Supporting Information for

Halide Perovskite-Lead Chalcohalide Nanocrystal Heterostructures

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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 μ L 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 μ L 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 CsPbBr₃-Pb₄S₃Br₂ 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 faceup projection: the individual CsPbBr₃ and Pb₄S₃Br₂ 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 CsPbBr₃ and Pb₄S₃Br₂ domains in each heterostructure are more easily distinguishable.



Figure S6. TEM image of CsPbBr₃ NCs obtained when the initial CsPbBr₃ nanoclusters were heated (at 200 °C) under the same conditions as in the synthesis of the CsPbBr₃-Pb₄S₃Br₂ 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 CsPbBr₃ NCs with an edge length of 15.9 ± 1.6 nm.



Figure S7. The XRPD patterns of CsPbBr₃-Pb₄S₃Br₂ heterostructure and of CsPbBr₃NCs (synthesis details for the CsPbBr₃NCs 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 CsPbBr₃ orthorhombic phase (Pnma, COD: 4510745).



Figure S8. From top to bottom: XRPD patterns of: (a) CsPbBr₃-Pb₄S₃Br₂ heterostructures (same pattern as in Figure S7). The much weaker and broader peaks ascribable to the chalcohalide 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 chalcohalide domain with respect to the perovskite domain. This difference in peak intensities and broadening is so large that the chalcohalide peaks are almost undetectable in the XRPD pattern of the heterostructure; (b) mixtures of CsPbBr₃ NCs and Pb₄S₃Br₂ NCs powders; (c) Pb₄S₃Br₂ NCs; (d) CsPbBr₃NCs (same pattern a in Figure S7). The sample whose XRPD pattern is shown in (b) was prepared by mixing powders of Pb₄S₃Br₂ NCs and CsPbBr₃ 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 Pb₄S₃Br₂ NCs and CsPbBr₃ NCs; (e) Pb₄S₃Br₂ 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 Pb₄S₃Br₂ (see ref.²) we preferred here to provide such experimental pattern of Pb₄S₃Br₂, instead of the reflection list, as a reference. (f) Bulk pattern for CsPbBr₃, (green histograms, reference code 96-153-3063).



Figure S9. Influence of reaction temperature on the formation of the CsPbBr₃-Pb₄S₃Br₂ 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 CsPbBr₃-**Pb**₄**S**₃**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 μ L. TEM images of samples prepared without dodecanethiol (a), and with 20 μ L (b), 40 μ L (c), and 100 μ L of dodecanethiol (d), respectively. In the absence of dodecanethiol (panel a), no CsPbBr₃-Pb₄S₃Br₂ heterostructures were formed, and instead we obtained large CsPbBr₃ NCs, each carrying though a tiny, low contras domain attached to it.



Figure S11. Role of lead oleate on the formation of the CsPbBr₃-Pb₄S₃Br₂ 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 $0.03 \text{ mmol of Pb}(OA)_2(c)$ respectively. We observed the formation of smaller domains of $Pb_4S_3Br_2$ in the absence of $Pb(OA)_2$, while instead an excess $Pb(OA)_2$ addition led to the formation of isolated Pb₄S₃Br₂ 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 $Pb_4S_3Br_2$) 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 μ L of PbBr₂ solution in ODE (see experimental section in the manuscript for the details) and 20 uL DDT was added into the vials. Thereafter, a mixture of Cs-oleate (100 μ L) and S-ODE (100 μ L) 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 μ L of previously prepared lead oleate (see experimental section for the details), 100 μ L Cs-oleate and 20 μ L DDT were separately added to the vial. Thereafter, a mixture of benzoyl bromide (0.1 mmol) and S-ODE (100 μ L) 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 μ L of PbBr₂ solution, together with 0.02 mmol OLA-Br and 20 μ L DDT was added into vial. Thereafter, a mixture of Cs-oleate (100 μ L) and S-ODE (100 μ L) 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 CsPbBr₃-Pb₄S₃Br₂ 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 CsPbBr₃-Pb₄S₃Br₂ 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 Pb₄S₃Br₂ domain has grown on the (101)/(010) facets of the CsPbBr₃ (FTs of the corresponding domains are reported in panel (b) and (c)).



Figure S17. (a) HRSTEM image of a single $CsPbBr_3-Pb_4S_3Br_2$ 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 $Pb4S_3Br_2$ (c) domains are oriented in the [010] direction and $Pb4S_3Br_2$ 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 CsPbBr₃ 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 CsPbBr₃ 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 CsPbBr₃-Pb₄S₃Br₂ 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 $CsPbBr_3-Pb_4S_3Br_2$ heterostructure (STEM image before the scan is provided in inset) with the perovskite domain on the left and the $Pb_4S_3Br_2$ 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.

Pb₄S₃Br₂ **CsPbBr** 0 0 00 0 00 0 00 0 00 0 00 0 00 0 00 0 m œ œ 0 00 00 0 C

Figure S22. Model of the cationic (Cs and Pb) sublattices of the CsPbBr₃-Pb₄S₃Br₂ 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 chalcohalide and the perovskite structures.



Figure S23. Electronic structure and IPR plots of a) a spherical $Pb_{548}S_{423}Br_{250}$ NC model of about 4.2 nm in diameter, b) three cubic $Cs_{200}Pb_{125}X_{450}$ NC models of about 3.2nm in size featuring X=Cl, X=Br and X=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 $Pb_4S_3Br_2$ -CsPbBr₃ heterostructure model computed for (magenta) the $Pb_4S_3Br_2$ interfacial layer, and (green) the CsPbBr₃ Pb-rich interfacial layer.



Figure S25. (a) PL spectra of $Pb_4Br_3S_2$ 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 $Pb_4Br_3S_2$ 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 S27. HAADF-STEM image and the corresponding EDX mapping of a group of $CsPbCl_3-Pb_4S_3Br_2$ heterostructures (obtained from $CsPbBr_3-Pb_4S_3Br_2$ 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 chalcohalide domain, suggesting a CsPbCl₃-Pb₄S₃Br₂ composition for the heterostructure.



Figure S28. (left) HAADF-STEM image of a group of three CsPbI₃-Pb₄S₃Br₂ heterostructures (obtained from the CsPbBr₃-Pb₄S₃Br₂ 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 Pb₄S₃Br₂ composition in those domains. The lower contrast domains, corresponding to the initial CsPbBr₃ 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 CsPbBr₃ to primarily CsPbI₃. 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 $CsPbBr_3-Pb_4S_3Br_2$ heterostructures and of the samples after anion exchange with Cl^{-} and I^{-} ions, respectively. For the comparison, the XRPD pattern of $Pb_4S_3Br_2$ is also reported along with the bulk diffraction patterns for the cubic $CsPbCl_3$, orthorhombic $CsPbBr_3$ and $CsPbI_3$ phases.



Figure S31. Anion exchange attempts on $Pb_4S_3Br_2$ NCs: Panel (a) shows the absorption spectra of the starting $Pb_4S_3Br_2$ NCs (black) and after treatment with chloride and iodide precursors (red and blue) respectively. XRPD patterns of the starting $Pb_4S_3Br_2$ NCs and of the chloride and iodide treated samples (b). TEM images of $Pb_4S_3Br_2$ NCs (d) and after treatment with the chloride (c) and iodide (e) ions, respectively.



Figure S32. Electronic structure and IPR plots of the three $Pb_4S_3Br_2$ -CsPbX₃ heterostructure NC models, with X=Cl, X=Br and X=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) $CsPbCl_3 NCs$ and $CsPbCl_3-Pb_4Br_3S_2$ heterostructures (blue and purple, respectively) and (b) $CsPbI_3 NCs$ and $CsPbI_3-Pb_4Br_3S_2$ 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) $CsPbCl_3 NCs$ and $CsPbCl_3-Pb_4Br_3S_2$ heterostructures and (f) $CsPbI_3 NCs$ and $CsPbI_3-Pb_4Br_3S_2$ 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 $CsPbI_3-Pb_4S_3Br_2$ heterostructures as prepared (fresh) and after 10 days of aging under air in closed vials. (b-c) The corresponding TEM images of the $CsPbI_3-Pb_4S_3Br_2$ 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 chalcohalide domains.

Pb-sublattices matching at the perovskite-chalcohalide interface for the $CsPbBr_3-Pb_4S_3Br_2$ and $CsPbI_3-Pb_4S_3Br_2$ 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 chalcohalide 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 $CsPbBr_3-Pb_4S_3Br_2$ and $CsPbI_3-Pb_4S_3Br_2$ heterostructures. The lead atoms of the chalcohalide are in red, the lead atoms of the perovskite are in black.

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