

Halide Perovskite–Lead Chalcogenide Nanocrystal Heterostructures

Muhammad Imran,[▽] Lucheng Peng,[▽] Andrea Pianetti, Valerio Pinchetti, Julien Ramade, Juliette Zito, Francesco Di Stasio, Joka Buha, Stefano Toso, Jun Song,^{*} Ivan Infante,^{*} Sara Bals,^{*} Sergio Brovelli,^{*} and Liberato Manna^{*}

Cite This: *J. Am. Chem. Soc.* 2021, 143, 1435–1446

Read Online

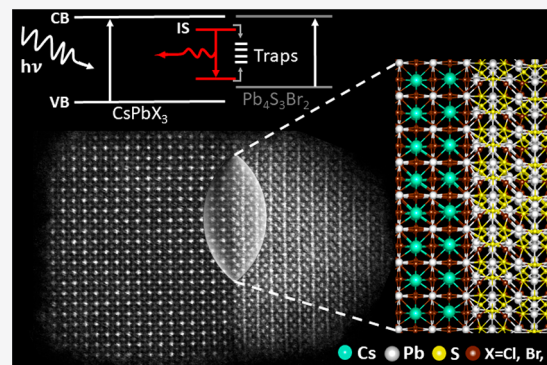
ACCESS |

Metrics & More

Article Recommendations

Supporting Information

ABSTRACT: We report the synthesis of colloidal $\text{CsPbX}_3\text{--Pb}_4\text{S}_3\text{Br}_2$ ($X = \text{Cl, Br, I}$) nanocrystal heterostructures, providing an example of a sharp and atomically resolved epitaxial interface between a metal halide perovskite and a non-perovskite lattice. The $\text{CsPbBr}_3\text{--Pb}_4\text{S}_3\text{Br}_2$ nanocrystals are prepared by a two-step direct synthesis using preformed subnanometer CsPbBr_3 clusters. Density functional theory calculations indicate the creation of a quasi-type II alignment at the heterointerface as well as the formation of localized trap states, promoting ultrafast separation of photogenerated excitons and carrier trapping, as confirmed by spectroscopic experiments. Postsynthesis reaction with either Cl^- or I^- ions delivers the corresponding $\text{CsPbCl}_3\text{--Pb}_4\text{S}_3\text{Br}_2$ and $\text{CsPbI}_3\text{--Pb}_4\text{S}_3\text{Br}_2$ heterostructures, thus enabling anion exchange only in the perovskite domain. An increased structural rigidity is conferred to the perovskite lattice when it is interfaced with the chalcogenide lattice. This is attested by the improved stability of the metastable γ phase (or “black” phase) of CsPbI_3 in the $\text{CsPbI}_3\text{--Pb}_4\text{S}_3\text{Br}_2$ heterostructure.



INTRODUCTION

Metal halide perovskites and especially CsPbX_3 ($X = \text{Cl, Br, I}$) in the form of colloidal nanocrystals (NCs) have witnessed a rapid development in the past few years due to their ease of processing, tunable band gaps, narrow emission line width, and defect-tolerant nature, all features that make them appealing for optoelectronic devices.^{1–11} Also, various groups have tackled the synthesis of NC heterostructures in which the perovskite domain is bound to a domain of another material.^{12,13} Examples include metal–perovskite (Au--CsPbBr_3),¹⁴ metal chalcogenide–perovskite (PbS--CsPbX_3 ,¹⁵ ZnS--CsPbX_3 ,^{16,17} and PbSe--CsPbX_3),¹⁸ metal dichalcogenide–perovskite ($\text{Cs}_2\text{SnI}_6/\text{SnS}_2$),¹⁹ CsPbX_3 /metal oxide Janus ($\text{TiO}_2\text{--CsPbBr}_3$,²⁰ $\text{CsPbX}_3/\text{SiO}_2$,²¹ $\text{CsPbX}_3/\text{ZrO}_2$,²² and $\text{CsPbBr}_3/\text{TiO}_2$),²³ CsBr--CsPbBr_3 ,²⁴ and $\text{Cs}_4\text{PbBr}_6\text{--CsPbBr}_3$ NCs.²⁵ The latter case is a particularly revealing example of an epitaxial heterointerface (recently disclosed by our group), in which it is possible to observe a continuity of the sublattice of Cs^+ cations across the interface between the two domains, a common theme underlying the various heterostructures involving metal halide NCs.²⁶ Many of these nano-heterostructures may find applications in various fields, such as solar cells, LEDs, and photocatalysis.^{23,27,28}

In the present work, we report a new type of heterostructure, in which a halide perovskite NC shares an epitaxial interface with a lead chalcogenide NC. Colloidal NCs of lead chalcogenides have been recently synthesized in our group:²⁹ they are characterized by an indirect band gap, are nonemissive

at room temperature, and are stable for months under ambient conditions.²⁹ The synthesis that we discuss in this work initially delivers $\text{CsPbBr}_3\text{--Pb}_4\text{S}_3\text{Br}_2$ NCs: from them, we could further prepare, by postsynthesis anion exchange, the corresponding heterostructures in which the perovskite domain is either CsPbCl_3 or CsPbI_3 . In other words, anion exchange only affects the perovskite region and not the chalcogenide one, which remains $\text{Pb}_4\text{S}_3\text{Br}_2$. In all these heterostructures, the two domains are separated by a sharp interface. Epitaxial relationships between the two domains are possible due to a favorable matching of the respective Pb sublattices in the two structures, when they are arranged in some specific mutual orientations.

In all the systems studied, density functional theory (DFT) calculations highlight that the interface joining CsPbX_3 and $\text{Pb}_4\text{S}_3\text{Br}_2$ leads to a significant change in the electronic structures of the individual components. In the heterostructure, the edge of the valence band is localized almost completely in the chalcogenide domain, whereas the edge of the conduction band is distributed almost evenly across the

Received: October 17, 2020

Published: January 13, 2021



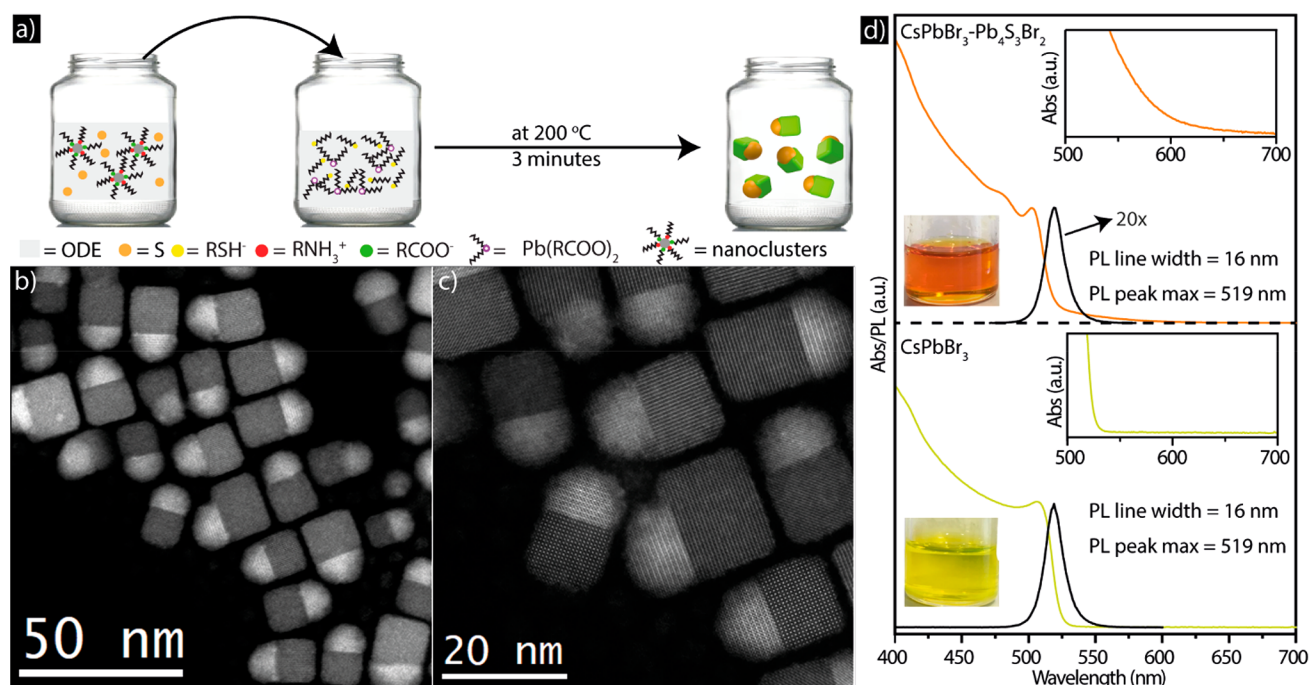


Figure 1. (a) Sketch describing the synthesis of the CsPbBr₃-Pb₄S₃Br₂ heterostructures. STEM images of (b, c) CsPbBr₃-Pb₄S₃Br₂ NCs at two different magnifications. (d) Absorbance and PL spectra of dispersions in toluene of the CsPbBr₃-Pb₄S₃Br₂ heterostructures and the CsPbBr₃ NCs, along with the photographs of the corresponding colloidal dispersions under room light. The insets are magnified absorption features in the 500–700 nm range for both samples.

heterostructure. This indicates that the overall system is not just the sum of its components but a potentially valuable platform for wave function engineering strategies that are not typically accessible with halide perovskite materials due to compositional alloying promoted by ion migration. The resulting quasi-type II-like energy level alignment at the heterojunction promotes the rapid splitting of photogenerated excitons with the photoexcited hole localized in the chalcogenide domain and the electron partially delocalized in the entire nanostructure. This, together with the rapid carrier trapping at interface localized states, as also predicted by DFT, leads to a nearly complete suppression of the photoluminescence (PL) with respect to the pure NCs. Nonetheless, low-temperature spectroscopic measurements reveal a red-shifted PL (compared to that from pure Pb₄S₃Br₂ NCs), which is likely due to the optical recombination of interface trapped carriers, whose efficiency is substantially affected by non-radiative channels. Notably, the presence of the interface confers higher structural rigidity to the perovskite lattice. This is evident in the CsPbI₃-Pb₄S₃Br₂ heterostructure, in which the CsPbI₃ domain over time does not transform to the thermodynamically stable δ “yellow” phase, as is well established for CsPbI₃ NCs, but remains in the metastable “black” γ phase.

RESULTS AND DISCUSSION

Synthesis. The synthesis of the heterostructures started with the preparation and purification of CsPbBr₃ nanoclusters, following a previously reported method.³⁰ These clusters, of subnanometer size, have an exciton absorption at 402 nm and are nonemissive at room temperature (Figure S1). They have been recently prepared and used as convenient “monomers” for the growth of perovskite NCs, as they enable a more precise control over size and shape than by using a standard

synthesis approach, including the possibility to access branched geometries.³¹ In the preparation of these clusters, both oleic acid and oleylamine were used. It is therefore likely that their surface is coated by both oleate and oleylammonium ions. In a typical synthesis, these nanoclusters were mixed with a solution of elemental sulfur dissolved in degassed octadecene (ODE), and the resulting mixture was injected in a vial containing a solution of dodecanethiol and lead oleate in degassed ODE, heated at 200 °C (Figure 1a). The reaction was allowed to proceed for 3 min and was subsequently quenched by immersing the vial in an ice water bath. The NCs were collected by centrifugation and were then redispersed in toluene for further use (see the Experimental Section for further details).

High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) analysis evidenced the presence of heterostructures formed by a cubic shaped domain bound to a more rounded and higher contrast domain with an edge length of 20.3 ± 2.2 nm, most often along one face of the cube (Figure 1b,c; see also the TEM images of Figures S2 and S3). A statistical analysis done on ~1300 NCs of Figure S2 indicated that only around 80 NCs (i.e., around 6% of the total) were cubes, apparently not carrying an additional domain attached to them. On the other hand, contrast variations in most of these cubes suggest that most of them were heterostructures as well, but they were simply sitting on the substrate in a vertical (face up) or lateral projection (see the examples in Figures S4 and S5). Overall, we can state that the fraction of isolated CsPbBr₃ NCs in this sample was definitely below 6%. If instead the initial CsPbBr₃ nanoclusters were heated under the same conditions as in the synthesis that we have just described for the heterostructures of Figure 1b,c, but in ODE alone (that is, with no elemental sulfur, dodecanethiol, and lead oleate), the product was represented

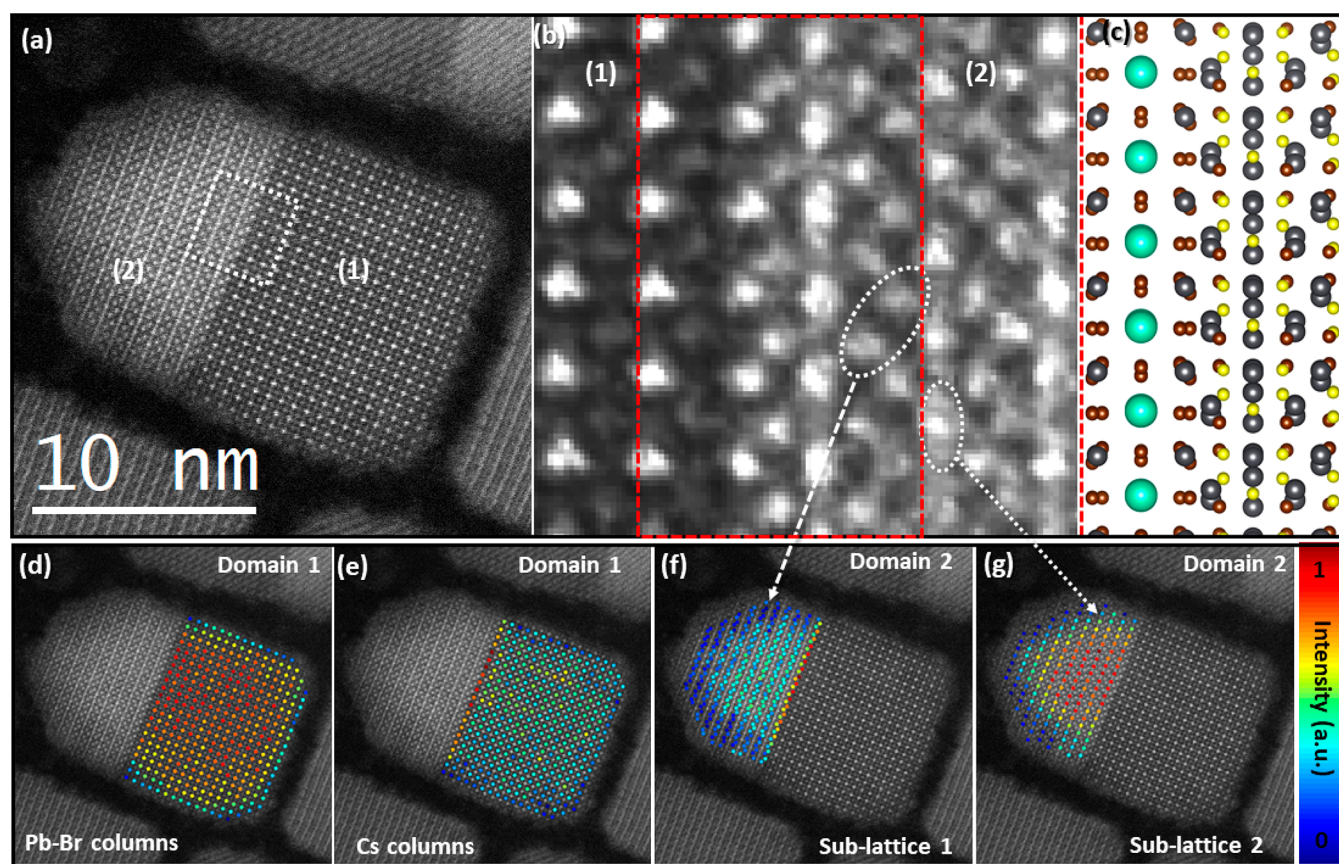


Figure 2. Structural analysis of a single CsPbBr_3 – $\text{Pb}_4\text{S}_3\text{Br}_2$ heterostructure. (a) High-resolution HAADF-STEM image of a single heterostructure composed by a CsPbBr_3 (1) and a $\text{Pb}_4\text{S}_3\text{Br}_2$ (2) domains. (b) Magnified image of the region highlighted in white in (a), depicting the interface between CsPbBr_3 and $\text{Pb}_4\text{S}_3\text{Br}_2$ domains. The region highlighted in red represent a $\text{Pb}_4\text{S}_3\text{Br}_2$ pattern oriented along the $[101]$ zone axis, as confirmed in (c) showing the CsPbBr_3 and $\text{Pb}_4\text{S}_3\text{Br}_2$ structural model along this orientation. (d) Column intensity map of Pb–Br columns of the perovskite phase. (e) Column intensity map of Cs columns of the perovskite phase. (f) and (g) represent the intensity map of Pb columns belonging to the $\text{Pb}_4\text{S}_3\text{Br}_2$ domain.

by nearly monodisperse CsPbBr_3 cube-shaped NCs with an edge length of 15.9 ± 1.6 nm (Figure S6).

Optical absorption and photoluminescence (PL) spectra of colloidal dispersions of the cube-shaped CsPbBr_3 NCs and of the heterostructures are reported in Figure 1d. Compared to the CsPbBr_3 NCs, the heterostructures exhibited an additional absorption tail at long wavelengths, which became more prominent for wavelengths shorter than 550 nm. The two insets of Figure 1d are magnified views of the absorption features in the range 500–700 nm for both samples. For the heterostructure, this feature matched closely the optical absorption spectrum of our recently synthesized $\text{Pb}_4\text{Br}_3\text{S}_2$ NCs.²⁹ The CsPbBr_3 NCs evidenced the typical narrow PL peak (full-width-half-maximum, FWHM, of 16–17 nm) at 519 nm. The formation of the heterostructure led to a substantial suppression of the CsPbBr_3 NC emission, as discussed in detail later. The much weaker emission from the heterostructures sample ($\sim 5\%$ of the CsPbBr_3 NC PL intensity) can be ascribed to the few CsPbBr_3 NCs present in solution that are not bound to a $\text{Pb}_4\text{S}_3\text{Br}_2$ domain, in quantitative agreement with the statistical analysis of the wide-field TEM images of Figure S2 (indicating less than $\sim 6\%$ residual CsPbBr_3 cubes).

The X-ray powder diffraction (XRPD) pattern of the cubes (Figure S7) contained diffraction features that are ascribable to the orthorhombic phase of CsPbBr_3 . The pattern of the heterostructures had the same features as that of the CsPbBr_3

cubes, with additional peaks appearing around 25° and 36° (2θ). To identify the origin of these extra peaks, we recorded XRPD patterns of $\text{Pb}_4\text{Br}_3\text{S}_2$ NC and of mixtures of CsPbBr_3 and $\text{Pb}_4\text{Br}_3\text{S}_2$ NC powders (see Figure S8 for an overall comparison of the XRPD patterns of the various samples). A comparison of these various patterns confirmed that the XRPD pattern of the heterostructures had contribution from both phases, albeit with strong predominance of the signal from the perovskite domain.

We tested the influence of reaction temperature, time, relative concentrations of dodecanethiol and of lead oleate, and addition of oleylammonium bromide (OLAM-Br) on the formation of the heterostructures, while keeping the concentration of CsPbBr_3 clusters constant. Details on all these tests are reported in the Supporting Information (Figures S9–S15). In brief, the optimal temperature window for growing the heterostructures was around 200°C . At sensibly lower temperatures (150°C or below) no heterostructures were formed, and at higher temperatures (230°C) the size and shape distributions worsened considerably (Figure S9). We then tested the influence of dodecanethiol in syntheses performed at the optimal temperature of 200°C . In the absence of dodecanethiol (Figure S10a), no CsPbBr_3 – $\text{Pb}_4\text{S}_3\text{Br}_2$ heterostructures were formed, and instead we obtained large CsPbBr_3 NCs, each carrying a tiny, low contrast domain attached to it. At increasing amounts of dodecanethiol

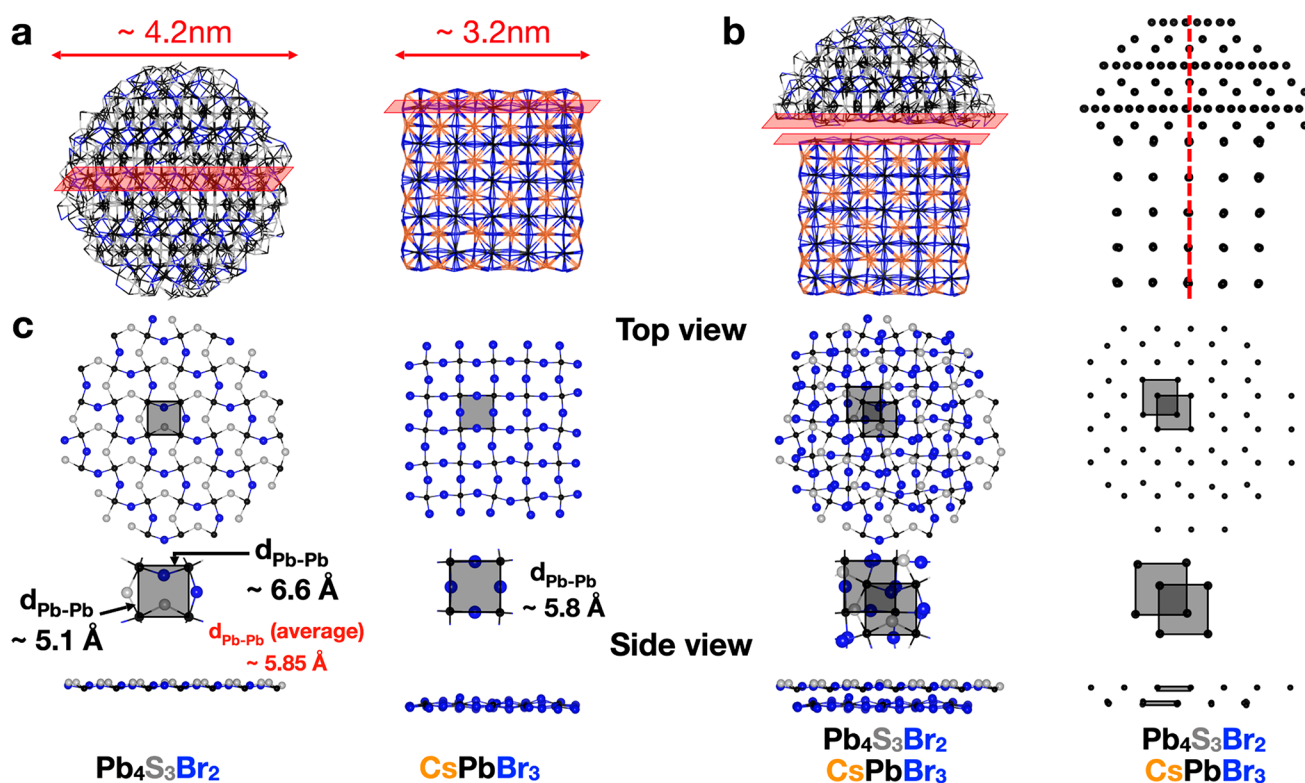


Figure 3. (a) Sticks representation of (left) a spherical $\sim 4.2\text{ nm}$ diameter $\text{Pb}_{548}\text{S}_{423}\text{Br}_{250}$ NC model and (right) a cubic $\sim 3.2\text{ nm}$ sided $\text{Cs}_{200}\text{Pb}_{125}\text{Br}_{450}$ NC model optimized at the DFT/PBE level of theory. (b) Preparation of the heterostructure NC model by (left) stacking of the $\text{Pb}_4\text{S}_3\text{Br}_2$ and CsPbBr_3 moieties and (right) alignment of their Pb ions along the [010] axis. (c) Top and side view of the interface layers of both the $\text{Pb}_4\text{S}_3\text{Br}_2$ and CsPbBr_3 nanocrystals. A cell of four Pb ions was taken to demonstrate the smooth alignment at the interface. The radial distribution function for the Pb–Pb pairs is sketched in Figure S24 and indicates that the Pb–Pb bond distances are similar in both domains.

added, past a range of concentrations that enabled the ideal growth of heterostructures (Figure S10b,c), the latter were still formed, but their size and shape distributions worsened considerably; additionally, PbS NCs appeared as a byproduct (Figure S10d). A controlled amount of lead oleate was also critical to prepare well-defined heterostructures. With excessive addition of lead oleate, isolated $\text{Pb}_4\text{S}_3\text{Br}_2$ particles were found as a byproduct (Figure S11).

To understand the growth mechanism, syntheses were run at varying reaction times, while all other reaction conditions were kept constant (including the synthesis temperature, always set at $200\text{ }^\circ\text{C}$). The TEM images of the sample obtained after 30 s of reaction time evidenced nearly cube-shaped NCs containing higher contrast domains (presumably $\text{Pb}_4\text{S}_3\text{Br}_2$) at their edges (Figure S12a). These higher contrast domains further grew in sizes at longer reaction times, while the perovskite domain remained nearly the same (Figure S12a–e). This trend was confirmed by optical absorption spectra of the corresponding samples (dominated by the features from CsPbBr_3), which remained almost unchanged over the course of the reaction (Figure S13). By crossing the TEM images and optical absorption data of various samples prepared with different reaction times, we conclude that the perovskite domains formed first, followed by the growth of $\text{Pb}_4\text{S}_3\text{Br}_2$. The optimal reaction time was around 3 min.

The CsPbBr_3 clusters that were used as “precursors” for the perovskite domain have a large surface-to-volume ratio; hence, their dissolution during the synthesis of the heterostructures should release a certain amount of oleylammonium ions. This is, however, negligible compared to the amount of oleate that

was added (as lead oleate) together with the CsPbBr_3 clusters. To test the influence of higher concentrations of oleylammonium ions, we also attempted the synthesis of CsPbBr_3 – $\text{Pb}_4\text{S}_3\text{Br}_2$ heterostructures under the same conditions as in the synthesis of Figure 1b,c and Figures S2–S5, but with the extra addition of 10^{-2} mmol of OLAM-Br. These attempts failed at producing heterostructures. TEM analysis revealed that the product was mainly represented by CsPbBr_3 nanoplatelets/lamellar structures (Figure S14).

As a final test, we also attempted to synthesize CsPbBr_3 – $\text{Pb}_4\text{S}_3\text{Br}_2$ heterostructures by following conventional hot injection-based syntheses used for the preparation of halide perovskite NC, that is, not employing preformed CsPbBr_3 nanoclusters,^{5,32,33} but none of them was successful (Figure S15). Therefore, we inferred that a controlled growth of the heterostructures was possible only through the use of CsPbBr_3 nanoclusters, most likely as they prevent a massive homogeneous nucleation of perovskite NCs, separately from the chalcogenide NCs.

Characterization by Electron Microscopy. Detailed analyses were performed on single heterostructures through high-resolution, high-angle annular dark field scanning TEM (HAADF-STEM) imaging. Figure 2a represents a high-resolution HAADF-STEM image of a typical CsPbBr_3 – $\text{Pb}_4\text{S}_3\text{Br}_2$ heterostructure. Both domains were single crystalline. The chalcogenide domain is facing the [101] zone axis, as demonstrated by its Fourier transform (FT, Figure S16), and is attached to one of the facets of the CsPbBr_3 cube-shaped NC. The orthorhombic perovskite domain FT can be matched with either the [101] or [010] zone axes, as those are almost

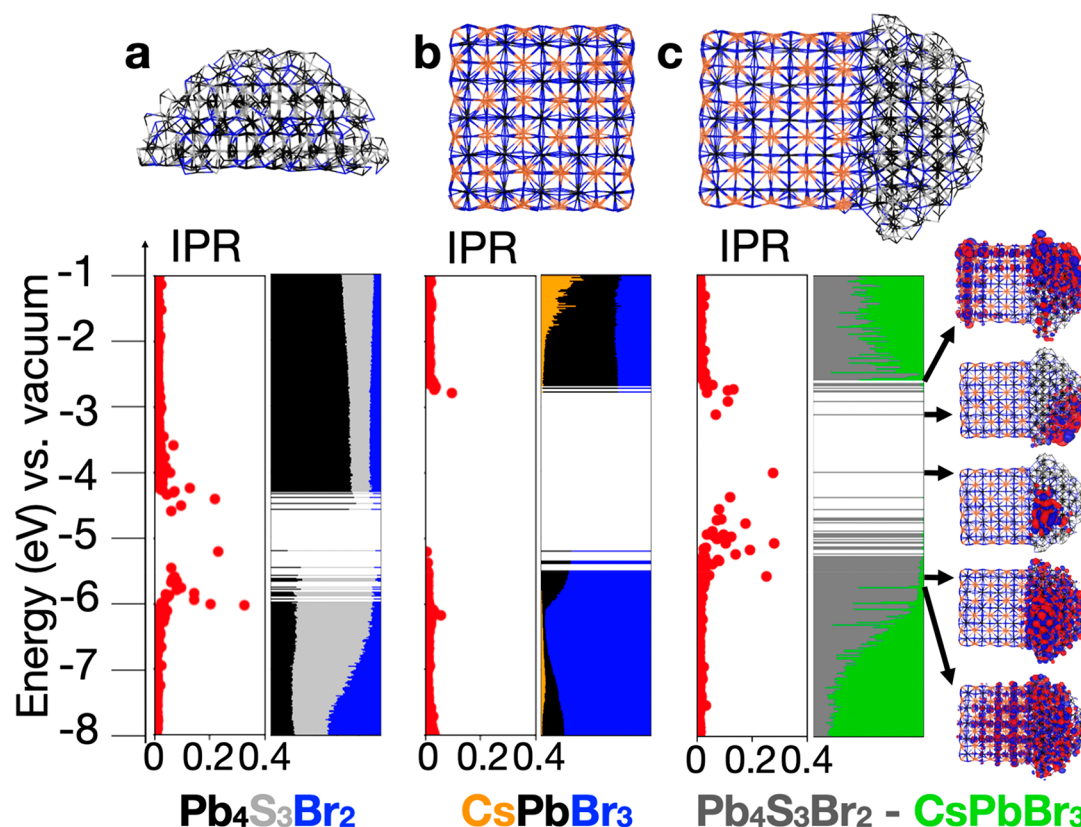


Figure 4. Electronic structure and IPR plots of the (a) $\text{Pb}_4\text{S}_3\text{Br}_2$ half-sphere model, (b) CsPbBr_3 cube model, and (c) heterostructure model computed at the DFT/PBE level of theory. The color code indicates the contribution of an atom/moieties type to each molecular orbitals. On the right we plotted both delocalized and localized molecular orbitals at the band edges.

indistinguishable because of the small deviation from the ideal cubic symmetry. The same is true for (101) and (010) planes, which are the planes exposed by the facets of NCs. From a close scrutiny of several heterostructures, we found that the lead chalcogenide domains can grow most commonly on the (101) facets and less commonly on the (010) and (001) facets of the orthorhombic CsPbBr_3 perovskite NC, with a mutual orientation of the two domains such that there is little or nearly no mismatch between the joining planes (Figures S17–S19). It is also interesting that although the CsPbBr_3 NCs present several sets of equivalent facets, basically all the heterostructures that we could observe were made of only one domain of chalcogenide, and not of multiple domains, attached to a CsPbBr_3 NC. This behavior is most likely due to a slow nucleation kinetics of the chalcogenide on the surface of the perovskite NC. Our interpretation is that as soon as a nucleus of chalcogenide is formed on one facet of a CsPbBr_3 NC, the energetic barrier for its further accretion is much lower than the energetic barrier for the formation of other chalcogenide nuclei on the other facets.

We then quantitatively analyzed the intensities of the individual atomic columns in a single heterostructure by using STAT-STEM.³⁴ In an HAADF-STEM image, the intensity of an atomic column depends on the material thickness (amount of atoms composing the column) and its atomic composition (Z number). Panels d and e of Figure 2 show the intensities of the Pb–Br and Cs columns of the perovskite domain, while panels f and g of Figure 2 represent the Pb column intensities of sublattices 1 and 2 from the $\text{Pb}_4\text{S}_3\text{Br}_2$ domain, respectively. The relatively homogeneous distribution confirmed the single-

phase character of both the perovskite and the lead chalcogenide domains. Notably, the atomic columns located at the interface presented higher intensities, especially the Cs columns and the columns belonging to the sublattice 2 of the $\text{Pb}_4\text{S}_3\text{Br}_2$ domain (Figure 2e,f). The intensity of the atomic columns located at the boundary of two materials can be affected by local strain that can change the alignment of the atoms, which in turn modifies the channeling effect that is at the base of the HAADF-STEM signal.³⁵ In this specific case, such rearrangement appears to bring the atoms close to a perfect alignment in the specific zone axis along which the heterostructure is being imaged.

The compositional analysis by energy dispersive X-ray spectroscopy (STEM-EDX) of individual heterostructures attested a uniform distribution of the corresponding elements in the respective domains and returned elemental ratios of Cs:Pb:Br equal to 1.05:1:2.7 for the perovskite domain and of Pb:S:Br equal to 4:2.9:2.6 for the lead chalcogenide domain (Figure S20). These values are in line with the respective stoichiometries of the two materials (i.e., $\text{Pb}_4\text{S}_3\text{Br}_2$ and CsPbBr_3). This was further supported by an EDX-line scan across a single heterostructure (Figure S21) which evidenced that the Cs signal was localized in the perovskite domain and the S signal was mainly present in the $\text{Pb}_4\text{S}_3\text{Br}_2$ domain.

A close look at the epitaxial relationship between the two domains, as sketched in Figure 2b, reveals that the lead and bromide ions in the perovskite are aligned with those of the chalcogenide. This is made clearer in Figure 3, showing how the interface monolayer of $\text{Pb}_4\text{S}_3\text{Br}_2$ presents an atomic arrangement similar to the perovskite orthorhombic lattice if

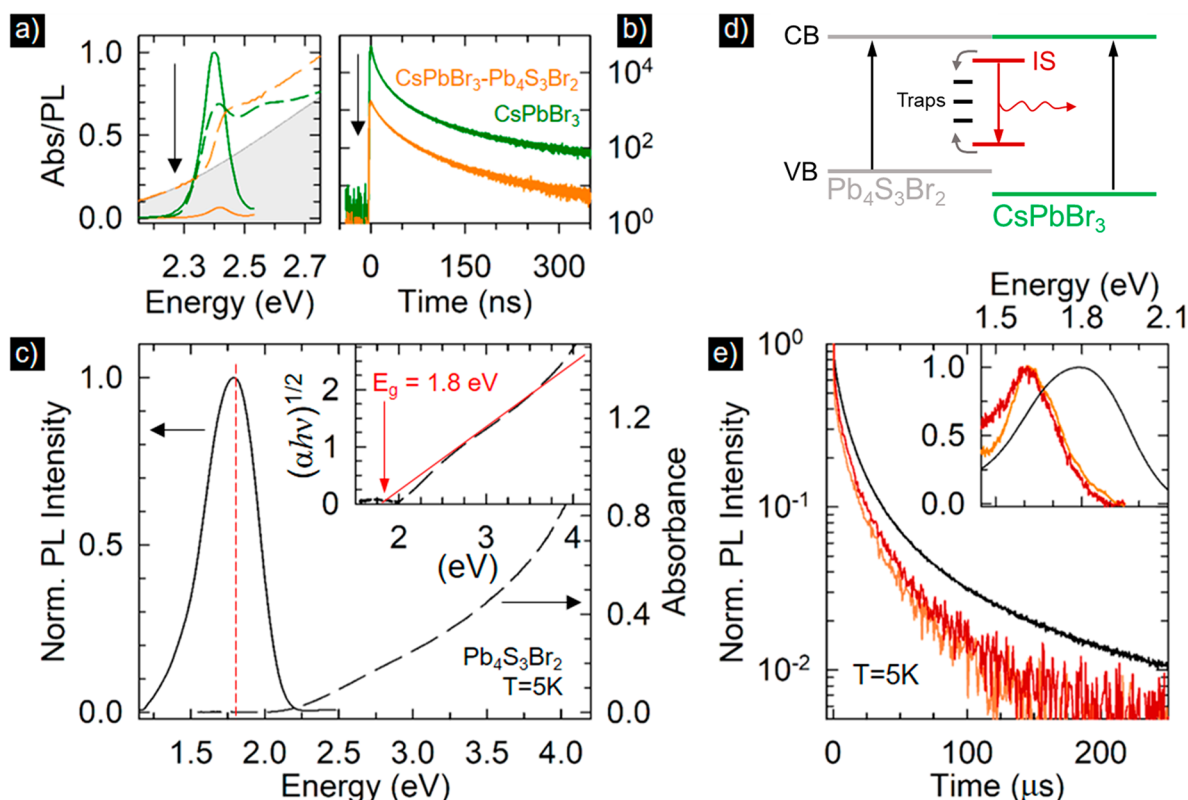


Figure 5. (a) Optical absorption PL spectra and (b) time-resolved PL decay curves of colloidal dispersions of CsPbBr₃ NCs and CsPbBr₃–Pb₄S₃Br₂ heterostructures (normalized to the intensity of bare CsPbBr₃ NCs). Green lines refer to CsPbBr₃ NCs, and orange lines refer to the heterostructure. The arrow highlights the quenching of the PL intensity in the heterostructure. (c) Optical absorption and PL spectra of Pb₄S₃Br₂ NCs (excitation at 3.5 eV). Inset: respective Tauc plot showing the linear dependence (red line) of $(\alpha h\nu)^{1/2}$ with the photon energy typical for indirect band gap transitions. The red arrow indicates the band gap energy that corresponds to the PL peak position. (d) Schematic depiction of the energy levels of the CsPbBr₃–Pb₄S₃Br₂ heterostructure highlighting the radiative recombination (red arrow) in interface localized states (IS) following excitation of either the perovskite or chalcobromide domains and the respective quenching by traps. (e) Time decay curves of the Pb₄S₃Br₂ PL from CsPbBr₃–Pb₄S₃Br₂ NCs at $T = 5$ K upon 2.33 and 3.5 eV excitation energy (orange and red lines, respectively) compared to the PL decay curve of bare Pb₄S₃Br₂ NCs (black line). Inset: PL spectra of CsPbBr₃–Pb₄S₃Br₂ NCs at $T = 5$ K upon 2.33 and 3.5 eV excitation energy (orange and red lines, respectively) compared to the PL spectrum of Pb₄S₃Br₂ NCs at the same temperature.

one focuses on the Pb atoms only. Figure S22 contains additional sketches that help to better visualize the epitaxial connection at the interface. The sketches show the connectivity of the cationic substructure at the interface in three different orientations. In the same figure, we also highlight the shared plane of lead atoms that is found almost unaltered within both the chalcobromide and the perovskite structures, pointing to an epitaxial interface. A model of the heterojunction in .xyz format is also provided as Supporting Information.

DFT Modeling. The models discussed above give us important hints on how to build a model of the heterostructure for our DFT calculations. For the CsPbX₃ perovskite cube we have simply taken one of our “trap-free” models of about 3.2 nm in size published earlier,²⁹ whereas for the lead chalcobromide we first cleaved the bulk into a sphere of 4.2 nm diameter with a charge balanced stoichiometry (Figure 3a), and then we relaxed the structure and computed its density of states. This shows a large number of surface defects, as evidenced by the inverse participation ratio (IPR) analysis (Figure 4a). IPR with values deviating significantly from zero provide a fingerprint for the presence of localized states in the electronic structure, which in the case of chalcobromide are mostly present at the conduction band (CB) and valence band (VB) edges. For comparison, the IPR analysis for the

perovskite systems exhibits only delocalized states, as expected (Figure 4b). IPR values can also be used to filter trap states in the electronic structure and deduce the actual intake of the CB and VB edges, here extrapolated (with IPR below 0.03) at about 1.6–1.7 eV (Figure 4a), in good agreement with the experimental value for the emission of 1.6–1.8 eV for Pb₄S₃Br₂ (see the discussion on the optical properties).

Note that as in the case of lead halide perovskites our DFT approach provides the correct band gap for the wrong reason: the lack of spin–orbit coupling in our calculations, which lowers the band gap but is computationally prohibitive for the heterostructure size, is compensated by the typical band gap underestimation for pure exchange–correlation functionals like the Perdew–Burke–Ernzerhof (PBE) employed here. The choice of IPR below 0.03 is arbitrary; however, it does indicate that trap states are present in various kinds, from very localized to less localized ones. After we assessed this part, we cut half of the chalcobromide sphere, relaxed it, and arranged it on top of the perovskite domain, following the alignment proposed above and sketched in Figure 3b,c. The relaxation of the heterostructure occurred smoothly, an indication that the structural alignment between the two domains was indeed the correct one.

We then computed the electronic structure and the density of states followed by the IPR analysis. As expected, by looking

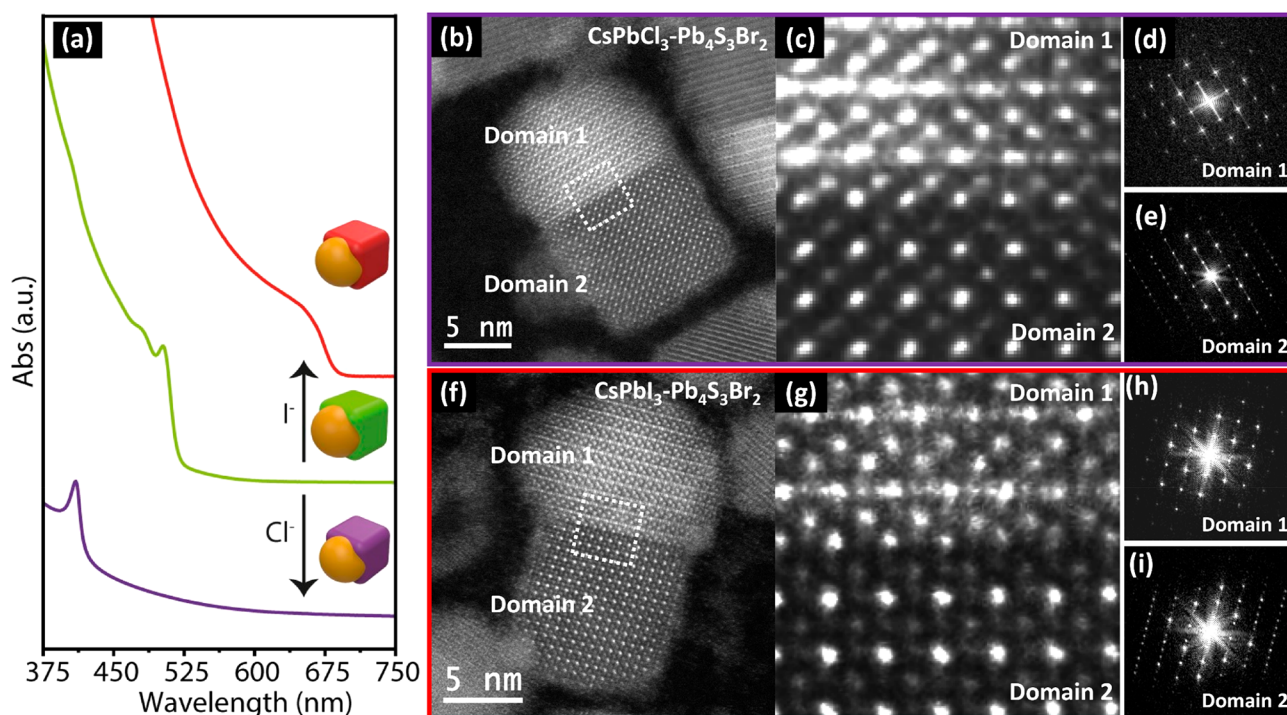


Figure 6. (a) Optical absorption spectra of pristine $\text{CsPbBr}_3\text{-Pb}_4\text{S}_3\text{Br}_2$ NCs and of the same NCs after halide exchange with either Cl^- or I^- recorded in colloidal dispersions. (b) HRSTEM image of $\text{CsPbCl}_3\text{-Pb}_4\text{S}_3\text{Br}_2$ NC. (c) Magnified image of the region highlighted in white dotted line. (d) and (e) show the FT of the regions labeled as domain 1 and domain 2 in (b), respectively. (f) HRSTEM image of a $\text{CsPbI}_3\text{-Pb}_4\text{S}_3\text{Br}_2$ NC. (g) Magnified image of the region highlighted in white dotted lines. (h) and (i) show the FTs of the domains labeled as domain 1 and domain 2 of panels f and g. The CsPbCl_3 and CsPbI_3 domains were in the $[100]$ and $[101]$ orientation, while the $\text{Pb}_4\text{S}_3\text{Br}_2$ domain was in the $[101]$ orientation, respectively, with respect to the viewing direction.

at the electronic structure of the domains computed separately, the CB edge of the heterostructure is apparently dominated by the $\text{Pb}_4\text{S}_3\text{Br}_2$ domain. Notably, although the band edge is fully defined by trap states, as expressed by the IPR values, the first delocalized states in the CB are present in both the chalcogenide and perovskite domains. To make this clear, we plotted the molecular orbitals for both the localized states and the first of the delocalized one (Figure 4c). Conversely, in the valence band region, the orbital contribution is different. The first states at the VB edge are still mostly localized in the chalcogenide domain, pointing toward the presence of an energy offset with the perovskite domain. The first delocalized molecular orbitals deeper in the VB appear intermixed, with some present only on the chalcogenide domain and others delocalized on both domains (Figure 4c). States even deeper exhibit mostly mixing between the two domains. Notably, there are no states at the VB edge region that belong solely to the perovskite domain. Overall, following the core-shell nomenclature,³⁶ these data suggest that the energy level alignment of the heterostructure is quasi-type II, with the VB localized on the chalcogenide domain and the CB mixed between the two domains.

Optical Properties. On the basis of theoretical insights provided by DFT, we proceeded to investigate the excitonic processes of the $\text{CsPbBr}_3\text{-Pb}_4\text{S}_3\text{Br}_2$ heterostructures. To this end, we prepared pure CsPbBr_3 and $\text{Pb}_4\text{S}_3\text{Br}_2$ NCs of nearly the same size as the respective domains in the heterostructure (namely, CsPbBr_3 NCs having an edge length of 14 nm and $\text{Pb}_4\text{S}_3\text{Br}_2$ NCs with a diameter of 8.5 nm) and performed side-by-side optical spectroscopy experiments. The optical spectra for CsPbBr_3 NCs and related heterostructures are shown in

Figure 5a. As anticipated, the pure CsPbBr_3 NCs featured the typical sharp absorption edge and a nearly resonant PL peak with $\text{PLQY} = 67 \pm 7\%$. The PL dynamic followed a multiexponential decay with effective lifetime of ~ 10 ns (Figure 5b). The spectral properties of the $\text{Pb}_4\text{S}_3\text{Br}_2$ NCs are reported in Figure 5c and show a nearly featureless absorption spectrum typical of an indirect band gap material,²⁹ as confirmed by the Tauc plot in the inset of Figure 5c, showing a linear dependence of the absorption profile on the square root of $(\alpha h\nu)$, where α is the absorption coefficient and $h\nu$ the energy of the incident photons. The fitting yields a band gap energy of ~ 1.8 eV, in good agreement with the band gap energy estimated by DFT (Figure 4a). The broad PL spectrum was also peaked at ~ 1.8 eV, thus indicating that the radiative recombination is due to an indirect transition coupling the band edge states, possibly promoted by partial relaxation of momentum conservation in nanoscale systems. The PLQY at room temperature was $< 1\%$, likely due to nonradiative quenching by carrier trapping in surface defects. Cooling the $\text{Pb}_4\text{S}_3\text{Br}_2$ NCs to cryogenic temperatures strongly suppressed such nonradiative losses, resulting in a substantial enhancement of the PL intensity at $T = 5$ K, accompanied by a concomitant lengthening of the PL lifetime that increased from 70 ns to 4.1 μs (Figure S25). This behavior suggests a recombination from an indirect transition.

Combining the $\text{Pb}_4\text{S}_3\text{Br}_2$ and CsPbBr_3 domains in the heterostructure strongly quenches the emission from both domains. The quenching of the PL from CsPbBr_3 in the heterostructure is consistent with an ultrafast hole transfer from the perovskite domain to the $\text{Pb}_4\text{S}_3\text{Br}_2$ domain (Figure 5d). The very weak green PL that was observed from the

sample of heterostructures had the same spectral position and decay kinetics as the sample of pure CsPbBr_3 NCs (Figure S4a,b). Hence, we ascribe this residual PL to the presence of isolated CsPbBr_3 NCs in the sample of heterostructures. Interestingly, by cooling the heterostructures to $T < 70$ K, an emission peak at 1.60 eV emerged, either under direct excitation of the CsPbBr_3 domain at 2.33 eV (that is, below the band gap of the CsPbBr_3 NCs) or under UV excitation at 3.5 eV. This emission was red-shifted by ~ 200 meV from that observed, at the same temperature, in the sample of pure $\text{Pb}_4\text{S}_3\text{Br}_2$ NCs and was thus ascribed to the recombination from intragap localized states in the heterostructures, consistent with the DFT analysis in Figure 4c. No such emission was observed from the heterostructures at room temperature, indicating substantial nonradiative losses, likely associated with carrier trapping. Also, the PL decay at 5 K associated with such 1.6 eV emission from the heterostructures was faster than the PL decay of the 1.8 eV emission from the $\text{Pb}_4\text{S}_3\text{Br}_2$ NCs ($1.6 \mu\text{s}$ vs $4.1 \mu\text{s}$) and was identical under either excitation conditions (2.33 and 3.5 eV). This behavior suggests that in the heterostructure the PL dynamics does not depend on the regions of the heterostructure where the photocarriers are initially generated and confirms the quenching effect of the interface.

CsPbCl_3 – $\text{Pb}_4\text{S}_3\text{Br}_2$ and CsPbI_3 – $\text{Pb}_4\text{S}_3\text{Br}_2$ Heterostructures. The exposure of the CsPbBr_3 – $\text{Pb}_4\text{S}_3\text{Br}_2$ heterostructures to either Cl^- or I^- ions resulted in anion exchange, as evidenced by the changes in the optical absorption spectra (Figure 6a). Notably, the Cl^- -treated sample exhibited a more evident absorption feature toward longer wavelengths in addition to the band edge absorption of the CsPbCl_3 domain. This tail, arising from the chalcogenide domain, is partially hidden in the initial sample and completely hidden in the iodide-exchanged sample. Morphological analysis by TEM showed that the NCs retained nearly the same size and shape as the initial NCs after anion exchange (Figure S26). Compositional mapping of individual heterostructures by STEM-EDX to assess anion distribution evidenced a clear segregation of the Cl and the Br signals in the two domains of the heterostructures (Figure S27), with Cl preferentially segregated in the perovskite domain and Br in the chalcogenide domain, compatible with a CsPbCl_3 – $\text{Pb}_4\text{S}_3\text{Br}_2$ composition for the heterostructure. Similar conclusions were drawn from EDX line scans on the heterostructures reacted with I^- ions (Figure S28), suggesting a CsPbI_3 – $\text{Pb}_4\text{S}_3\text{Br}_2$ composition in the latter case. HAADF-STEM analyses of these two samples revealed again a sharp interface between the two domains (Figure 6b–i), with the same epitaxial relationships as in the CsPbBr_3 – $\text{Pb}_4\text{S}_3\text{Br}_2$ sample discussed earlier (Figure 2), evidencing that anion exchange had not disrupted the overall structure of the initial CsPbBr_3 – $\text{Pb}_4\text{S}_3\text{Br}_2$ NCs. The sharpness of the interface was also obvious from the intensity maps of the various columns in the perovskite and chalcogenide domains in representative heterostructures belonging to these two samples (Figure S29). This was confirmed by the FT of the cubic CsPbCl_3 domain displayed in Figure 6d along its $[100]$ zone axis and is in agreement with the XRPD analysis of the same sample (Figure S30). The FT of the iodide exchange sample is reported in Figure 6h and does not show the additional diffraction spots typical of an orthorhombic structure whereas the chalcogenide domains was found to be unaffected, retaining the $\text{Pb}_4\text{S}_3\text{Br}_2$ phase. The XRPD pattern of the iodide-

exchanged sample unambiguously conformed to the “black” orthorhombic perovskite phase of CsPbI_3 (Figure S30).³⁷

As a further control, the attempt at halide exchange on pure $\text{Pb}_4\text{S}_3\text{Br}_2$ NCs left the NCs unaltered (see Figure S31 comparing optical absorption, XRPD, and TEM data of $\text{Pb}_4\text{S}_3\text{Br}_2$ NCs before and after treatment with either Cl^- or I^- ions). Taken together, these sets of data indicate that anion exchange took place only in the halide perovskite region of the heterostructures. The electronic structure and IPR analysis of these systems shows that also for the lead chloride and iodide perovskites the energy alignment is quasi-type II, with features similar to those of the bromide case (Figure S32).

Extensive spectroscopic analysis was performed on these two heterostructures as well, revealing, in both cases nearly complete quenching of the PL from the perovskite domain, as observed for the CsPbBr_3 – $\text{Pb}_4\text{S}_3\text{Br}_2$ systems. Notably, no acceleration was observed also for the kinetics of the CsPbCl_3 domain in the heterostructures with respect to the isolated CsPbCl_3 NCs. These kinetics, because of their fast decay time, were measured by using a streak camera with temporal resolution better than 7 ps (Figure S33), thus confirming the ultrafast nature of the hole transfer process.

One interesting question that arises in these nanostructures is whether the presence of the chalcogenide domain has any influence on the structural stability of the perovskite domain. This is particularly insightful for the “black” γ - CsPbI_3 phase, as this structure is metastable at room temperature and quickly undergoes a transition to the nonemitting “yellow” δ - CsPbI_3 phase in the case of colloidal NCs (on a time span of hours/days). The “yellow” δ - CsPbI_3 phase is characterized by linear arrays of edge-sharing $[\text{PbI}_6]^{4-}$ octahedra, very much different structurally from the perovskite structure. By monitoring the stability of the CsPbI_3 – $\text{Pb}_4\text{S}_3\text{Br}_2$ NCs both as colloidal dispersions and as solids films over time under air, and through a comparison with CsPbI_3 NCs of nearly the same size, we found the following: the CsPbI_3 NCs, as already well established, were very unstable, since they transformed to the yellow phase already within 1 day of storage under air, as revealed by XRPD analysis (Figure S34). On the other hand, after several days of aging, colloidal suspensions of CsPbI_3 – $\text{Pb}_4\text{S}_3\text{Br}_2$ heterostructures did not show any relevant change, neither in their optical features and morphology (Figure S35) nor in their XRPD patterns (Figure S36). Importantly, in the XRPD patterns of Figure S36 there are no additional diffraction peaks observed that belong to the δ - CsPbI_3 phase, even after 3 weeks of aging under air. We ascribe this structural stability to the presence of the interface joining CsPbI_3 and $\text{Pb}_4\text{S}_3\text{Br}_2$. This interface most likely confers higher structural rigidity to the perovskite CsPbI_3 lattice, preventing the reorganization both of the substructure of $[\text{PbI}_6]^{4-}$ octahedra and of the Cs^+ ions that would be necessary for the transition to the δ - CsPbI_3 phase to take place. This reorganization would disrupt the epitaxial connection of the two lattices, creating a new interface characterized by a much higher interfacial energy. Indeed, a hypothetical interface between the “yellow-phase” δ - CsPbI_3 and $\text{Pb}_4\text{S}_3\text{Br}_2$ heterostructure is extremely unlikely to exist: our observations demonstrate that the interfaces that we observe experimentally are based on the sharing of a plane of lead ions which produces a square pattern, as shown in Figure 3c and Figure S37. Such a squared plane of lead is not found in δ - CsPbI_3 in any orientation. Our conclusion is that the transformation of black CsPbI_3 into its

yellow polymorph is impossible without disrupting the heterostructure.

CONCLUSIONS

In conclusion, we have reported the synthesis of a series of $\text{CsPbX}_3\text{--Pb}_4\text{Br}_3\text{S}_2$ heterostructures and have studied their growth mechanisms as well as their structural and optical features and modeled their overall electronic structure. One likely reason for the affinity of this specific chalcogenide with lead halide perovskites is that its sublattice of Pb cations is similar to that of the perovskite, so that epitaxial heterostructures can be grown. In the present synthesis scheme, the use of preformed, subnanometer CsPbBr_3 clusters appears to be a very valuable strategy for preparing the initial $\text{CsPbBr}_3\text{--Pb}_4\text{Br}_3\text{S}_2$ heterostructures, from which the other two have been derived by selective anion exchange in the perovskite domain. It is likely that this synthesis strategy can be extended to other nanocrystal heterostructures containing a halide perovskite domain, providing new ground for materials scientists to develop new types of nanoscale materials. On the other hand, it remains to be seen whether other chalcogenides, not based on Pb, can also form heterostructures with lead halide perovskites as easily as in the present case. One potential issue is that the introduction of another cation, instead of Pb^{2+} , in the reaction environment, might render the lead halide perovskite unstable. There is also ample space for improving the optical properties of the nanocrystals developed in this present work, and a finer control of the interfacial structure could unlock the full potential of these heterostructures for optoelectronic or photonic applications. Finally, the increased structural rigidity conferred to the perovskite lattice by virtue of an epitaxial interface with another material is a fascinating aspect of these nanostructures and can provide a possible avenue for mitigating the well-known instability of halide perovskites.

EXPERIMENTAL SECTION

Chemicals. 1-Octadecene (ODE, tech, 90%), oleic acid (OA, tech, 90%), oleylamine (OLA, tech, 70%), lead(II) bromide (PbBr_2 , 98%), lead(II) chloride (PbCl_2 , 98%), lead(II) iodide (PbI_2 , 98%), cesium carbonate (Cs_2CO_3 , 99%), dodecanethiol (DDT, 99.9%), sulfur powder (S, 99.99%), and lead acetate trihydrate ($\text{Pb}(\text{OAc})_2\cdot 3\text{H}_2\text{O}$, 99.99%), were purchased from Sigma-Aldrich. All reagents were used as received without any further experimental purification.

Preparation of Cs-Oleate Precursor. In a typical synthesis, Cs_2CO_3 (0.652 g, 2 mmol), OA (2.5 mL, 7.5 mmol), and ODE (17.5 mL) were loaded into a 50 mL three-neck flask, dried for 1 h at 110 °C, and then heated under N_2 to 150 °C until the solution turned clear. The resulting mixture was transferred into a N_2 -filled glass vial and was stored inside a glovebox for further use.

Preparation of PbBr_2 Stock Solution. PbBr_2 powder (0.734 g, 2 mmol), OA (5 mL), and OLA (5 mL) were mixed with ODE (30 mL) in a 100 mL three-neck round-bottom flask. The reaction mixture was dried/degassed under vacuum for 30 min at 110 °C. Then, the flask was filled with N_2 , and the temperature was raised to 150 °C. After complete dissolution of PbBr_2 salt, the solution was cooled to room temperature (25 °C) and transferred into a N_2 -filled glass vial.

Preparation of $\text{Pb}(\text{OAc})_2$ Stock Solution. $\text{Pb}(\text{OAc})_2\cdot 3\text{H}_2\text{O}$ powder (0.76 g, 2 mmol) and OA (1.3 mL) were mixed with ODE (18.7 mL) in a 50 mL three-neck round-bottom flask. The reaction mixture was degassed under vacuum for 1 h at 110 °C and then heated under N_2 to 150 °C until all $\text{Pb}(\text{OAc})_2\cdot 3\text{H}_2\text{O}$ reacted with OA. Thereafter, the solution was cooled to room temperature (25 °C) and transferred into N_2 -filled glass vials.

Preparation of S-ODE Stock Solution. 1.5 mmol of S powder was mixed with 15 mL ODE (predegassed at 120 °C for an hour) in a 20 mL glass vial inside a glovebox. Then, the resulting mixture was sonicated until the complete dissolution of S.

Synthesis of CsPbBr_3 Nanoclusters. CsPbBr_3 nanoclusters were synthesized following a previously reported method.³⁰ Briefly, 4 mL of the above-mentioned PbBr_2 stock solution was transferred into the N_2 -filled 20 mL glass vial. Thereafter, 0.2 mL of Cs-oleate stock solution was injected into the PbBr_2 stock solution, and the resulting mixture was kept under stirring at room temperature (25 °C). After about 30 min, the resulting mixture was centrifuged at 8000 rpm for 5 min, the supernatant was discarded, and the precipitate was redispersed in 0.9 mL of degassed ODE.

Synthesis of $\text{CsPbBr}_3\text{--Pb}_4\text{S}_3\text{Br}_2$ Heterostructures. In a typical synthesis, 4.0 mL of degassed ODE was added to a 20 mL glass vial under the N_2 . Then the vial was heated to 200 °C, and 100 μL of the above-mentioned $\text{Pb}(\text{OAc})_2$ solution and 20 μL of DDT were added into the reaction system. Then, the mixture of S (0.1 mL) and CsPbBr_3 nanoclusters (0.9 mL) was swiftly injected into the reaction mixture. The reaction was allowed to proceed for 3 min and was subsequently quenched by immersing the vial in an ice water bath. Thereafter, the NCs were collected by centrifugation at 6000 rpm for 5 min, the supernatant was discarded, and the precipitate was redispersed in 5 mL of anhydrous toluene. The toluene dispersion of the NCs was centrifuged once again (at 4000 rpm for 5 min), the colloidal unstable fraction was discarded, and the supernatant was collected for further use.

Synthesis of $\text{Pb}_4\text{S}_3\text{Br}_2$ Nanocrystals. In a typical synthesis, 4.0 mL of degassed ODE was added to a 20 mL glass vial under the N_2 . Then the vial was heated to 150 °C, and 400 μL of the above-mentioned PbBr_2 solution and 100 μL of DDT were separately added into the reaction system. Then 100 μL of the above-mentioned S-ODE solution was swiftly injected, and the reaction mixture was annealed for 5 min at 150 °C. Subsequently, the mixture was cooled to room temperature and centrifuged at 4000 rpm for 5 min. After centrifugation, the precipitate was discarded, and the supernatant was centrifuged again (8000 rpm for 5 min) by adding 10 mL of acetone. Thereafter, the precipitate was redispersed in toluene for further use.

Synthesis of CsPbBr_3 Nanocrystals. In a typical synthesis, 4.0 mL of ODE was added to a 20 mL glass vial under the air and heated to 150 °C; then 1.0 mL of the above-mentioned seed cluster solution (CsPbBr_3 , without S-ODE) was swiftly injected, and the mixture was annealed for 3 min and cooled subsequently by using an ice water bath. Then, the resulting mixture was centrifuged at 8000 rpm for 5 min, the supernatant was discarded, and the precipitate was dispersed in 4 mL of toluene.

Anion Exchange Reactions. All the anion exchange reactions were performed under ambient conditions following previously reported methods.^{38,39} Briefly, 2 mL of the $\text{CsPbBr}_3\text{--Pb}_4\text{S}_3\text{Br}_2$ heterostructures (CsPbBr_3 or $\text{Pb}_4\text{S}_3\text{Br}_2$ NCs) solution was added into a 10 mL glass vial, and different amounts of PbX_2 stock solution (ranging from 30 to 300 μL) were added under vigorous stirring at RT to obtain the desired emission color. Thereafter, the heterostructures were collected by centrifugation at 6000 rpm for 5 min and redispersed in toluene for further use.

X-ray Powder Diffraction (XRPD) Characterization. The XRPD analysis was performed on a PANalytical Empyrean X-ray diffractometer, equipped with a 1.8 kW Cu $K\alpha$ ceramic X-ray tube, operating at 45 kV and 40 mA, and a PIXcel^{3D} 2 \times 2 area detector. To avoid preferred orientation effect, the concentrated dispersions of NCs were mixed with fumed silica powder prior to their deposition on zero-diffraction silicon substrate. All the diffraction patterns reported in this work were collected at room temperature under ambient conditions by using parallel beam geometry and symmetric reflection mode. Postacquisition XRPD data analysis was performed by using the HighScore 4.1 software from PANalytical.

Transmission Electron Microscopy (TEM) Characterization. Bright-field TEM images of the NC samples were acquired with a JEOL-1100 transmission electron microscope operating at an acceleration voltage of 100 kV. Samples were prepared by drop-

casting diluted solutions of NCs onto carbon film-coated 200 mesh copper grids for low-resolution TEM.

High-Resolution TEM and Energy Dispersive X-ray Spectroscopy. The characterization was performed by using a JEOL JEM2200 image corrected instrument operated at 200 kV and equipped with an in-column Omega energy filter and Bruker Quantax 400 EDX system with a 60 mm² XFlash detector. Partial HRSTEM and EDS characterization was taken on a ThermoFisher Scientific Titan Cubed Themis G2 300 transmission electron microscope with an acceleration voltage of 300 kV and equipped with a Super-X4 probe super energy spectrum.

High-Resolution High Angle Annular Dark Field Scanning Transmission Electron Microscopy Characterization. High-resolution HAADF-STEM images were acquired with a probe-corrected cubed Thermo Fisher Scientific Titan microscope operating at 300 kV with a probe semiconvergence angle of 20.5 mrad. Qualitative analyses of column intensities were performed by using STAT-STEM.³⁴ The total scattered intensity and location of all atomic columns were determined by fitting Gaussian functions to these columns.

Computational Modeling. For the electronic structure calculations, we have performed atomistic simulations at the density functional theory (DFT) level using the PBE exchange–correlation functional⁴⁰ and a double- ζ basis set plus polarization functions on all atoms as implemented in the CP2K 6.1 package.⁴¹ Scalar relativistic effects were incorporated as effective core potential functions in the basis set. All structures have been optimized in a vacuum. More details on how the models were built can be found in the main text. To identify surface localized states that could trap charge carriers, we have also computed the inverse participation ratio (IPR)⁴² for the chalcogenide and perovskite systems alone and in the heterostructure. The IPR, as also demonstrated for other nanocrystals,⁴³ quantifies the orbital localization of a given molecular orbital and is defined as

$$\text{IPR}_i = \frac{\sum_{\alpha} |P_{\alpha,i}|^4}{(\sum_{\alpha} |P_{\alpha,i}|^2)^2}$$

Here, $P_{\alpha,i}$ represents the weight of molecular orbital i on a given atom α expanded in an atomic orbital basis. For finite systems, the IPR provides an estimate of the number of atoms that contribute to a given electronic state i . It can range from the inverse of the number of atoms in the system when the wave function is distributed equally over all atoms in the system to 1 in the case of a localized state to a single atom. When values are near zero, the IPR identifies delocalized states.

Spectroscopic Studies. Optical absorption spectra were recorded on a Varian Cary 50 Scan UV–vis spectrophotometer under normal incidence in quartz cuvettes (optical path 0.1 cm). Absolute photoluminescence quantum yields of NC samples were measured by using an Edinburgh FLS900 fluorescence spectrometer equipped with a xenon lamp and a monochromator. The PLQY was measured by using a calibrated integrating sphere ($\lambda_{\text{ex}} = 350$ nm for all CsPbX₃ and CsPbX₃–Pb₄S₃Br₂ ($X = \text{Cl}, \text{Br}$) samples while the $\lambda_{\text{ex}} = 450$ nm was used for CsPbI₃/CsPbI₃–Pb₄S₃Br₂ NCs). All NC dispersions were diluted to an optical density of 0.1 at the corresponding excitation wavelength to minimize the amount of fluorophore being reabsorbed. The PL and PL dynamics were investigated by using a TM-C10083CA Hamamatsu spectrometer and a Hamamatsu R943-02 time-correlated single-photon counting unit coupled to an Oriel Instruments Cornerstone 260 monochromator using either an Edinburgh Inst. EPL 405 pulsed diode laser ($\lambda_{\text{exc}} = 405$ nm, pulse duration 40 ps, variable repetition rate) or a frequency-tripled/doubled pulsed Nd:YAG laser ($\lambda_{\text{exc}} = 355/532$ nm, pulse duration 5 ns, repetition rate 140 Hz) as excitation sources. The PL and time-resolved PL experiments on CsPbCl₃ and Pb₄S₃Br₂–CsPbCl₃ NCs were performed by using a frequency-doubled Ti:sapphire laser ($\lambda_{\text{exc}} = 360$ nm, pulse duration 150 fs, and repetition rate 76 MHz) as excitation source and a Hamamatsu streak camera as detector. To perform optical experiments at cryogenic temperatures, the NCs were

drop-casted onto glass substrates and placed in a variable-temperature insert of a closed-cycle helium cryostat ($T = 3.5\text{--}300$ K).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.0c10916>.

Detailed results of various control experiments including reaction temperature, role of various ligands and precursors on the formation of heterostructure, optical absorption, PL, PLQY, and PL decay curves, XRPD patterns, EDS compositional analysis, HR-TEM/STEM images, and computational analysis (PDF) 3D model of the heterojunction (XYZ)

■ AUTHOR INFORMATION

Corresponding Authors

Jun Song – Center for Biomedical Optics and Photonics (CBOP) & College of Physics and Optoelectronic Engineering, Key Laboratory of Optoelectronic Devices and Systems, Shenzhen University, Shenzhen 518060, P. R. China; orcid.org/0000-0002-2321-7064; Email: songjun@szu.edu.cn

Ivan Infante – Department of Nanochemistry, Istituto Italiano di Tecnologia, 16163 Genova, Italy; Department of Theoretical Chemistry, Faculty of Science, Vrije Universiteit Amsterdam, 1081 HV Amsterdam, The Netherlands; orcid.org/0000-0003-3467-9376; Email: ivan.infante@iit.it

Sara Bals – Electron Microscopy for Materials Science (EMAT) and NANOLab Center of Excellence, University of Antwerp, 2020 Antwerp, Belgium; Email: sara.bals@uantwerpen.be

Sergio Brovelli – Dipartimento di Scienza dei Materiali, Università degli Studi di Milano-Bicocca, 20125 Milano, Italy; orcid.org/0000-0002-5993-855X; Email: sergio.brovelli@unimib.it

Liberato Manna – Department of Nanochemistry, Istituto Italiano di Tecnologia, 16163 Genova, Italy; orcid.org/0000-0003-4386-7985; Email: liberato.manna@iit.it

Authors

Muhammad Imran – Department of Nanochemistry, Istituto Italiano di Tecnologia, 16163 Genova, Italy; orcid.org/0000-0001-7091-6514

Lucheng Peng – Department of Nanochemistry, Istituto Italiano di Tecnologia, 16163 Genova, Italy; Center for Biomedical Optics and Photonics (CBOP) & College of Physics and Optoelectronic Engineering, Key Laboratory of Optoelectronic Devices and Systems, Shenzhen University, Shenzhen 518060, P. R. China

Andrea Pianetti – Dipartimento di Scienza dei Materiali, Università degli Studi di Milano-Bicocca, 20125 Milano, Italy

Valerio Pinchetti – Dipartimento di Scienza dei Materiali, Università degli Studi di Milano-Bicocca, 20125 Milano, Italy; orcid.org/0000-0003-3792-3661

Julien Ramade – Electron Microscopy for Materials Science (EMAT), University of Antwerp, 2020 Antwerp, Belgium

Juliette Zito – Department of Nanochemistry, Istituto Italiano di Tecnologia, 16163 Genova, Italy; Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Genova, 16146 Genova, Italy

Francesco Di Stasio – Photonic Nanomaterials group, Istituto Italiano di Tecnologia, 16163 Genova, Italy; orcid.org/0000-0002-2079-3322

Joka Buha – Department of Nanochemistry, Istituto Italiano di Tecnologia, 16163 Genova, Italy

Stefano Toso – Department of Nanochemistry, Istituto Italiano di Tecnologia, 16163 Genova, Italy; International Doctoral Program in Science, Università Cattolica del Sacro Cuore, 25121 Brescia, Italy

Complete contact information is available at:
<https://pubs.acs.org/10.1021/jacs.0c10916>

Author Contributions

[†]M.I. and L.P. contributed equally to this work.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was performed on the Dutch national e-infra-structure with the support of SURF Cooperative. L.P. and J.S. are thankful for the support by the National Key R&D Program of China (2018YFC0910600) and the National Natural Science Foundation of China (61775145). F.D.S. and S.B. acknowledge support by the European Research Council via the ERC-StG “NANOLED” (851794) and the ERC-Cog “REALNANO” (815128). The authors acknowledge financial support from the European Commission under the Horizon 2020 Programme through Grant Agreement No. 731019 (EUSMI). S.B., A.P., and V.P. gratefully acknowledge the financial support from the Italian Ministry of University and Research (MIUR) through grant “Dipartimenti di Eccellenza-2017 Materials For Energy”.

REFERENCES

- (1) Kovalenko, M. V.; Protesescu, L.; Bodnarchuk, M. I. Properties and potential optoelectronic applications of lead halide perovskite nanocrystals. *Science* **2017**, *358* (6364), 745–750.
- (2) Sutherland, B. R.; Sargent, E. H. Perovskite photonic sources. *Nat. Photonics* **2016**, *10* (5), 295–302.
- (3) Akkerman, Q. A.; Rainò, G.; Kovalenko, M. V.; Manna, L. Genesis, challenges and opportunities for colloidal lead halide perovskite nanocrystals. *Nat. Mater.* **2018**, *17* (5), 394–405.
- (4) Quan, L. N.; Rand, B. P.; Friend, R. H.; Mhaisalkar, S. G.; Lee, T.-W.; Sargent, E. H. Perovskites for Next-Generation Optical Sources. *Chem. Rev.* **2019**, *119* (12), 7444–7477.
- (5) Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Krieg, F.; Caputo, R.; Hendon, C. H.; Yang, R. X.; Walsh, A.; Kovalenko, M. V. Nanocrystals of Cesium Lead Halide Perovskites (CsPbX₃, X = Cl, Br, and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut. *Nano Lett.* **2015**, *15* (6), 3692–3696.
- (6) Ten Brinck, S.; Zaccaria, F.; Infante, I. Defects in lead halide perovskite nanocrystals: Analogies and (many) differences with the bulk. *ACS Energy Lett.* **2019**, *4* (11), 2739–2747.
- (7) Shamsi, J.; Urban, A. S.; Imran, M.; De Trizio, L.; Manna, L. Metal halide perovskite nanocrystals: synthesis, post-synthesis modifications, and their optical properties. *Chem. Rev.* **2019**, *119* (5), 3296–3348.
- (8) Gandini, M.; Villa, I.; Beretta, M.; Gotti, C.; Imran, M.; Carulli, F.; Fantuzzi, E.; Sassi, M.; Zaffalon, M.; Brofferio, C.; et al. Efficient, fast and reabsorption-free perovskite nanocrystal-based sensitized plastic scintillators. *Nat. Nanotechnol.* **2020**, *15*, 462–468.
- (9) Ijaz, P.; Imran, M.; Soares, M. M.; Tolentino, H. C.; Martín-García, B.; Giannini, C.; Moreels, I.; Manna, L.; Krahne, R. Composition-, size-, and surface functionalization-dependent optical properties of lead bromide perovskite nanocrystals. *J. Phys. Chem. Lett.* **2020**, *11* (6), 2079–2085.
- (10) Yuan, J.; Hazarika, A.; Zhao, Q.; Ling, X.; Moot, T.; Ma, W.; Luther, J. M. Metal Halide Perovskites in Quantum Dot Solar Cells: Progress and Prospects. *Joule* **2020**, *4* (6), 1160–1185.
- (11) Imran, M.; Ijaz, P.; Baranov, D.; Goldoni, L.; Petralanda, U.; Akkerman, Q.; Abdelhady, A. L.; Prato, M.; Bianchini, P.; Infante, I.; Manna, L. Shape-pure, nearly monodispersed CsPbBr₃ nanocubes prepared using secondary aliphatic amines. *Nano Lett.* **2018**, *18* (12), 7822–7831.
- (12) Bera, S.; Pradhan, N. Perovskite Nanocrystal Heterostructures: Synthesis, Optical Properties, and Applications. *ACS Energy Lett.* **2020**, *5* (9), 2858–2872.
- (13) Kamat, P. V.; Pradhan, N.; Schanze, K.; Weiss, P. S.; Buriak, J.; Stang, P.; Odom, T. W.; Hartland, G. Challenges and Opportunities in Designing Perovskite Nanocrystal Heterostructures. *ACS Energy Lett.* **2020**, *5* (7), 2253–2255.
- (14) Balakrishnan, S. K.; Kamat, P. V. Au-CsPbBr₃ Hybrid Architecture: Anchoring Gold Nanoparticles on Cubic Perovskite Nanocrystals. *ACS Energy Lett.* **2017**, *2* (1), 88–93.
- (15) Zhang, X.; Wu, X.; Liu, X.; Chen, G.; Wang, Y.; Bao, J.; Xu, X.; Liu, X.; Zhang, Q.; Yu, K.; Wei, W.; Liu, J.; Xu, J.; Jiang, H.; Wang, P.; Wang, X. Heterostructural CsPbX₃-PbS (X = Cl, Br, I) Quantum Dots with Tunable Vis-NIR Dual Emission. *J. Am. Chem. Soc.* **2020**, *142* (9), 4464–4471.
- (16) Chen, W.; Hao, J.; Hu, W.; Zang, Z.; Tang, X.; Fang, L.; Niu, T.; Zhou, M. Enhanced stability and tunable photoluminescence in perovskite CsPbX₃/ZnS quantum dot heterostructure. *Small* **2017**, *13* (21), 1604085.
- (17) Ravi, V. K.; Saikia, S.; Yadav, S.; Nawale, V. V.; Nag, A. CsPbBr₃/ZnS Core/Shell Type Nanocrystals for Enhancing Luminescence Lifetime and Water Stability. *ACS Energy Lett.* **2020**, *5* (6), 1794–1796.
- (18) Nguyen, T. P.; Ozturk, A.; Park, J.; Sohn, W.; Lee, T. H.; Jang, H. W.; Kim, S. Y. Facile synthesis of CsPbBr₃/PbSe composite clusters. *Sci. Technol. Adv. Mater.* **2018**, *19* (1), 10–17.
- (19) Wang, X.-D.; Huang, Y.-H.; Liao, J.-F.; Jiang, Y.; Zhou, L.; Zhang, X.-Y.; Chen, H.-Y.; Kuang, D.-B. In situ construction of a Cs₂SnI₆ perovskite nanocrystal/SnS₂ nanosheet heterojunction with boosted interfacial charge transfer. *J. Am. Chem. Soc.* **2019**, *141* (34), 13434–13441.
- (20) Xu, F.; Meng, K.; Cheng, B.; Wang, S.; Xu, J.; Yu, J. Unique S-scheme heterojunctions in self-assembled TiO₂/CsPbBr₃ hybrids for CO₂ photoreduction. *Nat. Commun.* **2020**, *11* (1), 1–9.
- (21) Hu, H.; Wu, L.; Tan, Y.; Zhong, Q.; Chen, M.; Qiu, Y.; Yang, D.; Sun, B.; Zhang, Q.; Yin, Y. Interfacial synthesis of highly stable CsPbX₃/oxide Janus nanoparticles. *J. Am. Chem. Soc.* **2018**, *140* (1), 406–412.
- (22) Liu, H.; Tan, Y.; Cao, M.; Hu, H.; Wu, L.; Yu, X.; Wang, L.; Sun, B.; Zhang, Q. Fabricating CsPbX₃-based type I and type II heterostructures by tuning the halide composition of janus CsPbX₃/ZrO₂ nanocrystals. *ACS Nano* **2019**, *13* (5), 5366–5374.
- (23) Li, Z.-J.; Hofman, E.; Li, J.; Davis, A. H.; Tung, C.-H.; Wu, L.-Z.; Zheng, W. Photoelectrochemically Active and Environmentally Stable CsPbBr₃/TiO₂ Core/Shell Nanocrystals. *Adv. Funct. Mater.* **2018**, *28* (1), 1704288.
- (24) Shamsi, J.; Dang, Z.; Ijaz, P.; Abdelhady, A. L.; Bertoni, G.; Moreels, I.; Manna, L. Colloidal CsX (X = Cl, Br, I) Nanocrystals and Their Transformation to CsPbX₃ Nanocrystals by Cation Exchange. *Chem. Mater.* **2018**, *30* (1), 79–83.
- (25) Baranov, D.; Caputo, G.; Goldoni, L.; Dang, Z.; Scarfiello, R.; De Trizio, L.; Portone, A.; Fabbri, F.; Camposo, A.; Pisignano, D.; Manna, L. Transforming colloidal Cs₄PbBr₆ nanocrystals with poly(maleic anhydride-alt-1-octadecene) into stable CsPbBr₃ perovskite emitters through intermediate heterostructures. *Chem. Sci.* **2020**, *11* (15), 3986–3995.
- (26) Toso, S.; Baranov, D.; Manna, L. Hidden in Plain Sight: the Overlooked Influence of the Cs⁺ Substructure on Transformations in

Cesium Lead Halide Nano-crystals. *ACS Energy Lett.* **2020**, *5*, 3409–3414.

(27) Zhang, X.; Lu, M.; Zhang, Y.; Wu, H.; Shen, X.; Zhang, W.; Zheng, W.; Colvin, V. L.; Yu, W. W. PbS Capped CsPbI₃ Nanocrystals for Efficient and Stable Light-Emitting Devices Using p-i-n Structures. *ACS Cent. Sci.* **2018**, *4* (10), 1352–1359.

(28) Wang, S.; Bi, C.; Portniagin, A.; Yuan, J.; Ning, J.; Xiao, X.; Zhang, X.; Li, Y. Y.; Kershaw, S. V.; Tian, J.; Rogach, A. L. CsPbI₃/PbSe Heterostructured Nanocrystals for High-Efficiency Solar Cells. *ACS Energy Lett.* **2020**, *5* (7), 2401–2410.

(29) Toso, S.; Akkerman, Q. A.; Martín-García, B.; Prato, M.; Zito, J.; Infante, I.; Dang, Z.; Moliterni, A.; Giannini, C.; Bladt, E.; Lobato, I.; Ramade, J.; Bals, S.; Buha, J.; Spirito, D.; Mugnaioli, E.; Gemmi, M.; Manna, L. Nanocrystals of Lead Chalcogenides: A Series of Kinetically Trapped Metastable Nanostructures. *J. Am. Chem. Soc.* **2020**, *142* (22), 10198–10211.

(30) Peng, L.; Dutta, A.; Xie, R.; Yang, W.; Pradhan, N. Dot-Wire-Platelet-Cube: Step Growth and Structural Transformations in CsPbBr₃ Perovskite Nanocrystals. *ACS Energy Lett.* **2018**, *3* (8), 2014–2020.

(31) Peng, L.; Dutta, S. K.; Mondal, D.; Hudait, B.; Shyamal, S.; Xie, R.; Mahadevan, P.; Pradhan, N. Arm Growth and Facet Modulation in Perovskite Nanocrystals. *J. Am. Chem. Soc.* **2019**, *141* (40), 16160–16168.

(32) Imran, M.; Caligiuri, V.; Wang, M.; Goldoni, L.; Prato, M.; Krahne, R.; De Trizio, L.; Manna, L. Benzoyl halides as alternative precursors for the colloidal synthesis of lead-based halide perovskite nanocrystals. *J. Am. Chem. Soc.* **2018**, *140* (7), 2656–2664.

(33) Dutta, A.; Dutta, S. K.; Das Adhikari, S.; Pradhan, N. Tuning the size of CsPbBr₃ nanocrystals: all at one constant temperature. *ACS Energy Lett.* **2018**, *3* (2), 329–334.

(34) De Backer, A.; Van den Bos, K.; Van den Broek, W.; Sijbers, J.; Van Aert, S. StatSTEM: an efficient approach for accurate and precise model-based quantification of atomic resolution electron microscopy images. *Ultramicroscopy* **2016**, *171*, 104–116.

(35) Grillo, V. The effect of surface strain relaxation on HAADF imaging. *Ultramicroscopy* **2009**, *109* (12), 1453–1464.

(36) Wu, K.; Liang, G.; Kong, D.; Chen, J.; Chen, Z.; Shan, X.; McBride, J. R.; Lian, T. Quasi-type II CuInS₂/CdS core/shell quantum dots. *Chem. Sci.* **2016**, *7* (2), 1238–1244.

(37) Sutton, R. J.; Filip, M. R.; Haghighirad, A. A.; Sakai, N.; Wenger, B.; Giustino, F.; Snaith, H. J. Cubic or orthorhombic? Revealing the crystal structure of metastable black-phase CsPbI₃ by theory and experiment. *ACS Energy Lett.* **2018**, *3* (8), 1787–1794.

(38) Nedelcu, G.; Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Grotevent, M. J.; Kovalenko, M. V. Fast anion-exchange in highly luminescent nanocrystals of cesium lead halide perovskites (CsPbX₃, X = Cl, Br, I). *Nano Lett.* **2015**, *15* (8), 5635–5640.

(39) Akkerman, Q. A.; D'Innocenzo, V.; Accornero, S.; Scarpellini, A.; Petrozza, A.; Prato, M.; Manna, L. Tuning the optical properties of cesium lead halide perovskite nanocrystals by anion exchange reactions. *J. Am. Chem. Soc.* **2015**, *137* (32), 10276–10281.

(40) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, *77* (18), 3865.

(41) Hutter, J.; Iannuzzi, M.; Schiffmann, F.; VandeVondele, J. cp2k: atomistic simulations of condensed matter systems. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2014**, *4* (1), 15–25.

(42) Murphy, N.; Wortis, R.; Atkinson, W. Generalized inverse participation ratio as a possible measure of localization for interacting systems. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2011**, *83* (18), 184206.

(43) Houtepen, A. J.; Hens, Z.; Owen, J. S.; Infante, I. On the origin of surface traps in colloidal II-VI semiconductor nanocrystals. *Chem. Mater.* **2017**, *29* (2), 752–761.

Supporting Information for

Halide Perovskite-Lead Chalcogenide Nanocrystal Heterostructures

Muhammad Imran^{a,†}, Lucheng Peng^{a,b,†}, Andrea Pianetti^c, Valerio Pinchetti^c, Julien Ramade^d, Juliette Zito^{a,e}, Francesco Di Stasio^g, Joka Buha^a, Stefano Toso^{a,i}, Jun Song^{b,*}, Ivan Infante^{a,h,*}, Sara Bals^{d,f,*}, Sergio Brovelli^{c,*}, Liberato Manna^{a,*}

^a Department of Nanochemistry, Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy

^b Center for Biomedical Optics and Photonics (CBOP) & College of Physics and Optoelectronic Engineering, Key Laboratory of Optoelectronic Devices and Systems, Shenzhen University, Shenzhen 518060, P. R. China

^c Dipartimento di Scienza dei Materiali, Università degli Studi di Milano-Bicocca, via R. Cozzi 55, 20125 Milano, Italy

^d Electron Microscopy for Materials Science (EMAT), University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium

^e Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Genova, Via Dodecaneso 31, 16146 Genova, Italy

^f NANO lab Center of Excellence, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium

^g Photonic Nanomaterials group, Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy

^h Department of Theoretical Chemistry, Faculty of Science, Vrije Universiteit Amsterdam, de Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

ⁱ International Doctoral Program in Science, Università Cattolica del Sacro Cuore, 25121 Brescia, Italy

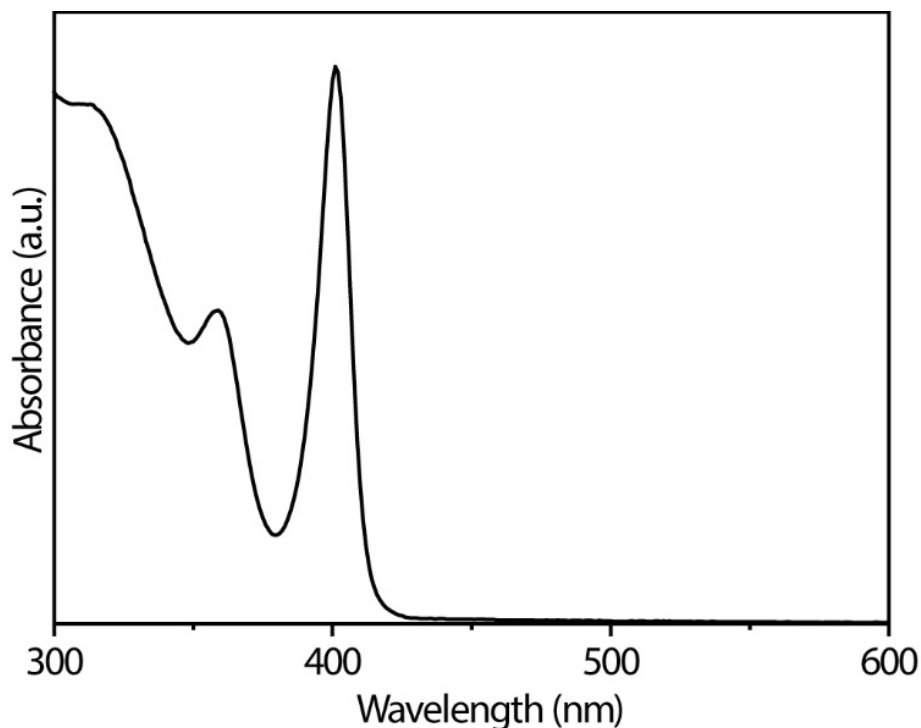


Figure S1. Optical absorption spectrum of sub-nm CsPbBr₃ nanoclusters, prepared following a previously reported method.¹ In a typical synthesis, 4 mL PbBr₂ stock solution (prepared separately by adding 2 mmol of PbBr₂ to a mixture of 5 mL OA, 5 mL OLA and 30 mL ODE, pumping the resulting solution to vacuum at 110 °C for an hour and subsequently heating it under N₂ to 150 °C till the complete dissolution of salt) was transferred into a N₂ filled 20 ml glass vial. Thereafter, 0.2 mL of Cs-oleate stock solution (prepared by dissolving 2 mmol of Cs₂CO₃ in a mixture of 2.5 mL OA and 17.5 mL ODE, pumping the resulting solution to vacuum at 110 °C for an hour and subsequently heating it under N₂ to 150 °C till the solution turned clear) was injected into the PbBr₂ solution and the resulting mixture was kept under stirring at room temperature (25 °C). After about 30 minutes, the mixture was centrifuged at 8000 rpm for 5 min, the supernatant was discarded and the precipitate was re-dispersed in 0.9 mL of degassed ODE by using a vortex mixer. These clusters, of sub-nm size, have an exciton absorption at 400 nm, they are non-emissive at room temperature and are used for the synthesis of CsPbBr₃-Pb₄S₃Br₂ NCs.

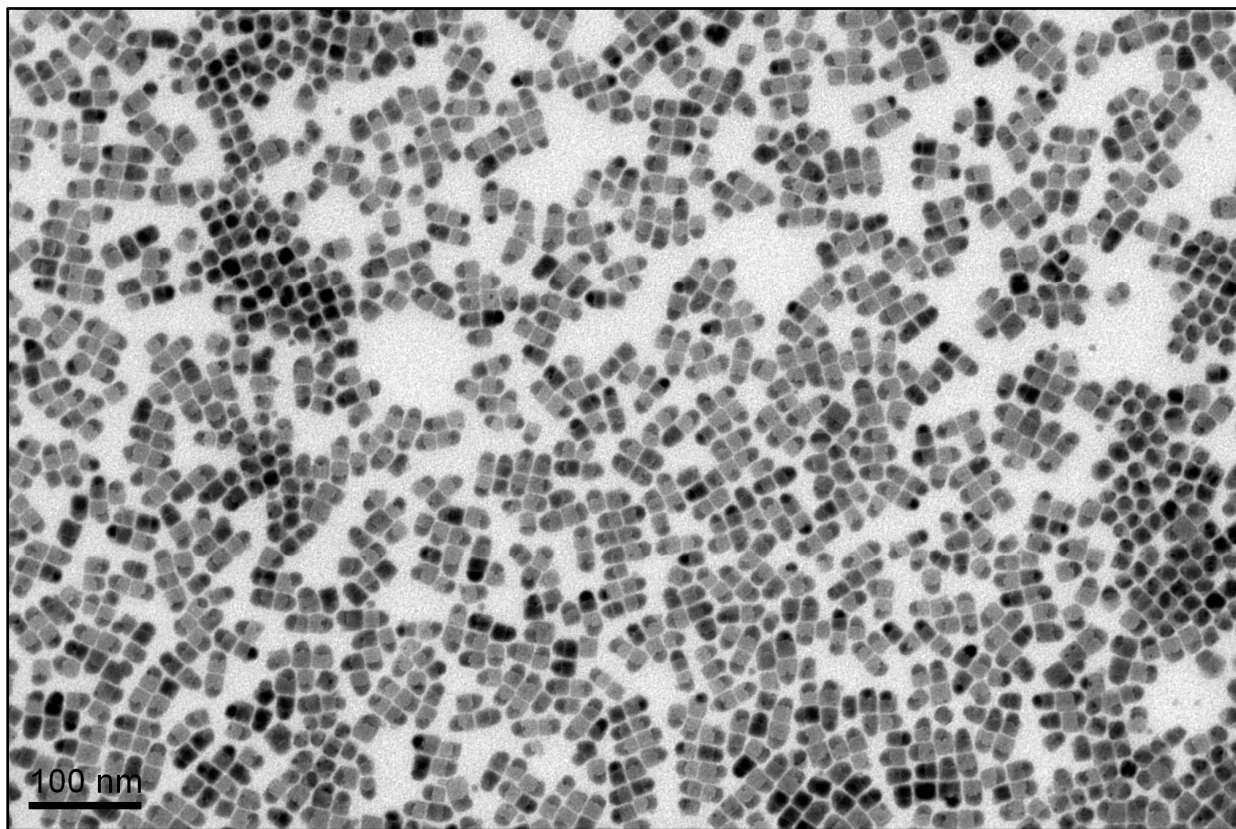


Figure S2. A representative low magnification TEM image of CsPbBr₃-Pb₄S₃Br₂ heterostructures. To synthesize CsPbBr₃-Pb₄S₃Br₂ NCs, 4.0 mL of degassed ODE was added to a 20 mL glass vial under N₂. Then, the vial was heated to 200 °C, and 100 µL of Pb(OA)₂ solution (separately prepared by adding 2 mmol of Pb(OAc)₂·3H₂O to a mixture of 1.3 mL OA and 18.7 mL ODE, pumping the resulting solution to vacuum at 110 °C for an hour and subsequently heating it under N₂ to 150 °C till the solution turned clear) and 20 µL of DDT were added to the vial. Then, 0.1 mL of S-ODE (prepared by dissolving 1.5 mmol of S powder into 15 mL of pre-dried ODE using ultra sonication) was mixed with 0.9 mL of the CsPbBr₃ nanoclusters solution (see the caption of Figure S1 for the detail about the synthesis of nanoclusters) and swiftly injected into the reaction mixture. Thereafter, the reaction was allowed to proceed for 3 min and was subsequently quenched by immersing the vial in an ice water bath. This image contains about 1300 NCs. The statistical analysis for the number of nanocrystals with or without Pb₄S₃Br₂ domain was carried out on this image.

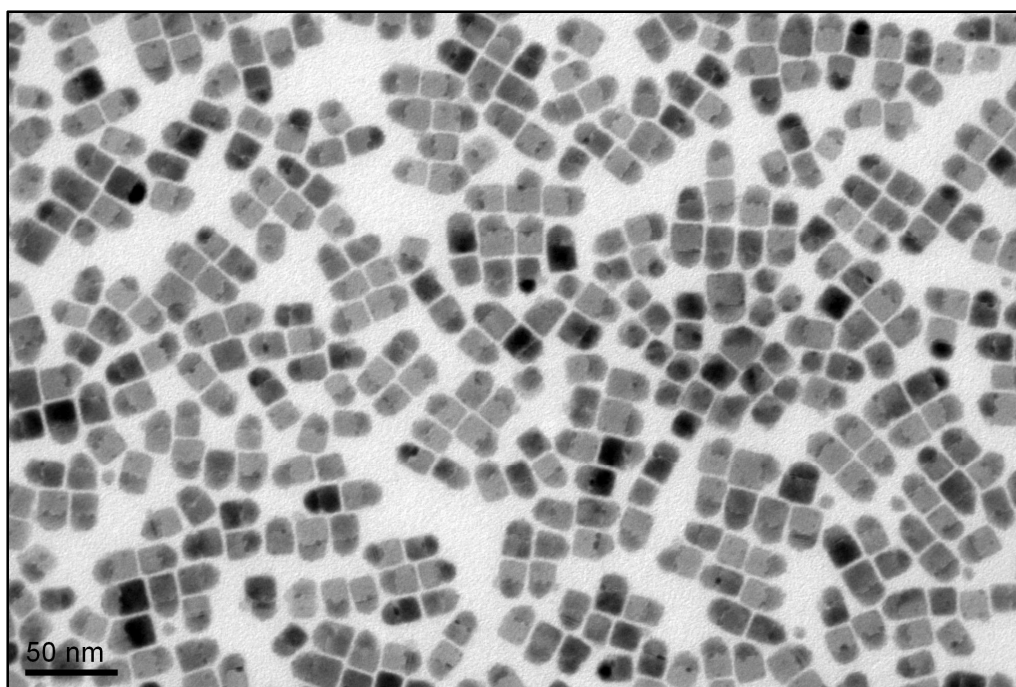


Figure S3. A higher magnification TEM image (compared to Figure S2) of CsPbBr₃-Pb₄S₃Br₂ heterostructures.

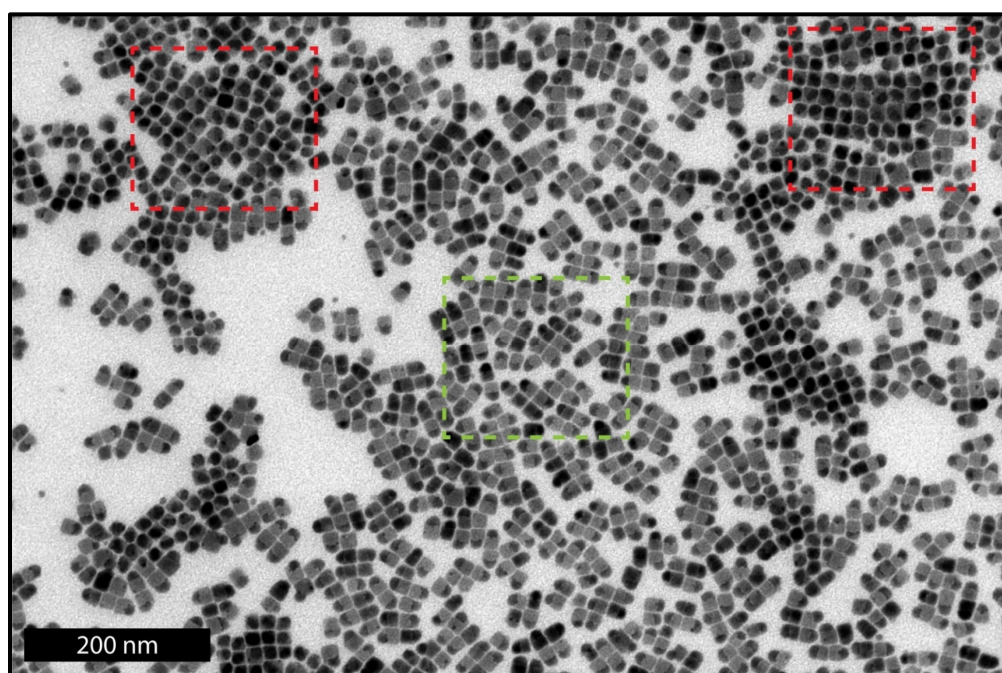


Figure S4. A low magnification TEM image of CsPbBr₃-Pb₄S₃Br₂ heterostructures showing different projections of the heterostructures on the substrate. For example, the two regions marked by red dotted lines encompass areas on the grid in which most heterostructures are sitting on the substrate in a face-up projection, such that the individual CsPbBr₃ and Pb₄S₃Br₂ domains in each heterostructure are on top of each other. On the other hand, the region marked by green dotted lines encompasses an area on the grid in which most heterostructures are sitting flat, so that the individual CsPbBr₃ and Pb₄S₃Br₂ domains in each heterostructure are more easily distinguishable.

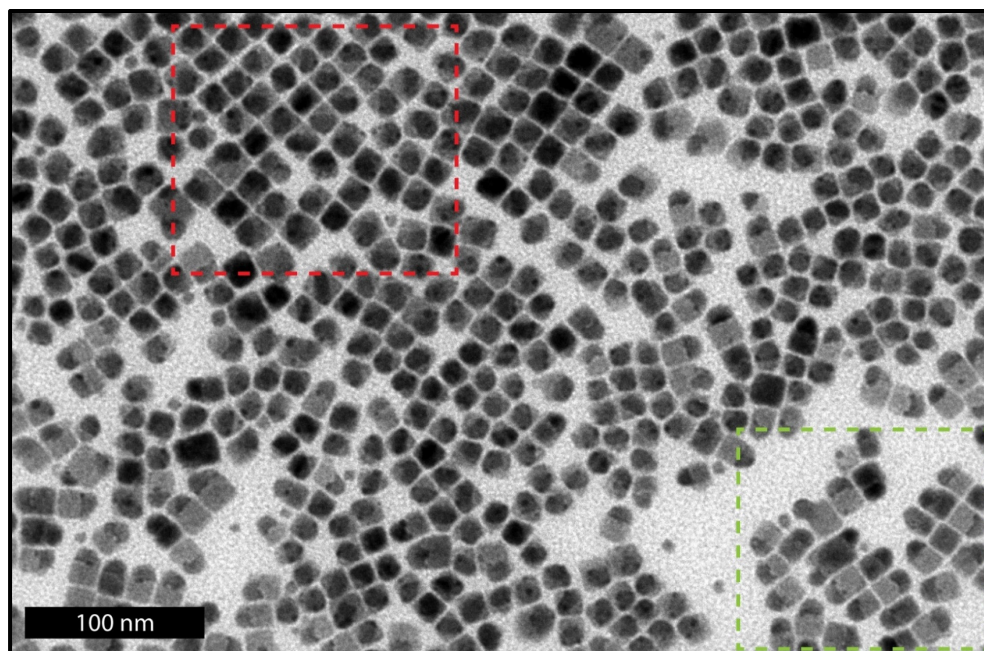


Figure S5. A higher magnification TEM image of $\text{CsPbBr}_3\text{-Pb}_4\text{S}_3\text{Br}_2$ heterostructures. The region marked by red dotted lines encompasses an area on the grid in which most heterostructures are sitting on the substrate in a face-up projection: the individual CsPbBr_3 and $\text{Pb}_4\text{S}_3\text{Br}_2$ domains in each heterostructure are on top of each other. The region marked by green dotted lines encompasses an area on the grid in which most heterostructures are sitting flat, so that the individual CsPbBr_3 and $\text{Pb}_4\text{S}_3\text{Br}_2$ domains in each heterostructure are more easily distinguishable.

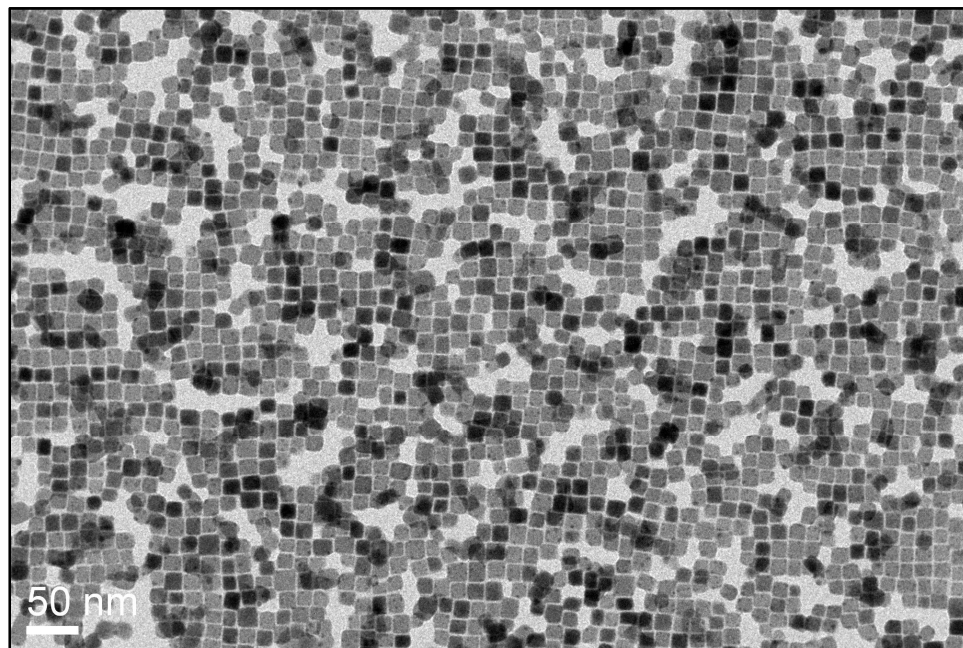


Figure S6. TEM image of CsPbBr_3 NCs obtained when the initial CsPbBr_3 nanoclusters were heated (at 200°C) under the same conditions as in the synthesis of the $\text{CsPbBr}_3\text{-Pb}_4\text{S}_3\text{Br}_2$ heterostructures of Figures 1b-c and S2-S5, but in ODE alone (that is, with no elemental sulfur, dodecanethiol and lead oleate). The product in this case was represented by nearly cube shaped CsPbBr_3 NCs with an edge length of 15.9 ± 1.6 nm.

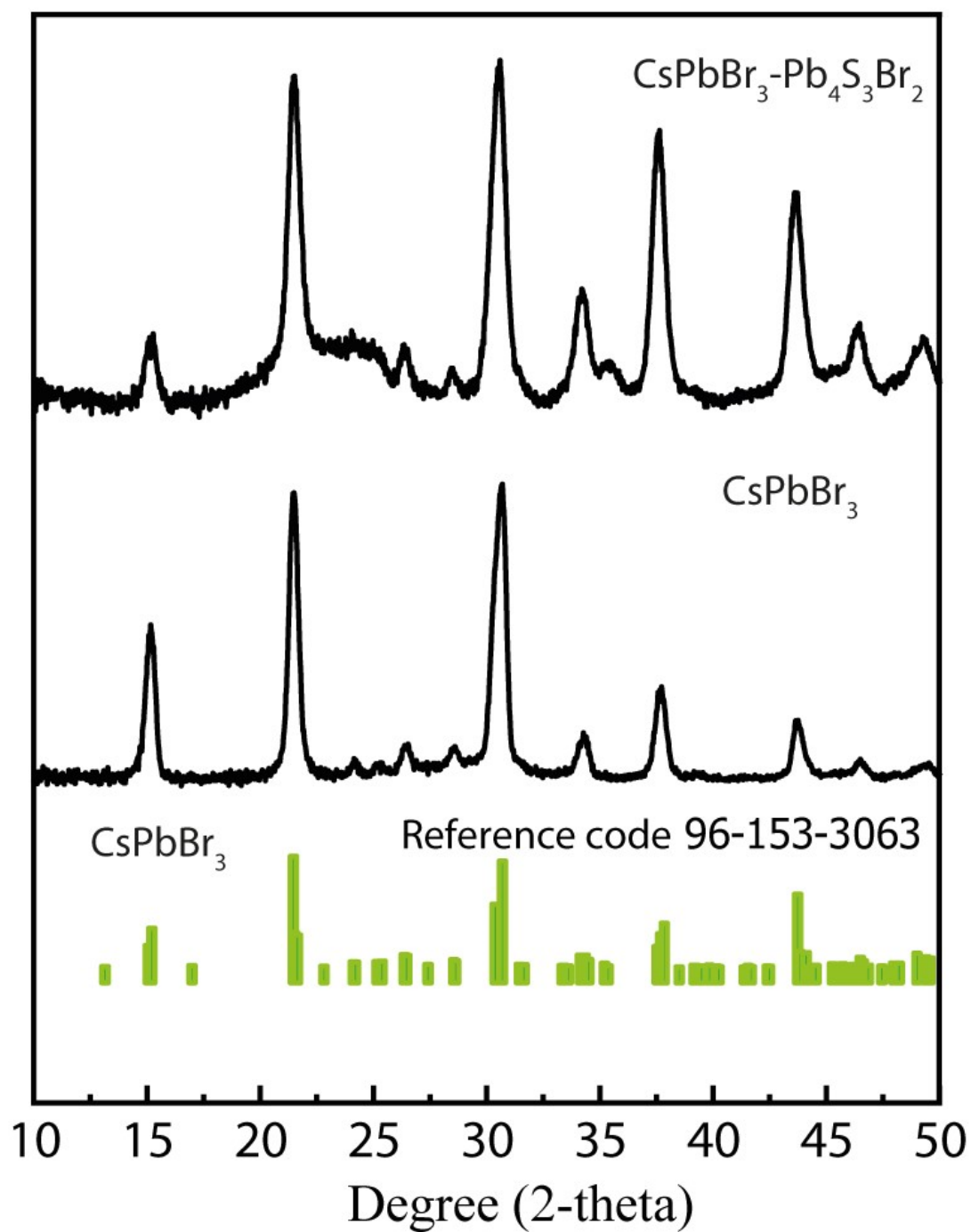


Figure S7. The XRPD patterns of $\text{CsPbBr}_3\text{-Pb}_4\text{S}_3\text{Br}_2$ heterostructure and of CsPbBr_3 NCs (synthesis details for the CsPbBr_3 NCs are reported in experimental section of the main text and the TEM analysis of same sample is reported in Figure S6) along with the bulk reference pattern of the CsPbBr_3 orthorhombic phase (Pnma, COD: 4510745).

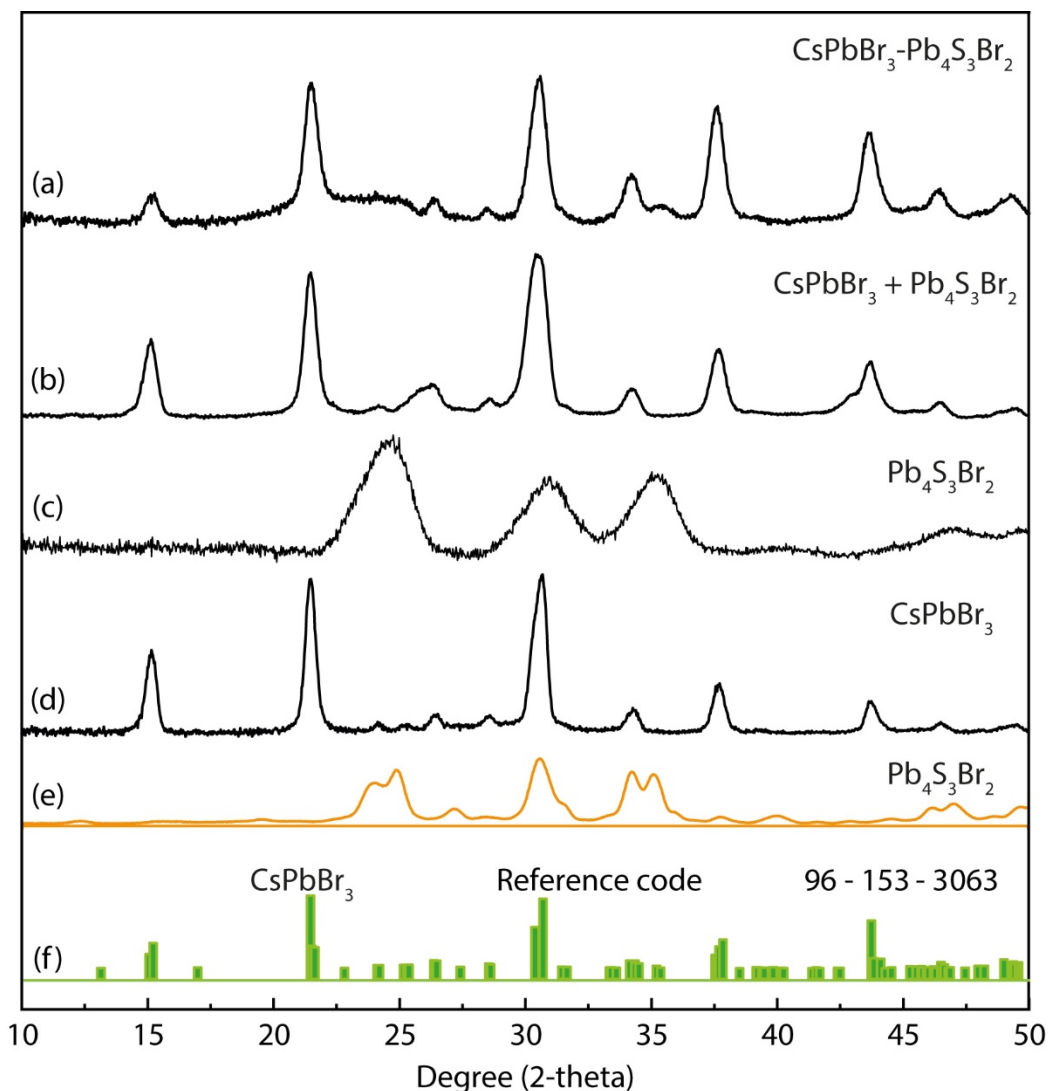


Figure S8. From top to bottom: XRPD patterns of: (a) $\text{CsPbBr}_3\text{-Pb}_4\text{S}_3\text{Br}_2$ heterostructures (same pattern as in Figure S7). The much weaker and broader peaks ascribable to the chalcogenide domain, compared to the sharper and more intense peaks ascribable to the perovskite domain, are due to the comparatively smaller size and lower volume fraction of the chalcogenide domain with respect to the perovskite domain. This difference in peak intensities and broadening is so large that the chalcogenide peaks are almost undetectable in the XRPD pattern of the heterostructure; (b) mixtures of CsPbBr_3 NCs and $\text{Pb}_4\text{S}_3\text{Br}_2$ NCs powders; (c) $\text{Pb}_4\text{S}_3\text{Br}_2$ NCs; (d) CsPbBr_3 NCs (same pattern as in Figure S7). The sample whose XRPD pattern is shown in (b) was prepared by mixing powders of $\text{Pb}_4\text{S}_3\text{Br}_2$ NCs and CsPbBr_3 NCs whose XRPD patterns are shown in (c) and (d), respectively. Also, see the experimental section of the main manuscript for the synthesis details of $\text{Pb}_4\text{S}_3\text{Br}_2$ NCs and CsPbBr_3 NCs; (e) $\text{Pb}_4\text{S}_3\text{Br}_2$ NCs (orange line) as reported in a previous work from our group.² This pattern is taken from ref.² with permission. Given the large number of reflections for $\text{Pb}_4\text{S}_3\text{Br}_2$ (see ref.²) we preferred here to provide such experimental pattern of $\text{Pb}_4\text{S}_3\text{Br}_2$, instead of the reflection list, as a reference. (f) Bulk pattern for CsPbBr_3 , (green histograms, reference code 96-153-3063).

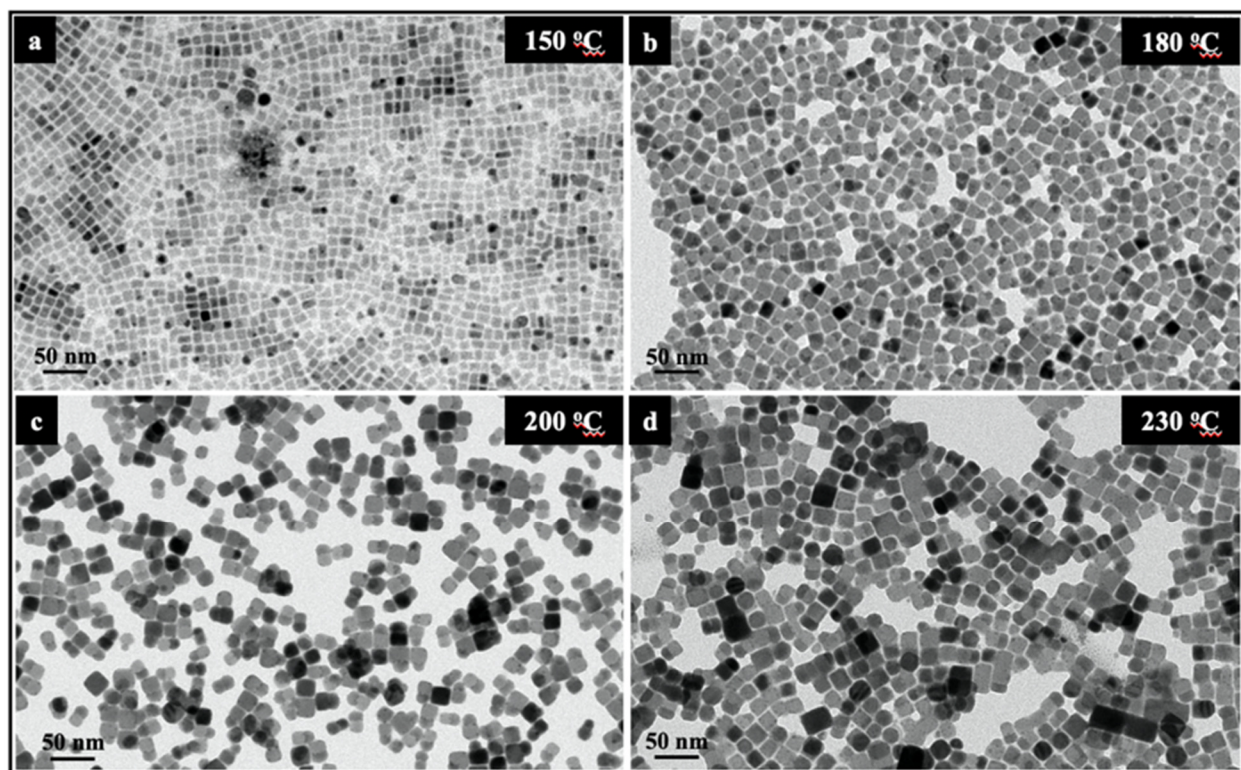


Figure S9. Influence of reaction temperature on the formation of the $\text{CsPbBr}_3\text{-Pb}_4\text{S}_3\text{Br}_2$ heterostructures: All the syntheses were carried under conditions that were identical to those of Figure S2, except for the temperature, which was varied from 150 to 230 °C. TEM images of the samples prepared at (a) 150 °C , (b) 180 °C , (c) 200 °C, (d) 230 °C respectively. A reaction temperature below 180 °C was not favorable for the growth of the heterostructure, whereas at higher temperatures (230 °C) the size and shape distributions of the heterostructures worsened considerably.

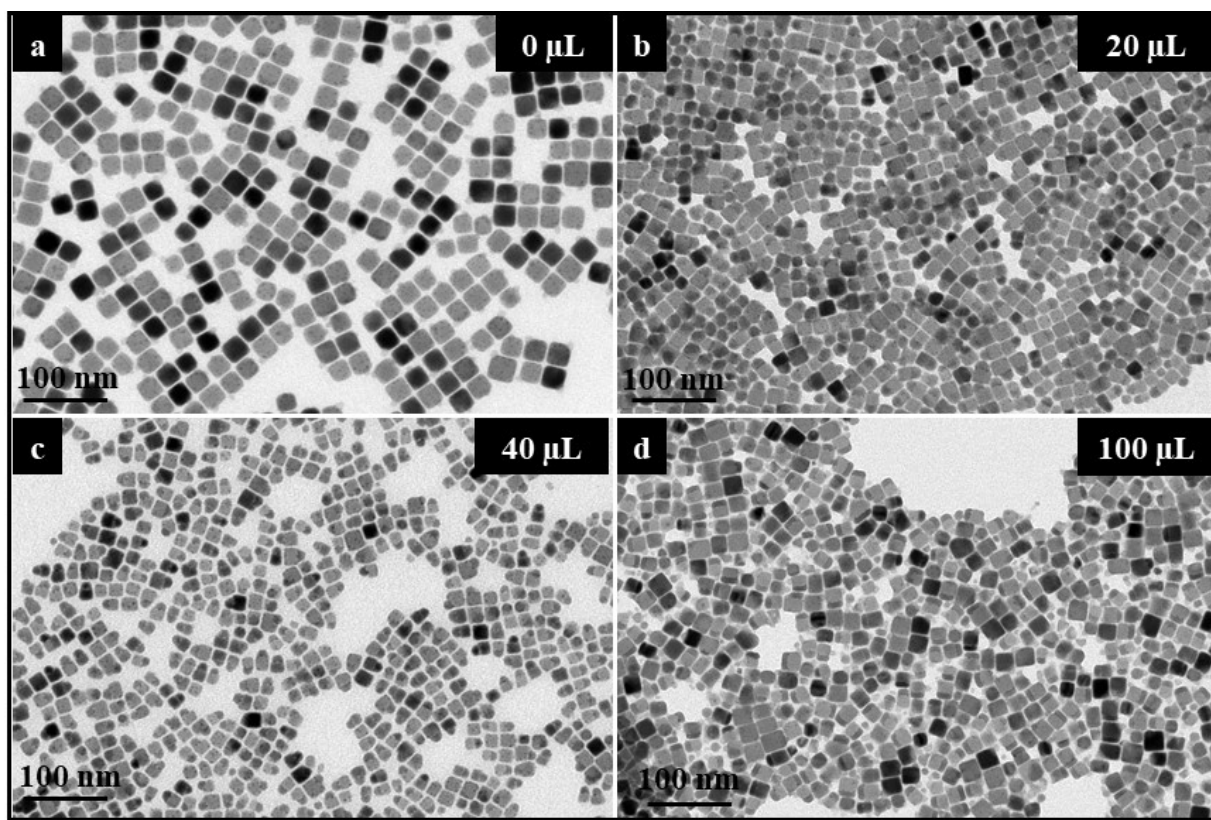


Figure S10. Role of dodecanethiol on the formation of the $\text{CsPbBr}_3\text{-Pb}_4\text{S}_3\text{Br}_2$ heterostructures. All the syntheses were carried under conditions identical to those of Figure S2 except for dodecanethiol, which was varied from 0 to 100 μL . TEM images of samples prepared without dodecanethiol (a), and with 20 μL (b), 40 μL (c), and 100 μL of dodecanethiol (d), respectively. In the absence of dodecanethiol (panel a), no $\text{CsPbBr}_3\text{-Pb}_4\text{S}_3\text{Br}_2$ heterostructures were formed, and instead we obtained large CsPbBr_3 NCs, each carrying though a tiny, low contrast domain attached to it.

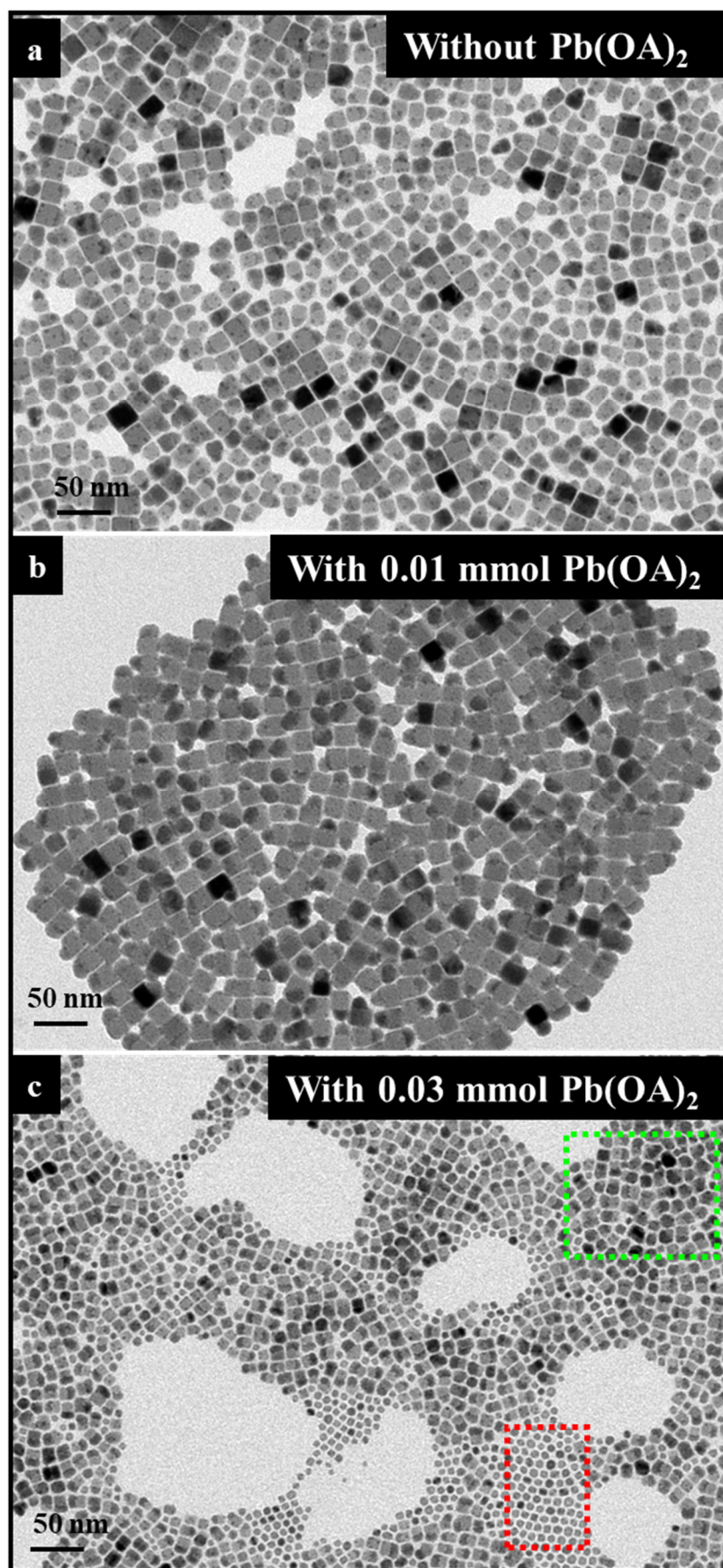


Figure S11. Role of lead oleate on the formation of the CsPbBr_3 - $\text{Pb}_4\text{S}_3\text{Br}_2$ heterostructures. All the syntheses were carried under conditions identical to those of Figure S2, except for the amount of Pb(OA)_2 , which was varied from 0 to 0.03 mmol. TEM images of the samples prepared without Pb(OA)_2 (a), with 0.01 mmol (b) and 0.03 mmol of Pb(OA)_2 (c) respectively. We observed the formation of smaller domains of $\text{Pb}_4\text{S}_3\text{Br}_2$ in the absence of Pb(OA)_2 , while instead an excess Pb(OA)_2 addition led to the formation of isolated $\text{Pb}_4\text{S}_3\text{Br}_2$ particles (highlighted by red dotted lines) as a byproduct in addition to the heterostructure (highlighted by green dotted lines).

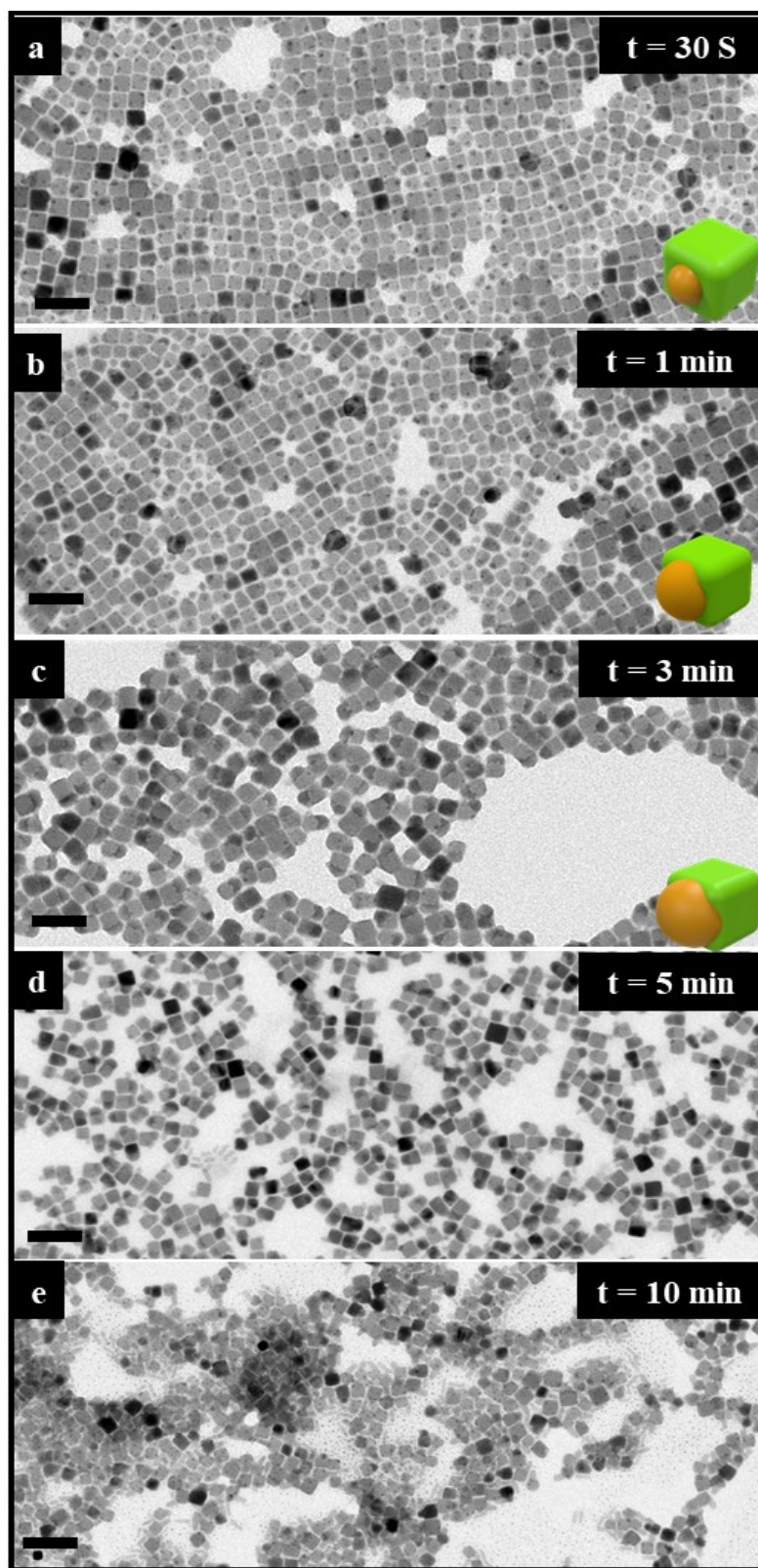


Figure S12. Influence of the reaction time on the formation of CsPbBr₃-Pb₄S₃Br₂ heterostructures. All the syntheses were carried under conditions identical to those of Figure S2 except for the reaction time, which was varied from 30 s to 10 min. TEM images of samples obtained after 30 s of reaction time (a), 1 min (b), 3 min (c), 5 min (d), and 10 min (e) respectively. Notably, after 30 s of reaction time sample showed nearly cubic shape NCs with higher contrast domains (presumably Pb₄S₃Br₂) at their edges. These domains grew in sizes by prolonging the reaction time. For more times longer than 3 minutes, we observed the formation of low contrast nanorods as a byproduct, and the quality of the heterostructures was much worse compared to the previous samples. Scale bars are 50 nm in all the TEM images.

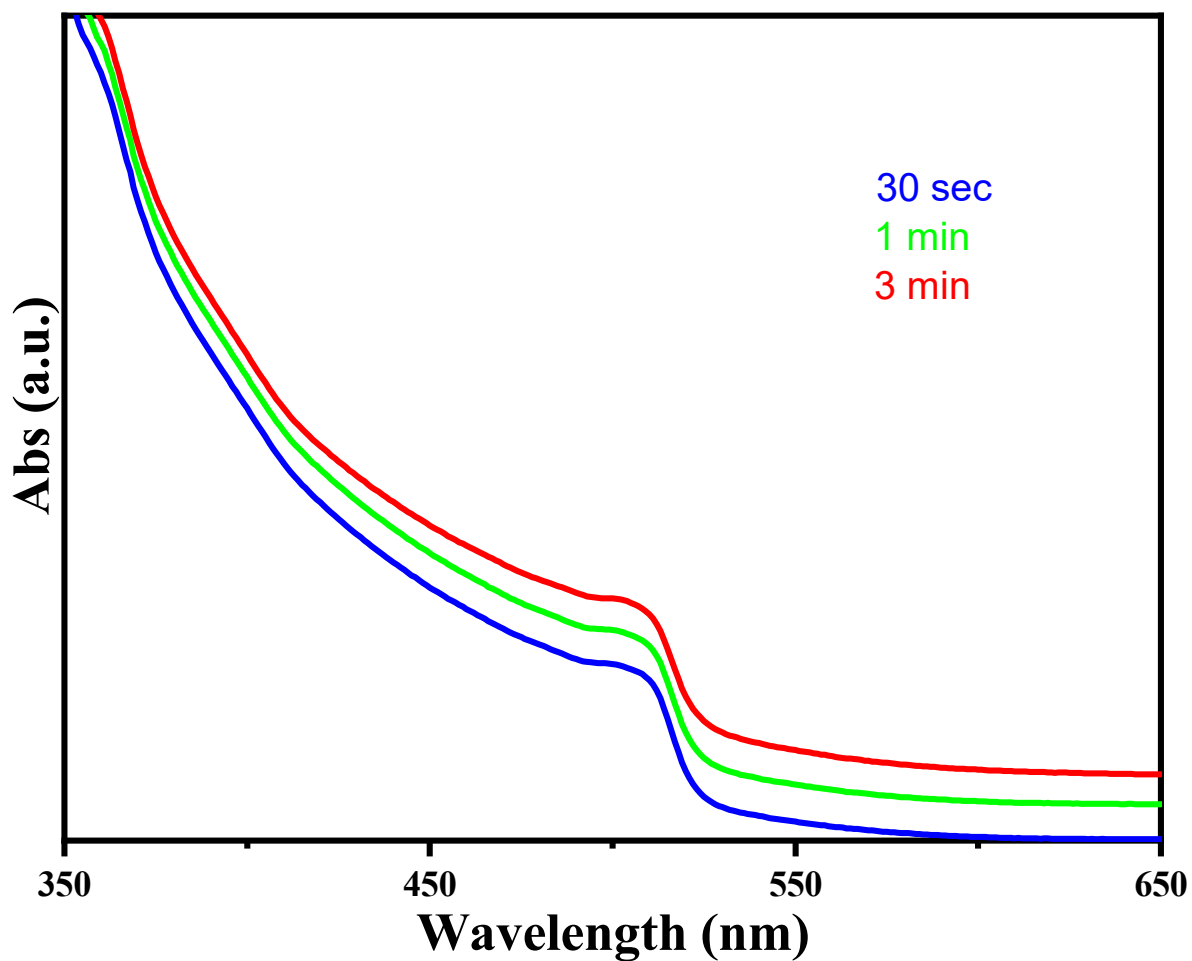


Figure S13. Influence of the reaction time on the formation of the CsPbBr₃-Pb₄S₃Br₂ heterostructures. This figure displays the absorption spectra of some of the samples reported in Figure S12, specifically the samples grown at 30 sec, 1 min and 3 min (see panels a-c of Figure S12). The absorption features remained nearly unchanged, during the time span from 30 sec to 3 min, suggesting that the perovskite NCs formed first (the spectra are dominated by absorption from the perovskite domains), followed by the nucleation and growth of Pb₄S₃Br₂ on top of them.

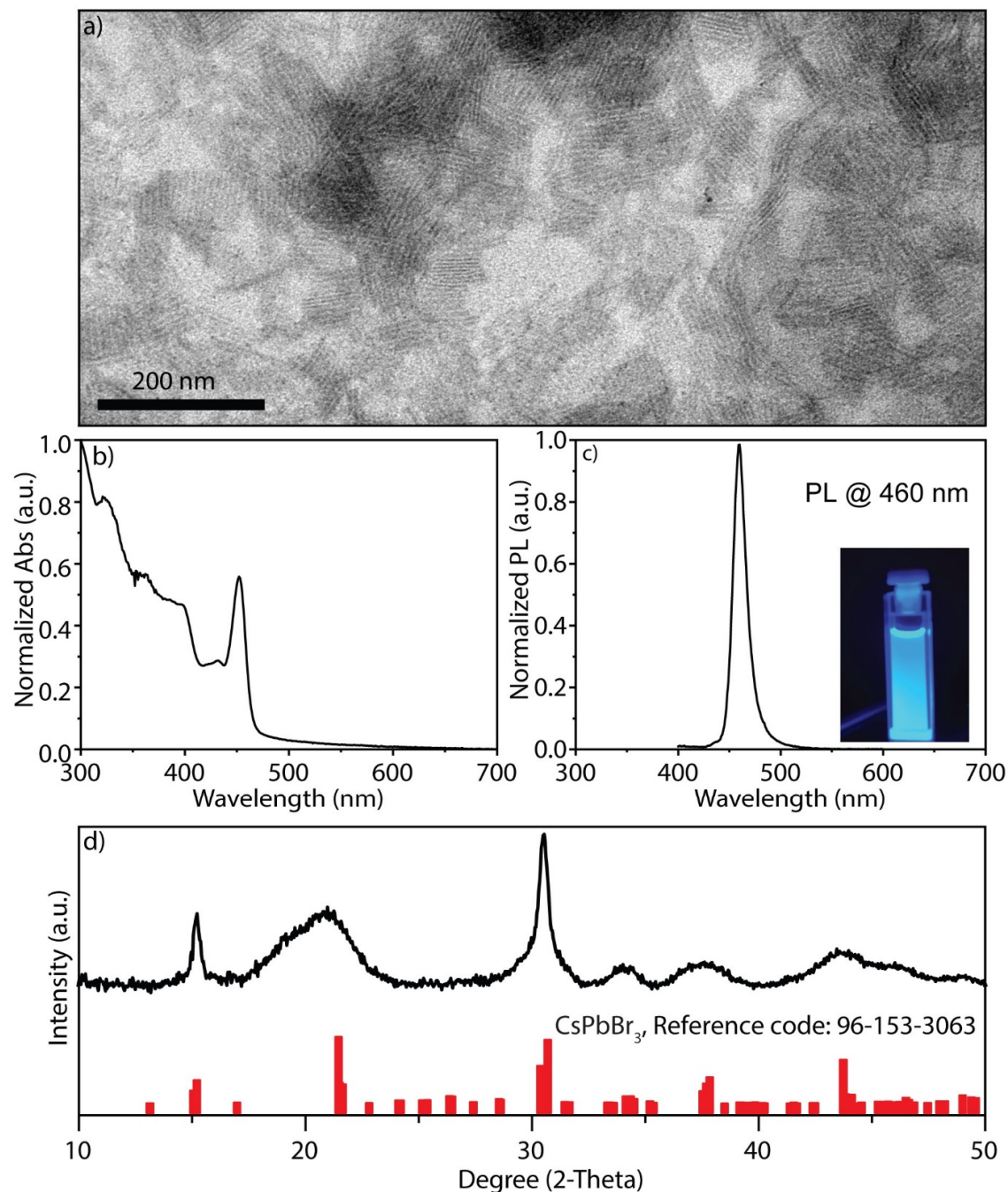


Figure S14. Inhibitor effect of oleylammonium bromide on the formation of the CsPbBr₃-Pb₄S₃Br₂ heterostructures: The experiment was performed under the same conditions as in the synthesis of the CsPbBr₃-Pb₄S₃Br₂ heterostructures of Figures 1b-c and S2-S5, but with the addition of 0.01 mmol OLAM-Br. Representative TEM image of NCs (a), optical absorbance (b) and photoluminescence spectra (c) recorded from colloidal dispersions. XRPD pattern of the corresponding sample along with the bulk reference pattern of the CsPbBr₃ orthorhombic phase (Pnma, COD: 4510745). Basically, no heterostructures were formed in this case, and the product was mainly represented by nanoplatelets/lamellar structures.

Synthesis of CsPbBr₃-Pb₄S₃Br₂ heterostructures by using conventional hot-injection based synthesis routes

Synthesis of CsPbBr₃-Pb₄S₃Br₂ heterostructure nanocrystals by using hot-injection method developed by Protesescu et al.³: In a typical synthesis, 4.0 mL of degassed ODE was added to a 20 mL glass vial under the N₂ and placed on a hot plate that was preset at 180 °C. Then, 500 µL of PbBr₂ solution in ODE (see experimental section in the manuscript for the details) and 20 µL DDT was added into the vials. Thereafter, a mixture of Cs-oleate (100 µL) and S-ODE (100 µL) was swiftly injected and the reaction was allowed to proceed for 3 min. The resulting mixture was centrifuged at 4000 rpm for 5 min. After centrifugation, the supernatant was discarded and the precipitate was dispersed in 4 mL toluene.

Synthesis of CsPbBr₃-Pb₄S₃Br₂ heterostructure nanocrystals by using hot-injection method developed by Imran et al.⁴: In a typical synthesis, 4.0 mL of degassed ODE was added to a 20 mL glass vial under the N₂ and placed on a hot plate that was preset at 180 °C. Then, 500 µL of previously prepared lead oleate (see experimental section for the details), 100 µL Cs-oleate and 20 µL DDT were separately added to the vial. Thereafter, a mixture of benzoyl bromide (0.1 mmol) and S-ODE (100 µL) was swiftly injected and the reaction was allowed to proceed for 3 min. Subsequently, the reaction mixture was cooled down to room temperature and centrifuged at 4000 rpm for 5 min. After centrifugation, the supernatant was discarded and the precipitate was re-dispersed in 4 mL toluene for further use.

Synthesis of CsPbBr₃-Pb₄S₃Br₂ heterostructure nanocrystals by using hot-injection method developed by Dutta et al.⁵: Briefly, 4.0 mL of degassed ODE was added to a 20 mL glass vial under the N₂. Then the vial was heated to 180 °C and 500 µL of PbBr₂ solution, together with 0.02 mmol OLA-Br and 20 µL DDT was added into vial. Thereafter, a mixture of Cs-oleate (100 µL) and S-ODE (100 µL) from previously prepared stock solutions (see experimental section in the manuscript for further details) was swiftly injected and the reaction was allowed to proceed for 3 min. Subsequently, the reaction mixture was cooled down to room temperature and centrifuged at 4000 rpm for 5 min. After centrifugation, the supernatant was discarded and the precipitate was re-dispersed in 4 mL toluene for further use.

The TEM of nanocrystals prepared following these methods are reported in Figure S15.

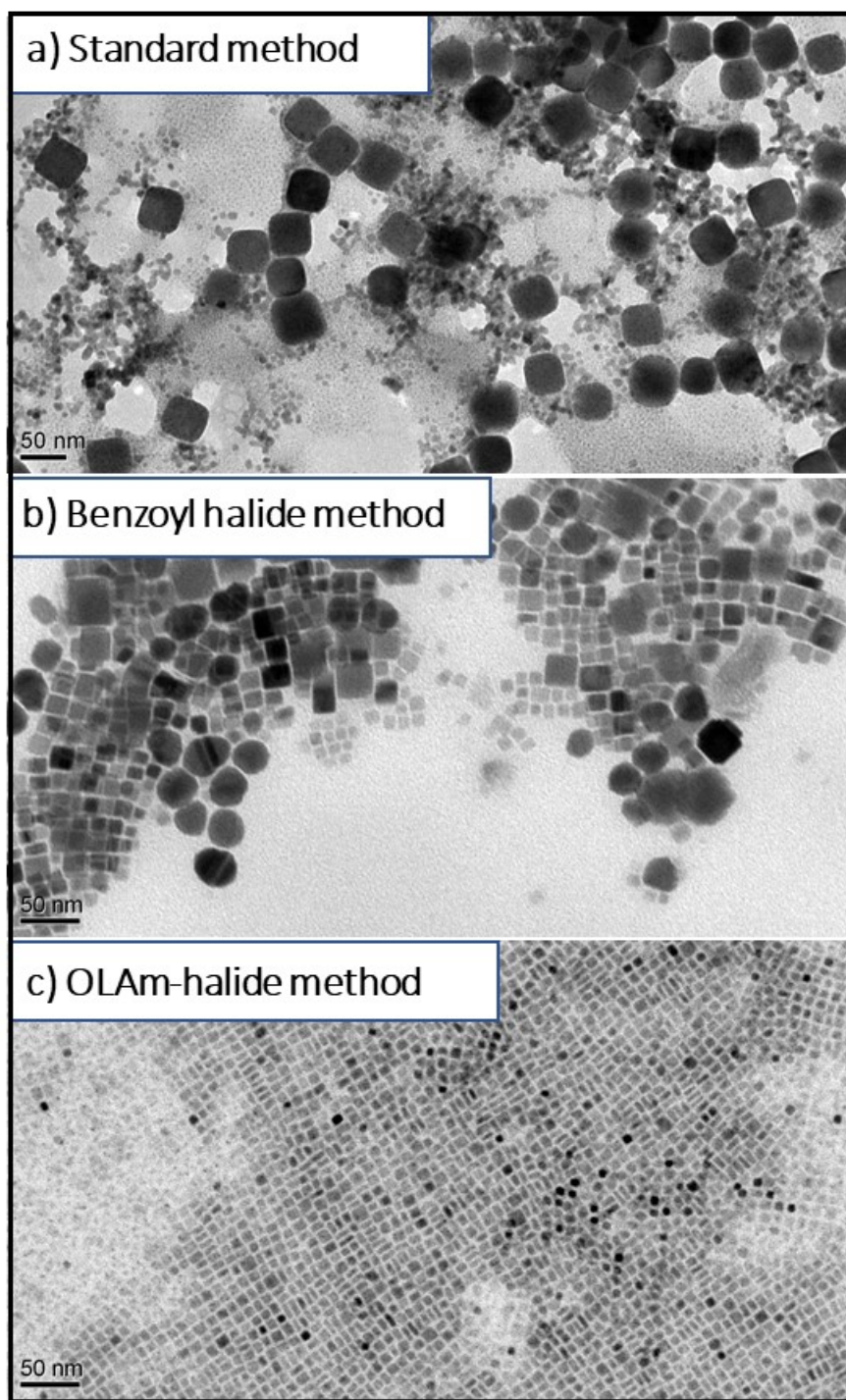


Figure S15. Attempts to synthesize the $\text{CsPbBr}_3\text{-Pb}_4\text{S}_3\text{Br}_2$ heterostructures by using conventional hot injection based methods. The syntheses were performed by using optimized sets of parameters, discussed above in detail. Panel (a) shows the NCs obtained using hot injection approaches developed by (a) Protesescu et al.², (b) Imran et al.³ and (c) Dutta et al.⁴, respectively. All attempts at growing the heterostructures by employing these approaches were not successful, despite using the optimized set of reaction conditions.

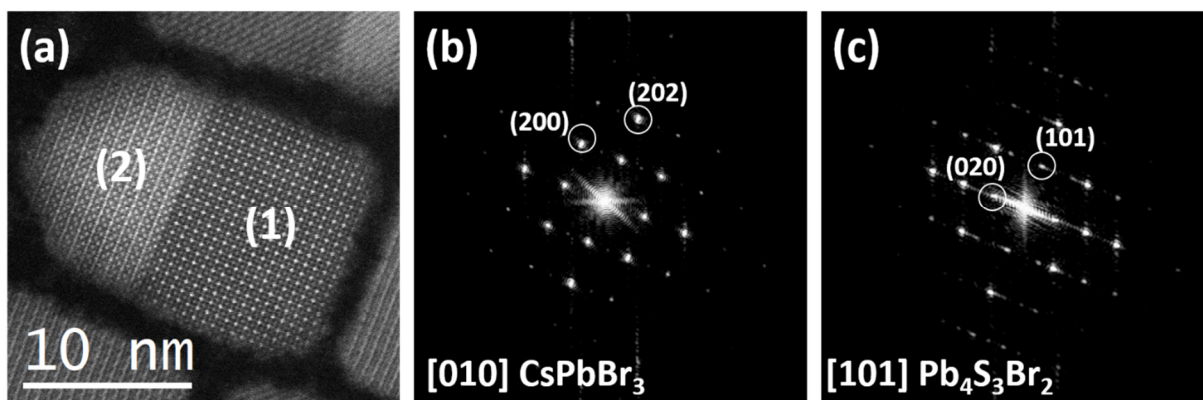


Figure S16. Fourier Transforms (FTs, b-c) of an individual CsPbBr_3 - $\text{Pb}_4\text{S}_3\text{Br}_2$ heterostructure (a). A detailed analysis of the interfaces and column intensities on the same heterostructure is reported in Figure 2 of the manuscript. FT analysis of the region (1) and the region (2) reveals that the $\text{Pb}_4\text{S}_3\text{Br}_2$ domain has grown on the (101)/(010) facets of the CsPbBr_3 (FTs of the corresponding domains are reported in panel (b) and (c)).

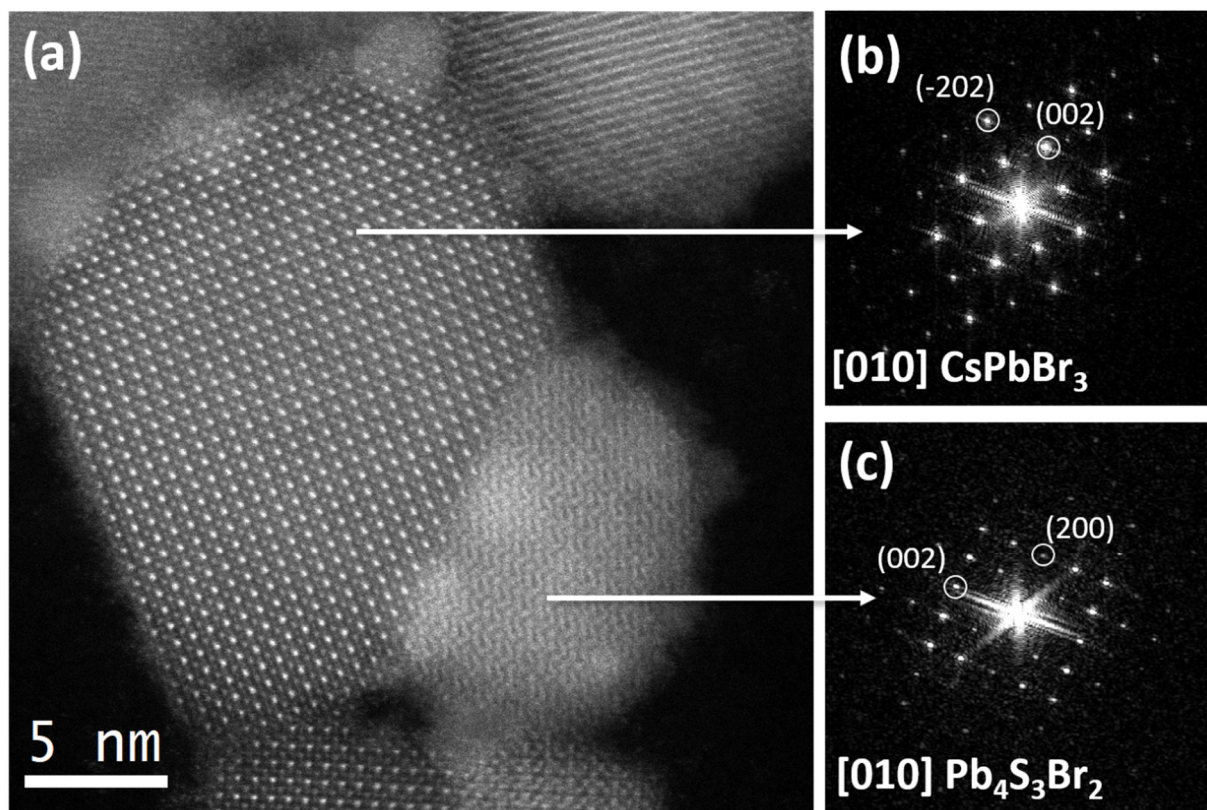


Figure S17. (a) HRSTEM image of a single CsPbBr_3 - $\text{Pb}_4\text{S}_3\text{Br}_2$ heterostructure with a different orientation relationship between the two domains compared to the case of Figure S16. The FT analysis shows that both CsPbBr_3 (b) and $\text{Pb}_4\text{S}_3\text{Br}_2$ (c) domains are oriented in the $[010]$ direction and $\text{Pb}_4\text{S}_3\text{Br}_2$ grows on the (001) facets of CsPbBr_3 .

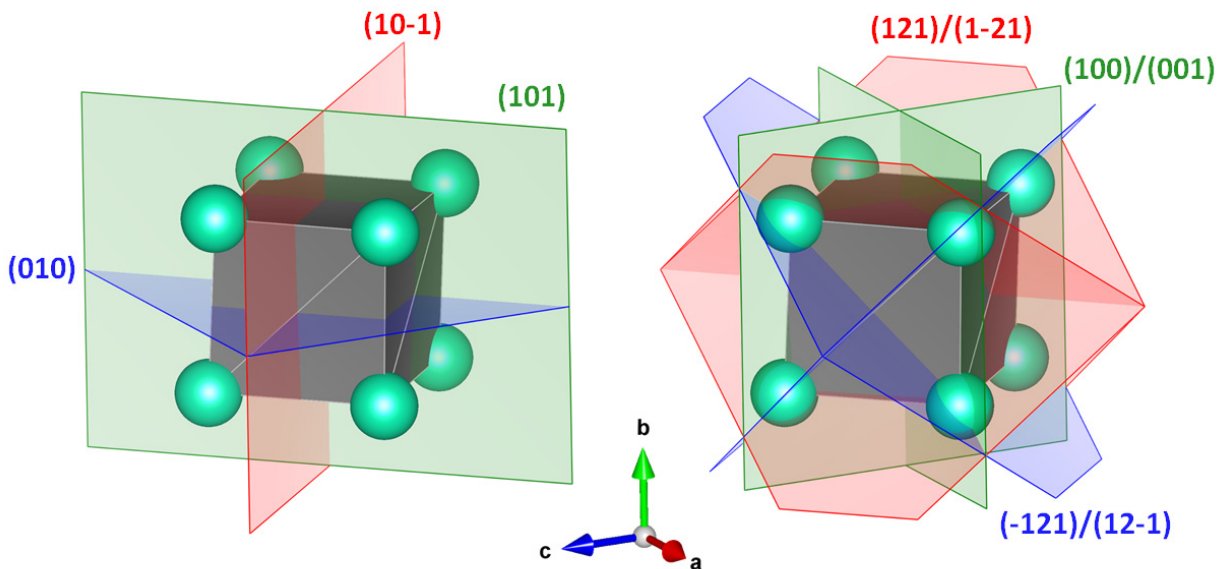


Figure S18: Illustration clarifying the orientations of crystal planes mentioned in the main text with respect to the crystallographic axes, the pseudo-cubic CsPbBr_3 unit cell (represented by the cyan cesium atoms) and the perovskite nanocrystal (represented by the grey cube). Planes parallel to the nanocrystal facets are shown on the left, those cutting the crystal edges are shown on the right. Given the CsPbBr_3 space group (the orthorhombic Pnma), planes within the same illustration are not equivalent one to the other from a crystallographic point of view. However, the distortion from the ideal cubic symmetry, in which they would be equivalent, is very small. For this reason distinguishing between them would be challenging, and since the differences are too small to affect their chemical behavior, this is beyond the scope of this work. Thus, we referred to the planes on the left as $(010)/(101)$, and to the planes on the right as $\{100\}/\{121\}$ for simplicity.

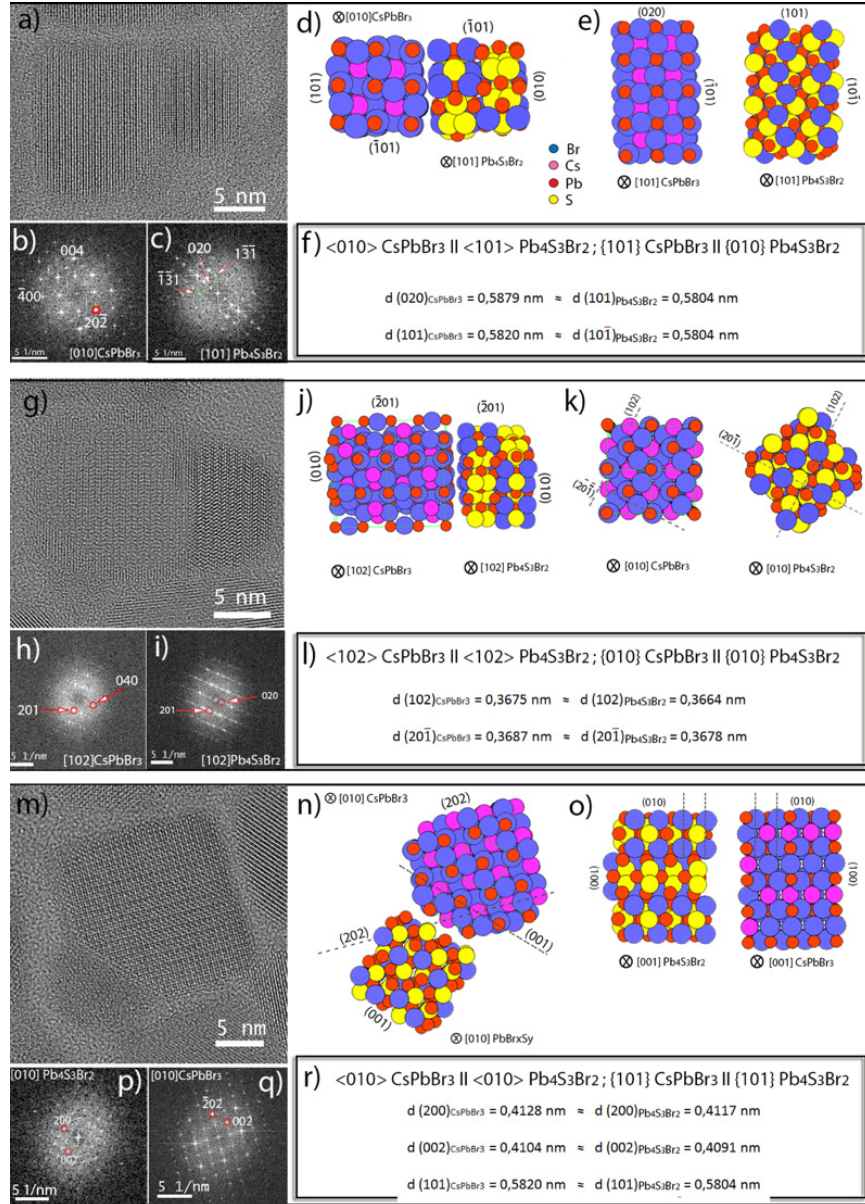


Figure S19. HRTEM characterization of the CsPbBr₃-Pb₄S₃Br₂ heterostructures and orientation relationships between (OR) the CsPbBr₃ and Pb₄S₃Br₂ domains. Three ORs between the CsPbBr₃ and Pb₄S₃Br₂ have been identified. Most commonly observed OR involved Pb₄S₃Br₂ domains growing on the {101} planes of the perovskite, as shown in HRTEM image in a). The CsPbBr₃ domain was in the [010] orientation (the corresponding FT is indexed in b)) while the Pb₄S₃Br₂ domain was in the [101] orientation with respect to the viewing direction (the corresponding FT is indexed in c)). The structural model of the two domains as observed experimentally is presented in d) with the view on the interface planes of the two domains shown in e). This OR between ensured almost no mismatch between the two domains of different structures, as indicated in f). A similar analysis is presented in g) to l) where Pb₄S₃Br₂ domains were found to grow on {010} facets perovskite structure. The least frequently observed OR involved Pb₄S₃Br₂ domains growing on the {001} planes of the CsPbBr₃ crystals (the analysis is shown in the panels from m) to r).

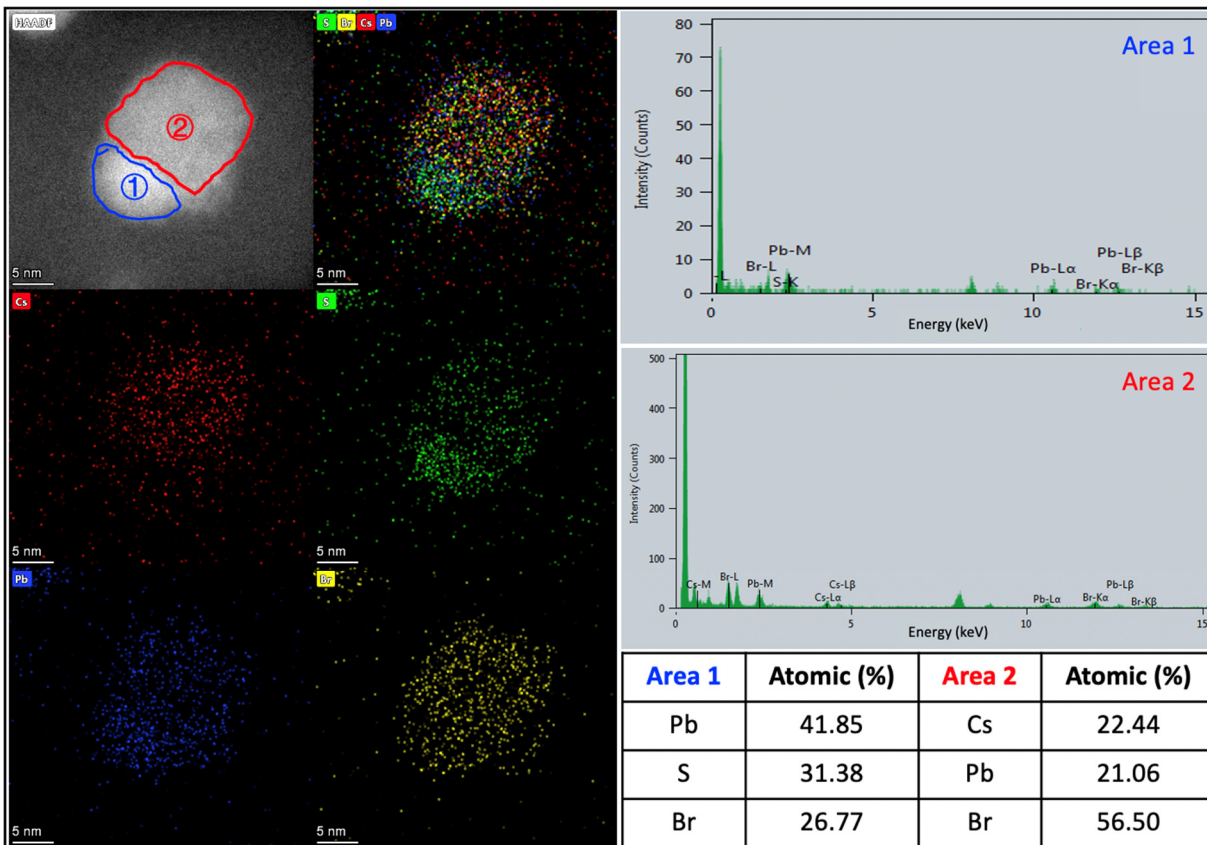


Figure S20. HAADF-STEM EDS analysis of the $\text{CsPbBr}_3\text{-Pb}_4\text{S}_3\text{Br}_2$ NCs: EDS analysis of the individual heterostructures evidenced uniform distribution of the corresponding elements in the respective domains and returned elemental ratios of Cs:Pb:Br equal to 1.05:1:2.7 for the perovskite domain, and of Pb:S:Br equal to 4:2.95:2.57 for the lead chalcobromide domain.

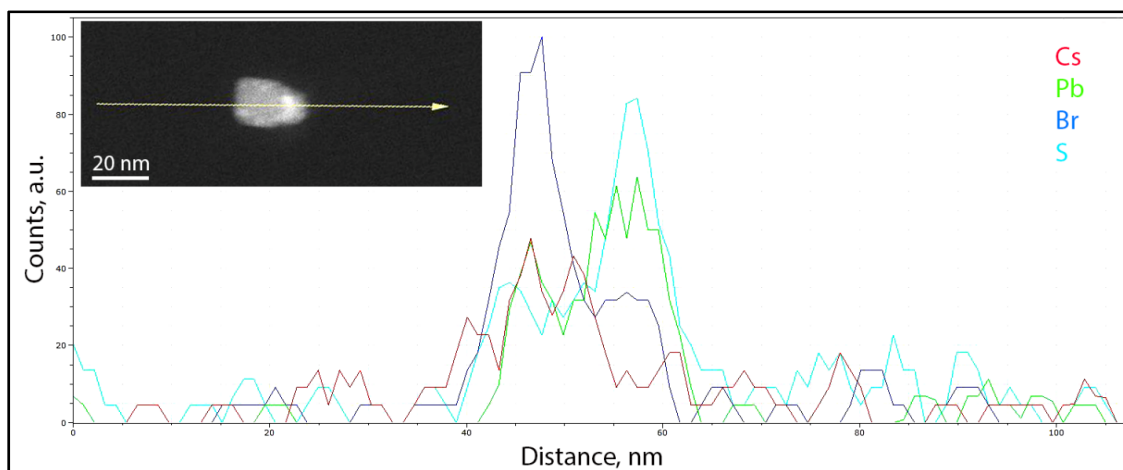


Figure S21. EDX line scan showing the distribution of Cs, Pb, Br and S across a single $\text{CsPbBr}_3\text{-Pb}_4\text{S}_3\text{Br}_2$ heterostructure (STEM image before the scan is provided in inset) with the perovskite domain on the left and the $\text{Pb}_4\text{S}_3\text{Br}_2$ domain on the right. The EDX line scans were collected using a short acquisition time (typically within less than 20 seconds) in order to minimize the effects of electron beam damage on the sample and stage drift.

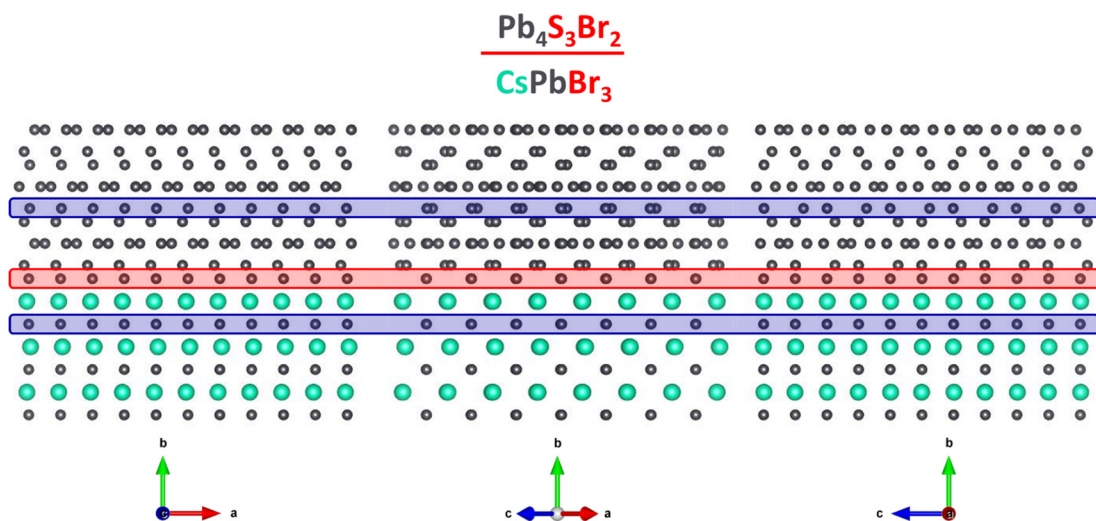


Figure S22. Model of the cationic (Cs and Pb) sublattices of the CsPbBr_3 - $\text{Pb}_4\text{S}_3\text{Br}_2$ heterostructure in three different projections, highlighting that the shared planes of Pb atoms remain unaltered across both domains, corroborating the formation of an epitaxial interface between the chalcogenide and the perovskite structures.

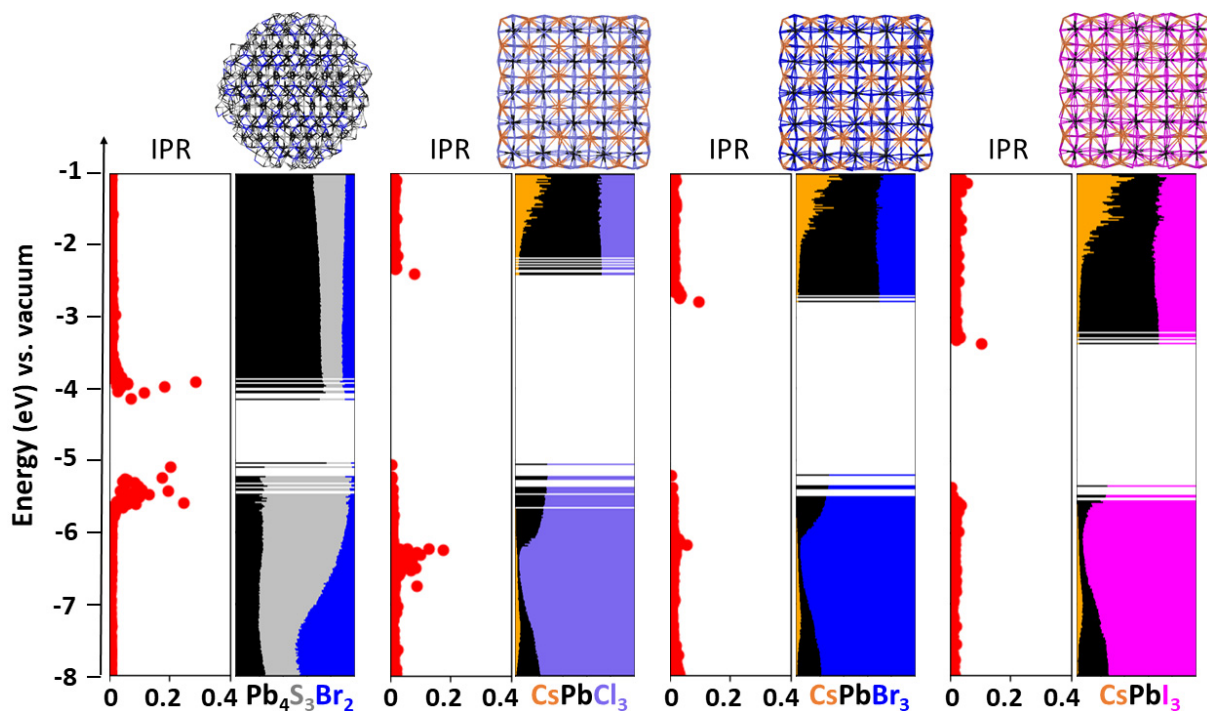


Figure S23. Electronic structure and IPR plots of a) a spherical $\text{Pb}_{548}\text{S}_{423}\text{Br}_{250}$ NC model of about 4.2 nm in diameter, b) three cubic $\text{Cs}_{200}\text{Pb}_{125}\text{X}_{450}$ NC models of about 3.2 nm in size featuring $\text{X}=\text{Cl}$, $\text{X}=\text{Br}$ and $\text{X}=\text{I}$ respectively computed at the DFT/PBE level of theory. Each orbital is decomposed by colors according to the contribution of each atom type.

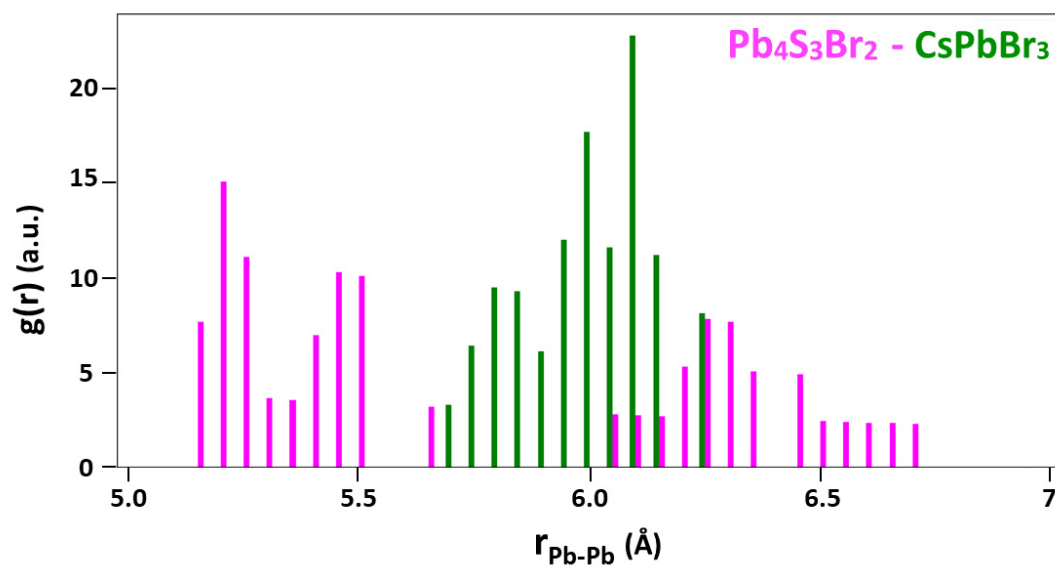


Figure S24. Radial distribution function between Pb ions at the interface of the $\text{Pb}_4\text{S}_3\text{Br}_2$ - CsPbBr_3 heterostructure model computed for (magenta) the $\text{Pb}_4\text{S}_3\text{Br}_2$ interfacial layer, and (green) the CsPbBr_3 Pb-rich interfacial layer.

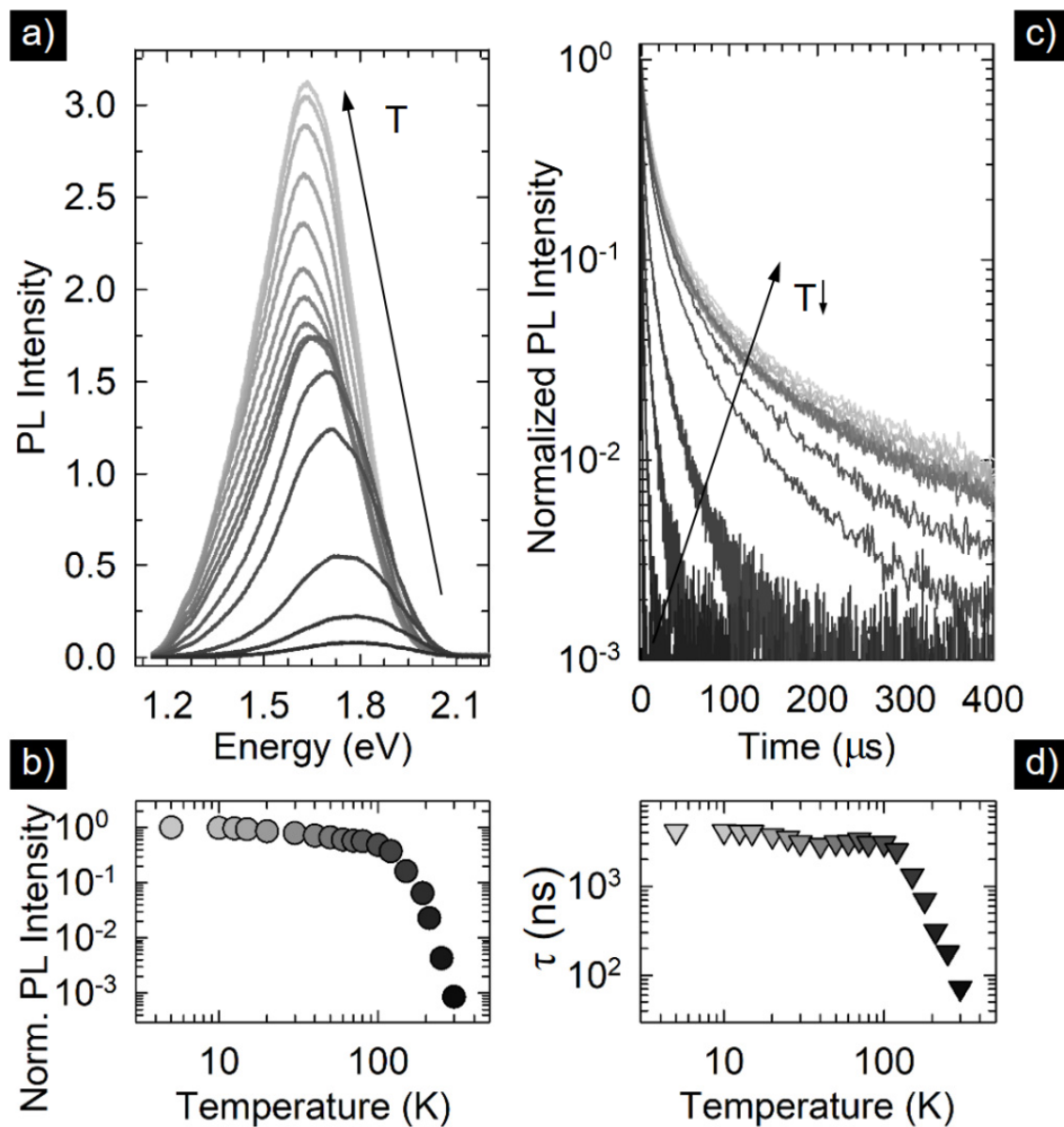


Figure S25. (a) PL spectra of $\text{Pb}_4\text{Br}_3\text{S}_2$ NCs upon lowering the temperature from $T=300$ K down to $T=5$ K (from black to light grey curves, respectively). (b) Integrated PL intensity values as a function of temperature extracted from the PL spectra reported in 'a' and normalized to the value at $T=5$ K. (c) Time-resolved PL traces of $\text{Pb}_4\text{Br}_3\text{S}_2$ NCs upon lowering the temperature from $T=300$ K to $T=5$ K (from black to light grey curves, respectively). (d) Temperature dependence of the effective PL decay lifetimes (τ , evaluated as the time after which the PL intensity drops by a factor of e) extracted from the PL decay curved reported in 'c'.

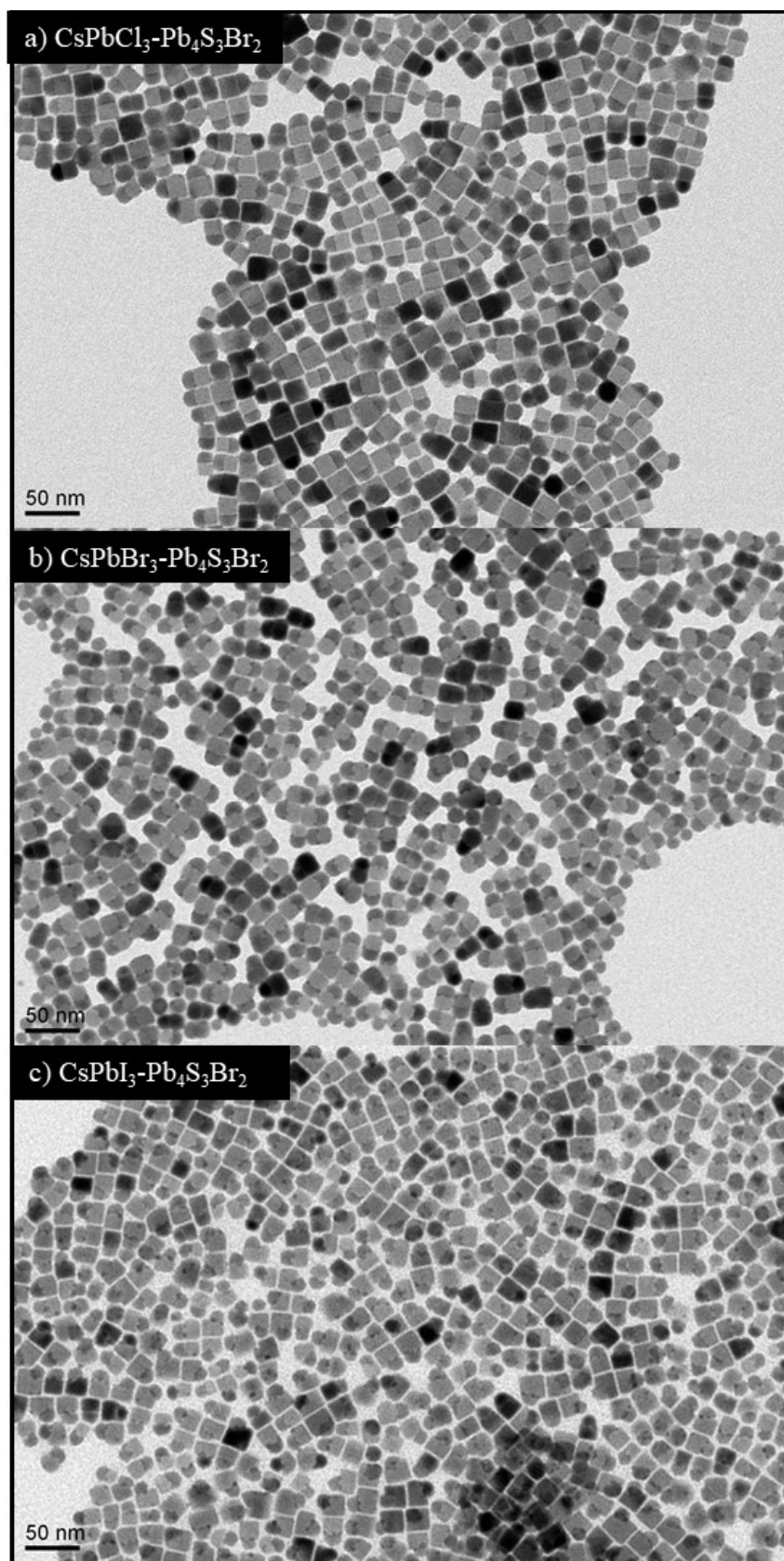


Figure S26. Representative TEM images of $\text{CsPbCl}_3\text{-Pb}_4\text{S}_3\text{Br}_2$ heterostructures (a) and $\text{CsPbI}_3\text{-Pb}_4\text{S}_3\text{Br}_2$ heterostructures (c) prepared by anion exchanged reactions starting from the $\text{CsPbBr}_3\text{-Pb}_4\text{S}_3\text{Br}_2$ heterostructures (b) (see the experimental section in the main text for the details about anion exchange reactions).

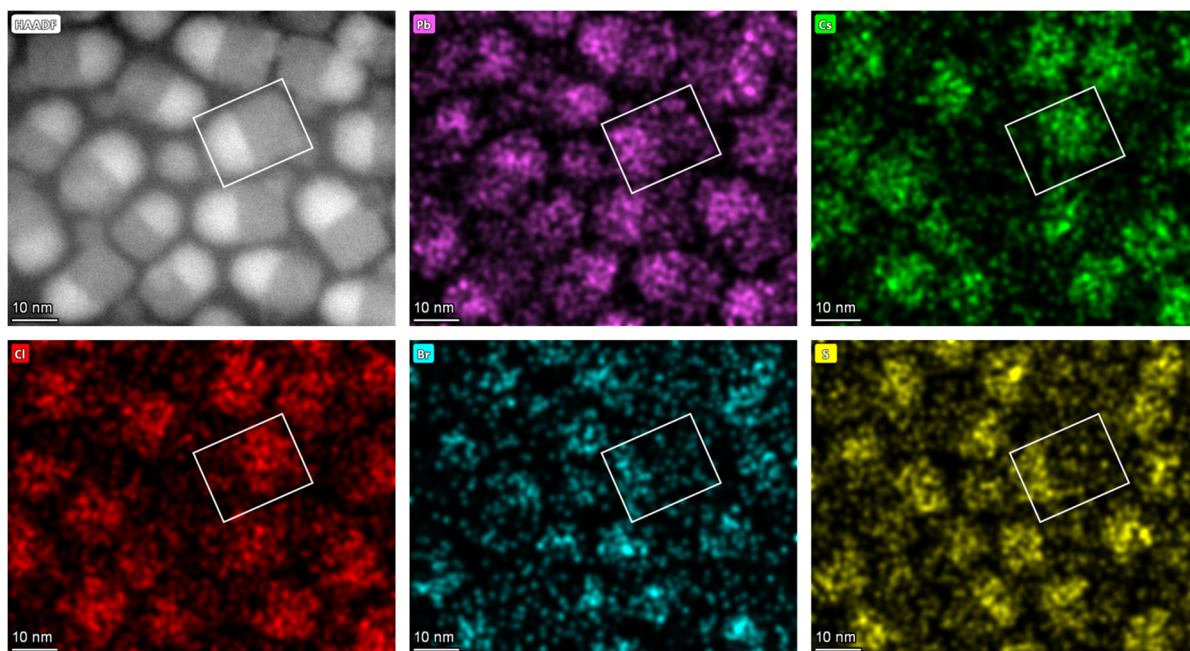


Figure S27. HAADF-STEM image and the corresponding EDX mapping of a group of $\text{CsPbCl}_3\text{-Pb}_4\text{S}_3\text{Br}_2$ heterostructures (obtained from $\text{CsPbBr}_3\text{-Pb}_4\text{S}_3\text{Br}_2$ heterostructures by anion exchange reaction with Cl^- ions). The maps point to a clear segregation of the Cl and the Br signals in the two domains of the heterostructures (Figure S26), with Cl preferentially segregated in the perovskite domain and Br in the chalcogenide domain, suggesting a $\text{CsPbCl}_3\text{-Pb}_4\text{S}_3\text{Br}_2$ composition for the heterostructure.

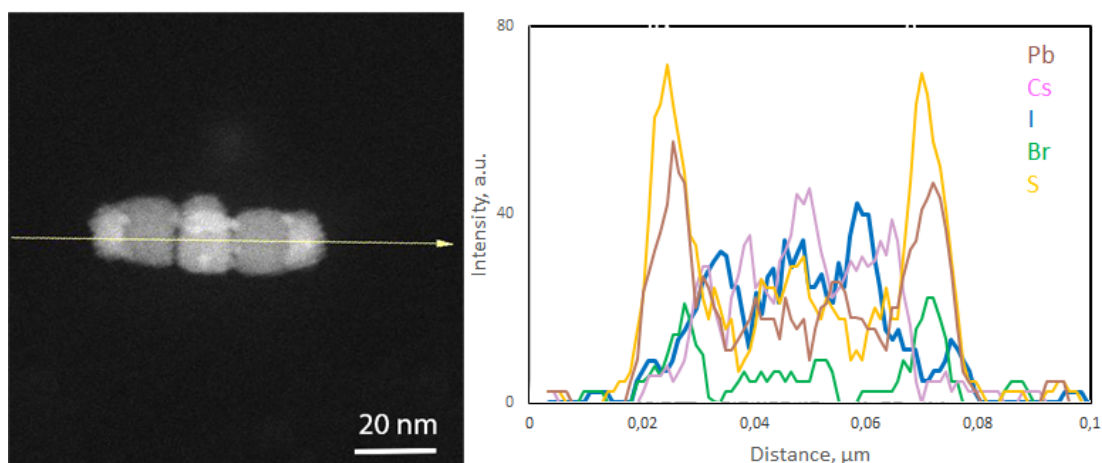


Figure S28. (left) HAADF-STEM image of a group of three $\text{CsPbI}_3\text{-Pb}_4\text{S}_3\text{Br}_2$ heterostructures (obtained from the $\text{CsPbBr}_3\text{-Pb}_4\text{S}_3\text{Br}_2$ heterostructures by anion exchange reaction with I^- ions) and (right) results from the corresponding EDS scan. The scans show the distribution of Cs, Pb, Br, I and S across the heterostructures. The S and Br were found to be localized mainly in the higher contrast domains, in line with a retention of the $\text{Pb}_4\text{S}_3\text{Br}_2$ composition in those domains. The lower contrast domains, corresponding to the initial CsPbBr_3 phase, contained predominantly signal from I and much less from Br, in line with a selective anion exchange reaction in those domains, which had transformed them from CsPbBr_3 to primarily CsPbI_3 . The EDX line scans were collected in a very short acquisition time (typically within less than 20 seconds) in order to minimize the effects of electron beam damage on the sample and stage drift.

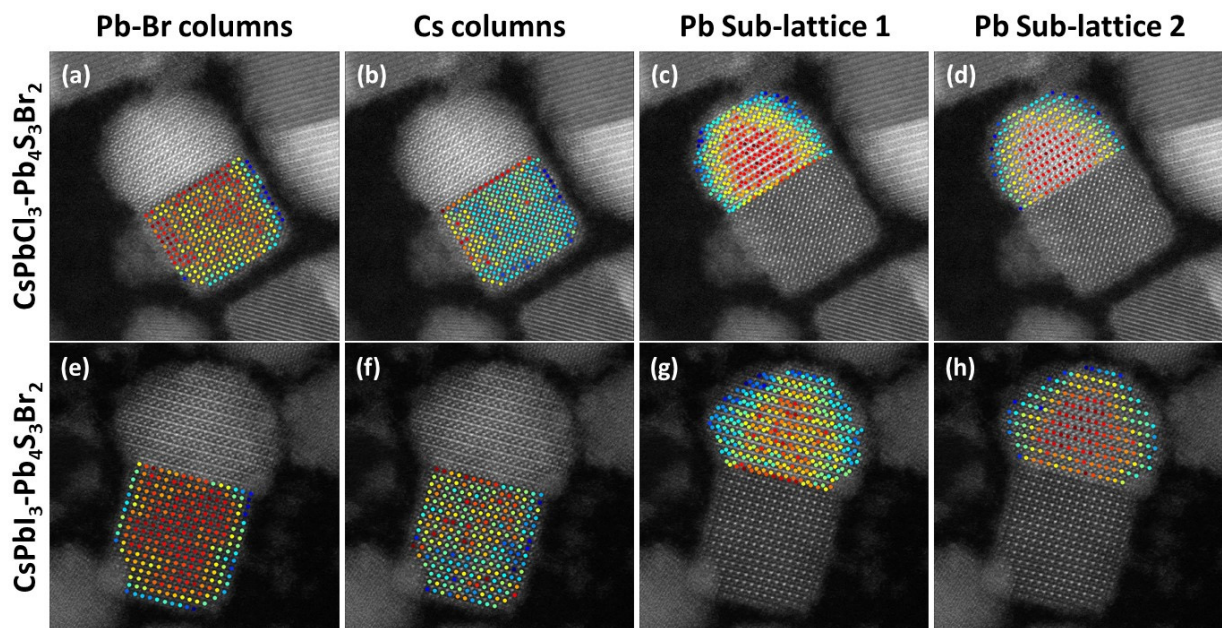


Figure S29. Structural analysis of a single CsPbCl₃-Pb₄S₃Br₂ heterostructure (top panels) and CsPbI₃-Pb₄S₃Br₂ heterostructure (bottom panels). (a-b) Column intensity map of Pb-Br columns (a) and Cs columns (b) of the perovskite phase for the CsPbCl₃-Pb₄S₃Br₂ heterostructure. Panels (c) and (d) represent the intensity maps of Pb columns (sub-lattices 1 and 2) belonging to the Pb₄S₃Br₂ domain of the same heterostructure. (e-f) Column intensity map of Pb-Br (e) columns and Cs columns (f) of the perovskite phase for the CsPbI₃-Pb₄S₃Br₂ heterostructure. Panels (g) and (h) represent the intensity maps of Pb columns (sub-lattices 1 and 2) belonging to the Pb₄S₃Br₂ domain for the same heterostructure.

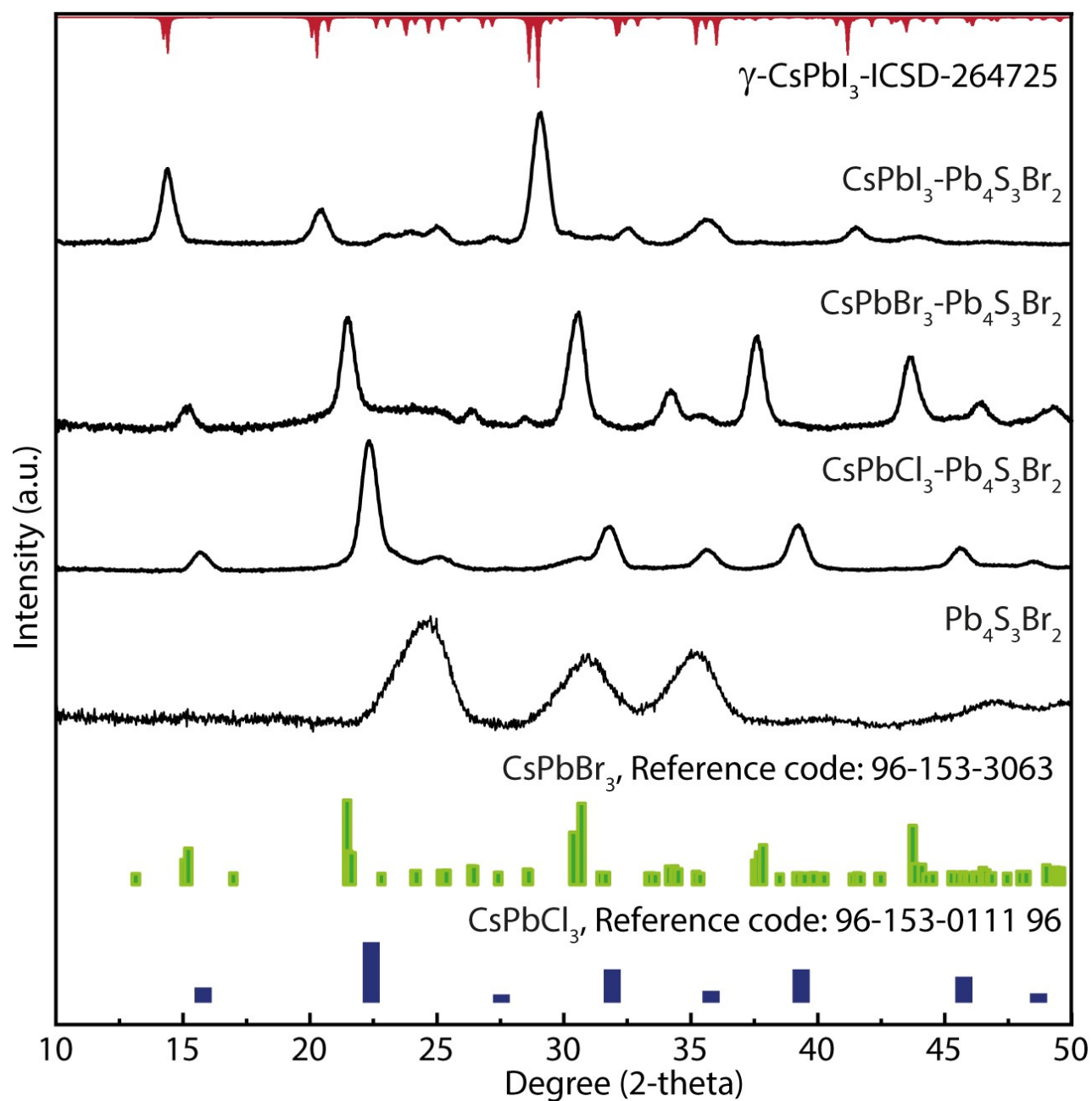


Figure S30. The XRPD patterns of CsPbBr₃-Pb₄S₃Br₂ heterostructures and of the samples after anion exchange with Cl⁻ and I⁻ ions, respectively. For the comparison, the XRPD pattern of Pb₄S₃Br₂ is also reported along with the bulk diffraction patterns for the cubic CsPbCl₃, orthorhombic CsPbBr₃ and CsPbI₃ phases.

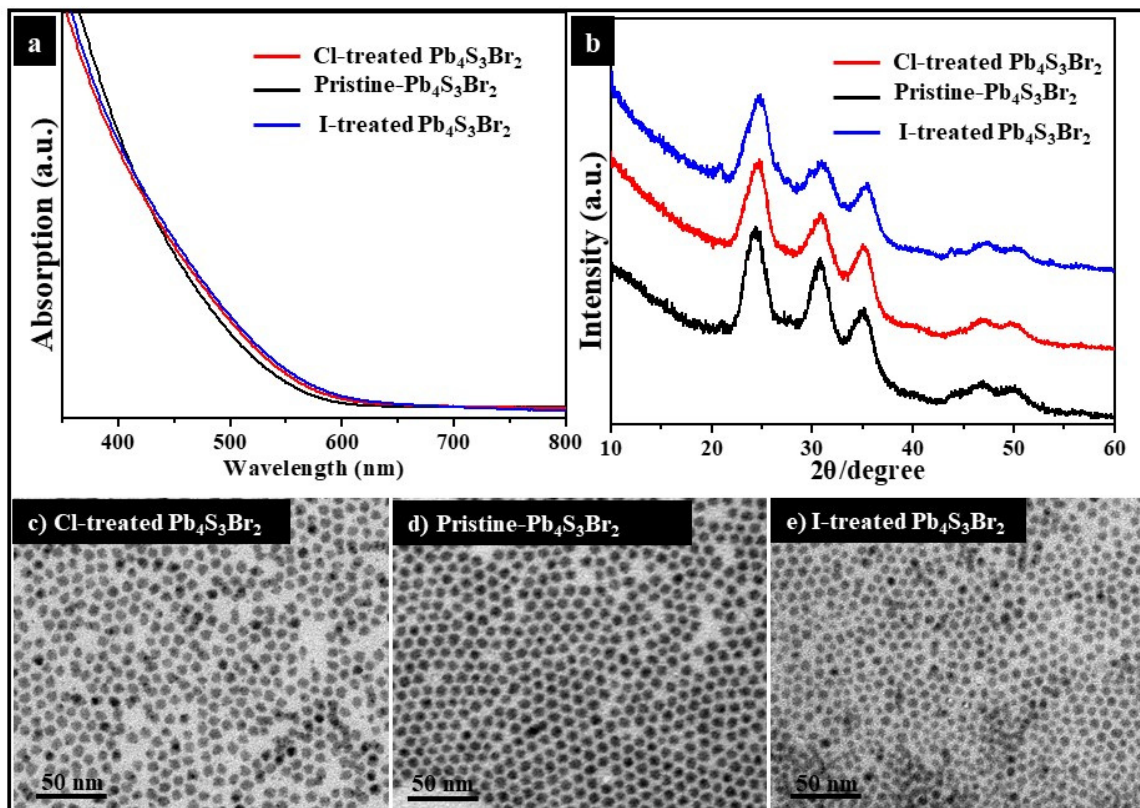


Figure S31. Anion exchange attempts on $\text{Pb}_4\text{S}_3\text{Br}_2$ NCs: Panel (a) shows the absorption spectra of the starting $\text{Pb}_4\text{S}_3\text{Br}_2$ NCs (black) and after treatment with chloride and iodide precursors (red and blue) respectively. XRPD patterns of the starting $\text{Pb}_4\text{S}_3\text{Br}_2$ NCs and of the chloride and iodide treated samples (b). TEM images of $\text{Pb}_4\text{S}_3\text{Br}_2$ NCs (d) and after treatment with the chloride (c) and iodide (e) ions, respectively.

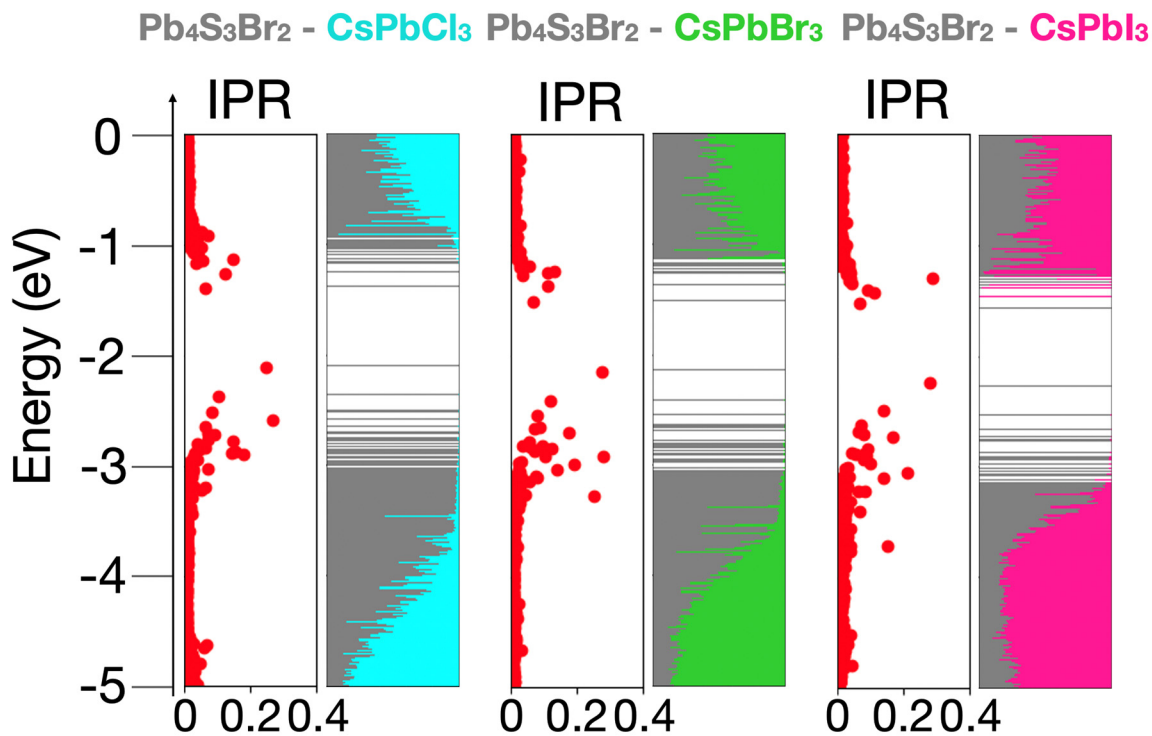


Figure S32. Electronic structure and IPR plots of the three $\text{Pb}_4\text{S}_3\text{Br}_2$ - CsPbX_3 heterostructure NC models, with $\text{X}=\text{Cl}$, $\text{X}=\text{Br}$ and $\text{X}=\text{I}$ respectively, computed at the DFT/PBE level of theory. Here the color code indicates the contribution of each moiety type to each molecular orbitals.

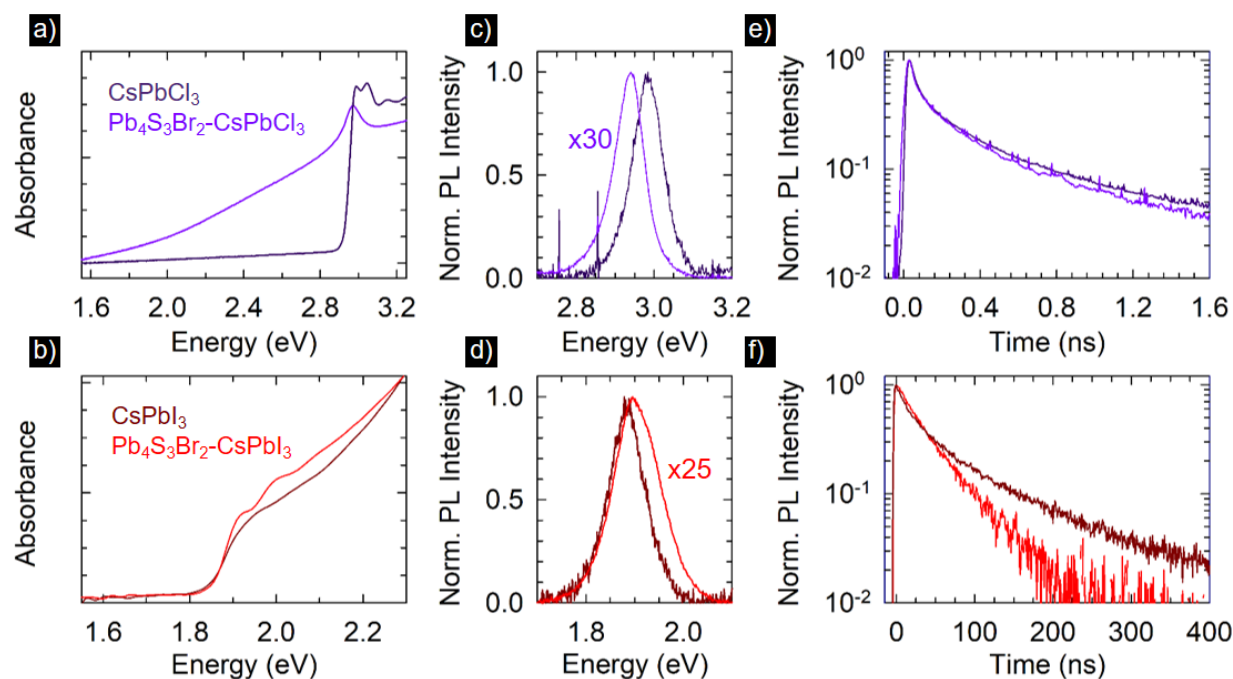


Figure S33. Absorption spectra of (a) CsPbCl₃ NCs and CsPbCl₃-Pb₄Br₃S₂ heterostructures (blue and purple, respectively) and (b) CsPbI₃ NCs and CsPbI₃-Pb₄Br₃S₂ heterostructures (dark and light red, respectively). PL spectra of (c) the chloride and (d) iodide-based samples. The spectra of the respective heterostructures have been multiplied as indicated. Normalized PL decay traces of (e) CsPbCl₃ NCs and CsPbCl₃-Pb₄Br₃S₂ heterostructures and (f) CsPbI₃ NCs and CsPbI₃-Pb₄Br₃S₂ heterostructures. The color scheme is the same for all panels. All measurements were performed on toluene dispersions at room temperature.

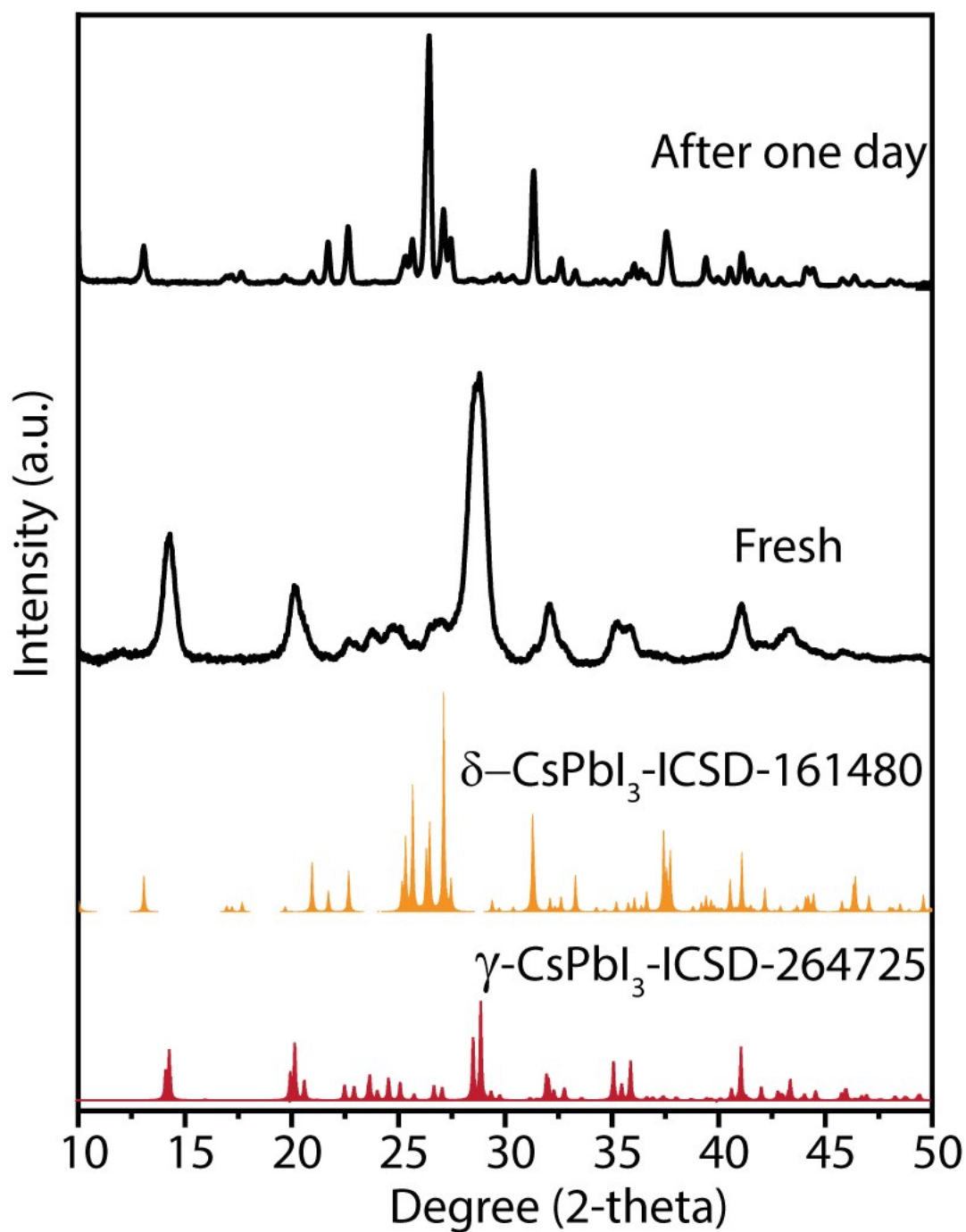


Figure S34. XRPD patterns of CsPbI₃ NCs, freshly prepared and after one day of aging under air. The phase transformation from the “black” γ -CsPbI₃ to non-emitting “yellow” phase δ -CsPbI₃ occurred within one day. The CsPbI₃ NCs were obtained by anion exchange reaction from the CsPbBr₃ NCs (see experimental section of the manuscript for further details).

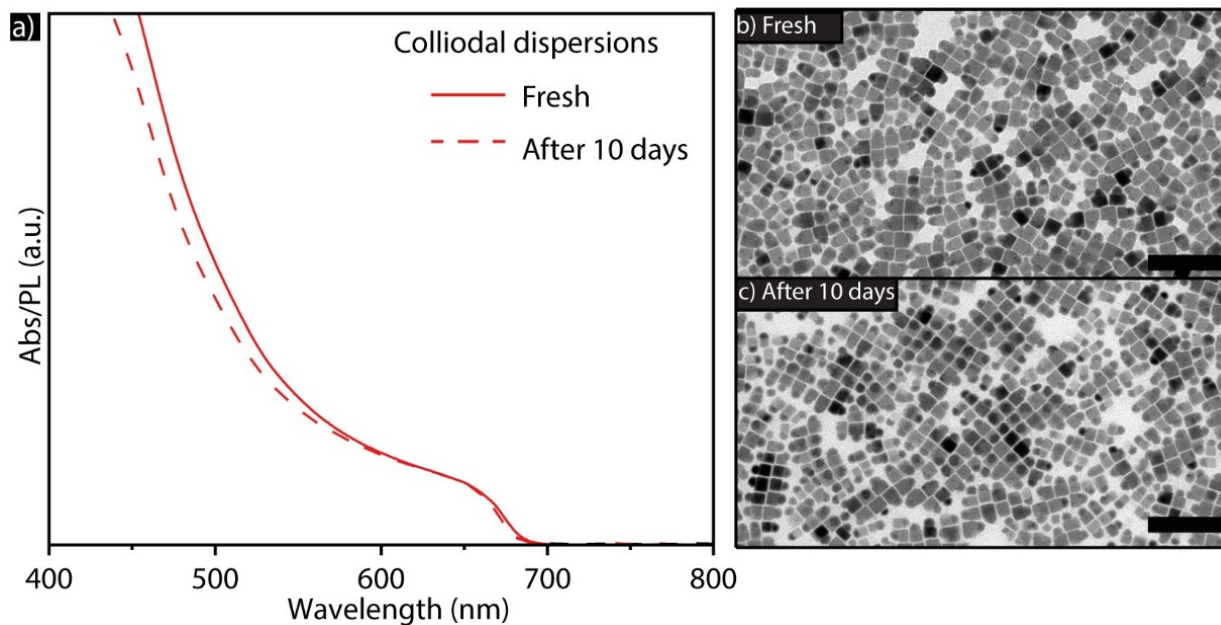


Figure S35. (a) Optical absorbance spectra of toluene dispersions of CsPbI₃-Pb₄S₃Br₂ heterostructures as prepared (fresh) and after 10 days of aging under air in closed vials. (b-c) The corresponding TEM images of the CsPbI₃-Pb₄S₃Br₂ heterostructures before and after aging (scale bars are 100 nm in both images).

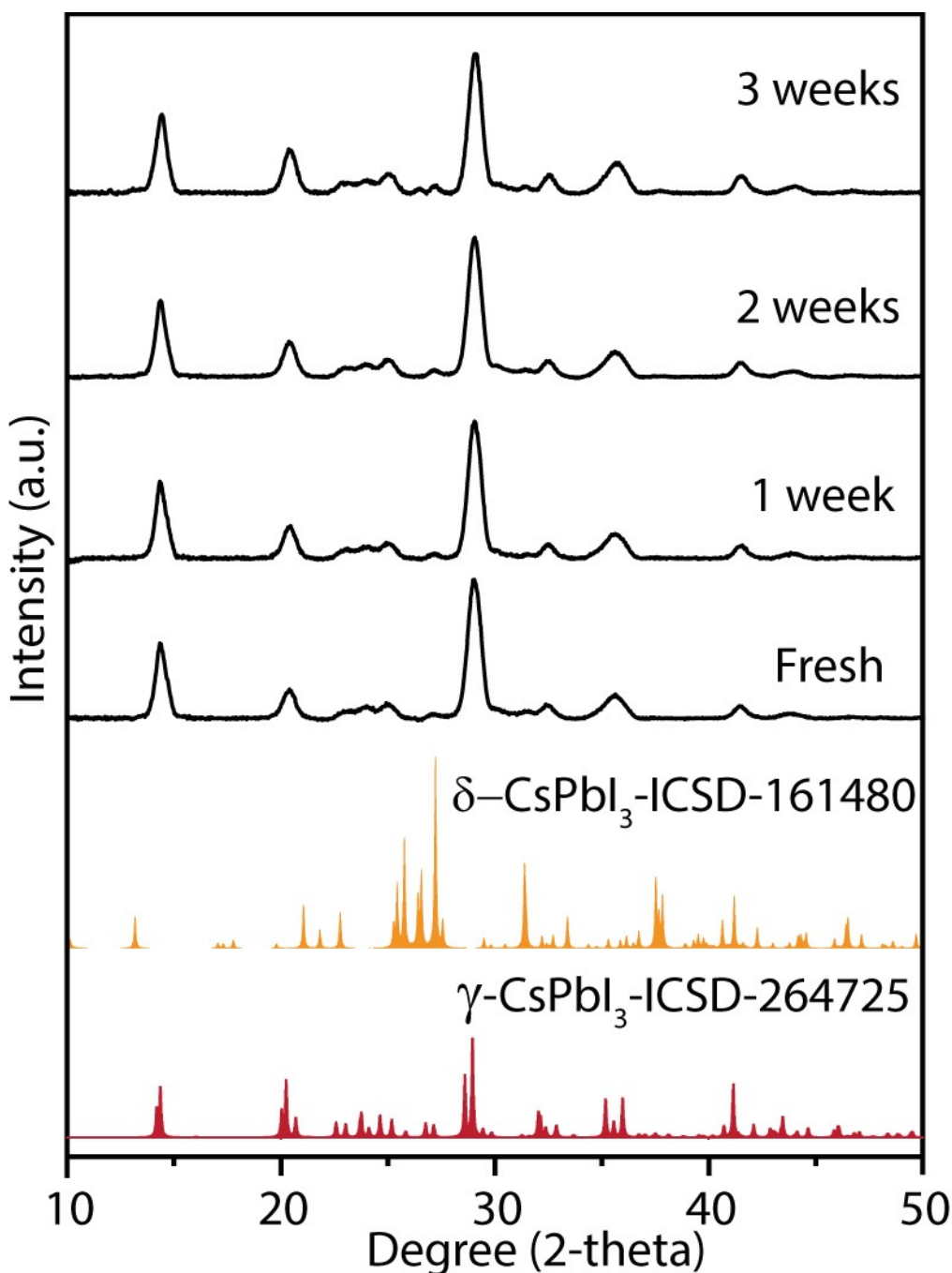


Figure S36. XRPD patterns of CsPbI₃-Pb₄S₃Br₂ heterostructures recorded over time along with the bulk diffraction patterns for the “black” γ -CsPbI₃ and non-emitting “yellow” phase δ -CsPbI₃. The colloidal dispersions of CsPbI₃-Pb₄Br₃S₂ heterostructures were drop-cast on zero-diffraction silicon wafers and the XRPD patterns were acquired over a time span of three weeks on the same film. No additional diffraction belonging to the δ -CsPbI₃ phase were observed even after 3 weeks of aging under air. We attribute the increase in stability of

the “black” γ -CsPbI₃ phase to the formation of an epitaxial interface between the perovskite and the chalcogenide domains.

Pb-sublattices matching at the perovskite-chalcogenide interface for the CsPbBr₃-Pb₄S₃Br₂ and CsPbI₃-Pb₄S₃Br₂ heterostructures

When compared, the CsPbBr₃-Pb₄S₃Br₂ and CsPbI₃-Pb₄S₃Br₂ heterostructures are actually very similar. There is only a better lattice matching in the case of the CsPbBr₃-Pb₄S₃Br₂ heterostructure, due to a closer similarity in bond lengths between CsPbBr₃ and Pb₄S₃Br₂. This can be evaluated by comparing the average first-neighbor Pb-Pb distances for the perovskite and the chalcogenide domains in both heterostructures. The difference is only 0.3% for CsPbBr₃-Pb₄S₃Br₂ and increases to 5.6% in CsPbI₃-Pb₄S₃Br₂. Even in the second case, the mismatch is small enough to allow the formation of the heterostructure, especially given the short spatial extension of the heterojunction layer. When instead evaluating the improved stability of the perovskite polymorph of CsPbI₃ in the CsPbI₃-Pb₄S₃Br₂ heterostructure, we should better compare the stability of our junction with that of a hypothetical “yellow-phase” δ -CsPbI₃-Pb₄S₃Br₂ heterostructure. This second heterostructure is extremely unlikely to exist: our observations demonstrate that the junction is based on the sharing of a plane of lead ions which produce a square pattern, as shown in Figure 3 of the manuscript (reproduced below for clarity). Such a squared plane of leads is not found in δ -CsPbI₃. Our conclusion is that the transformation of black CsPbI₃ into its yellow polymorph is impossible without disrupting the heterostructure.

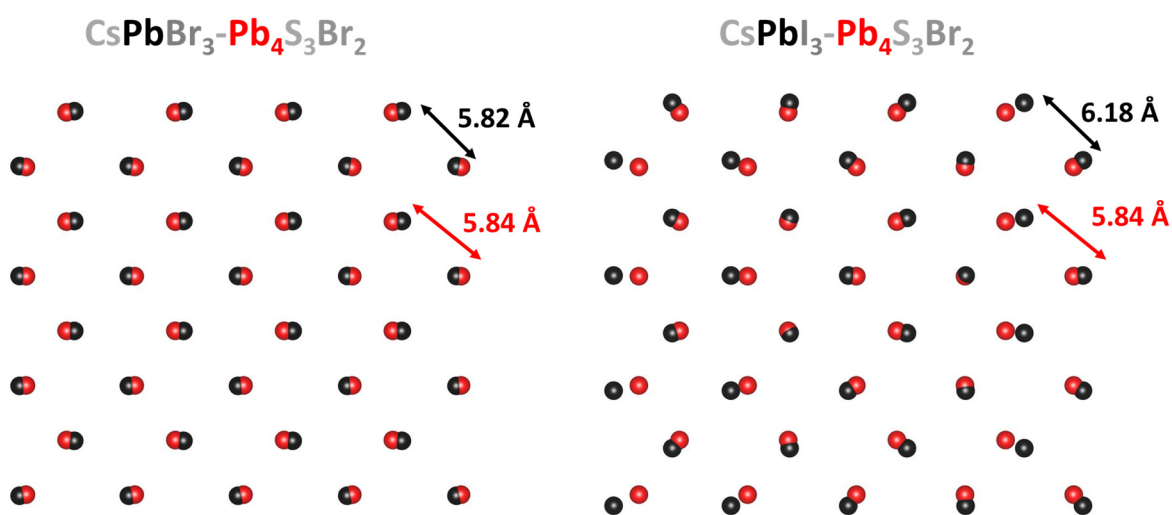


Figure S37: Positions of lead atoms on the shared lead layer for both $\text{CsPbBr}_3\text{-Pb}_4\text{S}_3\text{Br}_2$ and $\text{CsPbI}_3\text{-Pb}_4\text{S}_3\text{Br}_2$ heterostructures. The lead atoms of the chalcogenide are in red, the lead atoms of the perovskite are in black.

References

- 1) Peng, L.; Dutta, A.; Xie, R.; Yang, W.; Pradhan, N., Dot–Wire–Platelet–Cube: Step Growth and Structural Transformations in CsPbBr₃ Perovskite Nanocrystals. *ACS Energy Lett.* **2018**, 3 (8), 2014-2020.
- 2) Toso, S.; Akkerman, Q. A.; Martín-García, B.; Prato, M.; Zito, J.; Infante, I.; Dang, Z.; Moliterni, A.; Giannini, C.; Bladt, E.; Lobato, I.; Ramade, J.; Bals, S.; Buha, J.; Spirito, D.; Mugnaioli, E.; Gemmi, M.; Manna, L., Nanocrystals of Lead Chalcogenides: A Series of Kinetically Trapped Metastable Nanostructures. *J. Am. Chem. Soc.* **2020**, 142 (22), 10198-10211.
- 3) Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Krieg, F.; Caputo, R.; Hendon, C. H.; Yang, R. X.; Walsh, A.; Kovalenko, M. V., Nanocrystals of Cesium Lead Halide Perovskites (CsPbX₃, X = Cl, Br, and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut. *Nano Lett.* **2015**, 15 (6), 3692-3696.
- 4) Imran, M.; Caligiuri, V.; Wang, M.; Goldoni, L.; Prato, M.; Krahne, R.; De Trizio, L.; Manna, L., Benzoyl halides as alternative precursors for the colloidal synthesis of lead-based halide perovskite nanocrystals. *J. Am. Chem. Soc.* **2018**, 140 (7), 2656-2664.
- 5) Dutta, A.; Dutta, S. K.; Das Adhikari, S.; Pradhan, N., Tuning the size of CsPbBr₃ nanocrystals: all at one constant temperature. *ACS Energy Lett.* **2018**, 3 (2), 329-334.