

# ADVANCED ENERGY MATERIALS

## Supporting Information

for *Adv. Energy Mater.*, DOI 10.1002/aenm.202303405

Rationalizing Electron–Phonon Interactions and Hot Carriers Cooling in 2D to 3D Metal Halide Perovskites

*Arup Mahata\**, *Edoardo Mosconi*, *Daniele Meggiolaro\**, *Simona Fantacci* and *Filippo De Angelis\**

## Supporting Information

**Rationalizing Electron-Phonon Interactions and Hot Carriers Cooling in 2D to 3D Metal Halide Perovskites**

*Arup Mahata,\* Edoardo Mosconi, Daniele Meggiolaro,\* Simona Fantacci, Filippo De Angelis\**

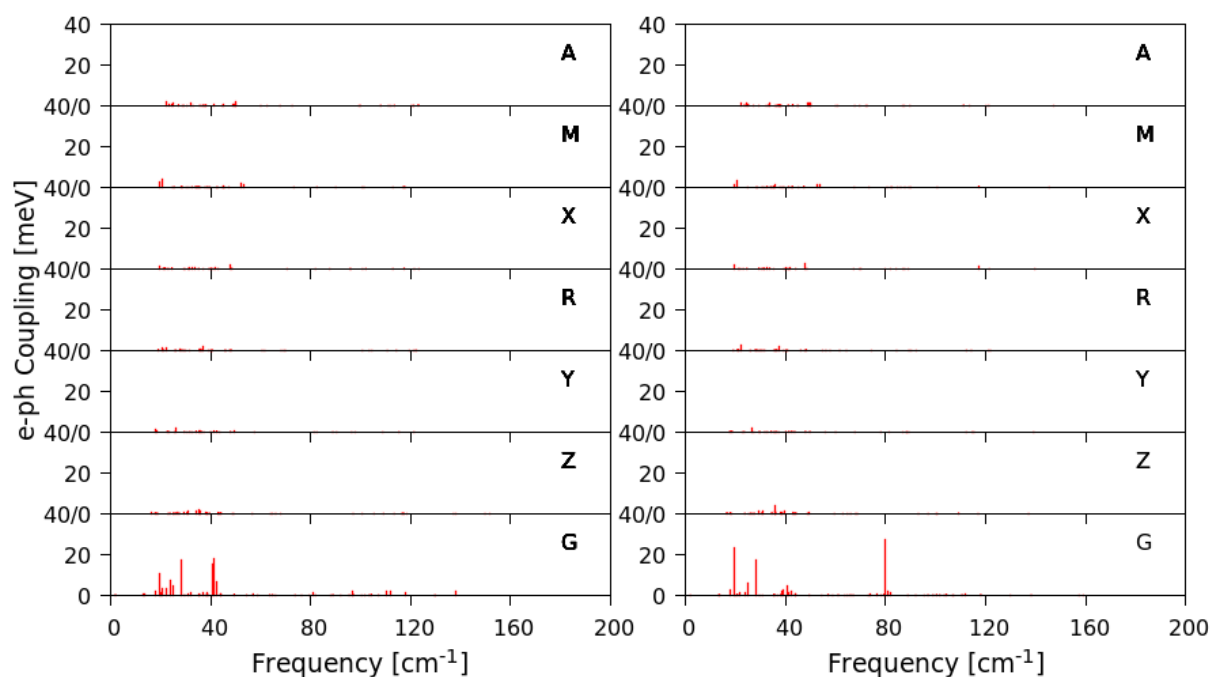
**Text S1.** Computational Details

The first-principles calculations based on density functional theory (DFT) are carried out as implemented in the PWSCF Quantum-Espresso package.<sup>1</sup> Geometry optimization is performed using GGA-PBE<sup>2</sup> level of theory, and the electrons-ions interactions were described by ultrasoft pseudo-potentials with electrons from I 5s, 5p; N, C 2s, 2p; H 1s; Pb 6s, 6p, 5d; shells explicitly included in calculations. The experimental cell parameters have been used in all the cases for the *a* and *b* directions of the lattice, whereas half of the cell parameter of *c* is considered in some cases, where two quantum wells are present in the experimental crystal structures. The cell parameters for MAPbI<sub>3</sub>, BA-n1, PEA-n1, BA-n3, PEA-n3, and OCTA-n1 have been taken from Ref<sup>3</sup>, Ref<sup>4</sup>, Ref<sup>5</sup>, Ref<sup>6</sup>, Ref<sup>7</sup>, Ref<sup>8</sup>, respectively. Geometry optimizations for 2×2×1 supercell are performed with a k-point sampling<sup>9</sup> of 4×4×2, along with plane-wave basis set cutoffs for the smooth part of the wave functions and augmented electronic density expansions of 25 and 200 Ry, respectively.

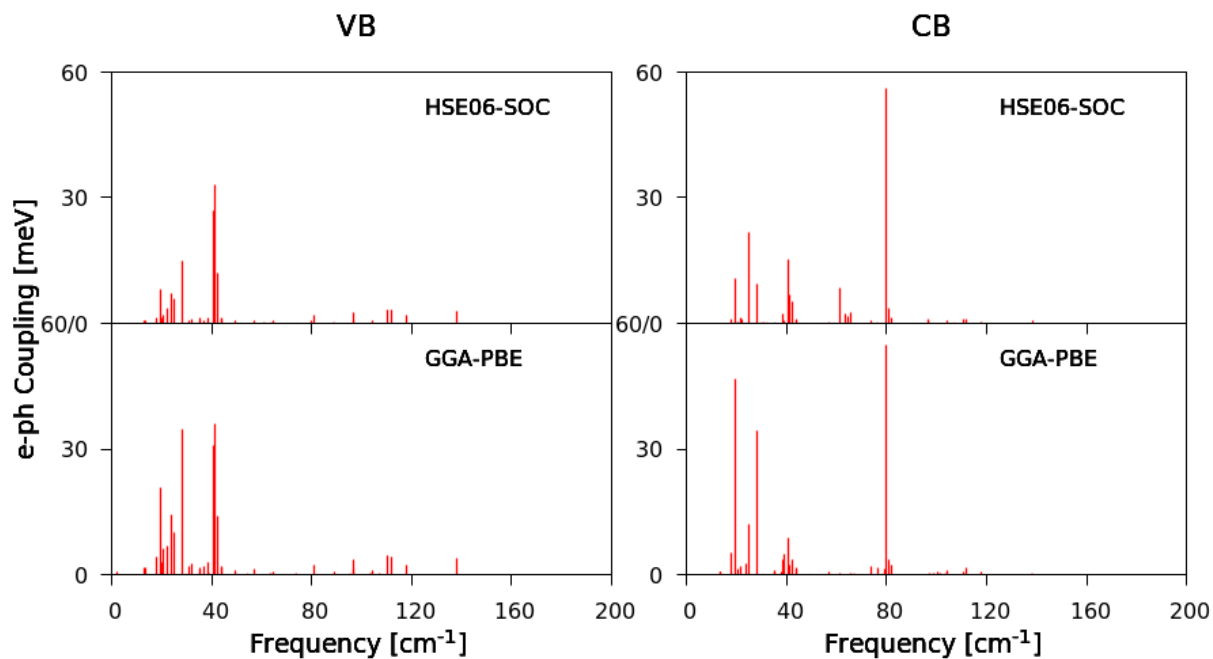
Electronic band gap is calculated by single-point hybrid calculations including spin-orbit coupling (SOC). These are conducted using the modified version of the HSE06 functional<sup>10</sup> including 43% Hartree-Fock exchange as in Ref<sup>11</sup> with norm-conserving pseudo-potentials with electrons from I 5s, 5p; N, C 2s, 2p; H 1s; Pb 5s, 5p, 6s, 6p, 5d; shells are explicitly included in calculations, with 2×2×1 k-point sampling with plane-wave basis set cutoffs for the

smooth part of the wave functions and augmented electronic density expansions of 40 and 80Ry, respectively.

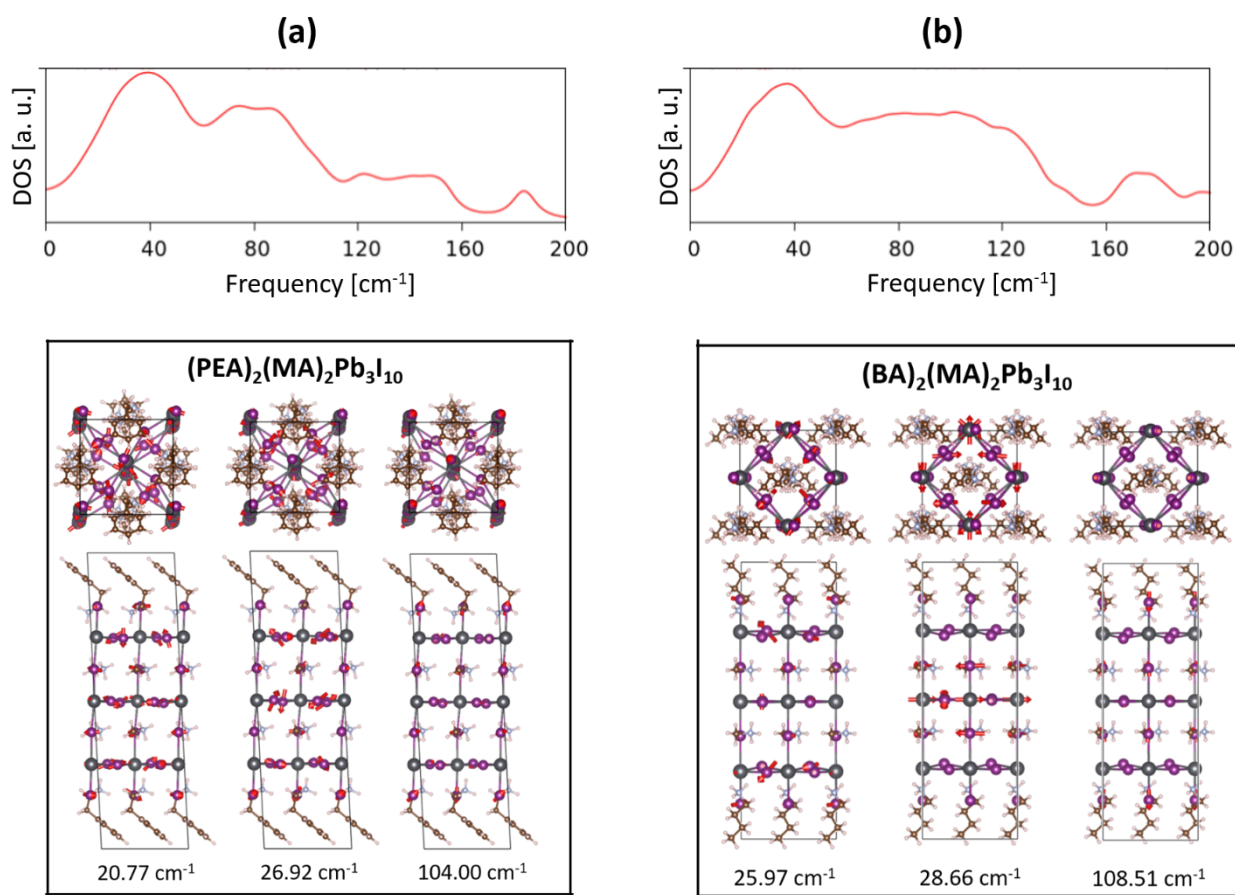
Frequency calculations have been performed by DFPT and by using PBE functional and ultrasoft pseudopotentials with a cutoff on the wavefunction of 25 Ry (200 Ry on the charge density) and uniform  $4 \times 4 \times 2$  grid of k-points in the Brillouin zone. Phonon DOS has been plotted from the interatomic force constant in real space, which was calculated from the dynamical matrices produced at  $\Gamma$  point followed by their Fourier-transformation. For MAPbI<sub>3</sub>, the phonon DOS is reported for  $2 \times 2 \times 2$  grid of k-points.



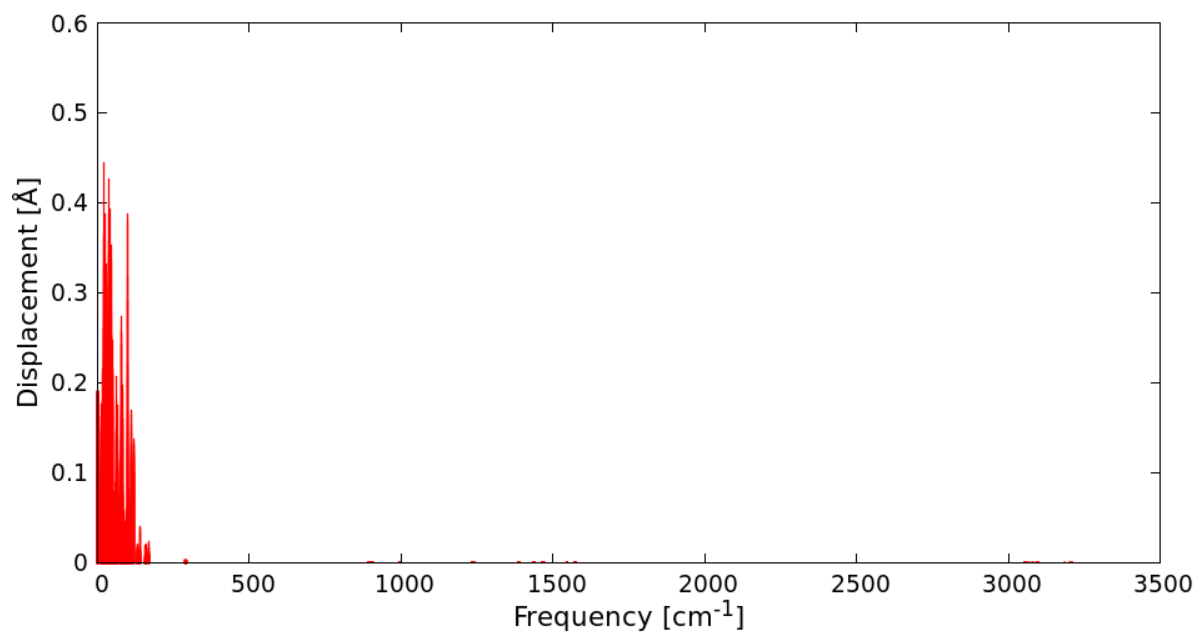
**Figure S1.** e-ph interaction of MAPbI<sub>3</sub> for the band edge states at different q-points in GGA-PBE level of theory. Left and right panels represent the e-ph coupling at VBM and CBM, respectively.



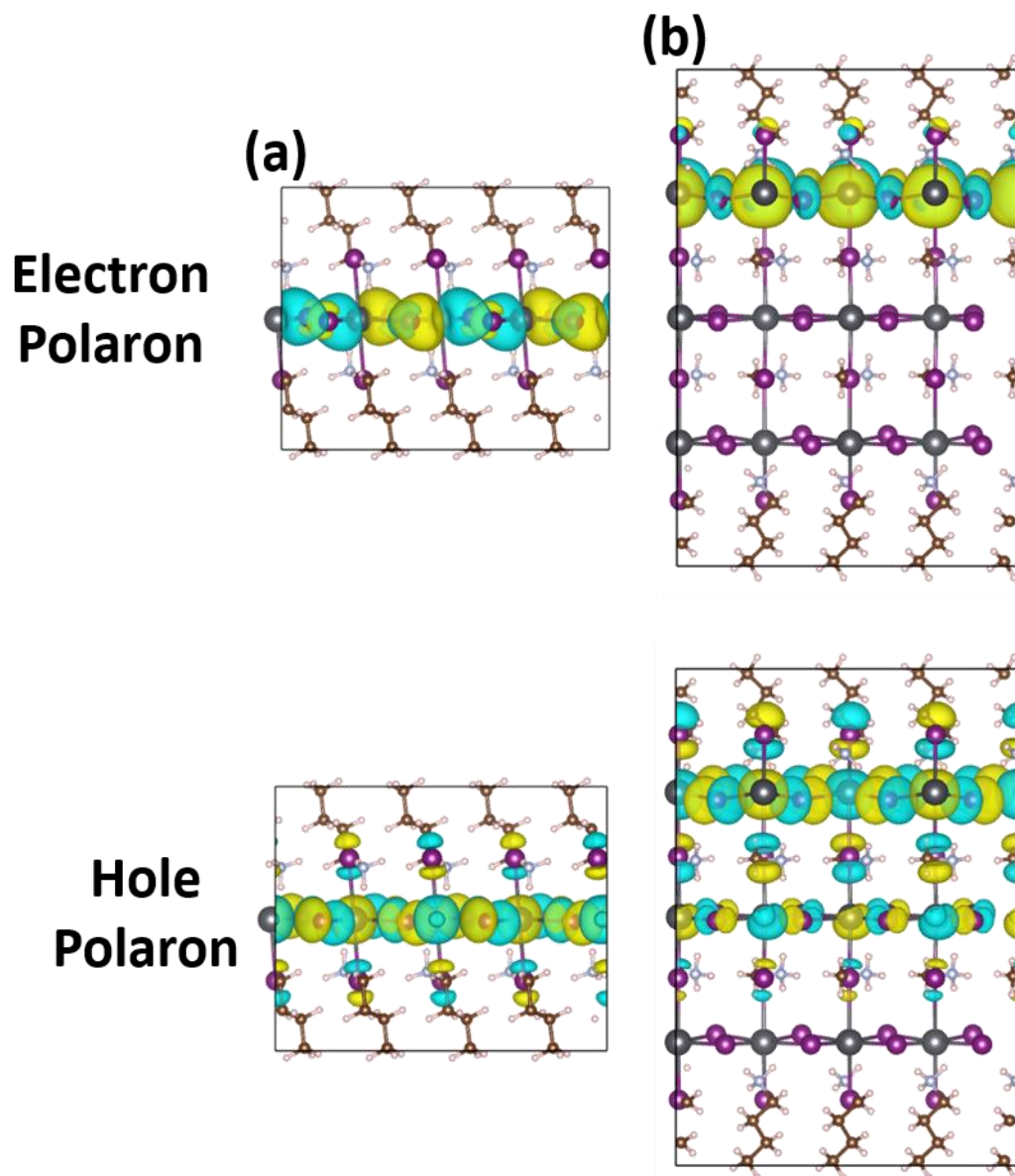
**Figure S2.** e-ph interaction of MAPbI<sub>3</sub> for the band edge state at  $\Gamma$  q-point at different level of theory



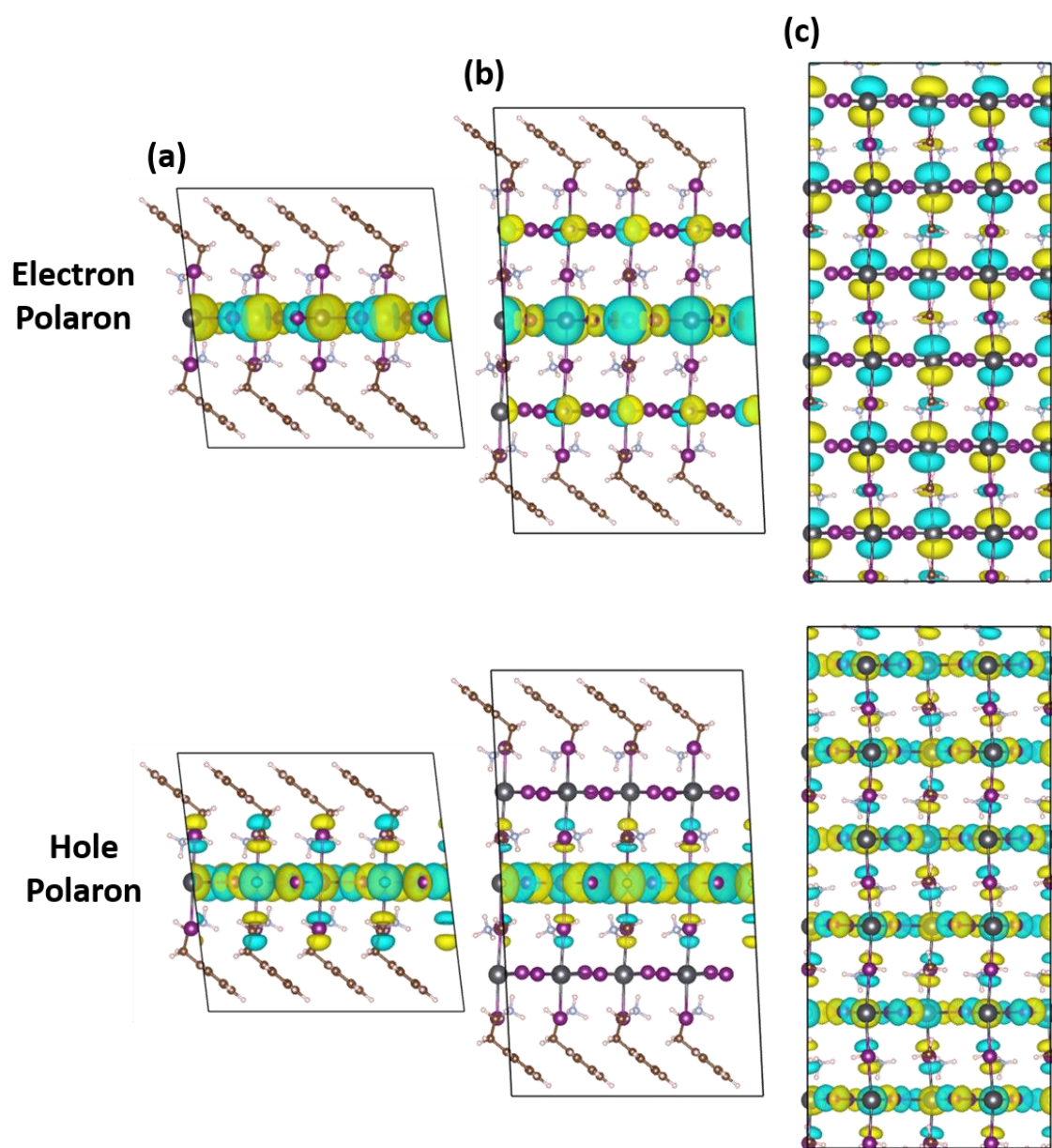
**Figure S3.** Phonon DOS and vibrations having significant e-ph coupling of (a) PEA-n3 and (b) BA-n3



**Figure S4.** Atomic displacements of the inorganic moiety for each normal mode of MAPbI<sub>3</sub>.



**Figure S5.** Wave function localization for the electron (upper panel) and hole (lower panel) polaron of (a) BA-n1 and (b) BA-n3.



**Figure S6.** Wave function localization for the electron (upper panel) and hole (lower panel) polaron of (a) PEA-n1, (b) PEA-n3 and, (c) MAPbI<sub>3</sub>.

**Table S1.** Cumulative e-ph coupling of two higher energy bands above CBM (~1.5, 2.0 and 0.5 eV energy window for 3D, 2D and 2D-n3 phases, respectively) in different frequency regions for the various systems.

Systems		Energy (eV)	e-ph coupling (meV) in different frequency ( $\text{cm}^{-1}$ ) regions			Ratio
			0-60	60-120	120-200	
MAPbI <sub>3</sub>	CBM	0.00	78	82	0	9 : 10 : 0
	CBM1	0.74	26	24	0	10 : 9 : 0
	CBM2	1.49	36	36	0	10 : 10 : 0
	<b>Total</b>		<b>140</b>	<b>142</b>	<b>0</b>	<b>10 : 10 : 0</b>
PEA <sub>2</sub> PbI <sub>4</sub>	CBM	0.00	54	404	0	1 : 10 : 0
	CBM1	1.27	42	226	0	2 : 10 : 0
	CBM2	1.99	82	642	0	1 : 10 : 0
	<b>Total</b>		<b>178</b>	<b>1272</b>	<b>0</b>	<b>1 : 10 : 0</b>
BA <sub>2</sub> PbI <sub>4</sub>	CBM	0.00	66	350	4	2 : 10 : 0
	CBM1	1.29	52	190	6	3 : 10 : 0
	CBM2	1.93	20	1170	2	0 : 10 : 0
	<b>Total</b>		<b>138</b>	<b>1710</b>	<b>12</b>	<b>1 : 10 : 0</b>
OCTA <sub>2</sub> PbI <sub>4</sub>	CBM	0.00	78	134	0	6 : 10 : 0
	CBM1	1.18	38	90	0	4 : 10 : 0
	CBM2	1.93	68	532	0	1 : 10 : 0
	<b>Total</b>		<b>184</b>	<b>756</b>	<b>0</b>	<b>2 : 10 : 0</b>
(BA) <sub>2</sub> (MA) <sub>2</sub> Pb <sub>3</sub> I <sub>10</sub>	CBM	0.00	62	104	20	6 : 10 : 1
	CBM1	0.24	40	104	6	4 : 10 : 0
	CBM2	0.45	124	78	8	10 : 6 : 0
	<b>Total</b>		<b>226</b>	<b>286</b>	<b>34</b>	<b>8 : 10 : 1</b>



**Table S2.** Cumulative e-ph coupling of five lower energy bands (~1.0 eV energy window for all phases) below VBM in different frequency regions for the various systems.

Systems		Energy (eV)	e-ph coupling (meV) in different frequency (cm <sup>-1</sup> ) regions			Ratio
			0-60	60-120	120-200	
MAPbI <sub>3</sub>	VBM	0.00	124	18	2	10 : 1 : 0
	VBM-1	0.39	44	20	4	10 : 4 : 1
	VBM-2	0.98	40	40	10	10 : 10 : 2
	VBM-3	1.04	40	22	0	10 : 5 : 0
	VBM-4	1.07	16	16	16	10 : 10 : 10
	VBM-5	1.20	46	32	20	10 : 7 : 4
	<b>Total</b>			<b>310</b>	<b>148</b>	<b>52</b>
PEA <sub>2</sub> PbI <sub>4</sub>	VBM	0.00	86	226	2	4 : 10 : 0
	VBM-1	0.76	30	154	0	2 : 10 : 0
	VBM-2	0.95	64	192	4	3 : 10 : 0
	VBM-3	0.98	60	126	2	10 : 5 : 0
	VBM-4	0.99	30	38	0	8 : 10 : 0
	VBM-5	1.07	48	38	0	10 : 8 : 0
	<b>Total</b>			<b>318</b>	<b>774</b>	<b>8</b>
BA <sub>2</sub> PbI <sub>4</sub>	VBM	0.00	74	366	8	2 : 10 : 0
	VBM-1	0.81	38	308	8	1 : 10 : 0
	VBM-2	0.89	66	194	10	3 : 10 : 0
	VBM-3	0.90	44	92	10	5 : 10 : 1
	VBM-4	1.00	30	92	4	3 : 10 : 0
	VBM-5	1.04	14	60	2	2 : 10 : 0
	<b>Total</b>			<b>266</b>	<b>1112</b>	<b>42</b>
OCTA <sub>2</sub> PbI <sub>4</sub>	VBM	0.00	128	204	0	6 : 10 : 0
	VBM-1	0.62	48	132	0	3 : 10 : 0
	VBM-2	0.80	74	118	0	6 : 10 : 0
	VBM-3	0.82	42	64	0	6 : 10 : 0
	VBM-4	0.93	20	44	0	4 : 10 : 0
	VBM-5 & CBM	0.99	32	58	0	5 : 10 : 0
	<b>Total</b>			<b>344</b>	<b>620</b>	<b>0</b>
(BA) <sub>2</sub> (MA) <sub>2</sub> Pb <sub>3</sub> I <sub>10</sub>	VBM	0.00	130	62	16	10 : 5 : 1
	VBM-1	0.31	62	72	32	9 : 10 : 4
	VBM-2	0.34	84	82	54	10 : 10 : 6
	VBM-3	0.85	34	36	2	10 : 10 : 0
	VBM-4	0.97	24	34	6	7 : 10 : 2
	VBM-5	1.00	18	22	8	8 : 10 : 4
	<b>Total</b>			<b>352</b>	<b>308</b>	<b>118</b>

**Table S3.** Cell parameters considered in this paper and the corresponding experimental references.

Systems	Cell Parameters (Å)	References
MAPbI <sub>3</sub>	8.849 0.000 0.00 0.000 8.849 0.000 0.000 0.000 12.642	Ref <sup>3</sup>
BA-n1	8.8512 0.0000 0.0000 0.0000 8.6543 0.0000 0.0000 0.0000 13.86765	Ref <sup>4</sup>
PEA-n1	8.7398 0.0000 0.0000 0.0152 8.7402 0.0000 1.0438 1.5916 16.5156	Ref <sup>5</sup>
BA-n3	8.9274 0.0000 0.0000 0.0000 25.9794 0.0000 0.0000 0.0000 8.8776	Ref <sup>6</sup>
PEA-n3	30.69 0.000 0.000 0.000 8.9 0.000 -0.43481 0.000 9.0195	Ref <sup>7</sup>
OCTA-n1	8.4541 0.0000 0.0000 0.0000 8.9916 0.0000 -2.0565 0.0000 18.6248	Ref <sup>8</sup>

## References

- [1] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, L. C. Guido, M. Cococcioni, I. Dabo, A. D. Corso, S. d. Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, R. M. Wentzcovitch, *J. Phys.: Condens. Matter* **2009**, *21*, 395502.
- [2] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865.
- [3] C. C. Stoumpos, C. D. Malliakas, M. G. Kanatzidis, *Inorg. Chem.* **2013**, *52*, 9019.
- [4] T. Yin, B. Liu, J. Yan, Y. Fang, M. Chen, W. K. Chong, S. Jiang, J.-L. Kuo, J. Fang, P. Liang, S. Wei, K. P. Loh, T. C. Sum, T. J. White, Z. X. Shen, *J. Am. Chem. Soc.* **2019**, *141*, 1235.
- [5] S. Liu, S. Sun, C. K. Gan, A. G. del Águila, Y. Fang, J. Xing, T. T. H. Do, T. J. White, H. Li, W. Huang, Q. Xiong, *Sci. Adv.* **2019**, *5*, eaav9445.
- [6] C. C. Stoumpos, D. H. Cao, D. J. Clark, J. Young, J. M. Rondinelli, J. I. Jang, J. T. Hupp, M. G. Kanatzidis. *Chem. Mater.* **2016**, *28*, 2852.
- [7] J. Yin, P. Maity, L. Xu, A. M. El-Zohry, H. Li, O. M. Bakr, J.-L. Brédas, O. F. Mohammed, *Chem. Mater.* **2018**, *30*, 8538.
- [8] A. Lemmerer, D. G. Billing, *Dalton Trans.* **2012**, *41*, 1146.
- [9] H. J. Monkhorst, J. D. Pack, *Phys. Rev. B* **1976**, *13*, 5188.
- [10] J. Heyd, G. E. Scuseria, M. Ernzerhof, *J. Chem. Phys.* **2003**, *118*, 8207.
- [11] M.-H. Du, *J. Phys. Chem. Lett.* **2015**, *6*, 1461.