

# Hydrogen Bonding and Stability of Hybrid Organic– Inorganic Perovskites

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In the past few years, the efficiency of solar cells based on hybrid organic-inorganic perovskites has exceeded the level needed for commercialization. However, existing perovskites solar cells (PSCs) suffer from several intrinsic instabilities, which prevent them from reaching industrial maturity, and stabilizing PSCs has become a critically important problem. Here we propose to stabilize PSCs chemically by strengthening the interactions between the organic cation and inorganic anion of the perovskite framework. In particular, we show that replacing the methylammonium cation with alternative protonated cations allows an increase in the stability of the perovskite by forming strong hydrogen bonds with the halide anions. This interaction also provides opportunities for tuning the electronic states near the bandgap. These mechanisms should have a universal character in different hybrid organic–inorganic framework materials that are widely used.

### Introduction

In the past few years, hybrid organic–inorganic perovskite solar cells (PSCs)<sup>[1–3]</sup> have aroused great interest owing to the dramatic shot up of their power conversion efficiency, which now exceeds 20%.<sup>[4]</sup> Although hybrid perovskites with composition AMX<sub>3</sub> [A=methylammonium (MA<sup>+</sup>) and/or formamidinium (FA<sup>+</sup>); M=Sn<sup>2+</sup> or Pb<sup>2+</sup>; and X=I<sup>-</sup>, Br<sup>-</sup>, and/or Cl<sup>-</sup>] were known for more than two decades,<sup>[5]</sup> it was recently recognized that they show outstanding performance in solar cell applications and may be synthesized by relatively inexpensive processing methods, such as spin-coating, dip-coating, and vapor deposition techniques.<sup>[6-8]</sup>

PSCs should be considered as a part of a more general group of hybrid organic-inorganic framework materials formed by binding multi-dentate molecules to multi-coordinate metal complexes. These frameworks provide unlimited combinations of physical and chemical properties that allow their use in many applications,<sup>[9]</sup> including chemical sensing,<sup>[10]</sup> gas stor-

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age,<sup>[11]</sup> catalysis,<sup>[12]</sup> optical and semiconductor devices, and batteries.<sup>[13]</sup> Some dense organic–inorganic frameworks exhibit wide range of ferroelectric and multiferroic properties.<sup>[14, 15]</sup>

High PSC power conversion efficiency in photovoltaics is a result of a combination of different properties, such as favorable balance between strong absorption and long carrier lifetimes,<sup>[16,17]</sup> outstanding transport,<sup>[18–20]</sup> and excellent fault tolerance.<sup>[21]</sup> It was also suggested that defect tolerance in these perovskites as well as in other organic–inorganic frameworks may be related to the presence of van der Waals interactions and hydrogen bonding.<sup>[3,22,23]</sup> Also, recent molecular dynamics simulations indicate that in MAPbl<sub>3</sub>,  $\Gamma$  anions form dynamic short-lived hydrogen bonds with H atoms located on MA<sup>+</sup> ions, which causes charge fluctuations, resulting in a significant increase of the dielectric function.<sup>[24]</sup>

It is well known that MAPbl<sub>3</sub> is unstable and sensitive to external factors, such as moisture, UV exposure, and oxygen.<sup>[3,25]</sup> Poor crystal quality also contributes to stability issues<sup>[26]</sup> as well as the dynamics of the polarized molecular cations.<sup>[27,28]</sup> At the fundamental level, MAPbl<sub>3</sub> suffers from intrinsic instability that can result in disorder and assist phase transitions. Recently, it was computationally confirmed that this compound is thermodynamically unstable, and although a kinetic barrier that prevents its spontaneous decomposition to MAI and Pbl<sub>2</sub> exists, it is very low (i.e., decomposition is unavoidable with time).<sup>[25]</sup>

It was experimentally shown that stability of PSC could be significantly increased by mixing MA<sup>+</sup> with FA<sup>+</sup> and Cs<sup>+</sup> cations.<sup>[29,30]</sup> Detailed structural investigations indicated that the resulting sample is not homogeneous, but consists of a mixture of grains of different materials.<sup>[31]</sup> This granulated structure, however, may enhance the stability of the perovskite by limiting ion migration, which is assumed to be one of the instability causes.



Another possible way to stabilize the structure is to manipulate the electronic coupling between the molecular cation A and the MX<sub>6</sub> octahedra of the perovskite structure. For example, 3D MAPbl<sub>3</sub> is composed of a network of corner-sharing Pbl<sub>6</sub> octahedra and molecular cations MA<sup>+</sup> hosted between the cages. The cohesion between Pbl<sub>6</sub> octahedra and MA<sup>+</sup> is mainly owing to weak electrostatic interactions,[32] thus, the electronic coupling between the octahedron and the cation is negligible. This argument is supported by the fact that electronic states owing to the MA<sup>+</sup> orbitals are located several eV above and below the band gap edges (formed mainly by 5p orbitals of iodine and 6p orbitals of lead) and do not contribute directly to the optical properties within the solar spectrum range or electronic transport.[16,33] Therefore, the resulting cohesion is weak<sup>[3]</sup> as characterized by relatively small site Madelung potential,<sup>[32,34]</sup> which leads to chemical instability.

Another interesting consequence that originates from these results is the possibility to use cations and anions to tune the optical and electrical properties by distorting the octahedral network. Filip et al.<sup>[33]</sup> and Knutson et al.<sup>[35]</sup> utilized this concept to tune the gap in 3D and 2D hybrid perovskites, respectively.

In this work, we employed density functional theory (DFT) to investigate pathways to strengthen the electronic coupling between the molecular cation and MX<sub>6</sub> octahedra to enhance the stability of hybrid perovskites. This stability enhancement mechanism is alternative to the approach based on mixing different cations employed before,<sup>[29,30]</sup> and focuses on atomic-scale changes within one unit cell of the perovskite material. Therefore, it potentially provides the possibility to grow higher quality crystal structures that are free of segregation on different phases and do not form granulated microstructures.

We found that the electronic coupling between the molecular cation  $A^{\scriptscriptstyle +}$  and the  $MX_6$  octahedra may be manipulated in two ways: (i) by modification of the molecular cation A<sup>+</sup>, and (ii) by modification of the anion  $X^-$ . For example, in the most popular PSC material MAPbl<sub>3</sub>, the MA<sup>+</sup> cation contains a strong electronegative N atom. The electronegativity of I<sup>-</sup> is rather low, so the H atoms are strongly bonded to the MA<sup>+</sup>, whereas their interaction with the Pbl<sub>6</sub> octahedron is fairly small. By replacing the nitrogen atom by a less electronegative atom, the binding of the H atoms to the cation can be reduced, thus enhancing the electronic coupling of H with Pbl<sub>6</sub> octahedron. It is also possible to change the whole MA<sup>+</sup> cation by another protonated cation to obtain a similar result. Another possibility of strengthening electronic coupling is to substitute the I<sup>-</sup> anion with more electronegative elements (e.g., F, Cl, and/or Br). Although the molecular cation design and substitution approach were considered in the past, this research was mainly focused on tuning the optoelectronic properties through control of the band gap.<sup>[33,34,36]</sup> In this work, we prove that both cation and anion manipulations can be used as a mechanism to enhance the stability of perovskite by initiating stronger electronic coupling and electrostatic interactions.[37-40]

This approach is an attempt to employ mechanisms that were routinely utilized in other areas (e.g., for the construction of polymers and metal–organic frameworks<sup>[38,41–43]</sup>) to the

world of PSC. We confirm the possibility of stabilizing hybrid organic–inorganic PSC materials using hydrogen bonds, or electrostatic binding of hydrogen to a nearby highly electro-negative atom (e.g., N, O, and F). This type of bonding occurs in both inorganic (water) and organic (DNA and proteins) molecules and plays an important role in determining the 3D structures formed by these molecules (e.g., a double helical DNA structure).<sup>[44–46]</sup> Also, many polymers are strengthened by hydrogen bonds in their main chains.

## **Results and Discussion**

#### Electronegativity Factor: Halide Substitution in MAPbl<sub>3</sub>

First, we investigated the role of electronegative anion in hybrid organic–inorganic perovskites. For this purpose we start with the most popular PSC material, MAPbl<sub>3</sub>, and substitute I<sup>-</sup> with halides having higher electronegativity (i.e., Br, Cl, and F). For the sake of systematic analysis, we focused only of the tetragonal phase ( $\beta$ -phase) in which MAPbl<sub>3</sub> crystallizes at room temperature.

To characterize the strength of hydrogen bonds, we employed the recently developed noncovalent interactions (NCI) index that enables real-space visualization of both attractive (van der Waals and hydrogen bonding) and repulsive interactions based on the electron density.<sup>[47–49]</sup> This approach allows description of the interplay between stabilizing and destabilizing contributions that determine the stable minima on hydrogen-bonding potential-energy surfaces. It relies on two scalar fields to map local bonding properties: 1) the electron density ( $\rho$ ) and 2) the so-called reduced density gradient (RDG, *s*) defined as [Eq. (1)]:

$$s(\text{RDG}) = \frac{1}{2(3\pi)^{1/3}} \frac{|\nabla \rho|}{\rho^{4/3}}.$$
 (1)

Three principle interaction regions define the real space when combining the electron density and its gradient. The region of the non-interacting density tails is characterized by a high s and low  $\rho$ . However, a low s and high  $\rho$  define the covalent bonds region, where a low s and low  $\rho$  correspond to a non-covalent interaction. The non-covalent interactions are also classified into attractive or repulsive according to the sign of the second density eigenvalue ( $\lambda_2$ ) of the electron-density Hessian (second derivative) matrix.

The calculations of the NCI index approach is not discussed in detail here. An important issue is that it allows differentiating van der Waals interactions and hydrogen bonds by densities at the corresponding bond critical point.<sup>[47]</sup> Typically, characteristic densities of van der Waals interactions are much smaller than densities at which hydrogen bonds appear. At the same time, both van der Waals interactions and hydrogen bonds show negatives value  $\lambda_2$  at the critical point, with a very low  $\lambda_2$  (very near zero) for van der Waals interactions. A detailed analysis of the interaction type can be performed by plotting diagrams of *s* vs. sign( $\lambda_2$ ) $\rho$ . When there is an overlap between atomic orbitals, a trough in the NCI diagram appears.



The points forming this trough identify the interaction when they are mapped back to real space.<sup>[47]</sup>

In practice, the computational procedure of constructing an NCI diagram requires a grid-based representation of the selfconsistent electron density, which is obtained from quantummechanical calculations. When the real-space region of interest is chosen, a regular grid is built to encompass it. At each grid point,  $\rho$  and *s* are numerically calculated and  $\rho$  is multiplied by the sign of  $\lambda_2$ . Figure 1 shows NCI diagrams [*s* vs. sign( $\lambda_2$ ) $\rho$ ] for four perovskites with the same organic cation and different halide anions (MAPbX<sub>3</sub>, X = I, Br, CI, and F). For visualization of the NCI regions we also plot RDG isosurfaces in real space, which allows interpretation of different troughs in the NCI diagram as well as comparison of the strength of different NCI components. Figure 2 shows RDG isosurfaces for the same four perovskite materials.

The main feature of all NCI diagrams shown in Figure 1 is the presence of several peaks at negative values of  $\operatorname{sign}(\lambda_2)\rho$ corresponding to H···X hydrogen bonds of different lengths. The higher the electronegativity of the anion, the more negative the values of the abscissa at which these peaks are located (i.e., stronger hydrogen bonding). It is apparent that in MAPbl<sub>3</sub>, the H···I interaction is much weaker than H···F interaction in MAPbF<sub>3</sub>. In MAPbBr<sub>3</sub>, the two peaks at  $\operatorname{sign}(\lambda_2)\rho =$ -0.023 and -0.027 correspond to the shortest H···X bonds (2.34 and 2.42 Å), whereas the third peak that appears at higher  $\operatorname{sign}(\lambda_2)\rho =$  -0.012 relates to longer H···X bonds (2.89 and 2.90 Å). In MAPbCl<sub>3</sub>, these peaks move to more negative values (-0.032, -0.031, and -0.021) and correspond to the bond lengths of 2.20, 2.22, and 2.41 Å, respectively. In MAPbF<sub>3</sub>, the H…F bonds are even stronger and correspond to shorter bonds (1.68, 1.70, and 1.80 Å).

The increase of hydrogen bond strength with increase of the anion electronegativity can also be seen from the NCI isosurfaces in real space (Figure 2). When we move from I<sup>-</sup> to F<sup>-</sup>, the isosurface color in the region between the X and H from the NH<sub>3</sub> group of the MA<sup>+</sup> cation changes from green (for I) to bright red (for F), which corresponds to significant strengthening of the attraction between H and X anion, where the electrons are more localized.

The chemical stability of the considered materials was also quantified by the reaction<sup>[50]</sup> and the hull<sup>[51–53]</sup> energies. The reaction energy is the difference between the total energy of a reaction and reactants, whereas the hull energy is the difference in formation energies and it effectively evaluates the stability of a given compound against any linear combination. Whereas many possibilities for phase separation exist; we used the separation into the most stable binary and ternary compounds based on phase diagrams constructed from the Materials' Project database.<sup>[54]</sup>

Table 1 shows the reaction and hull energies for all considered MAPbX<sub>3</sub> (X = I, Br, CI, and F) perovskites. One can say that MAPbI<sub>3</sub> and MAPbCI<sub>3</sub> are marginally stable with reaction energies ranged between -25 and -30 meVatom<sup>-1</sup>. So, the ther-



**Figure 1.** NCI diagrams [RDG, or *s* vs. sign( $\lambda_2$ ) $\rho$ ] for several methylammonium lead halides in tetragonal ( $\beta$ -) phase: A) CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>, B) CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub>, C) CH<sub>3</sub>NH<sub>3</sub>PbCI<sub>3</sub>, and D) CH<sub>3</sub>NH<sub>3</sub>PbF<sub>3</sub>. The dotted square corresponds to the region of the N–H···X bonds, at *s*=0.3

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**Figure 2.** NCI isosurfaces in real space (perovskite tetragonal unit cell) for: A)  $CH_3NH_3PbI_3$ , B)  $CH_3NH_3PbBr_3$ , C)  $CH_3NH_3PbCI_3$ , and D)  $CH_3NH_3PbF_3$ . Atoms C (cyan), N (blue), H (light pink), I (magenta), Br (brown), Cl (green), and F (purple). The isosurfaces are generated at s = 0.3.

<b>Table 1.</b> Calculated bandgap ( $E_g$ ), reaction ( $E_{react}$ ), formation ( $E_{form}$ ), and hull energies ( $E_{hull}$ ); bond length elongation (BLE); <sup>[a]</sup> tolerance factor ( $t$ ); and octahedra tilting ( $\theta$ )/rotation ( $\Phi$ ) angles for different PSC tetragonal phase materials considered in this work.											
Material	E <sub>g</sub> [eV]	E <sub>react</sub> [eVatom <sup>-1</sup> ]	E <sub>form</sub> [eVatom <sup>-1</sup> ]	E <sub>hull</sub> [eVatom <sup>-1</sup> ]	BLE [%]	t	θ [°]	Φ [°]			
CH <sub>3</sub> NH <sub>3</sub> Pbl <sub>3</sub>	1.79	-0.033	-0.579	-0.033	0.97	0.847	1.3	0.5			
CH <sub>3</sub> NH <sub>3</sub> PbBr <sub>3</sub>	1.92	-0.200	-0.684	-0.147	0.87	0.809	2.0	2.1			
CH <sub>3</sub> NH <sub>3</sub> PbCl <sub>3</sub>	2.30	-0.035	-0.924	-0.036	0.99	0.833	2.0	1.5			
CH <sub>3</sub> NH <sub>3</sub> PbF <sub>3</sub>	3.70	0.072	-1.757	0.066	1.50	0.800	2.7	0.5			
CH <sub>3</sub> PH <sub>3</sub> Pbl <sub>3</sub>	1.81	-0.108	-0.442	-0.110	2.14	0.970	0.5	0.0			
CH <sub>3</sub> PH <sub>3</sub> PbBr <sub>3</sub>	0.81	0.101	-0.337	0.099	10.71	0.806	4.2	0.5			
CH₃SH₂Pbl₃	1.55	-0.227	-0.434	-0.226	2.79	0.895	4.6	0.5			
CH <sub>3</sub> SH <sub>2</sub> PbBr <sub>3</sub>	1.95	-0.189	-0.540	-0.189	2.21	0.878	4.9	0.5			
SH₃Pbl₃	1.73	-0.175	-0.442	-0.258	4.44	0.836	7.0	30.0			
SH₃PbBr₃	2.06	-0.386	-0.612	-0.229	2.55	0.863	8.4	17.0			
[a] Bond length elongation between the bridging H and its associated atom in the cation within the crystal (e.g., N, P, S) compared to its length in a standalone cation.											

mal energy at room temperature can decompose the materials. At the same time, MAPbF<sub>3</sub> should be considered as unstable because the reaction and hull energies are slightly positive. At the same time, here the considered phase for MAPbF<sub>3</sub> was tetragonal  $\beta$ -phase. Meanwhile, it is known that the cubic phase for this perovskite is more stable. Anyway, the bandgap in this material is above 3 eV, which makes it unsuitable of solar cells. However, it may be used in other optoelectronic applications (e.g., in some UV devices and sensors).

### Manipulating electronic coupling by cation substitution

Now we consider the effect of cation substitution. For this purpose, we start with two halides widely used for PSC (i.e., MAPbl<sub>3</sub> and MAPbBr<sub>3</sub>) and replace MA<sup>+</sup> by another protonated cation. Our target is to improve the stability of perovskite without deteriorating the energy bandgap that should be small enough to guarantee a significant light absorption by the material at the solar spectra frequency range. For this purpose,

the cation must be small to ensure that a 3D hybrid perovskite structure is obtained and must not contain any elements with high electronegativity that will allow H-bonding with Pbl<sub>6</sub> or PbBr<sub>6</sub> octahedron accompanied by breaking the original bond between H and the protonated cation. There are many protonated cations fulfilling this condition and not limited to the ones considered in this work, namely CH<sub>3</sub>PH<sub>3</sub><sup>+</sup> ,  $CH_3SH_2^+$ , and  $SH_3^+$ . The calculated gaps of these materials are shown in Table 1. Evidently, the bandgap is altered by cation substitution, but is still appropriate for solar cells except for CH<sub>3</sub>PH<sub>3</sub>PbBr<sub>3</sub>, where it is reduced drastically owing to the emergence of a state resulting from a bond formed between Br, the bridging H atom, and P<sup>[55]</sup>, which results in losing the electrostatic balance and hence, weakening the electronic coupling and chemical stability.

As explained in the Experimental Section, we also

generated phase diagrams for the relaxed structures. These diagrams are then used for finding the decomposition route to the most stable binary and ternary compounds. The calculated reaction and hull energies of these reactions are also shown in Table 1. These energies are negative for all materials with  $CH_3PH_3^+$ ,  $CH_3SH_2^+$ , and  $SH_3^+$  cations (the calculated reaction and hull energies stand between -230 and -100 meVatom<sup>-1</sup>), except for the  $CH_3PH_3PbBr_3$  perovskite where both reaction and hull energies are positive, thus confirming the instability of this material. This behavior is correlated with elongation of the bridging bond between the H atom and its donating atom in the cation compared to the standalone molecule. The relevant bridging bond is between the electron donating element in the cation (i.e., P, N, S) and its farthest H atom forming a bridge with the halide atom (i.e., I, Br).

To understand the nature of instability in the  $CH_3PH_3PbBr_3$ material, we compared the NCI diagrams and NCI isosurfaces for  $CH_3PH_3PbBr_3$  and  $CH_3PH_3PbI_3$  (Figure 3). Clearly, the peaks corresponding to hydrogen bonds between H atoms positioned at the cation and halogen anion significantly shifted to



**Figure 3.** NCI diagrams [*s* vs. sign( $\lambda_2$ ) $\rho$ ] for A) CH<sub>3</sub>PH<sub>3</sub>Pbl<sub>3</sub>, and B) CH<sub>3</sub>PH<sub>3</sub>PbBr<sub>3</sub> in tetragonal ( $\beta$ ) phase and C–D) NCI isosurfaces for the same materials. Atoms C (cyan), P (olive green), H (light pink), I (magenta), and Br (brown). The dotted line corresponds to the region of the P–H···X bonds, at *s*=0.3.

more negative values in  $CH_3PH_3PbBr_3$ . Indeed, the shortest  $H \cdots Br$  bond is 1.88 Å in  $CH_3PH_3PbBr_3$  compared to the shortest  $H \cdots I$  bond of 2.60 Å in  $CH_3PH_3PbI_3$ . Also, the dark brown color of NCI isosurface for this bond in  $CH_3PH_3PbBr_3$  means a stronger hydrogen-halogen interaction compared to the more green color isosurface for this bond in  $CH_3PH_3PbI_3$ .

From Table 1 it is clear that in the cases of MAPbl<sub>3</sub> and MAPbBr<sub>3</sub>, the H-I and H-B bonds are barely stretched (by 0.97 and 0.87%, respectively). This is mainly a result of the high electronegativity of the N atom, which keeps the bonded H atoms bound tightly. It means that the contributions from both of them to the bridging states are small, implying that the associated H atom is highly localized within the cation and interacts with the octahedron only weakly. The bridging P-H and S-H bonds are elongated much further, and for the stable materials, the elongation ranges between 2.14 and 4.44%, which is mainly a result of the attraction of the H atom to the halide and the bridge formation. So, the electronic densities of P, S, and H are delocalized owing to elongation. This attraction becomes even more substantial in CH<sub>3</sub>PH<sub>3</sub>PbBr<sub>3</sub> where the bond is stretched by 10.71%. In this particular case, the bridging H atom is attracted significantly by the halide, which breaks the balance around it. We attribute this phenomena to the electronegativity difference between Br (2.96) and P (2.19).[56]

Further understanding of the effects of enhanced electronic coupling between the cation and the octahedron requires a close look at the electronic structure. Table 2 contains normalized participation ratios (relative contributions to the norm of the wavefunction from atoms of a given sort) of the bridging states between the cation and octahedron for MAPbX<sub>3</sub> and  $CH_3PH_3PbX_3$  (X = I and Br). For each material, the bridging state was identified by analyzing the projected density of states

 
 Table 2. The normalized participation ratios for the bridging states between the cations and the octahedron.

Material	N or P	Н	l or Br
CH <sub>3</sub> NH <sub>3</sub> Pbl <sub>3</sub>	0.018	0.009	0.973
CH <sub>3</sub> NH <sub>3</sub> PbBr <sub>3</sub>	0.049	0.005	0.946
CH <sub>3</sub> PH <sub>3</sub> PDI <sub>3</sub> CH <sub>3</sub> PH <sub>3</sub> PbBr <sub>3</sub>	0.694	0.056	0.898

(PDOS) in the vicinity of the valence band edge. First, the energy point near the top of the valence band was found at which the PDOS for the electron donating atom of the cation (i.e., N, P, or S) has a maximum. Second, the electronic band (bands) contributing to this peak was (were) identified, and contributions to this band (bands) from H and halide atoms were also analyzed. For MAPbI<sub>3</sub> and MAPbBr<sub>3</sub>, the contributions of  $MA^+$  are deep in the valence and conduction bands. There are nearly no signs for interactions between the cation and Pbl<sub>6</sub> and PbBr<sub>6</sub> octahedra. This is severely altered when the MA<sup>+</sup> cation is replaced by the suggested protonated cations CH<sub>3</sub>PH<sub>3</sub><sup>+</sup>, CH<sub>3</sub>SH<sub>2</sub><sup>+</sup>, and SH<sub>3</sub><sup>+</sup>. In particular, for CH<sub>3</sub>PH<sub>3</sub>PbBr<sub>3</sub>, several molecular states caused by the enhanced electronic coupling appear at the top of the valence band. In the extreme case of very strong interaction between hydrogen of the cation with halide atom [reflected in the participation ratio (PR), which indicates that main contribution to the bridging state is given by the Br atoms], it results in emerging states occupying the top of the valance band and considerably shifting its edge as in the case of CH<sub>3</sub>PH<sub>3</sub>PbBr<sub>3</sub>. In such a case, one can say that electronic coupling between the cation and the halides in the octahedron lost a balance.



# Tolerance factor and structural and chemical stability of hybrid perovskites

The tolerance factor [t, Eq. (2)] was introduced to evaluate ionic size mismatches that the perovskite structure will tolerate until transformation into another structure,

$$t = (r_{\rm A} + r_{\rm X})/\sqrt{2}(r_{\rm B} + r_{\rm X}),$$
 (2)

where  $r_i$  are the radii of the ions in the perovskite ABX<sub>3</sub>, and i = A, B, and X, respectively.<sup>[57]</sup> This is a semi-empirical relationship that continues to be widely used as a guiding principle in the study of perovskite structures. It is widely accepted that cubic perovskite structure is stable for the values of t in the range 0.9–1.0, while values of 0.80–0.89 correspond to distorted perovskites that can be classified by using the concept of octahedral tilting.<sup>[58, 59]</sup> Below 0.80, other structures, such as the ilmenite-type (FeTiO<sub>3</sub>), are more stable owing to similar sizes of the cations A and B, and values larger than 1 lead to hexagonal structures where layers of face-sharing octahedra are introduced into the structure.<sup>[58]</sup>

Tilting and rotation of the octahedra play an important role in stabilizing the perovskite structures (Figure 4). They generate lower-symmetry distorted structures, in which the coordination numbers of A cations, B cations, or both are reduced. For example, the TiO<sub>6</sub> octahedron rotation and tilt angles are likely to be responsible for the metal-insulator transition in oxide superlattices.<sup>[60]</sup> Octahedral rotation and tilt angles are also related to structural and magnetic phase transitions in different perovskite materials.<sup>[61]</sup> It was experimentally shown that tunable optical bandgaps in metal-halide perovskites could be achieved by controlling the degree of the Pbl<sub>6</sub> octahedral tilting through the steric size of the molecular cation.<sup>[33]</sup> In particular, the bandgap can be reduced by decreasing the degree of the octahedral tilting, which can be achieved by adjusting the degree of the hydrogen-bonding interactions between the halides and H atoms bonded to the MA group.  $^{\scriptscriptstyle [33,36]}$ 

We calculated t and octahedron tilt/rotation angles for all considered perovskites (Table 1). A crucial point here is the def-

в



inition of ionic radii of protonated cations containing several atoms. An attempt to make several steps in this direction was considered in Ref. [58] where an effective molecular cation radius was defined. Also, it was suggested that the shape of some anions could be approximated by cylinders.

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In this work, we used different approach. If one assumes that ionic spheres are touching, there is no need to define each of them individually. Instead, one needs to find the averaged  $(r_A + r_X)$  and  $(r_B + r_X)$  only. Assuming that the center of molecular cation X is positioned in its center of mass, we could calculate both quantities from the atomic structure of the material that is geometrically relaxed by employing some first-principles calculations method.

Table 1 shows that for nearly all considered perovskites, the tolerance factor lies in the range between 0.8 and 0.9, which indicates that distorted perovskite structure with some tilt and rotation angles ( $\theta$  and  $\Phi$ ) is stable for them. The only exception is CH<sub>3</sub>PH<sub>3</sub>Pbl<sub>3</sub> with t=0.97, which means that cubic perovskite structure should be preferable for this compound. Actually, the rotation angle for this perovskite is zero while the tilt angle is only 0.5°, which is lower than for any other perovskite considered here (i.e., the structure is nearly cubic).

An interesting observation is that for two perovskites (unstable  $CH_3PH_3PbBr_3$  and marginally stable  $MAPbF_3$ ), the value of *t* is very close to 0.8, which means that these perovskites have cations (A and B) of similar size so transformations to other structures may be possible. However, taking into account a very limited character of the tolerance factor concept, we would avoid making any conclusions here. Another interesting observation is the observance of very high rotation angles for perovskites based on the  $SH_3^+$  cation. The reason for that behavior could be a very anisotropic character of this molecular cation so accommodating such species in the perovskite structure could become a very complicated problem.

### Conclusions

We show the possibility to chemically stabilize the hybrid organic–inorganic perovskites by replacing methylammonium molecular cation (MA<sup>+</sup>) with other protonated cations (CH<sub>3</sub>PH<sub>3</sub><sup>+</sup>, CH<sub>3</sub>SH<sub>2</sub><sup>+</sup>, and SH<sub>3</sub><sup>+</sup>) to enhance the electronic coupling between the cation and the perovskite structure octahedrons. We also show that similar effects could be reached by substitution of widely used halide anions (I<sup>-</sup>, Br<sup>-</sup>) by halide anions with higher electronegativity (Cl<sup>-</sup>, F<sup>-</sup>). At the same time, the bandgap energy could be maintained within the range suitable for solar cells applications. In practice, the search of new cations and anions can be performed by analyzing the electronegativity of the material constituents and the resulting electrostatic interactions.

For each material, we checked the stability in several different ways including analyzing: (i) the reaction, formation, and hull energies; (ii) calculating the tolerance factor and octahedron tilt/rotation angles; and (iii) checking electronic balance for bridge states using normalized participation ratios. In particular, it was found that to be stable, the material should have negative reaction and formation energies, the tolerance factor

A

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should lie in the stability range, and electronic coupling between the halides in the octahedron and protonated cations should be balanced. If any of these criteria is violated, the material most likely is unstable with respect to some structural transformation and unsuitable for protovoltaic and other optoelectronic applications. In addition to the protonated cations (CH<sub>3</sub>PH<sub>3</sub><sup>+</sup>, CH<sub>3</sub>SH<sub>2</sub><sup>+</sup>, and SH<sub>3</sub><sup>+</sup>) considered in this work, we expect that several other molecular cations with enhanced coupling and stability could be used.

## **Experimental Section**

First principles calculations are used to compute the electronic structure and to estimate the stability of the proposed materials. DFT calculations are done using the projected augmented wave (PAW) method as built in the Vienna ab initio Simulation Package (VASP).<sup>[62]</sup> All calculations were performed using spin polarized generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) parametrization for the exchange and correlation energy of interacting electrons.<sup>[63]</sup> The energy cutoff for the planewave basis set was set to 520 eV and a  $8 \times 8 \times 8$  Monkhorst–Pack *k*-point mesh was employed. Long-range van der Waals interactions have been taken into account through the Tkatchenko and Scheffler (TS) scheme.<sup>[64]</sup> The convergence of the final forces is set to 0.01 eV Å<sup>-1</sup>.

The participation ratio is obtained directly from VASP output. For the stability calculations, the phase diagrams are generated for the given stoichiometry using PyMatGen with the Material Project (MP) DataBase.<sup>[54]</sup> Then, we construct the decomposition route to the most stable binary and ternary compounds and calculate the reaction and hull energies.<sup>[51-53]</sup> A material is considered stable if the reaction and hull energies are negative. To consider the calculation errors, the stability is considered marginal if the magnitude of the calculated energy is below 100 meVatom<sup>-1</sup>.<sup>[65]</sup>

To characterize the strength of hydrogen bonds as well as other noncovalent interactions, we used noncovalent interactions (NCI) index that enables real-space visualization of both attractive (van der Waals and hydrogen bonding) and repulsive interactions based on properties of the electron density.<sup>[47–49]</sup> This approach allows the description of the interplay between stabilizing and destabilizing contributions that determine stable minima on hydrogen-bonding potential-energy surfaces. The hydrogen bonds are visualized using the NCIPLOT technique. NCI isosurfaces correspond to s = 0.3 and the color scale is  $-0.04 < \operatorname{sign}(\lambda_2)\rho < 0.04$ 

The simulation box used in the calculations is based on the 48 atoms unit cell (4 unit formula) where both the halides and cations are subsequently substituted followed by a full geometrical optimization using DFT. The simulation box is optimal to allow the octahedral rotations and tilts and hence, a better assessment of the stability. For preparation of the NCI diagrams and isosurfaces, calculations on a very fine mesh within a subregion positioned inside the simulation box (a 3D cube targeting one organic molecule and its first neighbor halides) were performed.

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# **FULL PAPERS**

**Bound together:** Density functional theory is used to investigate the effect of internal hydrogen bonds on the stability of methylammonium lead halide perovskite layers for solar cell applications. Calculations show that replacing the methylammonium cation with alternative protonated cations allows an increase in the stability of the perovskite by forming strong hydrogen bonds with the halide anions.



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Hydrogen Bonding and Stability of Hybrid Organic–Inorganic Perovskites