Why choosing the right partner is important: stabilization of ternary Cs$_y$GUA$_x$FA$_{(1-y-x)}$PbI$_3$ perovskites - Supporting Information

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Band gap benchmarks

As a test case for the performance of different computational protocols, we considered α-FAPbI$_3$. The results are summarized in Table S1. For the PBE0 and PBE0+SOC calculations, PBEsol geometries have been used. Both PBEsol and PBE0+SOC offer an accurate description of the band gap of α-FAPbI$_3$. However, recently published band gap calculations of 2D halide perovskites[1] and lead-free double perovskites[2] have shown that the employment of PBE0+SOC using geometries that have been relaxed at the PBEsol level provides an accurate description of the band gaps of a broader range of halide perovskites.

Goldschmidt tolerance factors

For the calculations of the Goldschmidt tolerance factor of both pure compounds and binary and ternary mixtures, the extension by Kieslich *et al.*[6, 7] for organic cations has been employed. According to this the effective ionic radii for mixtures of monovalent cation can be estimated by a rigid sphere model that can freely rotate around the center of mass. The effective ionic radii for FA$^+$, GUA$^+$ are 253 pm and 278 pm, respectively. The ionic radii of Cs$^+$, Pb^{2+} and I$^-$ are 167 pm, 119 pm and 220 pm, respectively. The effective ionic radii of the mixed cations have been estimated by considering the fraction of FA$^+$ substituted by either GUA$^+$ or Cs$^+$.

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Table S1: Effect of different exchange-correlation functionals on the band gap of α-FAPbI$_3$.

Functional	Band gap (eV)
PBE	1.71
PBEsol	1.46
PBE0	2.60
PBE0+SOC	1.47
Experimental values	1.43-1.48[3, 4, 5]

In addition, a new tolerance factor for the prediction of the stability of oxide and halide perovskites has been proposed by Bartel *et al.*. According to this new scheme a structure can be classified as a perovskite one if the calculated tolerance factor is less than 4.18. As shown in Tables S4 and S5 the calculated tolerance factor is less than 4.18. The use of this criterion for the systems investigated here leads to the prediction that the perovskite phase of all mixtures should be stable. However this observation is in contrast with our mixing free energy calculations and MD simulations and the solid-state NMR studies,[8] that reveal that although black $GUA_xFA_{(1-x)}PbI_3$ is initially formed, it is thermodynamically unstable, turning into the yellow δ-phase within hours after annealing. On the other hand, the Goldschmidt tolerance factor seems to be more suited for the prediction of the stability of the cation mixtures considered here.

Table S2: Goldschmidt tolerance factors calculated for both pure compounds and binary mixtures.[6, 7] A Goldschmidt tolerance factor > 1 indicates that the perovskite structure should not be stable.

Fraction (x) of FA$^+$ substituted by GUA$^+$ in the FAPbI$_3$ structure	Goldschmidt tolerance factor
0%	0.99
8%	0.99
17%	1.00
25%	1.00
33%	1.00
42%	1.01
50%	1.01
100%	1.04

Table S3: Goldschmidt tolerance factors calculated for the ternary mixtures.[6, 7]

Fraction (x) of FA^+ substituted by GUA^+ in the $FAPbI_3$ structure	Goldschmidt tolerance factor (8% of Cs^+)	Goldschmidt tolerance factor (17% of Cs^+)
8%	0.98	0.96
17%	0.98	0.97
33%	1.00	0.97
50%	1.00	0.98

Table S4: New tolerance factors calculated for both pure compounds and binary mixtures, according to [9]. Values < 4.18 indicate stability of the perovskite phase.

Fraction (x) of FA^+ substituted by GUA^+ in the $FAPbI_3$ structure	New tolerance factor
0%	3.67
8%	3.66
17%	3.65
25%	3.65
33%	3.64
42%	3.63
50%	3.63
100%	3.60

Table S5: New tolerance factors calculated for the ternary mixtures.[9]

Fraction (x) of FA^+ substituted by GUA^+ in the $FAPbI_3$ structure	New tolerance factor (8% of Cs^+)	New tolerance factor (17% of Cs^+)
8%	3.69	3.72
17%	3.68	3.71
33%	3.66	3.69
50%	3.64	3.68

Density of states

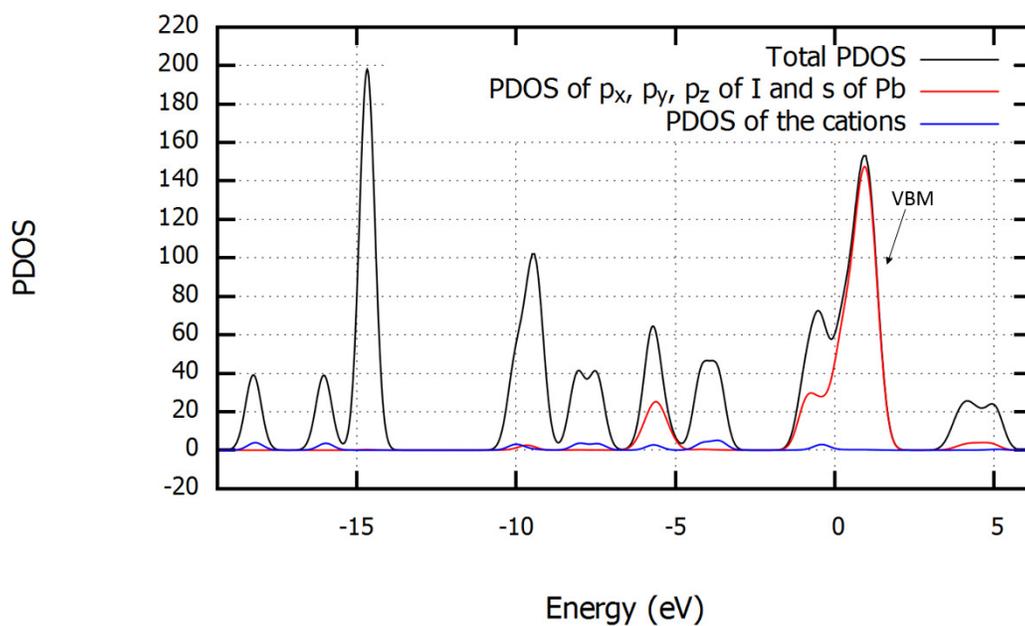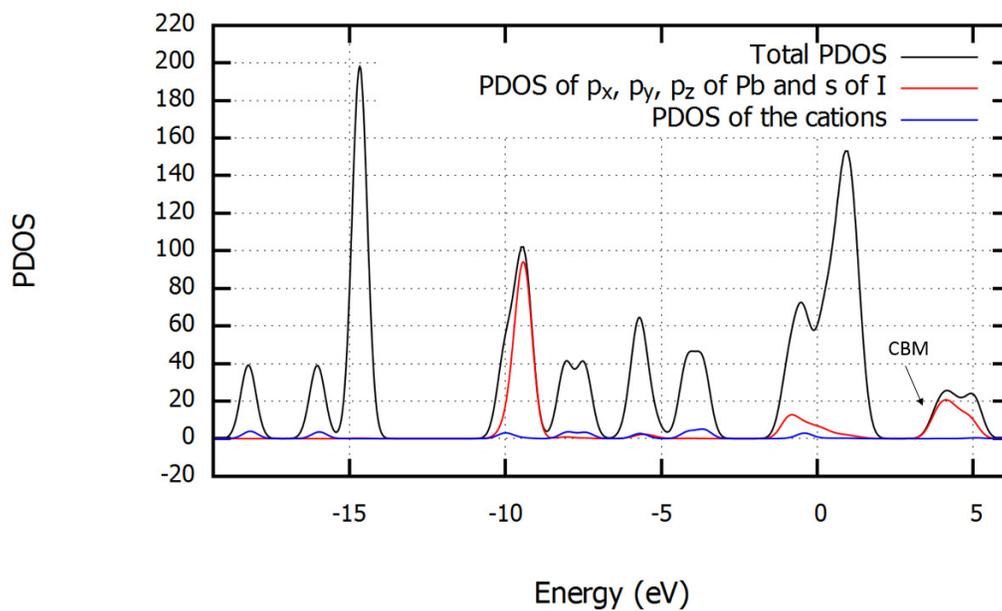Fig. S1: PDOS of β-FAPbI$_3$. The VBM consists of an antibonding overlap of Pb s and I p orbitals.

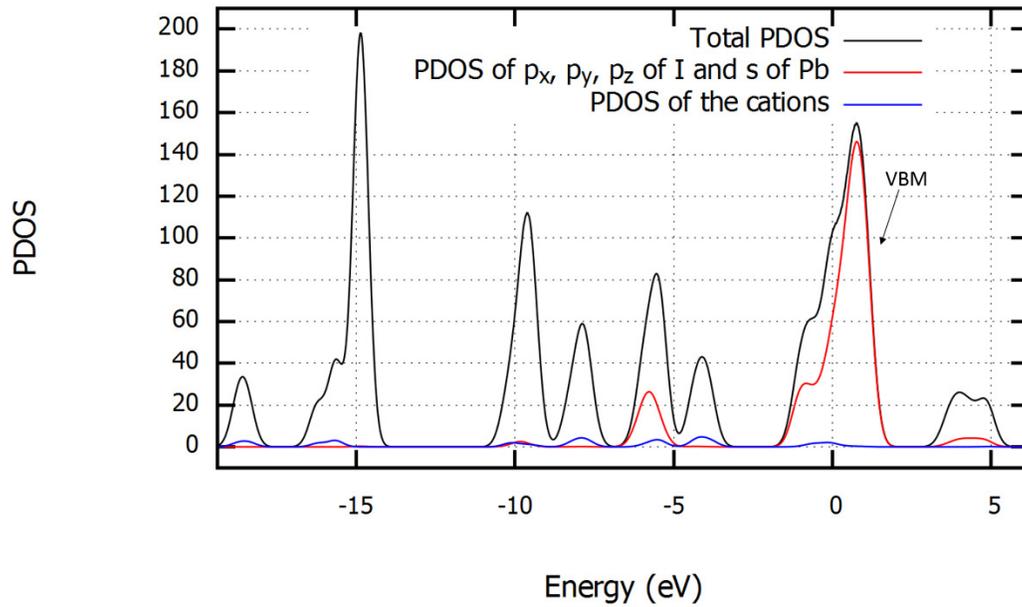Fig. S2: PDOS of β-FAPbI$_3$. The CBM consists of an antibonding overlap of I s and Pb p orbitals.

Fig. S3: PDOS of β-GUA$_{0.5}$FA$_{0.5}$PbI$_3$. The VBM consists of an antibonding overlap of Pb s and I p orbitals.

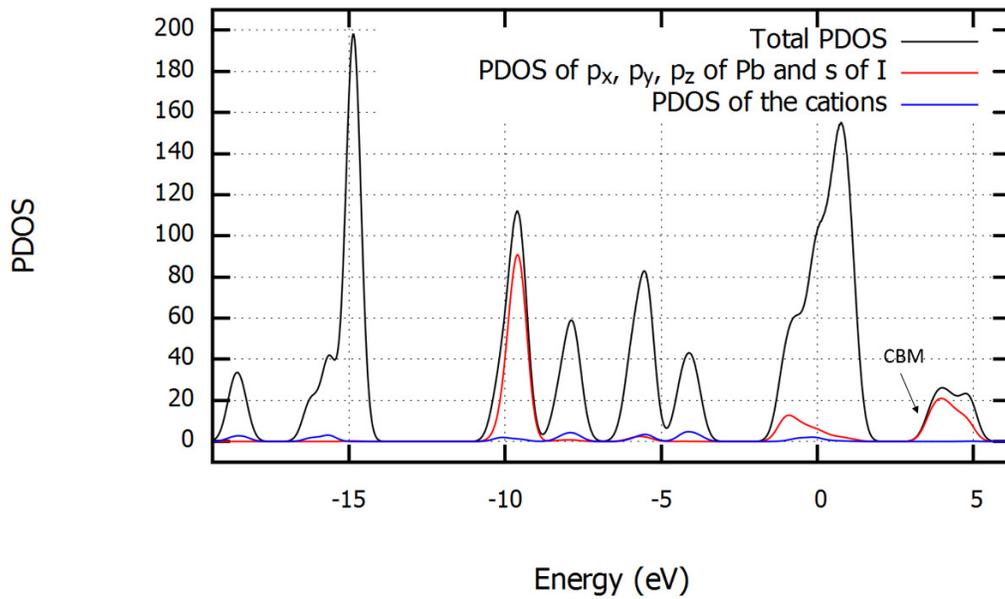Fig. S4: PDOS of β-GUA$_{0.5}$FA$_{0.5}$PbI$_3$. The CBM consists of an antibonding overlap of I s and Pb p orbitals.

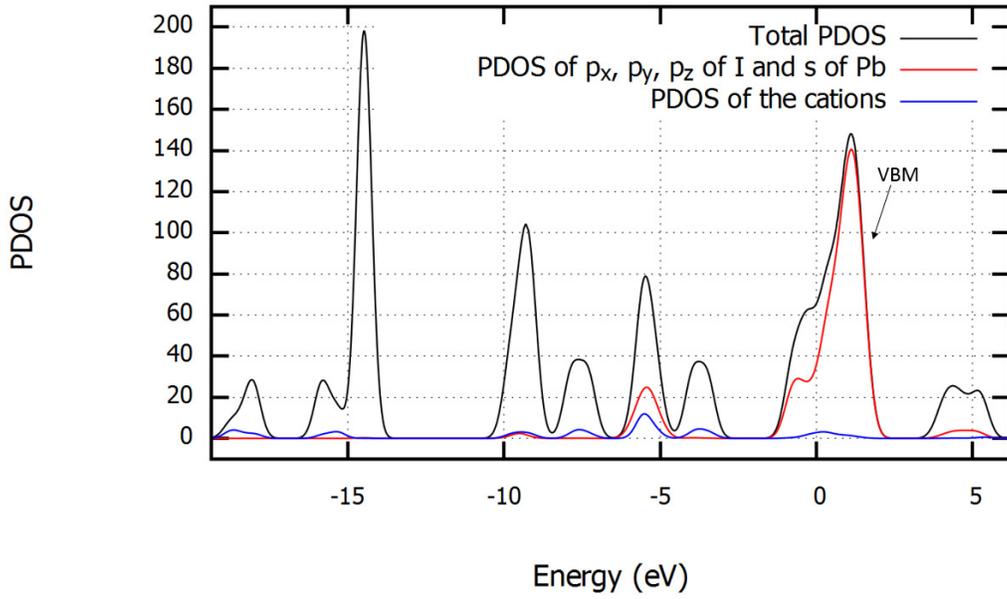Fig. S5: PDOS of β-$Cs_{0.17}GUA_{0.17}FA_{0.66}PbI_3$. The VBM consists of an antibonding overlap of Pb s and I p orbitals.
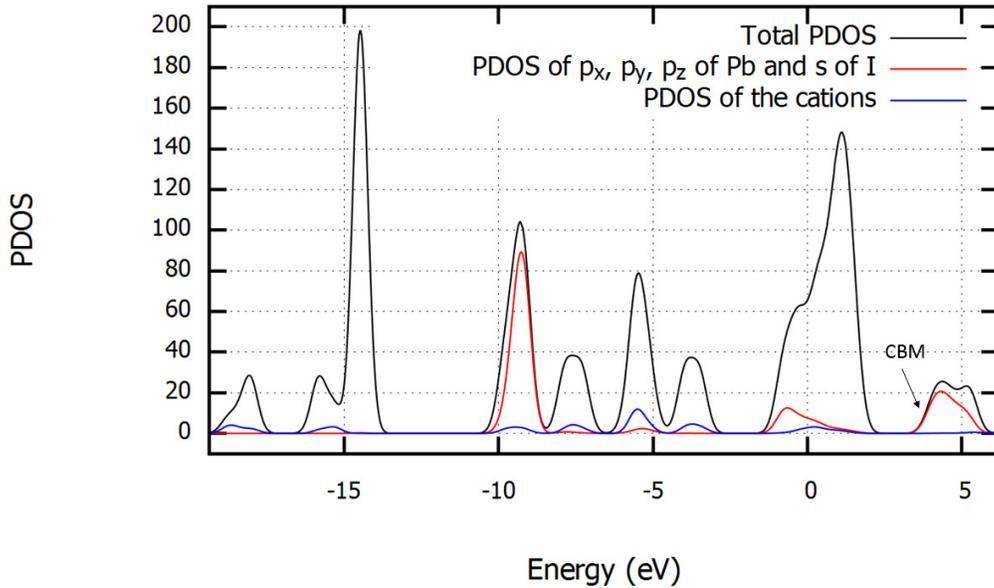

Fig. S6: PDOS of β-$Cs_{0.17}GUA_{0.17}FA_{0.66}PbI_3$. The CBM consists of an antibonding overlap of I s and Pb p orbitals.
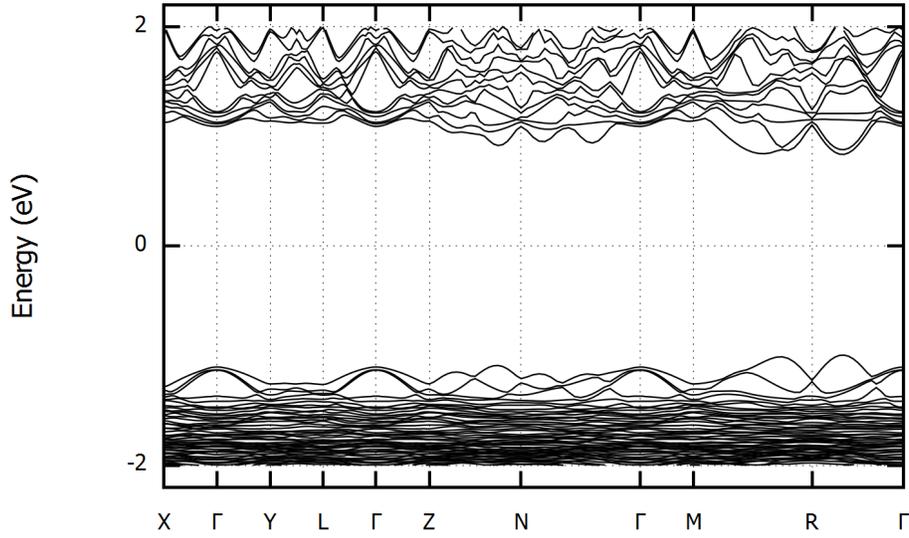
Band structure

Fig. S7: Band structure of β-FAPbI$_3$, calculated at PBEsol level. The zero corresponds to the Fermi energy of the systems. (X = 0.0, -0.5, 0.0; Γ= 0.0, 0.0, 0.0; Y = 0.5, 0.0, 0.0; L = 0.5, -0.5, 0.0; Z = -0.5, 0.0, 0.0; N = -0.5, -0.5, -0.5; M = 0.5, 0.0, 0.0; R = 0.0, -0.5, 0.5.)

Fig. S8: Band structure of β-GUA$_{0.5}$FA$_{0.5}$PbI$_3$, calculated at PBEsol level. The zero corresponds to the Fermi energy of the systems. (X = 0.0, -0.5, 0.0; Γ= 0.0, 0.0, 0.0; Y = 0.5, 0.0, 0.0; L = 0.5, -0.5, 0.0; Z = -0.5, 0.0, 0.0; N = -0.5, -0.5, -0.5; M = 0.5, 0.0, 0.0; R = 0.0, -0.5, 0.5.)

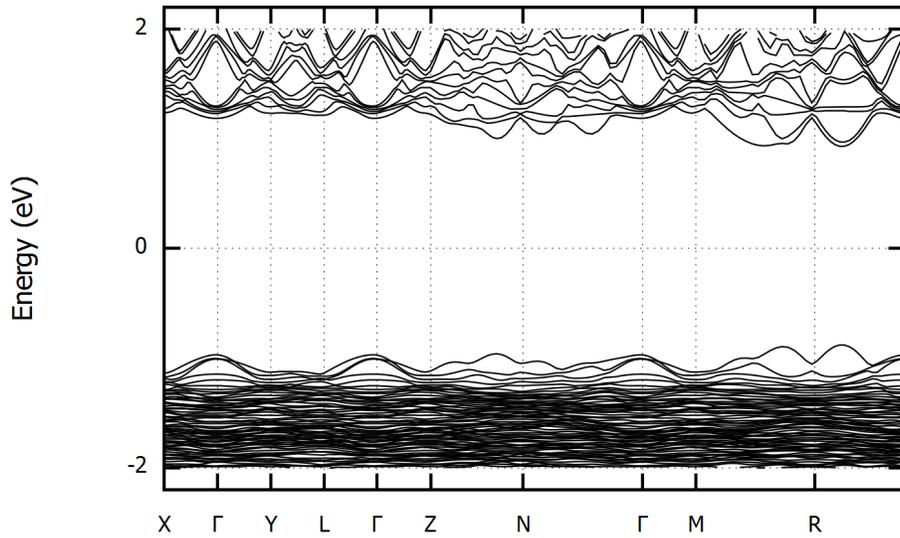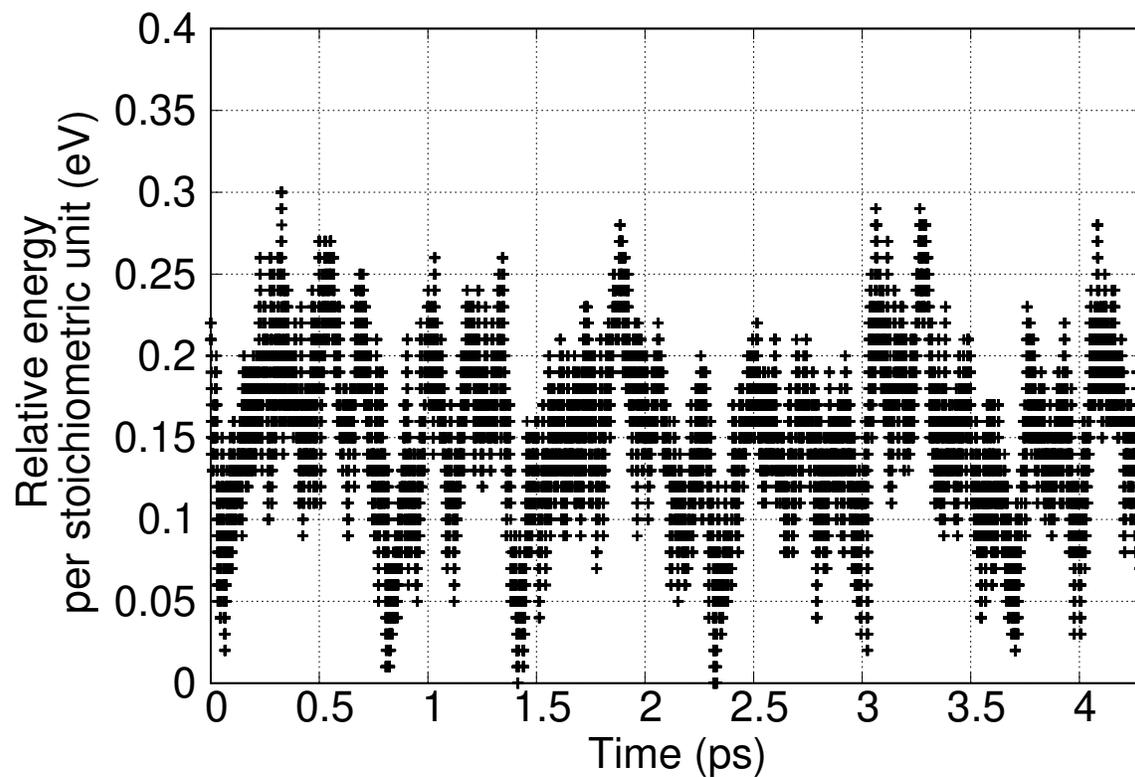# Data of MD simulations

Fig. S9: Relative energy difference per stoichiometric unit between β and δ GUA$_{0.17}$FA$_{0.83}$PbI$_3$ mixtures across a 4.3 ps trajectory from MD simulations. The δ-phase is always lower in energy than the β-phase.

References

[1] Negar Ashari-Astani, Farzaneh Jahanbakhshi, Marko Mladenović, Anwar Q. M. Alanazi, Iman Ahmadabadi, Mohammad Reza Ejtehadi, M. Ibrahim Dar, Michael Grätzel, and Ursula Rothlisberger. Ruddlesden-popper phases of methylammonium-based two-dimensional perovskites with 5-ammonium valeric acid $AVA_2MA_{n-1}Pb_nI_{3n+1}$ with n = 1, 2, and 3. *J. Phys. Chem. Lett.*, 10(13):3543–3549, 2019.

[2] Hung Q. Pham, Russell J. Holmes, Eray S. Aydil, and Laura Gagliardi. Lead-free double perovskites $Cs_2InCuCl_6$ and $(CH_3NH_3)_2InCuCl_6$: electronic, optical, and electrical properties. *Nanoscale*, 11:11173–11182, 2019.

[3] Shuping Pang, Hao Hu, Jiliang Zhang, Siliu Lv, Yaming Yu, Feng Wei, Tianshi Qin, Hongxia Xu, Zhihong Liu, and Guanglei Cui. $NH_2CH=NH_2PbI_3$: An alternative organolead iodide perovskite sensitizer for mesoscopic solar cells. *Chem. Mater.*, 26(3):1485–1491, 2014.

[4] Giles E. Eperon, Samuel D. Stranks, Christopher Menelaou, Michael B. Johnston, Laura M. Herz, and Henry J. Snaith. Formamidinium lead trihalide: a broadly tunable perovskite for efficient planar heterojunction solar cells. *Energy Environ. Sci.*, 7:982–988, 2014.

[5] Teck Ming Koh, Kunwu Fu, Yanan Fang, Shi Chen, T. C. Sum, Nripan Mathews, Subodh G. Mhaisalkar, Pablo P. Boix, and Tom Baikie. Formamidinium-containing metal-halide: An alternative material for near-IR absorption perovskite solar cells. *J. Phys. Chem. C*, 118(30):16458–16462, 2014.

[6] Gregor Kieslich, Shijing Sun, and Anthony K Cheetham. Solid-state principles applied to organic–inorganic perovskites: new tricks for an old dog. *Chem. Sci.*, 5(12):4712–4715, 2014.

[7] Gregor Kieslich, Shijing Sun, and Anthony K Cheetham. An extended tolerance factor approach for organic–inorganic perovskites. *Chem. Sci.*, 6(6):3430–3433, 2015.

[8] Dominik J. Kubicki, Daniel Prochowicz, Albert Hofstetter, Marcin Saski, Pankaj Yadav, Dongqin Bi, Norman Pellet, Janusz Lewiński, Shaik M. Zakeeruddin, Michael Grätzel, and Lyndon Emsley. Formation of stable mixed guanidinium-methylammonium phases with exceptionally long carrier lifetimes for high-efficiency lead iodide-based perovskite photovoltaics. *Journal of the American Chemical Society*, 140(9):3345–3351, 2018.

[9] Christopher J. Bartel, Christopher Sutton, Bryan R. Goldsmith, Runhai Ouyang, Charles B. Musgrave, Luca M. Ghiringhelli, and Matthias Scheffler. New tolerance factor to predict the stability of perovskite oxides and halides. *Sci. Adv.*, 5(2), 2019.