Quantum confinement and dielectric profiles of colloidal halide inorganic and hybrid organic-inorganic perovskites nanoplatelets – Electronic Supplementary Information

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Microscopic to macroscopic dielectric constant (Even et al., Phys. Chem. Chem. Phys., 16, 25182)

The connection between the microscopic dielectric constant $\varepsilon_{G,G'}(q)$ for a bulk periodic solid and a Fourier component $\varepsilon_M(q)$ with a short wavevector q of the macroscopic dielectric constant for an homogeneous medium $\varepsilon_M(\vec{r} - \vec{r'})$ is well-established.¹⁻⁴ It involves the inversion of the $\varepsilon_{G,G'}(q)$ matrix to extract the macroscopic dielectric including local field effects $\varepsilon(q) = 1/\varepsilon_{0,0}^{-1}(q)$. On the other hand, the macroscopic dielectric constant computed without inversion does not contain local field effects. The same connection between the microscopic and macroscopic quantities is realized when the microscopic field is averaged over a cell volume in real space, thus keeping only Fourier components inside the Brillouin zone.¹⁻³ Local fields effects are taken into account for the macroscopic dielectric constant computed in this work. However, it should be noticed that non-local effects on the self-energy cannot be evaluated from $\varepsilon_M(q)$ in periodic solids, since these effects arise typically over a bond length.⁵

Quantum confinement



Fig. S1 Band structure for the bulk all inorganic perovskites CsPbX₃ (X = I, Br, Cl).

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Fig. S2 Band structure for 8, 4, 2 and 1-layer slabs of (a) CsPbBr3 and (b) CsPbCl3.



Fig. S3 Band structure for 8, 4, 2 and 1-layer slabs of CH₃NH₃PbBr₃.

High frequency dielectric profiles



Fig. S4 High frequency dielectric profiles for 8, 4, 2 and 1-layer slabs of (a) CsPbBr₃, and (b) CsPbCl₃.



Fig. S5 High frequency dielectric profiles for 8 and 1-layer slabs of CH₃NH₃PbI₃ in the (a) [100], and (b) [001] directions.



Fig. S6 High frequency dielectric profiles for 8 and 1-layer slabs of CH₃NH₃PbBr₃ in the [010] direction.

Table S1 Calculated high frequency dielectric constants at slabs centre for 3D all-inorganic and organic-inorganic perovskites.

Cation	Cs ⁺			CH ₃ NH ₃ ⁺				
Halogen	Ι	Br	Cl		Ι		Br	
				[010]	[100]	[001]	[010]	
8-layer	5.0	3.8	3.2	5.6	4.9	4.8	4.2	
1-layer	3.7	3.1	2.7	4.2	4.1	4.1	3.3	

Table S2 Calculated high frequency dielectric constants for organic and inorganic layers in 2D and 2D/3D HOP.

	2D aromatic	2D aliphatic (short)	2D aliphatic (long)	2D/3D
inorganic	4.0	3.9	4.0	4.8
organic	2.9	2.1	2.1	2.9

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