Electronic Supplementary Information (ESI)

Post-synthetic Oriented Attachment of CsPbBr₃ Perovskite Nanocrystal Building Blocks: From First Principle Calculation to Experimental Demonstration of Size and Dimensionality (0D/1D/2D)

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Fig. S1 TEM images of $CsPbBr_3$ NCs processed using various polar solvents with different polarities and boiling points.



Fig. S2 XRD patterns of $CsPbBr_3$ NCs exposed to various polar solvents with different polarities and boiling points.



Fig. S3 TEM images of CsPbBr₃ NCs exposed to DEG.



Fig. S4 AFM image of a fabricated nanoplatelet and height profile of the nanoplatelet.



Fig. S5 Dependence of PLQY values of $CsPbBr_3$ on dimensionality.



Fig. S6 TEM images of transition states during self-assembly at the liquid-air interface.



Fig. S7 HR-TEM images of the oriented attachment of two NCs while exposed to the electron

beam of the transmission electron microscope.



Fig. S8 (a, b) Structures that were calculated to simulate the total energy of NW formation.

Discussion of the effect of the solvent polarity on the CsPbBr₃ NCs.

Because the solvent polarity plays a critical role in both the miscibility of solvents and the ionization of materials, the effects of solvent polarity on the structural properties of cesium lead(II) bromide perovskite nanocrystals (CsPbBr₃ NCs) were analyzed using TEM and XRD (Fig. S1, S2). As discussed in the article, in miscible solvents, as the polarity increased, the degree of destruction of the CsPbBr₃ NCs also increased. In contrast, in immiscible solvents, the degree of destruction decreased. To investigate only the effect of solvent polarity, we divided the solvents into two groups based on their boiling point: a low boiling point group (methanol and water), and a high boiling point group (DEG, EG, Gly). As observed by TEM and XRD, the tendency of the degree of destruction decreasing as the polarity increases was found for both groups. This unusual phenomenon, where high polarity causes less destruction in an immiscible group, can be explained by the interaction between molecules of the two solvents. For a polar and non-polar solvent to be mixed, the dipole of the polar solvent and the induced dipole of the non-polar solvent need to interact. However, as the difference in the polarity of the two solvents increased, the relatively stronger dipole (polar solvent molecule)-dipole (polar solvent molecule) interaction becomes significantly more dominant than the interaction between the relatively weaker dipole (polar solvent molecule) and the induced dipole (non-polar solvent molecule). In this case, the solvents become immiscible. When the difference in polarity increased significantly, the interaction between two solvent molecules is minimized. Consequently, the effect of polar solvent molecules cannot fully reach the NCs surrounded by non-polar solvent molecules. Therefore, solvents with a higher polarity have less effect on the NCs, whereby the destruction of the CsPbBr₃ NCs can be minimized in ISPM.

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Discussion of the effect of the boiling point of the solvent on the CsPbBr₃ NCs.

The effect of the boiling point of the solvents on the NCs was also investigated, as it represents intermolecular bonding strength. To elucidate this effect on the CsPbBr₃ NCs, DEG and EG were chosen as the polar solvents and compared with MeOH. This is because both DEG and EG have similarly high boiling points compared to methanol, but all three contain one or more hydroxyl group(s). Furthermore, because DEG is less polar and EG is more polar than MeOH, the effect of the boiling point can be isolated from the effect of polarity. DEG-processed CsPbBr₃ shows large-sized, integrated CsPbBr₃ assemblages with a highly crystalline perovskite lattice. However, the sizes of the CsPbBr₃ assemblages were quite varied, and some destruction of structures was observed (Fig. S1, S3). The XRD analysis (Fig. S2) revealed monoclinic CsPbBr₃ peaks and decreased FWHM, which indicates the destruction of the perovskite structure. As discussed in the main text, EG caused minimized destruction of the CsPbBr₃ NC structure. In both cases, the degree of destruction of the NC structure was significantly reduced compared with that caused by methanol. Considering that both the less polar DEG and more polar EG exhibited a lower degree of destruction, the non-aggressive action is attributed to a high boiling point.

Discussion of NW fabrication

To understand the origin of NW formation, the total energy differences were calculated by increasing length perovskite (Fig. S8a, S8b). We computed the of $\Delta E_{n,facet} = E_{n \times 2 \times 2} - (E_{(n-2) \times 2 \times 2} + E_{2 \times 2 \times 2}),$ which represents the total energy difference per atom between the $n \times 2 \times 2$ cluster and the sum of the two separated clusters $(n-2) \times 2 \times 2$ and $2 \times 2 \times 2$. Each cluster has a different facet. In this calculation, we also use two surface conditions, which are the same as those in the $\Delta E_{(100)}$ and $\Delta E_{(110)}$ calculations. $\Delta E_{6,(100)}$ and $\Delta E_{8,(100)}$ yielded –34.66 meV/atom and –26.5 meV/atom, and $\Delta E_{6,(110)}$ and $\Delta E_{8,(110)}$ yielded – 104.98 meV/atom and -78.38 meV/atom. Regardless of the n value or facet, the value of $\Delta E_{n,facet}$ was negative, meaning NW fabrication can reduce the total energy of the system and occur spontaneously. This phenomenon, where the driving force of NW formation occurs thermodynamically, is in good agreement with our experimental results. By increasing the length of the rod (the *n* value) from 4 to 8, one can observe the decreasing trend of ΔE_n in both cases. This is attributed simply to the reduced surface-to-volume ratio. The same tendency is observed for the case in which we fixed the surface termination and simply compared the total energy depending on the increase in the rod length (Fig. S8). In summary, the oriented attachment that drives the changes in the size and dimensionality of perovskite is attributed to the decrease in the total energy of the system.

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