Supplementary Information (SI) for Nanoscale.

Theoretical Insights into Spacer Molecule Design to Tune Stability, Dielectric, and Exciton Properties in 2D Perovskites

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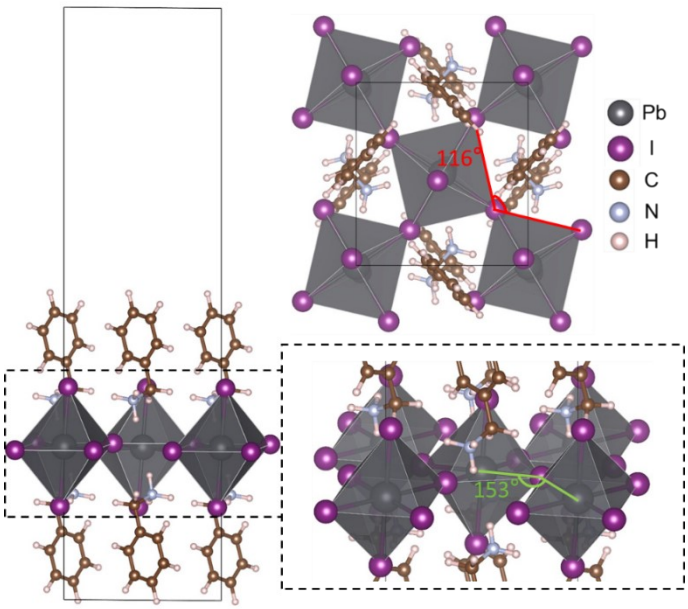

Figure S1. Relaxed crystal structure of monolayer (PMA)PbI_4 perovskite. Pb-I-Pb bond angle and I-I-I bond angle are highlighted in the enlarged figure and the figure viewed along c axis.

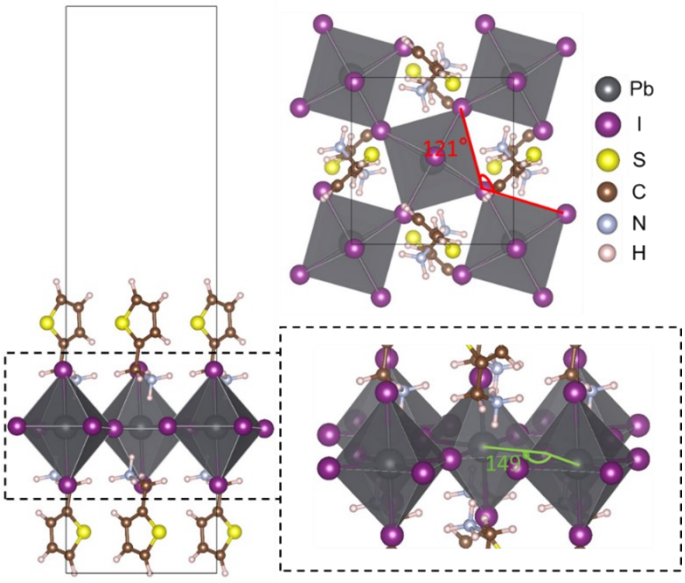

Figure S2. Relaxed crystal structure of monolayer (THMA)PbI_4 perovskite. Pb-I-Pb bond angle and I-I-I bond angle are highlighted in the enlarged figure and the figure viewed along c axis.

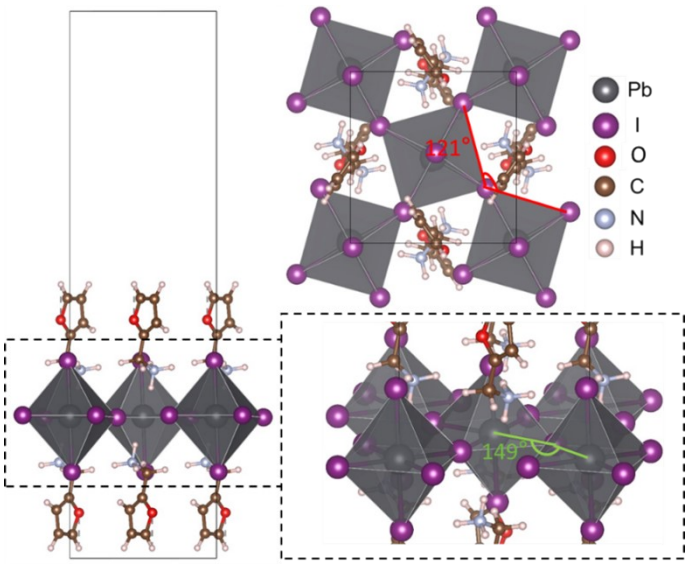

Figure S3. Relaxed crystal structure of monolayer (FUMA)PbI_4 perovskite. Pb-I-Pb bond angle and I-I-I bond angle are highlighted in the enlarged figure and the figure viewed along c axis.

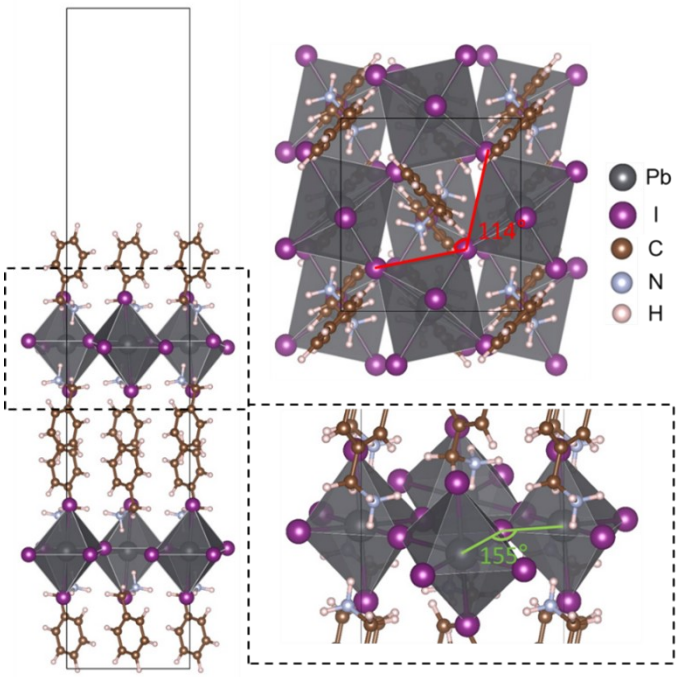

Figure S4. Relaxed crystal structure of bilayer (PMA)PbI_4 perovskite. Pb-I-Pb bond angle and I-I-I bond angle are highlighted in the enlarged figure and the figure viewed along c axis.

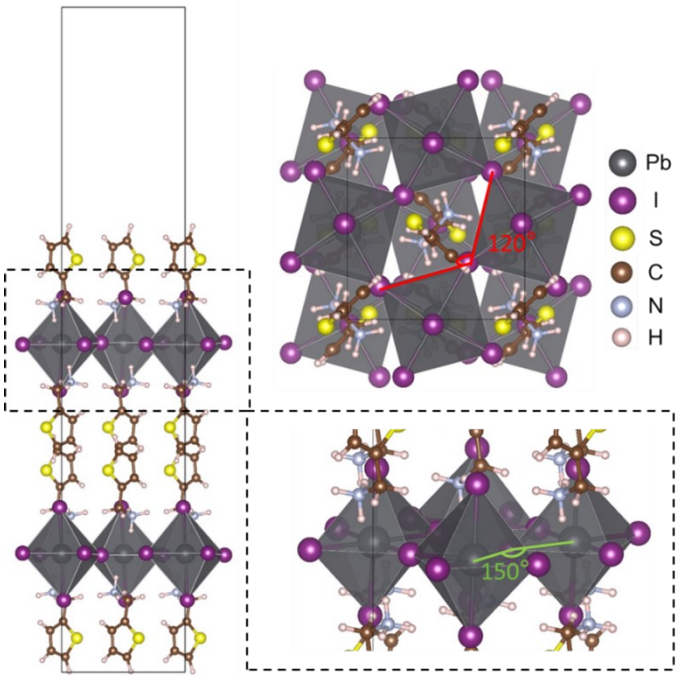

Figure S5. Relaxed crystal structure of bilayer (THMA)PbI_4 perovskite. Pb-I-Pb bond angle and I-I-I bond angle are highlighted in the enlarged figure and the figure viewed along c axis.

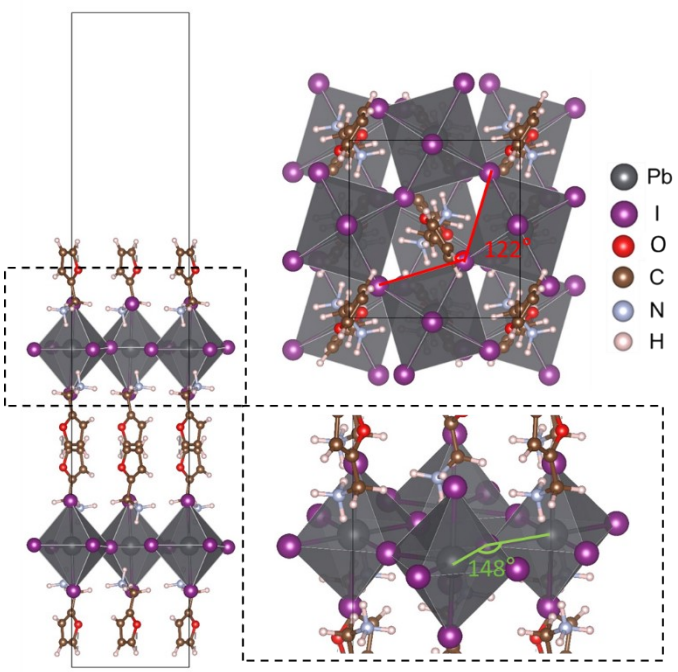

Figure S6. Relaxed crystal structure of bilayer (FUMA)PbI_4 perovskite. Pb-I-Pb bond angle and I-I-I bond angle are highlighted in the enlarged figure and the figure viewed along c axis.

Table S1 Relaxed lattice constants of 2D RP phase of Pb-I perovskites (n=1) with different spacer molecules of PMA, THMA and FUMA.

		a(Å)	b(Å)	α(°)	β(°)	γ(°)
Monolayer	$(PMA)_2PbI_4$	8.49, 8.67[a]	9.05, 9.14[a]	90.00	89.57	90.00
	$(THMA)_2PbI_4$	8.53, 8.70[b]	8.78, 8.83[b]	89.76	90.00	90.00
	$(FUMA)_2PbI_4$	8.55	8.81	90.07	90.00	90.00
Bilayer	$(PMA)_2PbI_4$	8.56, 8.67[a]	9.14, 9.14[a]	90.00	90.00	90.00
	$(THMA)_2PbI_4$	8.60, 8.70[b]	8.81, 8.83[b]	90.00	90.00	90.00
	$(FUMA)_2PbI_4$	8.45	8.82	90.00	90.00	90.00

[a] Data from ref. 1. [b] Data from ref. 2.

Table S2 Geometrical characteristics of octohedra in relaxed 2D RP phase of Pb-I perovskites (n=1) with different spacer molecules of PMA, THMA and FUMA.

		Pb-I-Pb (°)	I-I-I (°)	Thickness (Å)	Pb-I equatorial (Å)	Pb-I vertical (Å)
Monolayer	$(PMA)_2PbI_4$	153	116	16.61	3.191	3.236
	$(THMA)_2PbI_4$	149	121	16.47	3.177	3.245
	$(FUMA)_2PbI_4$	149	121	15.34	3.184	3.231
Bilayer	$(PMA)_2PbI_4$	155	114	30.90	3.208	3.236
	$(THMA)_2PbI_4$	150	120	31.06	3.183	3.251
	$(FUMA)_2PbI_4$	148	122	29.79	3.179	3.245

Table S3 Structural parameters quantifying internal distortions in relaxed 2D RP phase of Pb-I perovskites (*n*=1) with different spacer molecules of PMA, THMA and FUMA.

		Average octahedral angle variance (σ_{oct}^{2})	Average octahedron distortion parameter (Δ)	Average quadratic elongation (‹λ›)
Monolayer	$(PMA)_2PbI_4$	13.25	4.65E-05	1.00005
	$(THMA)_2PbI_4$	5.59	9.97E-05	1.00010
	$(FUMA)_2PbI_4$	5.84	4.92E-05	1.00005
Bilayer	$(PMA)_2PbI_4$	14.46	1.18E-05	1.00001
	$(THMA)_2PbI_4$	7.14	7.95E-05	1.00008
	$(FUMA)_2PbI_4$	5.88	7.97E-05	1.00008

Reference

1. M.-H. Tremblay, J. Bacsa, B. Zhao, F. Pulvirenti, S. Barlow and S. R. Marder, Chem. Mater., 2019, 31, 6145-6153.
2. C. Ni, Y. Huang, T. Zeng, D. Chen, H. Chen, M. Wei, A. Johnston, A. H. Proppe, Z. Ning, E. H. Sargent, P. Hu and Z. Yang, Angew Chem Int Ed Engl, 2020, 59, 13977-13983.