Supporting Information for

The Origin of Broad Emission in <100> Two-Dimensional Perovskites: Extrinsic vs. Intrinsic Processes

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**Figure S1:** Absorbance and photoluminescence spectrum of PEA$_2$PbCl$_4$ (excited at 4.6 eV) at room temperature.

**Figure S2:** Power-dependent PL of the BE of PEA$_2$SnI$_4$ at 5.4 K. Steady state spectra (a) and integrated intensity on a double-logarithmic plot indicating the sub-linear dependence.

### DFT simulations

**Electronic structure of (PEA)$_2$SnI$_4$ and (PEA)$_2$PbI$_4$**

The impact of the level of theory on the electronic properties of 2D perovskites is illustrated in the following for the PEA$_2$SnI$_4$ and PEA$_2$PbI$_4$ phases. Calculations have been carried out on the relaxed structures of the phases obtained by using the PBE functional (DFT-D3 dispersions included) and by fixing cell parameters to the experimental values.
At the PBE level of theory, spin-orbit coupling (SOC) included, the PEA$_2$SnI$_4$ and PEA$_2$PbI$_4$ phases show direct band gaps at the $\Gamma$ point in the Brillouin zone (BZ) of 1.32 eV and 0.99 eV, respectively, see Figure S3 and Table S1. Similar to the 3D bulk phase, the top of the valence band (VBM) is associated to I-p orbitals, while the conduction band minimum (CBM) is mainly associated with the p-states of the metal. As expected, the calculated band gaps at the PBE-SOC level are underestimated, as demonstrated by the higher optical band gaps measured in absorption experiments.

In order to provide a more accurate prediction of the optoelectronic properties of the phases, the band gaps of the PEA$_2$PbI$_4$ and PEA$_2$SnI$_4$ phases have been calculated by the $G_0W_0$ method, by using the Yambo code.

In Table S1 the calculated band gaps at the $G_0W_0$-SOC level are reported. A renormalization of the band gaps to values of 1.88 and 2.51 eV is reported for PEA$_2$SnI$_4$ and PEA$_2$PbI$_4$, respectively. The calculated band gaps are in good agreement with experimental works reporting values of 2.08 and 2.61 eV for PEA$_2$SnI$_4$ and PEA$_2$PbI$_4$, respectively.

The accuracy of hybrid functionals in the description of the electronic structure of the phases has been checked by recalculating the band gaps at the PBE0-SOC level, see Table S1. A good agreement with $G_0W_0$ calculations is found for lead, while for tin perovskite the band gap is slightly overestimated by the PBE0 functional. This analysis shows that PBE0 functional (SOC included) provides an accurate description of the electronic properties of these systems. Notably, small deviations of the calculated PBE0-SOC band gaps of PEA$_2$SnI$_4$ and PEA$_2$PbI$_4$ can be noticed between Table S1 and Table 1 of the main text. These variations are due to the slightly different structures of the phases obtained at the PBE and PBE0 levels of theory (band gaps reported in Table 1 of the main text have been calculated at the PBE0 relaxed structures obtained by the CP2K code).
Figure S3. Projected density of states (PDOS) and electronic band structure of the (PEA)$_2$PbI$_4$ and (PEA)$_2$SnI$_4$ phases calculated at the PBE-SOC level of theory.

Table S1. Electronic band gaps of 2D perovskites calculated at different levels of theory.

| System     | PBE-SOC (eV) | PBE0-SOC (eV) | $G_0W_0$-SOC (eV) | Experiments (eV) |
|------------|--------------|---------------|--------------------|------------------|
| (PEA)$_2$SnI$_4$ | 0.99         | 2.12          | 1.88               | 2.08$^3$         |
| (PEA)$_2$PbI$_4$ | 1.32         | 2.57          | 2.51               | 2.61$^2$         |

Defect calculations
Defect formation energies (DFE) and thermodynamic ionization levels (TIL) of defects were calculated by using the following relations$^3$

$$DFE[\chi^q] = E[\chi^q] - E[perf] - \sum_i n_i \mu_i + q(\varepsilon_{VB} + \varepsilon_{F}) + E^q_{corr}$$  

(1)
\[ \varepsilon(q/q') = \frac{E[X^q] - E[X^{q'}]}{q' - q} + \frac{E_{\text{corr}}^q - E_{\text{corr}}^{q'}}{q' - q} - \varepsilon_{VB} \]  

where \( E[X^q] \) is the energy of the supercell with defect \( X \) in the charge state \( q \); \( E(\text{perf}) \) is the energy of the perfect (non-defective) supercell; \( n \) and \( \mu \) are, respectively, the number and the chemical potentials of the species added or subtracted to the non-defective system; \( \varepsilon_{VB} \) and \( \varepsilon_F \) are the valence band energy and the Fermi level; \( E_{\text{corr}}^q \) is the correction term due to the charge. Charge corrections have been applied by following the Makov-Payne scheme by using the ionic dielectric constant of the phases calculated at the PBE level by following the approach of Umari et al\(^4\) (see Table S4). 

The chemical potentials of the elements in the calculation of PEA\(_2\)SnI\(_4\) and PEA\(_2\)PbI\(_4\) DFEs have been set by imposing the thermodynamic stability of the 2D perovskites and the equilibrium between the 2D perovskites and the relative metal precursors (SnI\(_2\) and PbI\(_2\))

\[ 2\mu(\text{PEA}) + \mu(\text{Pb/Sn}) + 4\mu(I) = \mu(\text{PEA}_2(\text{Pb/Sn})I_4) \]  

\[ \mu(\text{Pb}) + 2\mu(I) = \mu(\text{PbI}_2) \]  

\[ \mu(\text{Sn}) + 2\mu(I) = \mu(\text{SnI}_2) \]  

I-rich conditions have been simulated by setting the chemical potential of iodine to the value in solid I\(_2\) (\( \mu(I) = \frac{1}{2} \mu(I_2) \)), while I-poor conditions by setting the chemical potentials of lead / tin to the values in the respective metal bulks. The chemical potentials of other species have been calculated by considering equilibriums 3-5. For I-medium conditions the average values of the chemical potentials between I-rich and I-poor conditions have been used. A comparison of the calculated DFEs (I-medium conditions) and TILs in the 2D perovskites and in the 3D analogues is reported in Figures S4 and S5. 

The electronic structure analysis highlights that quantum confinement into two dimensions increases the band gap energy through a down/up-shift of the VBM/CBM for both tin and lead perovskites compared to their 3D counterparts (see Figure S4). At the PBE0 level of
theory, spin-orbit corrections (SOC) included, a down-shift of 0.42 eV and an upshift of 0.45 eV are observed for the VBM and CBM of PEA$_2$PbI$_4$ with respect to 3D MAPbI$_3$ (see Figure S4 and Figure S5). Shifts of 0.59 and 0.25 eV of the VBM and CBM are observed in the case of PEA$_2$SnI$_4$. These shifts and the associated band gaps opening leads to a widening of the stability field of defects and to a deepening of the VB and CB-related ionization levels compared with 3D analogues. As an example, (+/0) levels of V$_I$, which are shallow in MAPbI$_3$, become deep in PEA$_2$PbI$_4$; (0/-) transitions associated to I$_I$, which are shallow in MASnI$_3$, become deep in PEA$_2$SnI$_4$.

**Figure S4.** a-b) Defect formation energies of 2D and c-d) 3D perovskites calculated in I-medium condition at the PBE0 level. The band gaps and VB / CB alignments are those calculated at the PBE0-SOC level of theory.
**Figure S5.** Thermodynamic ionization levels of main defects in 2D and 3D lead and tin perovskites, calculated at the PBE0 level of theory. The band gaps and VB / CB alignments are those calculated at the PBE0-SOC level of theory.

**Figure S6.** Equilibrium structures of the iodine interstitial in the a) negative; b) neutral and c) positive charged forms.
Table S2. Predicted band gaps; (0/-) and (+/0) transitions of STEs; (+/0) transitions of halogen vacancies (equatorial = eq; apical = ap); calculated PL emission energies of the STE and $V_X$. A comparison of the values calculated at the PBE0 level of theory with and without SOC (in parenthesis) is provided.

| Phase   | TIL / eV          | PL emission Theory / eV |
|---------|-------------------|-------------------------|
|         |                   |                         |
| PEA$_2$SnI$_4$ | $E_g = 2.26$ eV (2.42 eV) |                         |
| STE     |                   |                         |
| $V_{I\text{ eq}}$ | (+/0) 1.42 (1.45) | 0.82 (0.85) |
| $V_{I\text{ ap}}$ | (+/0) 1.84 (1.99) | 1.75 (1.90) |
| PEA$_2$PbI$_4$ | $E_g = 2.58$ eV (3.33 eV) |                         |
| STE     |                   |                         |
| $V_{I\text{ eq}}$ | (+/0) 1.94 (2.29) | 1.27 (1.62) |
| $V_{I\text{ ap}}$ | (+/0) 2.07 (2.86) | 1.97 (2.76) |
| PEA$_2$PbBr$_4$ | $E_g = 3.26$ eV (4.13 eV) |                         |
| STE     | (0/-) 3.48 (4.01) | 2.19 (2.72) |
|         | (+/0) (0.05)      |                         |
| $V_{Br\text{ eq}}$ | (+/0) 2.56 (2.79) | 1.78 (2.02) |
| $V_{Br\text{ ap}}$ | (+/0) 2.93 (3.30) | 1.73 (2.11) |
| PEA$_2$PbCl$_4$ | $E_g = 3.91$ eV (4.62 eV) |                         |
| STE     | (0/-) 3.88 (4.21) | 1.89 (2.23) |
|         | (+/0) (0.12)      |                         |
| $V_{Cl\text{ eq}}$ | (+/0) 2.89 (3.02) | 1.97 (2.09) |
| $V_{Cl\text{ ap}}$ | (+/0) 3.29 (3.52) | 1.85 (2.08) |
Table S3. Optimized cell parameters and band gaps at different levels of theory (PBE and PBE+SOC) with the inclusion of DFT-D3 dispersions. DFT relaxations have been performed by using the CP2K and Quantum Espresso codes (small variations in the optimized cell parameters are ascribed to the different used pseudopotentials for Pb, i.e. 4 valence electrons CP2k vs 14 valence electrons QE). Variations of the DFE and (+/0) TIL energy of V\textsubscript{I} eq in fully relaxed supercells with respect to values calculated with cell parameters fixed at the experimental values.

|                      | a, b, c, α, β, γ          | E\textsubscript{gap} (eV) |
|----------------------|---------------------------|---------------------------|
| Experimental cell    | a=8.739 Å, b=8.740 Å, c=32.995 Å, α=84.6°, β=84.6°, γ=89.6° | 2.13                       |
| Optimized cell (PBE-D3, CP2K) | a=8.650 Å, b=8.633 Å, c=32.260 Å, α=85.6°, β=85.8°, γ=89.2° | 2.12                       |
| Optimized cell (PBE-D3, QE)  | a=8.694 Å, b=8.688 Å, c=32.945 Å, α=85.5°, β=85.5°, γ=89.3° | 2.13                       |
| Optimized cell (PBE-SOC-D3, QE) | a=8.694 Å, b=8.688 Å, c=32.945 Å, α=85.5°, β=85.5°, γ=89.3° | 1.32                       |
| Defect               | ΔDFE (eV)                 | Δ(+/0) TIL (eV)            |
| V\textsubscript{i}\textsuperscript{+} eq (PBE-D3, CP2K) | +0.02                     | -0.10                      |
| V\textsubscript{i}\textsuperscript{0} eq (PBE-D3, CP2K) | -0.08                     |                            |
**Table S4.** Calculated high frequency ($\varepsilon_\infty$) and static ($\varepsilon_0$) dielectric constants for the studied 2D phases at the PBE level. In the last column the Makov-Payne (MP) corrections to charged defect energies (charge q) in the respective supercells are also reported.

| System       | $\varepsilon_\infty$ | $\varepsilon_0$ | MP correction (eV) |
|--------------|-----------------------|------------------|---------------------|
| PEA$_2$SnI$_4$ | $\varepsilon_{xx} = 4.3$ | $\varepsilon_{xx} = 10.3$ | (q=1) +0.05 |
|              | $\varepsilon_{yy} = 4.3$ | $\varepsilon_{yy} = 10.2$ |         |
|              | $\varepsilon_{zz} = 3.1$ | $\varepsilon_{zz} = 4.2$ | (q=2) +0.22 |
| PEA$_2$PbI$_4$ | $\varepsilon_{xx} = 3.6$ | $\varepsilon_{xx} = 7.1$ | (q=1) +0.10 |
|              | $\varepsilon_{yy} = 3.6$ | $\varepsilon_{yy} = 7.2$ |         |
|              | $\varepsilon_{zz} = 3.0$ | $\varepsilon_{zz} = 4.0$ | (q=2) +0.40 |
| PEA$_2$PbBr$_4$ | $\varepsilon_{xx} = 3.2$ | $\varepsilon_{xx} = 6.5$ | (q=1) +0.10 |
|              | $\varepsilon_{yy} = 3.2$ | $\varepsilon_{yy} = 6.7$ |         |
|              | $\varepsilon_{zz} = 2.7$ | $\varepsilon_{zz} = 3.8$ |         |
| PEA$_2$PbCl$_4$ | $\varepsilon_{xx} = 3.0$ | $\varepsilon_{xx} = 7.4$ | (q=1) +0.16 |
|              | $\varepsilon_{yy} = 3.0$ | $\varepsilon_{yy} = 7.3$ |         |
|              | $\varepsilon_{zz} = 2.7$ | $\varepsilon_{zz} = 3.9$ |         |
Figure S7. Diagrams representing the simulated PL emission from a) STE and b) halide vacancy. \( E^{T_1}[\text{STE}] \) and \( E^{S_0}[\text{STE}] \) represent the energies of the triplet and singlet states, respectively, calculated at the equilibrium geometry of the STE; \( E^+[V_X^0] \) and \( E^+[V_X^+] \) represent the energies of the positive vacancy at the equilibrium geometries of the neutral and positive halide vacancy, respectively.

Table S5. Optimized structures of the positive / neutral equatorial and apical iodine vacancies in PEA\(_2\)PbI\(_4\) and the self-trapped exciton in PEA\(_2\)PbCl\(_4\), as calculated in the 2x2x1 supercells at the PBE0-D3 level of theory and by fixing cell parameters to the experimental values. Calculations have been carried out by using the CP2K code (version 6.1). Ion positions and supercell vector parameters (a, b, c) are in Å. Hydrogens have been removed for brevity.
PEA\textsubscript{2}Pb\textsubscript{4}

\begin{align*}
\text{a} &= 17.487 \quad 0.000 \\
\text{b} &= 17.480 \quad 0.000 \\
\text{c} &= 3.071 \quad 3.057 \quad 32.709
\end{align*}

PEA\textsubscript{2}Pb\textsubscript{4}

\begin{align*}
\text{a} &= 22.230 \quad 0.000 \\
\text{b} &= 22.240 \quad 0.000 \\
\text{c} &= -4.413 \quad -2.803 \quad 16.796
\end{align*}
| C | 8.793809976 | 12.690272881 | 26.149904724 |
| C | 8.561606900 | 16.274995896 | 0.602700009 |
| C | 9.213992025 | 22.197683835 | 26.149904724 |
| C | 9.569709297 | 15.473060762 | 3.998910942 |
| C | 3.579752239 | 3.048725605 | 3.000000000 |
| C | 3.235779949 | 15.206959861 | 3.000000000 |
| C | 9.591232199 | 13.344310306 | 7.000000000 |
| C | 1.313659796 | 14.876514330 | 2.617784771 |
| C | 5.590966029 | 11.434604002 | 22.552278183 |
| C | 5.205908532 | 11.434604002 | 12.304003235 |
| C | 7.752476020 | 16.258019164 | 3.998910942 |
| C | 6.170549374 | 18.747972567 | 20.256333243 |
| C | 4.862923839 | 13.746305769 | 21.310246236 |
| C | 3.040003661 | 16.305776464 | 20.256333243 |
| C | 7.126626834 | 12.162194830 | 21.310246236 |
| C | 7.126626834 | 18.569631736 | 21.310246236 |
| C | 4.862923839 | 7.900857841 | 20.256333243 |
| C | 4.862923839 | 7.900857841 | 20.256333243 |
| C | 12.6540645 | 10.787752876 | 21.250033325 |
| C | 12.6540645 | 10.787752876 | 21.250033325 |
| C | 8.18107645 | 12.955436120 | 5.875382757 |
| C | 8.18107645 | 12.955436120 | 5.875382757 |
| C | 13.1421158 | 18.747972567 | 2.617784771 |
| C | 8.573237542 | 18.747972567 | 2.617784771 |
| C | 18.110562713 | 18.736323564 | 2.617784771 |
| C | 18.110562713 | 18.736323564 | 2.617784771 |
| C | 13.1421158 | 18.747972567 | 2.617784771 |
| C | 18.110562713 | 18.736323564 | 2.617784771 |
| C | 18.110562713 | 18.736323564 | 2.617784771 |
| C | 18.110562713 | 18.736323564 | 2.617784771 |
| C | 18.110562713 | 18.736323564 | 2.617784771 |
| C | 18.110562713 | 18.736323564 | 2.617784771 |
| C | 18.110562713 | 18.736323564 | 2.617784771 |
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| C | 18.110562713 | 18.736323564 | 2.617784771 |
| C | 18.110562713 | 18.736323564 | 2.617784771 |
| C | 18.110562713 | 18.736323564 | 2.617784771 |
| C         | 9.90712E+001 | 10.8977E+013 | 6.9774E+02730 | 9.90006E+072 | 10.9107E+049 | 6.99235E+048 |
|-----------|--------------|--------------|----------------|--------------|--------------|--------------|

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