Electronic Supplementary Information

Self-Trapped Emissions in 2D Lead-Free Halide Perovskites Driven by Divalent Spacer Cations

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1.   Materials and Methods

Materials: Sodium chloride (NaCl), Indium III acetate (InAc), hydrochloric acid (HCl), phenethylamine (PEA), 1,3-diaminopropane (DAP), and toluene.

Synthesis details: The preparation of two-dimensional double perovskites was conducted using a procedure adapted from the literature.[1] The synthesis of Na-In based perovskite with n=1 was prepared using two organic molecules: PEA and DAP, resulting in two different 2D perovskite structures, Ruddsdlen-Popper (RP) and Dion-Jacobson (DJ), respectively. Both structures were prepared by following the procedure with the steps outlined below:

(i) $(PEA)_4NaInCl_8$ 2D-RP double perovskite structure (n=1):
1 mmol of NaCl was mixed with 1 mmol of In (III) acetate in 5 mL of HCl under a temperature of 110°C with high magnetic stirring. The precursor mixture was then heated and stirred for approximately 10-15 minutes to reach the temperature equilibrium. Once the salts were completely dissolved and the solution became colorless, 5 mmol of PEA was quickly added to the synthesis to achieve the desired n=1 stoichiometry. After the incorporation of the organic molecule, the reaction was maintained under temperature and stirring for approximately 20 minutes, after which the heating was removed, and the mixture was allowed to cool naturally to room temperature. Over time, small crystals started to be formed into the solution, which was reserved for washing the following day. To purify the sample, successive washes with

toluene and a slow-pass filter were used to remove any excess acid present. After washing, the sample was dried and stored for future characterizations.

(ii) (DAP)$_2$NaInCl$_8$ 2D-DJ double perovskite structure (n=1):

For the preparation of the 2D-DJ structure, a similar experimental procedure to that previously described for the 2D-RP structure prepared with the PEA molecule was followed. However, in this case, 5 mmol of the bi-protonated molecule DAP was added after all solids were dissolved in the acidic solution at 110°C. It is worth noting that the reaction is highly exothermic and was conducted inside a fume hood with exhaust to prevent potential accidents. After the molecule was incorporated, stirring was maintained for 20 minutes to ensure complete ion solubilization, and then the sample was allowed to cool naturally overnight. Similar to the previous method, the sample was washed with toluene and filtered to remove any remaining acid excess from the synthesis. The sample was dried and stored for further characterizations.

2.   Experimental characterizations:

After the synthetic process, the samples had their morphology characterized through scanning electron microscopy (SEM) using a JEOL JSM-670LA microscope. Confirmation of the different synthesized structures was conducted through X-ray diffraction analysis using a STADI-P diffractometer (Stoe®, Darmstadt, Germany) operating in transmission mode (40 kV and 40 mA) with a CuKα1 line source (λ = 1.54056 Å) and Mythen 1K linear detector. The chemical environment profile of the material was evaluated through X-ray photoelectron spectroscopy (XPS), revealing differences in relation to the different stoichiometries. Emission properties were evaluated through static photoluminescence measurements on a Varian Cary Xe-lamp spectrophotometer with scanning process and data acquisition at medium speed.

3.   Computational methods and Theoretical Approach:

We used the Fritz-Haber-Institute ab initio materials simulations (FHI-aims) code[2] to perform all density-functional theory (DFT) calculations. Hence, all the Kohn-Sham orbitals were expanded into numerical atom-centered orbitals (NAOs) and we used the "intermediate" basis set improvements for all atoms. The geometries were optimized with the Perdew-Burke-Ernzerhof exchange-functional corrected for solids (PBESol)[3]

plus the Tkatchenko-Scheffler (TS) van der Waals (vdW) correction[4] to accurately take into account the long-rang interactions taking place in the crystals. We performed electronic structure calculations, i.e., band structures, partial density-of-states, and electronic isosurfaces, using the Heyd-Scuseria-Ernzerhof (HSE06) hybrid-functional (25% Hartree-Fock exchange and a screening parameter of 0.11 bohr^{-1})[5,6] plus the second-variation non-self-consistent spin-orbit coupling (SOC)[7], since GGA functionals are prone to electronic delocalization error.[8]
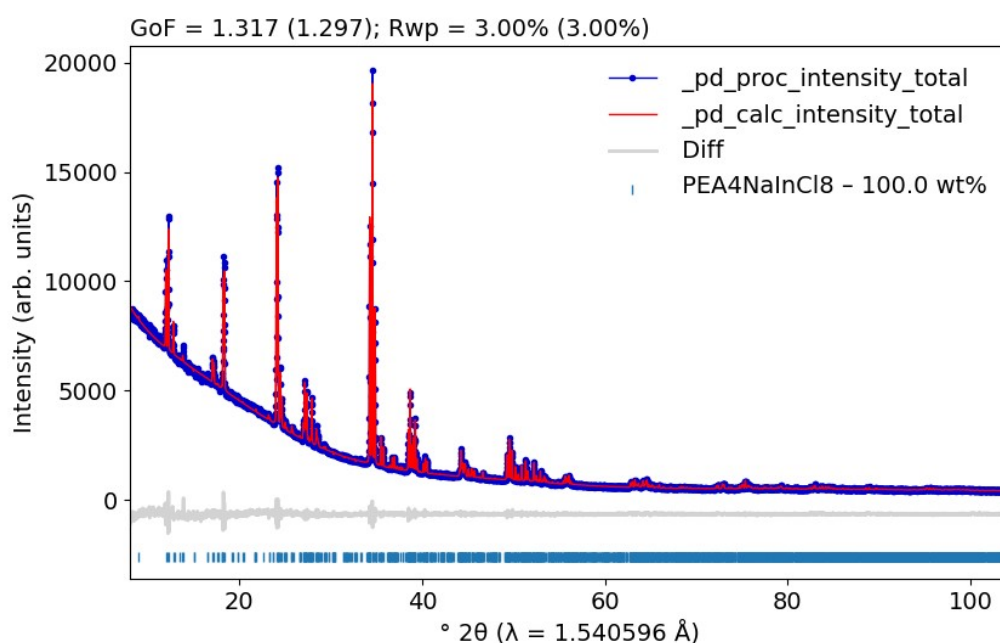

Fig. S1 Rietveld refinement of powder X-ray diffraction patterns of as-grown $(PEA)_4NaInCl_8$.

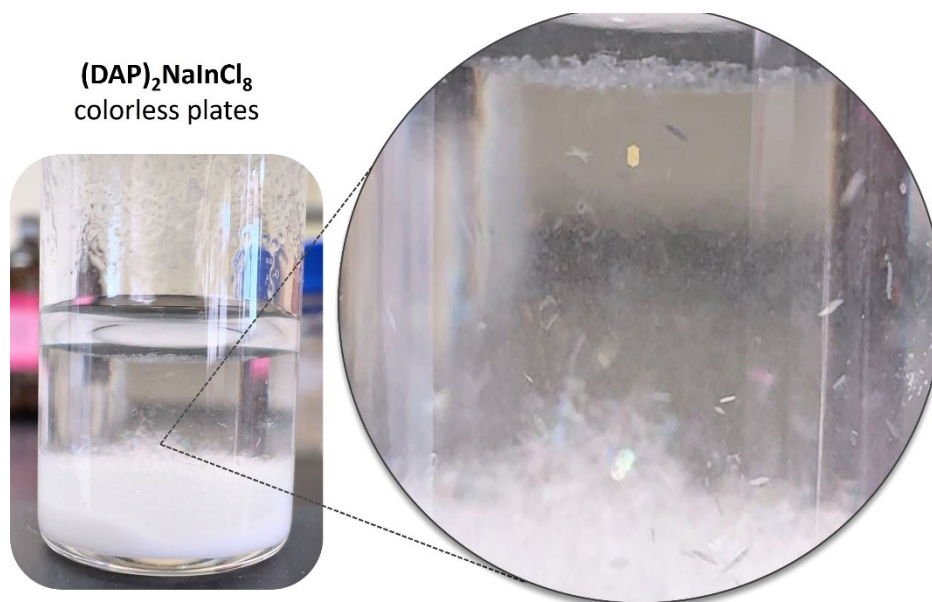**(DAP)₂NaInCl₈**
colorless plates

Fig. S2 Image of precipitated colorless plates of $(DAP)_2NaInCl_8$ in acidic solution during synthetic growth procedure.

(DPA)₂NaInCl₈

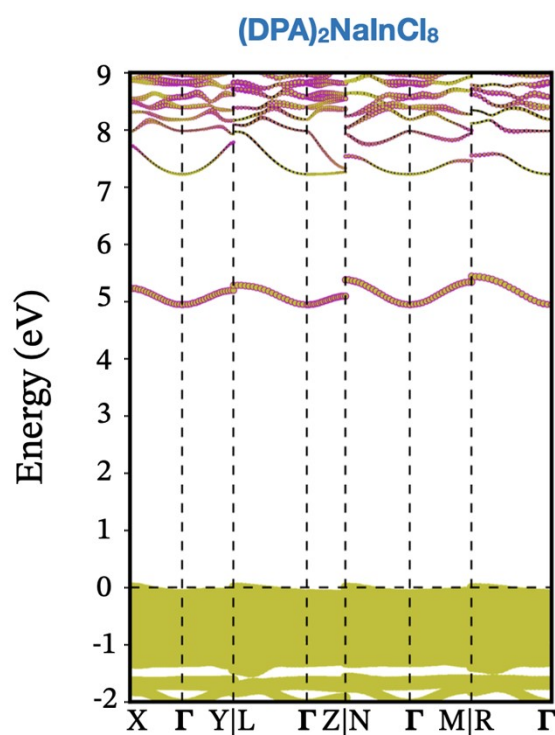**Fig. S3** Species-decomposed HSE06+SOC band structures for $(DAP)_2NaInX_8$, X = Br, Cl, where the magenta and yellow dots represent metallic and halogen contributions to the bands, respectively.

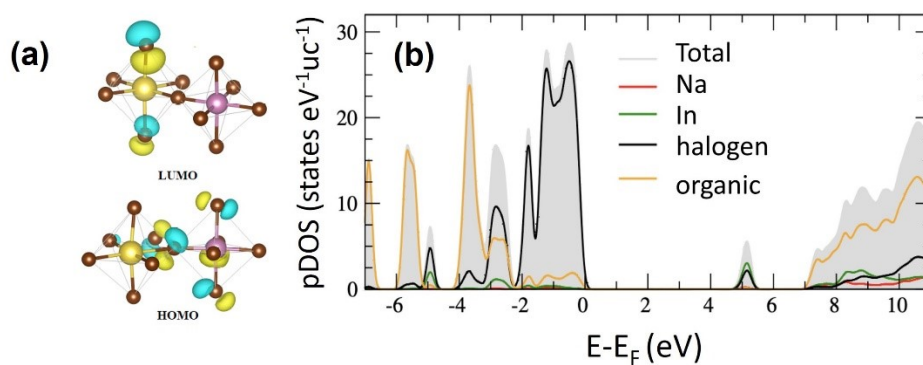**Fig. S4** (a) Ground-state electronic isosurfaces associated to the valence (HOMO) and conduction (LUMO) bands for $(DAP)_2NaInCl_8$. (b) Partial density of states of $(DAP)_2NaInCl_8$.

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