar SLs and do not find evidence of SF characteristics as well. While we could not find strongly accelerated luminescence decay, A₃B₅-type lamellar SLs comprising 5.3 nm CsPbBr₃ NCs and 6.5 nm LaF₃ disks feature a strongly red-shifted band from coupled NCs, with typical shifts ranging from 80 to 100 meV (Figure 11ef). The emission of coupled NCs is still far from the expected bulk emission (ca. 2.3 eV, 535–540 nm) and strongly varies from spot to spot on the same sample because of differently sized, coupled domains (Figure 11f), thus contrasting the hypothesis that the red-shifted emission band would emerge from merged, bulk-like microcrystals. Such large photoluminescence red shifts might originate from the shorter NC-to-NC distance, which enhances the NC coupling, irrespective of whether being mediated by a near-field effect with wave function tunneling, a partial necking involving the NC corners, or dipolar coupling. The apparent absence of coherent coupling and SF in thus far studied NC assemblies of small CsPbBr₃ NCs can be attributed to the higher static coupling and stronger superradiant emission rate enhancement with wave function tunneling, a partial necking involving the shorter NC-to-NC distance, which enhances the NC coupling, etc.

EXPERIMENTAL SECTION

Synthesis of Cesium Oleate Stock Solution. Cs₂CO₃ (0.2 g, Sigma-Aldrich, 99.9%), oleic acid (0.6 mL, OA, Sigma-Aldrich, 90%, vacuum-dried at 100 °C), and 1-octadecene (7.5 mL, ODE, Sigma-Aldrich, 90%, distilled) were dissolved in toluene (16 mL, Sigma-Aldrich, 99.9%, Sigma-Aldrich, 98%) and 1-octadecene (7.5 mL, Sigma-Aldrich, 90%, distilled) was added. The mixture was cooled immediately to room temperature with an ice bath. The crude solution was centrifuged at 20 130 relative centrifugal force (rcf) for 3 min. The supernatant was discarded, and the precipitate was dispersed in hexane (0.3 mL, Sigma-Aldrich, anhydrous, 95%) with a stirrer for 3 min, and the precipitate was discarded. Then, OLA/OA ligands were exchanged by didodecyldimethylammonium bromide (DDAB) treatment. Then, 0.3 mL of hexane, toluene (0.6 mL, Sigma-Aldrich, anhydrous, 99.8%), and DDAB (0.14 mL, 0.05 M in toluene, Sigma-Aldrich, 98%) were added to the supernatant and stirred for 1 h, followed by centrifugation at 13 750 rcf and 0.6 mL of toluene. Synthesis of 5.3 nm CsPbBr₃ NCs was adopted from ref 50 followed by DDAB treatment.

Synthesis of LaF₃ Nanodisks Was Adopted from Ref 19. LaF₃ nanodisks were synthesized using a modified Stöber method with anisotropic shape. The procedure involved the preparation of 10 mL of anhydrous alcohol (ethanol 97%, distilled) and 10 mL of deionized water, which were cooled to 10 °C and rapidly stirred for 2 min. The solution was then heated to 200 °C under nitrogen at 10 °C min under nitrogen and kept at this temperature for 32 min. The reaction mixture was cooled to room temperature, and 3 mL of hexane along with ethanol (30 mL, Merck, 99.8%) was added to destabilize the colloidal solution. The NCs were precipitated by centrifugation at 2200 rcf for 5 min and washed with 20 mL of hexane, and the precipitate was discarded. Then, 0.3 mL of hexane, toluene (0.6 mL, Sigma-Aldrich, anhydrous, 99.8%), and DDAB (0.14 mL, 0.05 M in toluene, Sigma-Aldrich, 98%) were added to the supernatant and stirred for 5 min, followed by centrifugation at 13 750 rcf for 5 min, and the precipitate was discarded. Then, OLA/OA ligands were exchanged by didodecyldimethylammonium bromide (DDAB) treatment. Then, 0.3 mL of hexane, toluene (0.6 mL, Sigma-Aldrich, anhydrous, 99.8%), and DDAB (0.14 mL, 0.05 M in toluene, Sigma-Aldrich, 98%) were added to the supernatant and stirred for 5 min, followed by centrifugation at 13 750 rcf for 5 min and redispersion in 0.6 mL of toluene. Synthesis of 5.3 nm CsPbBr₃ NCs was adopted from ref 50 followed by DDAB treatment.

CONCLUSIONS

This study contributed to the exploration of the structural space of multicomponent SLs derived from nonspherical, shape-engineered NC building blocks. Specifically, co-assembly of lead halide perovskite NCs of sharp, nontruncated cubic morphology (5.3 and 8.6 nm edge length) and size-tunable LaF₃ nanodisks yielded a number of columnar and three-dimensional structures, which are not common for mixtures of spherical NCs. Most of the obtained assemblies are characterized by not only positional but also orientational disorder of constituent building blocks. Columnar and lamellar lattices are characterized by alternating pillars of disks and cubes, forming long-range ordered patterns in two dimensions. All columnar structures were observed at cube edge length-to-disk diameter ratios γ ≤ 0.555. When the sizes of disks and cubes become similar, three-dimensional lattices form, wherein cubes interact with disks through flat faces in all three directions. Besides maximizing the packing density, the observed propensity to maximize the surface of contact by aligning nanodisks to cube facets agrees well with the increased interaction potential between flat surfaces of anisotropic NCs. Explicit free energy calculations are required to rationalize the formation of the observed structures and to guide further work in this area.
Synthesis of 6.0 nm PbS NCs Was Adopted from Ref 61. Lead(II) acetate trihydrate (379 mg, Sigma-Aldrich, 99.99%) along with 6.9 mL of OA and 3.1 mL of ODE were loaded in a three-neck flask and dried under a vacuum at 105 °C for 1 h. The atmosphere was changed to nitrogen, and the solution was heated up to 145 °C. Then, the heating mantle was removed, and hexamethyldisilathiane solution (0.105 mL, Sigma-Aldrich, synthesis grade, in 5 mL ODE) was swiftly injected. After 3 min of stirring the reaction was quenched with an ice-water bath. The NCs were purified by rinsing with 10 mL of hexane and destabilization with 10 mL of ethanol. The washing was repeated twice with hexane (10 mL along with 15 μL OA) and ethanol (5 mL) as a solvent–antisolvent pair, and the NCs were dispersed in 4 mL of hexane.

Preparation of Multicomponent SLs. NC SLs were prepared using a drying-mediated self-assembly method on carbon-coated TEM grids (carbon type B, Ted Pella, Formvar protective layer removed by immersing the grid in toluene for 10 s) as substrates. A mixture of NCs in octane or anhydrous toluene had an overall particle concentration of 0.5–2.5 μM and NC number ratios (CsPbBr3 to LaF3) in the range of 0.5–20. A total of 30–35 μL of NC mixture was transferred into a tilted 2 mL glass vial with a substrate inside. The solvent was evaporated under 0.45 atm pressure at room temperature. For example, AB2(II)-type SL with high yield was obtained from the solution prepared by mixing 12.5 nm LaF3 NCs (0.6 μL, 18 mg/mL), 5.3 nm CsPbBr3 NCs (5.0 μL, 7.0 μM), and 25 μL toluene. AB2-type SL: 21.0 nm LaF3 NCs (2.2 μL, 10 mg/mL), 5.3 nm CsPbBr3 NCs (7.5 μL, 7.4 μM), and 25 μL toluene. Lamellar AB(II)-type SL: 18.5 nm LaF3 NCs (1.5 μL, 17 mg/mL), 8.6 nm CsPbBr3 NCs (2 μL, 5.1 μM), and 25 μL toluene. ReO3-type SL: 9.0 nm LaF3 NCs (0.9 μL, 9 mg/mL), 8.6 nm CsPbBr3 NCs (1.8 μL, 5.9 μM), and 25 μL toluene.

Optical Measurements. Absorption spectra of NCs dispersed in toluene were measured with a Jasco V770 spectrometer in transmission mode. Photoluminescence (PL) spectra were measured in a 90° configuration using Horiba Fluoromax-4 equipped with a photomultiplier tube and a monochromatized 150 W xenon lamp as an excitation source. For PL and time-resolved PL measurements, the collected light was dispersed via a 300-lines-per-millimeter grating inside a 0.5-m-long monochromator and detected by an EMCCD camera.

Electron Microscopy Characterization. Transmission electron microscopy (TEM) and high-angle annular dark-field scanning TEM (HAADF-STEM) images as well as wide- and small-angle electron diffraction (ED) patterns were collected with the use of JEOL JEM2200FS microscope operating at a 200 kV accelerating voltage. Energy-dispersive X-ray (EDX-STEM) maps and HAADF-STEM were recorded using an FEI Titan Themis microscope operated at 300 kV. SEM images were obtained on a FEI Helios 660 operated at 3 kV using an immersion mode.

Atomic Force Microscopy. ScanAsyst-AirR probes were used to analyze the topography of the SLs on the Bruker Icon 3 Atomic Force Microscope.

ASSOCIATED CONTENT

*Supporting Information* The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.1c06047.

Packing analysis of columnar SLs comprising disks with cubes and disks with spheres; optical characterization of CsPbBr3 NCs and TEM images of NC building blocks used for self-assembly; TEM characterization of columnar, lamellar, three-dimensional SLs; and results on the assembly of LaF3 nanodisks with spherical PbS NCs (PDF)

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Notes

The authors declare no competing financial interest.

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