Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

Impact of the Organic Cation on the Band-Edge Emission of Two-Dimensional Lead-Bromide Perovskites

Seda Kutkan, Balaji Dhanabalan, Miao-Ling Lin, Ping-Heng Tan, Alexander Schleusener, Milena P. Arciniegas, and Roman Krahne

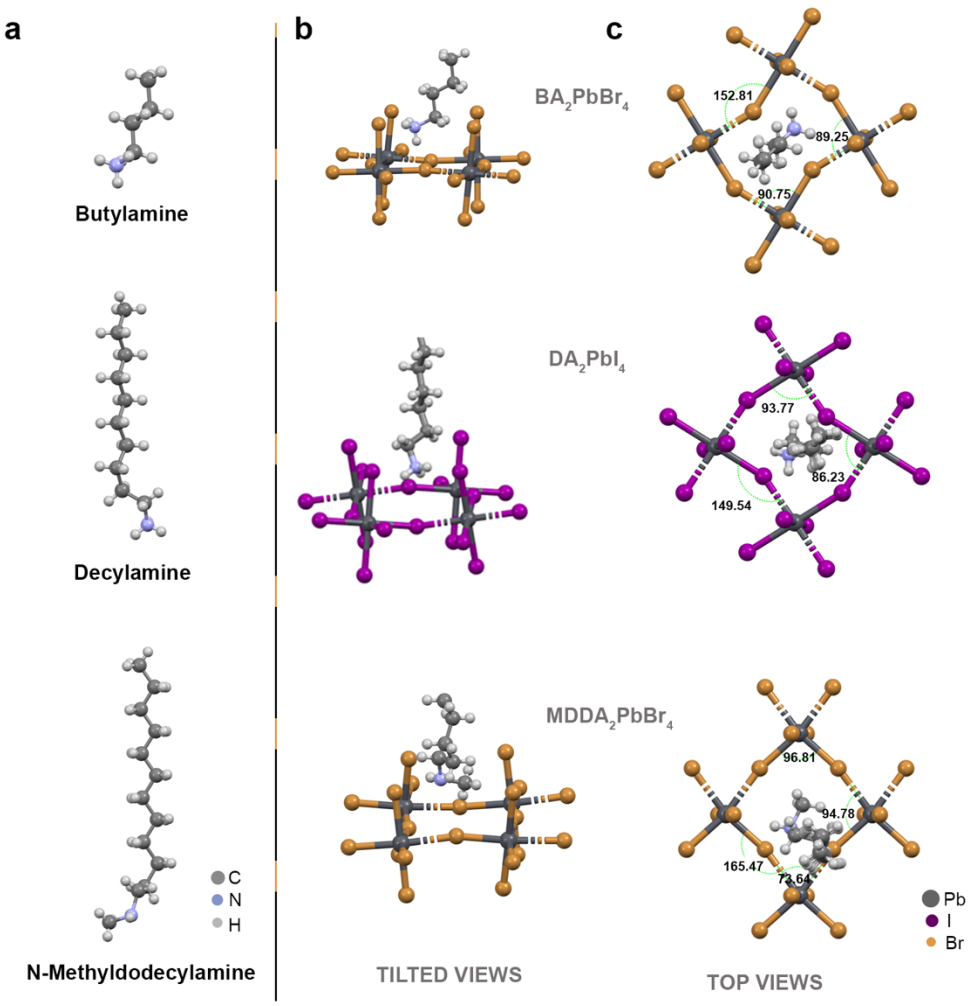

Figure S1. a. Front view of the organic cations showing how the amines are anchored in the void formed by four Pb-halide octahedra (omitted in the views) extracted from the corresponding crystallographic data. **b-c.** Representative tilted (b) and top (c) structural views of the 2D Ruddlesden-Popper layered perovskites derived from crystallographic data collected at low temperature for $(BA)_2PbBr_4$ (4K),[1] $(DA)_2PbI_4$ (CCDC No. 805436; 268K),[2] and $(N\text{-}MDDA)_2PbBr_4$ (100K).[3] The in-plane angles are denoted in the top views. For better visualization, the DA and MDDA organic cations are partially shown in panel (b).

In the discussion on the tilting and in-plane angles for $(UDA)_2PbBr_4$ we refer to the crystallographic data recorded from $(DA)_2PbI_4$. Although the change in the halide anion can

lead to different crystallographic angles, we think that these variations will be minor, considering the data in Table S1.

Table S1. Crystallographic angles $(BA)_2PbI_4$ (I-BA), $(DA)_2PbI_4$ (I-DA), and $(BA)_2PbBr_4$ (Br-BA) taken from data in the literature that was collected at low temperature, and which results in the orthorhombic crystal structure and same space group (pbca/61), see refs. 1, 2.

	I-BA	I-DA	Br-BA
Angle 1 Internal I-Pb-I	88.74°	86.23°	89.25°
Angle 2 Internal I-Pb-I	91.26°	93.77°	90.75°
Angle 3 External Pb-I-Pb	155.2°	149.54°	152.81°

We see that the in-plane angles overall vary only by a few degrees within these systems, and therefore we expect similar values for $(UDA)_2PbBr_4$ and $(DA)2PbBr_4$. This means a relatively strong in-plane distortion together with some out-of-plane tilting of the octahedra, which is the significant trend for the discussion of our optical data.

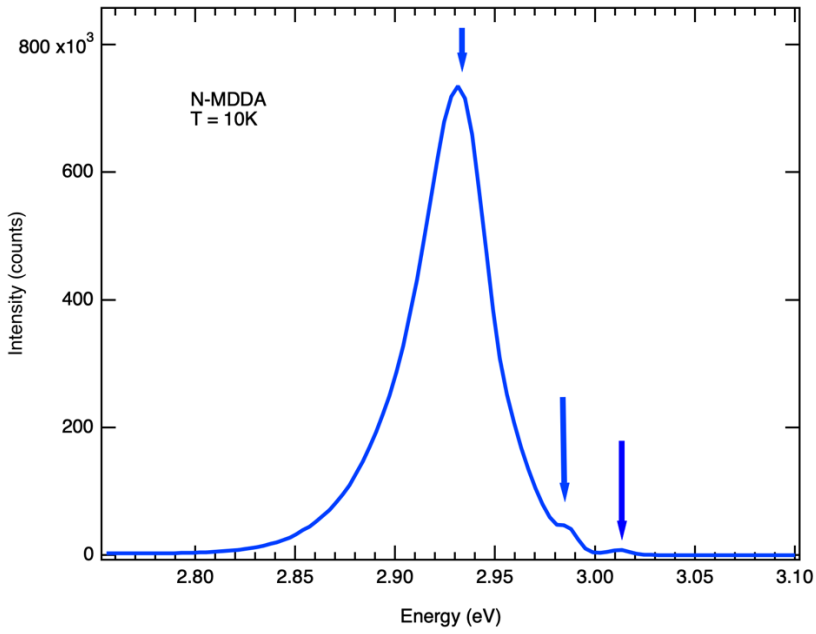

Figure S2. Spectrum of *N-MDDA* recorded at T=10K. Three distinct peaks marked by the arrows can be identified.

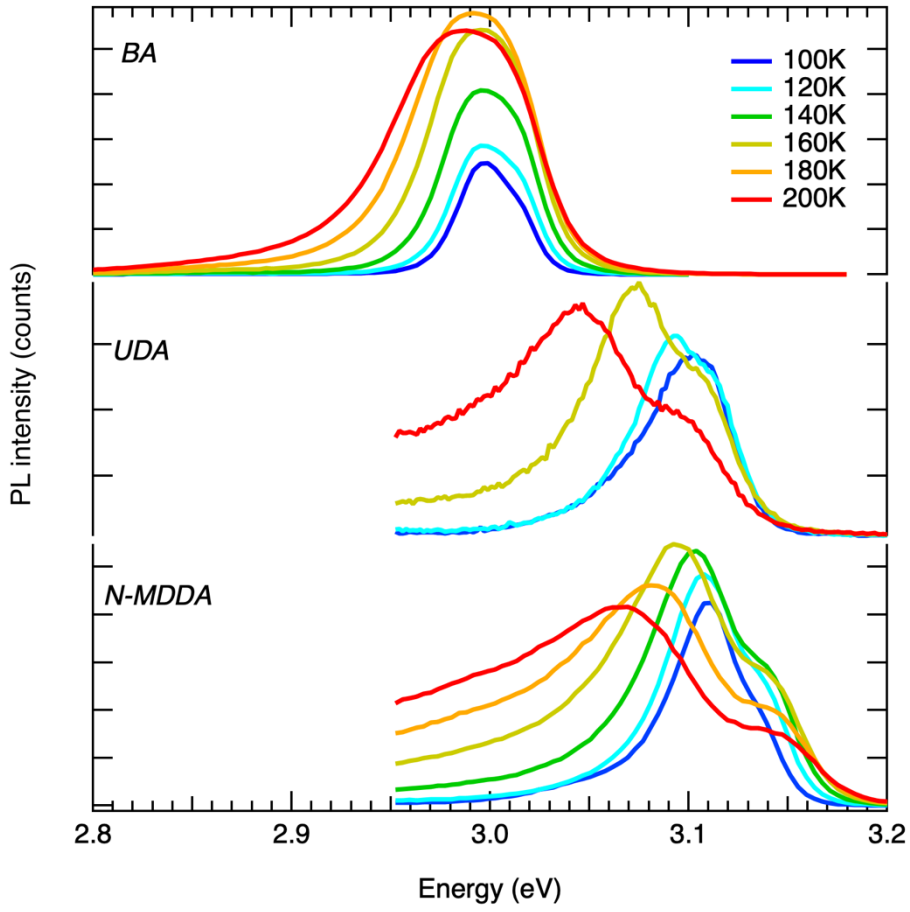

Figure S3. PL spectra of the *BA*, *UDA*, and *N-MDDA* 2DLP samples at higher temperatures, in the range from 100-200 K.

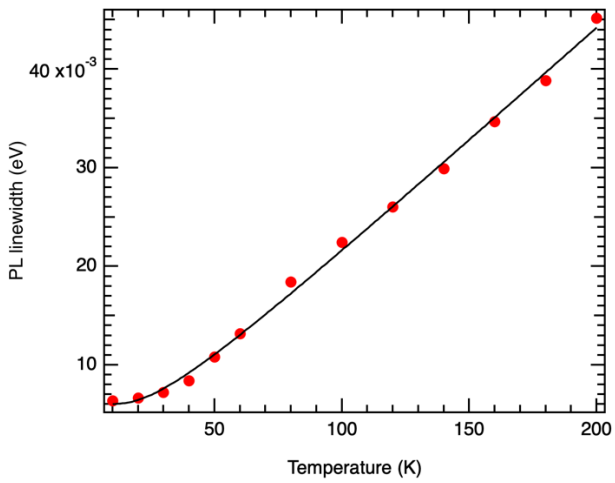

Figure S4. PL linewidth fitting of the *BA*-sample with Equation 2 of the main text. Fitting parameters are. Γ_0=6 meV, E_{LO}=6.3 meV, Γ_{LO}=17 meV.

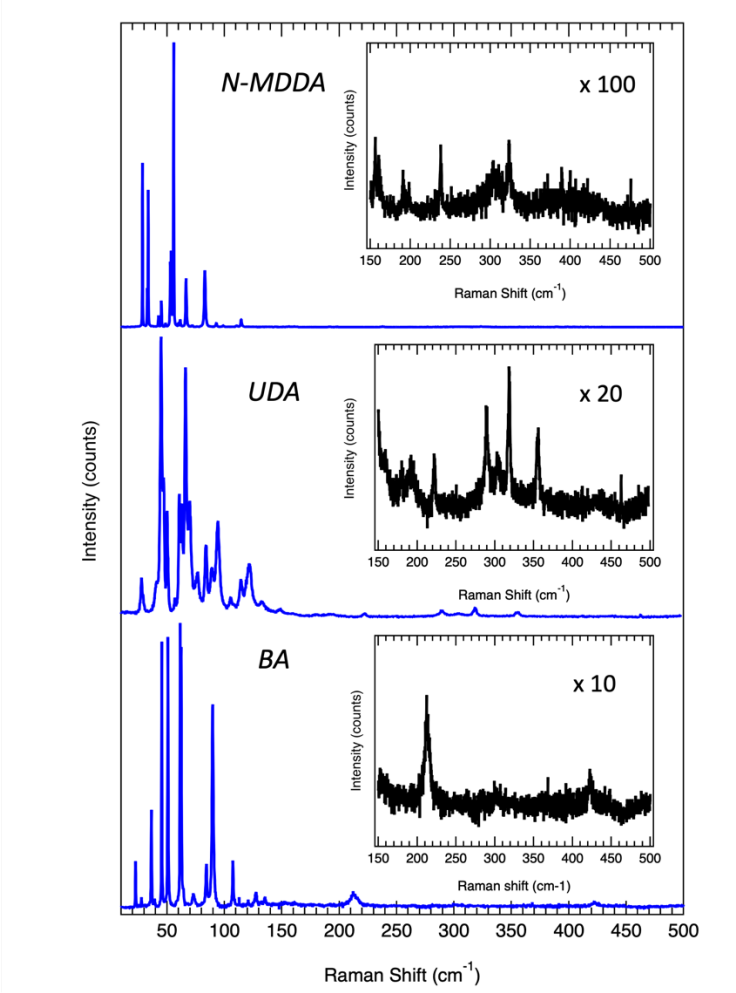

Figure S5. Raman spectra recorded at low temperature (5K) in the range from 8-500 cm^{-1} (1-62 meV) from the 2DLP samples discussed in this work. The insets show the high-frequency part of the spectra on an enlarged scale.

We recorded Raman spectra of our samples covering an energy range from 8-500 cm^{-1} (1-60 meV), Figure S5, to investigate if such phonons from the organic cations are present in our systems and could play a dominant role in the emission dynamics. We find that for all samples

the spectra are dominated by phonon modes with frequencies below 150 cm^{-1} that can be attributed to vibrations of the inorganic lattice.[4] On a magnified scale as shown in the insets of Figure S5 we can distinguish some weak Raman peaks in the range from 160-480 cm^{-1} (20-60 meV), in particular at 212 cm^{-1} for BA (with a second harmonic at 420 cm^{-1}), at 222 cm^{-1}, 290 cm^{-1}, 318 cm^{-1}, and 355 cm^{-1} for UDA, and very weak peaks at 238 cm^{-1} and 323 cm^{-1} for N-MDDA.

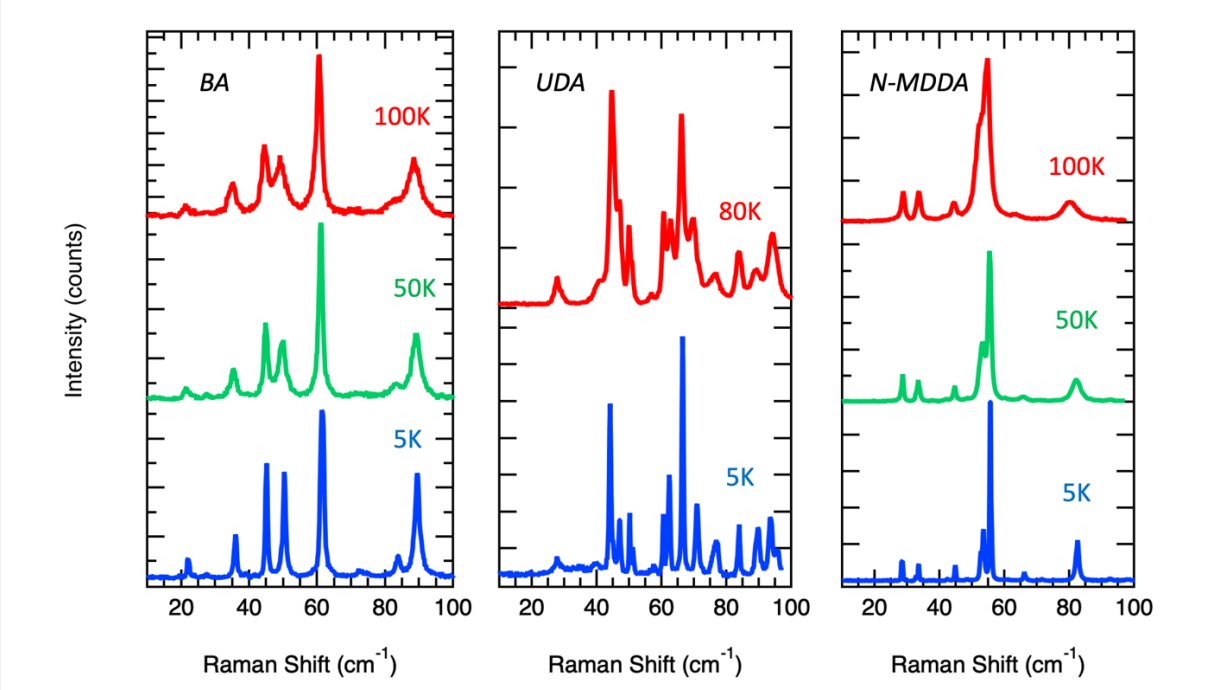

Figure S6. Raman spectra recorded from the BA, UDA and N-MDDA samples at different temperatures. Excitation wavelength was 633 nm.

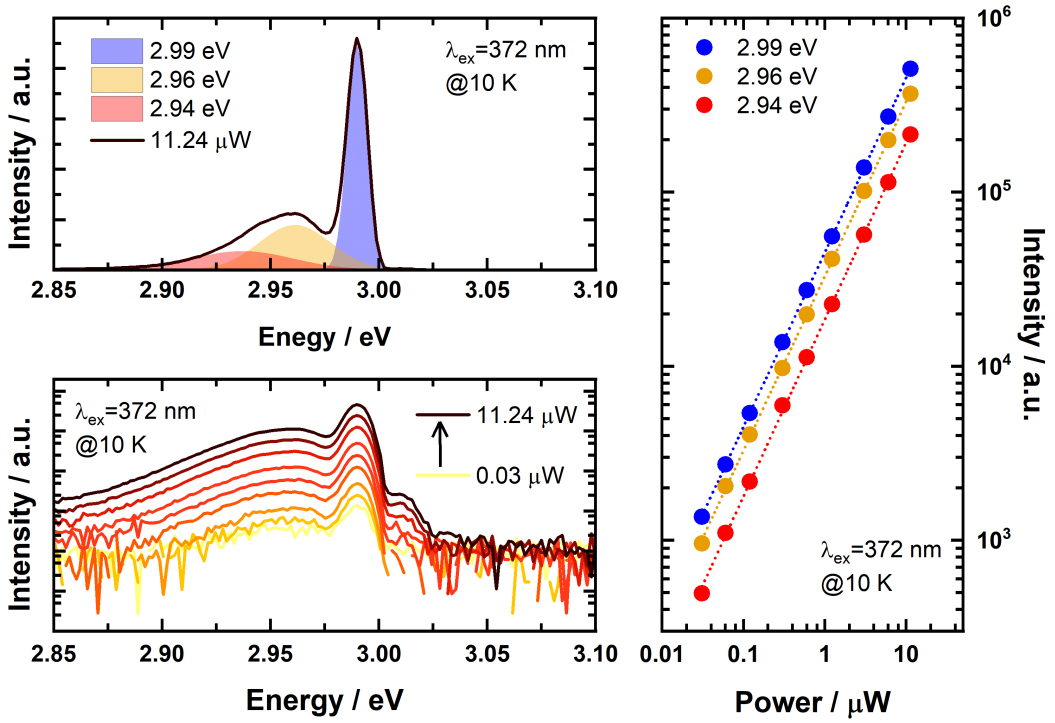

Figure S7. PL spectra recorded from the BA sample at 10K for different excitation power with a laser at 372 nm wavelength. The illumination spot had a diameter of 2 mm.

References

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2. A. Lemmerer and D. G. Billing, *Dalton Trans.*, 2012, **41**, 1146-1157.
3. B. Dhanabalan, G. Biffi, A. Moliterni, V. Olieric, C. Giannini, G. Saleh, L. Ponet, M. Prato, M. Imran, L. Manna, R. Krahne, S. Artyukhin and M. P. Arciniegas, *Adv. Mater.*, 2021, **33**, 2008004.
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