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#### Introduction

The introduction of the Hybrid Organic Inorganic Halide Perovskites (hereafter OIHPs) in solar cells (PSCs) represents the most important breakthrough in the realm of photovoltaics (PV) in the last decade, as testified by the interest of the community and by the huge number of publications appearing in the literature after the pioneering work of Miyasaka.<sup>1</sup> The relevance of such a class of materials characterized by the stoichiometric relationship ABX<sub>3</sub> (A = organic cation; B = Pb<sup>2+</sup>, Sn<sup>2+</sup>, Ge<sup>2+</sup>; X = halide) is associated with the appealing properties that perfectly satisfy the requirements of an optimal material for solar-to-energy conversion.

# First-principles investigation of the Lewis acid-base adduct formation at the methylammonium lead iodide surface<sup>†</sup>

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We have here performed a campaign of ab initio calculations focusing on the anchoring mechanism and adduct formation of some Lewis bases, both aliphatic and aromatic, on a Pbl2-rich flat (001) methylammonium lead iodide (MAPI) surface. Our goal is to provide theoretical support to the recently reported experimental techniques of MAPI surface passivation via Lewis acid-base neutralization and similarly of MAI-Pbl<sub>2</sub> (Lewis base) adduct formation. We tested several X-donor bases (X = :N, :O, :S), paying attention to the thermodynamic stability of the final MAPI base adducts and to their electronic properties. Factors that impact on the passivation mechanism are the directionality of the Lewis base lone pair and its enhanced/reduced overlap with MAPI Pb p orbitals, the dipole moment of the base and, similarly, the electronegativity of the X donor atom. Also non-covalent interactions, both at the surface side (intra, MAPI) and at the very interface (inter, MAPI-Lewis base), seem to contribute to the stability of the final adducts. Here we show that the thermodynamic stability does not necessarily correspond to the most effective base  $\rightarrow$  acid dative bond formation. Starting from a low coverage (12.5% of the undercoordinated Pb atoms available at the surface are passivated) this paper paves the way towards the study of cooperative and steric effects among Lewis bases at higher coverages representing, to the best of our knowledge, one of the very first studies focusing on the molecular anchoring on the surfaces of this very important class of materials.

> The length of the organic cation<sup>2</sup> in the A-site determines the dimensionality of the OIHPs and accordingly their usage in devices. Noticeably, in the mid '90s 2D OIHPs had already found applicability in optoelectronics.<sup>3–9</sup> Later on, after Miyasaka,<sup>1</sup> excellent photovoltaic (PV) performances were initially reported for 3D,<sup>10</sup> and more recently also for a particular polymorphic form of 2D<sup>11,12</sup> OIHPs, *i.e.* the Ruddlesden–Popper OIHPs. To complete the scenario, clusters (0D), both organic–inorganic and fully inorganic, have been investigated for their high potentiality not only in optoelectronics<sup>13</sup> but also in lasing applications.<sup>14</sup>

> The device applicability of OIHPs has motivated not only experimental but also theoretical deep research on their fundamental properties (see among others<sup>15–19</sup>). Concerning 3D OIHPs and their archetypal compound MAPbI<sub>3</sub> (MA = <sup>+</sup>CH<sub>3</sub>NH<sub>3</sub>, methylammonium), hereafter also MAPI, the excellent performances in PV stem from the fact this class satisfies all the main requirements a material for PV should have, *i.e.* a high compatibility with solution-based processing (low cost), a very long carrier diffusion length,<sup>20,21</sup> the ambipolar nature of the carriers that makes the OIHPs not only very good solar harvesters but also photocarrier conductor materials,<sup>22–27</sup> and not secondarily, a bandgap that is close to the ideal for a single-junction solar device. Different experimental architectures characterize the

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fabrication of PSCs.<sup>28</sup> Perovskite Sensitized Solar Cells (PSSCs) characterized by the use of mesoporous  $\text{TiO}_{2}$ ,<sup>25,29,30</sup> Meso-Superstructured Solar Cells (MSSCs)<sup>25</sup> where an insulating scaffold (alumina) is used instead of semiconducting TiO<sub>2</sub>, and thin-film, planar heterojunction cells,<sup>31–33</sup> have been all reported to provide excellent power conversion efficiencies (PCEs).

To further improve the quality of the OIHP layer, recent experimental papers have reported the possibility of passivating techniques able to improve the performances of the final device,<sup>34,35</sup> a technique which has been previously demonstrated to efficiently improve the performances of quantum dots.<sup>36</sup> Abate *et al.*<sup>37</sup> have demonstrated that undercoordinated halide atoms at the OIHP surface worsen the cell performances because of the positive charge trapping at the perovskite/hole conductor heterojunction and shown that coating with iodopentafluorobenzene (halogen bonding donor–acceptor formation) is the strategy to reduce this detrimental effect, obtaining a stable power output of over 15%.

Also, Lewis acid–base adduct (MAI·PbI<sub>2</sub>·base) mediated approaches<sup>38–40</sup> have been reported to be a very appealing technique able to provide highly efficient<sup>40</sup> solar cells characterized by the best PCEs of ~20%,<sup>38,39</sup> and are, very importantly, highly reproducible. Such a technique takes advantage of the favoured formation of adducts between Lewis bases containing nitrogen (N-donor), oxygen (O-donor), and sulphur (S-donor) with the acidic species PbI<sub>2</sub>.

On the other hand, Snaith's group<sup>41</sup> has reported on MAPI surfaces passivated still with Lewis bases characterized by a significant reduction of the non-radiative carrier recombination, by higher photoluminescence (PL) lifetimes and the PCEs of the planar heterojunction solar cells assembled via such procedure are quantitatively higher than those of untreated cells. This is clearly ascribed to the formation of a dative bond between the Lewis base and the undercoordinated Pb atoms at the surface.<sup>42</sup> Together with the high PL lifetimes, that in some experimental setups exceed 8 µs, also the PL quantum yield of the thin films results are highly improved (>30%) by means of the ligand passivation technique.<sup>43</sup> In this context several bases have been employed. In particular, N,N-dimethyl sulfoxide  $((CH_3)_2SO$ , also known as DMSO), an aprotic polar solvent, is found to work better in the case of MAPI, while thiourea ((NH<sub>2</sub>)<sub>2</sub>CS) provides the best results when methylammonium is replaced with formamidinium (FA =  $^{+}HC(NH_2)_2$ ), *i.e.* in the case of FAPbI<sub>3</sub> (FAPI).<sup>40</sup> Other aromatic, heterocyclic, Lewis bases like the pyridine (C<sub>5</sub>H<sub>5</sub>N), molecule reported also to remediate nonradiative defects in the MAPI film inducing bright domains,<sup>43</sup> and thiophene (C<sub>4</sub>H<sub>4</sub>S),<sup>41</sup> are used as passivating agents. It is furthermore evident from the available data<sup>40</sup> that the formation of the intermediate adduct MAI·PbI<sub>2</sub>·base improves over the direct annealing (no base) in terms of the morphology of the final layer, whose surface results in being extremely flat and uniform. Regardless of the nature of the experimental procedure, the interaction between the Lewis base and the OIHP is one of the key steps of the final device setup procedure. Noticeably, as recently reported by Zhu et al.,44 the presence of the Lewis base in the annealing process could highly promote the perovskite grain growth, further stressing the significance of the interaction between the Lewis bases and OIHPs.

Here, to get a better understanding of the processes involved in the Lewis acid–base adduct formation (passivation), we provide a theoretical analysis of the reaction/interaction of some of the most used X-donor systems (X = :N, :O, :S) with MAPI. In particular, after very carefully calibrating our theoretical setup, we report the results of the anchoring of three Lewis bases, *i.e.* pyridine (Py), thiourea (Thu), and *N*,*N*-dimethyl sulfoxide (DMSO) on the surface of MAPI. To the best of our knowledge, this is not only the first theoretical study on the topic but, in a wider context, this is one of the very first theoretical studies focusing on the molecular anchoring mechanism on MAPI surfaces.<sup>45–47</sup>

#### Computational details

Density functional based simulations have been performed by means of a numerical atomic based approach SIESTA code.<sup>48,49</sup> The generalized gradient approximation (GGA) for the exchange and correlation functional of Perdew, Burke, and Ernzerhof (PBE) was employed<sup>50</sup> along with the norm-conserving pseudopotentials of the Troullier-Martins (TM) type<sup>51</sup> for the description of the core electrons. For the heaviest atoms, *i.e.* Pb,<sup>14,52</sup> I, and S<sup>53</sup> we have used a scalar relativistic pseudopotential. In particular, the lead potential is described with 14 valence electrons,<sup>14,51</sup> 10 as semicore states (5d<sup>10</sup>) associated with a single- $\zeta$  plus polarization basis set, and 4 in the valence state  $(6s^26p^2)$  with a double- $\zeta$  plus polarization basis set; iodine is described by 7 valence electrons associated with a double- z plus polarization basis set. For the remaining species, nonrelativistic pseudopotentials with a standard triple- $\zeta$  plus polarization basis set were employed. The force threshold was set to 0.04 eV  $Å^{-1}$ . Noteworthily, the plane wave cut-off for the pseudopotential is set to 400.0 Ry.

To further assess the reliability of our results, considering the weak interactions existing between the organic moieties/ Lewis bases and the semiconductor barrier,<sup>2</sup> the initial analysis based on the DFT approach has been then refined by means of the vdW-DF2 (LMKLL)<sup>54,55</sup> non-local density functional for the most stable DFT calculated anchoring attacks. This latter approach leads to a larger adsorption energy without, in any case, either inducing large geometrical rearrangements with respect to the DFT optimized structure or impacting on the order of stability of the anchoring mechanisms previously obtained at the bare DFT level.

To initially validate our setup, we calculated the structural and electronic properties of the tetragonal phase of MAPI. The optimization of the bulk is carried on using an  $8 \times 8 \times 6$  *k*-point,  $\Gamma$ -centred, sampling of the Brillouin Zone (BZ), corresponding to 223 *k*-points.

On the optimized structure we have calculated the electronic properties with a 12 × 12 × 8 *k*-point,  $\Gamma$ -centred, mesh (634 *k*-points). The obtained lattice parameters and electronic bandgap are a = b = 8.84 Å, c = 12.74 Å, and  $E_{\rm G}(\Gamma) = 1.60$  eV

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(Fig. S1 in ESI<sup>†</sup>), respectively, in perfect agreement with the experimentally reported<sup>56–58</sup> and theoretically calculated (both by means of atomic orbitals<sup>14</sup> and plane wave based approaches<sup>59–61</sup>) values. Still, the charge density of the valence band maximum (VBM) and that of the conduction band minimum (CBM) (reported in Fig. S1 in ESI<sup>†</sup>) results from the antibonding linear combination of the Pb 6s and I 5p orbitals and of the Pb 6p orbitals with minor antibonding contributions of the I 5s ones, respectively, in agreement with previous results. It is worth noticing that our vdW-DF2 calculated volume for *t*-MAPI slightly increases (compared with the case of DFT/PBE) in a comparable amount with the previously reported data for the orthorhombic phase of MAPI<sup>62</sup> (~3%).

As widely documented in the literature,<sup>26,61,63</sup> the agreement between the DFT calculated electronic bandgap and experiments is fortuitous; the inclusion of fully relativistic effects (SOC) induces indeed a giant effect on the band edges<sup>63</sup> and on their dispersion, with the calculated bandgap reduced by more than 50% compared to the experimental one. Recovering the experimental gap of the bulk MAPbI<sub>3</sub> at the DFT level is thus due to the compensation of errors, *i.e.* no relativistic effect inclusion and DFT bandgap calculation shortcomings. To be rigorous, the true experimental bandgap would be reproduced at the theoretical level by adding many body corrections to the fully relativistic calculated systems (SOC+GW). The very large computational burden of this latter computational setup would not allow us to adopt a realistic modellization for our surfaces and for the Lewis base-acid mechanisms we plan here to study. Similarly, a DFT + SOC approach would highly underestimate the gap, reducing the impact of our analysis. In this sense the agreement between "bare" DFT and experiments due to the mentioned cancellation of errors makes our computational choice totally meaningful for the purpose of our present research, as also demonstrated by previous literature.<sup>14,64</sup>

#### Slab modellization

We studied anchoring mechanisms on the (001) surface of *t*-MAPI since such facet is widely recognized to be one of the most stable.<sup>65,66</sup> Due to the experimentally reported slight understoichiometry of N and I atoms<sup>67</sup> we have discarded the MAI-rich terminations,<sup>65,68</sup> focusing only on the PbI<sub>2</sub>-terminated flat surface. For our present purpose the first check is the convergence of the surface energy ( $E_{surf}$ ) vs. the slab thickness. To do this we refer to the equation:<sup>69</sup>

$$E_{\rm surf} = \frac{E_{\rm slab} - \left(n \cdot E_{\rm MAPI} + m \cdot E_{\rm PbI_2}\right)}{2 \cdot S} \tag{1}$$

where  $E_{\text{slab}}$  is the energy of the slab considered,  $E_{\text{MAPI}}$  is the chemical potential of bulk *t*-MAPI, *S* (considered twice, since the system is symmetric, see below) is the area of the exposed surface of the slab, and  $E_{\text{PbI}_2}$  is the chemical potential of PbI<sub>2</sub>. *n* and *m* are the number of MAPI and PbI<sub>2</sub> units in the slab, respectively. The polymorphism of PbI<sub>2</sub>, in our case, does not represent a serious issue since we are not here interested in determining the exact order of stability of different surfaces.<sup>65</sup> In other words, the PbI<sub>2</sub> chemical potential works as a constant

value included to take into account the non-stoichiometry of the flat PbI<sub>2</sub>(001) surface. Accordingly, we have optimized the experimental structure reported in literature and used the calculated energy in eqn (1).<sup>70</sup> The surface energies calculated with eqn (1) for two slabs consisting of three  $(1 \times 1 \times 3)$  and four  $(1 \times 1 \times 4)$  layers of *t*-MAPI along the non-periodic direction are 0.2808 and 0.2765 J  $m^{-2}$ , respectively, clearly showing that three layers along *c* are sufficient for the surface energy to converge. Similarly, the bandgap of  $(1 \times 1 \times 3)$  slab is 1.34 eV, slightly smaller than the same calculated with plane waves approaches.<sup>65</sup> The origin of this small difference relies on the fact that the previous literature considered thinner, and thus more confined, slabs (two layers along c), and also because the PAO based approaches may slightly underestimate the description of 2D electronic gaps because of the localized nature of the atomic orbitals.<sup>71</sup> This latter feature does not alter in any case the main findings of the paper.

For the sake of completeness, in order to assess the suitability of our slabs for evaluating the electronic properties, we have calculated at first the vacuum electrostatic potential of the  $(1 \times 1 \times 3)$  and  $(1 \times 1 \times 4)$  slabs finding a difference smaller than 0.002 V and then the difference between the vacuum electrostatic potential and mid-slab electrostatic potential  $(\Delta V \text{ in Fig. S2 in ESI}^{\dagger})$  for the same two slabs. We assume the convergence achieved within three layers along c since the difference in the latter case is  $\sim 1\%$ .<sup>72</sup> A vacuum thickness ranging between 60 and 65 Å is considered for both the  $(1 \times 1 \times 3)$ and  $(1 \times 1 \times 4)$  systems, a "safe" value to ensure the absence of spurious interactions once the Lewis base is adsorbed on both the surfaces of the slab. Fig. S2 in ESI<sup>†</sup> shows the planar averaged (PAV) and nanosmoothed (MAV) electrostatic potential for the  $(1 \times 1 \times 3)$  and  $(1 \times 1 \times 4)$  slabs, respectively. The choice of the symmetric modellization is motivated by the fact that such an approach, at variance with the asymmetric one,<sup>73,74</sup> allows studying both the thermodynamics and electronic properties of the attack, minimizing any residual dipole inside the slab. It is also worth noticing that, following Tateyama and Mosconi, 59,65,68 MA molecules are oriented in a "AB BA AB BA AB BA" fashion along the non-periodic direction further reducing any possible net polarization along the slab. Several studies indeed based on an asymmetric modellization have led to unrealistic wavefunction distribution. Concerning the adsorption energy calculations, the Basis Set Superposition Error (BSSE) has been calculated and included in order to overcome the possible basis set shortage associated with the DFT/PAO (vdW-DF2/PAO) theoretical setup.

#### Results and discussion

To analyse the adsorption mechanism, we have considered a  $(2 \times 2)$  supercell of the previously introduced  $(1 \times 1 \times 3)$  slab, consisting of a 600 atoms' slab. All the geometrical optimizations involving such slabs are performed by means of a  $4 \times 4 \times 1$  *k*-point,  $\Gamma$ -centred, BZ sampling, while the electronic properties are calculated by means of a  $6 \times 6 \times 1$  mesh on top of the optimized structure.

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**Fig. 1** DFT/PAO calculated PDOS of the (001) flat Pbl<sub>2</sub>-rich surface (Fermi energy is set to zero). In the inset PDOS for the same surface calculated at the plane-waves' level. Adapted with permission from ref. 65. Copyright (2014) American Chemical Society.

It is interesting to notice that the Projected Density of States (PDOS) close to the band edge region are in good agreement with those previously calculated for the same slab at a different level of theory.<sup>65</sup> Furthermore, we have compared the wavefunction localization at the band edges for both the flat and PbI<sub>2</sub>-vacant (001) surfaces.<sup>65</sup> It is extremely encouraging to notice the almost identical distribution of the CBM (see Fig. S7 of ref. 65) with those calculated here and reported in Fig. 1. Interestingly enough our setup seems to capture features typical of the fully relativistic effect inclusion, where I atoms of the flat (001) surface are essentially not involved in the CBM (Fig. 2(b)). Similarly, the CBM of the PbI<sub>2</sub>-vacant surface is uniformly distributed in the Pb atoms (prevalently in the internal region, Fig. 2(d)), while the

(b)

(d)

Fig. 2 DFT/PAO calculated wavefunction distribution for the (a) valence band maximum and (b) conduction band minimum for the Pbl<sub>2</sub>-rich (001) flat surface. (c and d) Are the same for the (001) Pbl<sub>2</sub>-vacant surface.

VBM of the same model (Fig. 2(c)) is completely buried in the subsuperficial region. The static picture that emerges from this theoretical description of the two different models,  $PbI_2$ -rich and vacant, is the fact that for the former case both the electron and hole are available at the surface, while for the latter only the electron is, making the carriers of the flat surface more accessible to any scavenger or transport material. This means that in principle, in the  $PbI_2$ -vacant surface the recombination may occur more easily, potentially making it a surface of scarce interest for solar-to-energy oriented applications.<sup>75</sup> Accordingly, we hereafter report results of the Lewis base adsorption only on the flat,  $PbI_2$ -rich (001) surface.

#### The anchoring mechanism

The almost complete lack of theoretical and experimental knowledge about the structures and mechanisms of adduct formation motivates us to initially focus on the study of single molecule interaction with the MAPI(001) surface. This is the main reason we have considered a reasonably large area  $(312.6 \text{ Å}^2)$  and a coverage of 12.5% of the available undercoordinated Pb atoms at the surface. The full coverage, although of clear interest, goes beyond the scope of the present paper, and accordingly we address the readers to further publications, now in preparation, for such extended analysis. In one sense, we are aware that our procedure partly neglects the steric or inductive effects that potentially could impact on the passivation.<sup>41</sup> On the other hand, we can easily compare and rationalize the structural/thermodynamic and electronic properties for each single different base in an unbiased way.

To possibly find out the most stable Lewis acid-base adduct for all the bases investigated, and also considering their planar geometry (only DMSO has a triangular pyramid structure where methyl C and O atoms describe a plane, *i.e.* the pyramid base), we considered two configurations, as initial guesses. In the first (the second) the molecule plane is oriented along the  $\langle 100 \rangle$ ( $\langle 010 \rangle$ ) direction, always pointing the donor atom (N, O, and S) towards an undercoordinated Pb atom at the surface. Lead atoms at the surface are formally equivalent, thus no main differences in the results are expected from choosing different Pb-sites at the surface. The initial orientation and the Pb atoms involved in the anchoring are reported in Fig. 3.

All the optimized geometries of the Lewis bases investigated are reported in Fig. 4, while Table S1 in ESI<sup>†</sup> reports the main geometrical parameters of the same systems at different levels of calculation. As can be observed four different levels of theory (two atomic orbitals-<sup>48,49,76</sup> and one plane wave-based<sup>77–81</sup>), provide very similar optimized structures, further validating the reliability of our setup. We thus calculate the adsorption energy for the different Lewis bases according to the equation:

$$E_{\rm ads} = (E_{\rm surf} + E_{\rm base}) - E_{\rm adduct}$$
(2)

Here,  $E_{ads}$  is the adsorption energy,  $E_{surf}(E_{base})$  is the optimized surface (base) energy, while  $E_{adduct}$  is the energy of the final MAPI base adduct. According to eqn (2), the larger the  $E_{ads}$ , the more stable the adduct.

(a)

(c)

(Isosurface level 0.02 eV Å<sup>-3</sup>.)



**Fig. 3** Left: Top view of the initial orientation of the anchoring of the Lewis base along the  $\langle 100 \rangle$  direction (red stripe) and the  $\langle 010 \rangle$  direction (green stripe). Right: Lateral view of Pb atoms (grey) involved in the anchoring mechanism on the top and bottom layers.



**Fig. 4** DFT/PAO optimized structures of the four Lewis bases here considered. From left (a), (a) pyridine (Py), (b) dimethylsulfoxide (DMSO), (c) thiourea (Thu). Numbers and Greek italic letters are legends of Tables S1, ESI.† Arrow and number are the direction and value of the calculated<sup>76</sup> dipole moment (Debye) [brown: C; yellow: S; cyan: N; red: O; white: H atoms].

The first base investigated is pyridine, Py (see Fig. 4(a)). We initially considered two different initial guesses whose optimization has collapsed into a single final geometry with an identical  $E_{ads}$  of 0.958 eV per Py at the vdW-DF2 level (0.850 eV per Py at the DFT/PBE level) (**Py**<sub>1</sub>). Interestingly, in the optimized geometry Py is not bent, featuring a geometry of the aromatic ring plane almost perpendicular to the (001) surface. This result motivated us to start from another initial guess with the Py aromatic ring plane already parallel to the (001) facet. Noticeably, the optimization of this structure (**Py**<sub>2</sub>) has led to the most stable MAPI-Py adduct with an  $E_{ads} = 1.315$  eV per Py at the vdW-DF2 level (1.065 eV per Py at the DFT/PBE level) whose geometry together with that of **Py**<sub>1</sub> is reported in Fig. 5.

The reason for the possible co-existence of the two structures must be ascribed to the extremely localized orientation of the N lone pair in an sp<sup>2</sup> orbital, which is perpendicular to the C  $\pi$  density of the aromatic system and which geometrically points towards the p orbitals of the undercoordinated Pb atom at the surface (the Lewis acid). In this sense the **Py**<sub>1</sub> geometry should result in the most effective geometry for the dative bond formation. The Py molecule is bulky enough to show a reduced tendency towards the bent geometry since the centre of mass of the overall system is more shifted towards the anchored molecule.

We believe that a main role in the adduct formation process is played by the sub-superficial MA cation orientation. The  $Py_2$ geometry is accompanied by an evident MA rearrangement that maximizes the aminic  $H \cdots I$  stabilizing Coulomb interactions. The same characteristic is not found in the other, less stable,  $Py_1$  structure where the MA cation orientation is very similar to that in the bare surface.

As stated, we are clearly aware of the methodological shortcomings of DFT in predicting electronic properties. In any case, we are similarly aware that as widely reported DFT well reproduces the electronic features of this class of materials (due to the previously mentioned cancellation of errors) and that, in this sense, our setup perfectly reproduces the experimental bandgap of bulk *t*-MAPI. We can accordingly compare, once aligned to the vacuum level, the VBM positioning of the flat PbI<sub>2</sub>-rich (001) surface and that of the  $Py_1$  and  $Py_2$  adducts. Furthermore, the VBM results are highly reliable since DFT is by definition a ground state theory. The comparison among CBMs will be more uncertain, but still extremely meaningful, since the chemical homogeneity of the systems is considered.

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Fig. 5 Lateral (a and d) and top (b and e) view of the two DFT/PAO optimized mechanisms found in the case of Py, Py1 and Py2, respectively. (c and f) DFT/PBE calculated PDOS of the two structures.

Following previous literature<sup>82</sup> we used our slabs to evaluate the band edge position as a function of the passivation. We accordingly considered the Kohn–Sham (KS) eigenvalue of the slab ( $\varepsilon_{\text{VBM}}^s$ ) and aligned it to the vacuum level ( $V_{\text{vac}}$  is the vacuum electrostatic potential taken at z = 0 Å, e is the electron charge) according to:

$$\varepsilon_{\rm VBM} = \varepsilon_{\rm VBM}^{\rm s} + e \cdot V_{\rm vac} \tag{3}$$

In this way, indeed, we can establish the downshift/upshift of the band edges of the anchored systems with respect to the flat  $PbI_2$ -rich (001) MAPI surface. Due to the perfect agreement between the experimental gap and the DFT calculated one we previously demonstrated in the bulk case, the CBM level is determined by adding the DFT calculated gap to the valence band eigenvalue. We have thus compared the Planar Averaged (PAV) and nanosmoothed (MAV) Potential of the bare PbI<sub>2</sub>-rich (001) surface and of the **Py**<sub>1</sub> and **Py**<sub>2</sub> adducts and accordingly established the relationship among the band edges of the three systems, as reported in Fig. 6.

The PDOS analysis reveals a different behaviour for the different anchorings. In particular, the  $Py_2$  structure is characterized by



**Fig. 6** (a) Left, Planar Averaged (PAV) and nanosmoothed (MAV) Potential for the bare  $Pbl_2$ -rich flat surface, **Py1**, and **Py2** structures and, right, relative CBM and VBM still for the bare  $Pbl_2$ -rich flat (001) surface (green), **Py1** (blue) and **Py2** (red) structure. The vacuum level is used as energy zero. (b) VBM and CBM for the bare  $Pbl_2$ -rich flat (001) surface (green), **Py2** (red) and **Py1** (blue) structure. The bare  $Pbl_2$ -rich flat (001) surface (green), **Py2** (red) and **Py1** (blue) structure. The bare  $Pbl_2$ -rich flat (001) surface (green), **Py2** (red) and **Py1** (blue) structure. The bare  $Pbl_2$ -rich flat (001) surface (green), **Py2** (red) and **Py1** (blue) structure. The bare  $Pbl_2$ -rich flat (001) surface (green), **Py2** (red) and **Py1** (blue) structure. The bare  $Pbl_2$ -rich flat (001) surface (green), **Py2** (red) and **Py3** (blue) structure. The bare  $Pbl_2$ -rich flat (001) surface (green), **Py2** (red) and **Py3** (blue) structure. The bare  $Pbl_2$ -rich flat (001) surface (green), **Py3** (red) and **Py3** (blue) structure. The bare  $Pbl_2$ -rich flat (001) surface (green), **Py3** (red) and **Py3** (blue) structure. The bare  $Pbl_2$ -rich flat (001) surface (green), **Py3** (red) and **Py3** (blue) structure. The bare  $Pbl_2$ -rich flat (001) surface (green), **Py3** (red) and **Py3** (blue) structure. The bare  $Pbl_2$ -rich flat (001) surface (green), **Py3** (red) and **Py3** (blue) structure. The bare  $Pbl_2$ -rich flat (001) surface (green), **Py3** (red) and **Py3** (blue) structure. The bare  $Pbl_2$ -rich flat (001) surface (green), **Py3** (red) and **Py3** (blue) structure. The bare  $Pbl_2$ -rich flat (001) surface (green), **Py3** (red) and **Py3** (blue) structure. The bare  $Pbl_2$ -rich flat (001) surface (green), **Py3** (red) and **Py3** (red) structure. The bare  $Pbl_2$ -rich flat (001) structure.

a gap pretty larger than the **Py**<sub>1</sub> one, that is 1.718 *vs.* 1.517 eV ( $\Gamma$ -point at the DFT/PBE level).

Following eqn (3), we have here aligned the VBM vs. the vacuum energy level for the three slabs, the bare, flat PbI<sub>2</sub>-rich (001) surface, Py<sub>1</sub>, and Py<sub>2</sub> adducts, and then compared the band edge levels. Here,  $Py_2$  VBM is stabilized with respect to the bare surface VBM. This downshift is reasonably large ( $\sim 0.25$  eV). Together with the previously discussed thermodynamic stability, this finding further supports the idea of Py as a performing passivating agent.<sup>40</sup> In this case, the difference between the Py<sub>2</sub> and  $Py_1$  electronic properties is slightly more complex and needs to be discussed. There is indeed the expected stabilization (0.163 eV) of the VBM of  $Py_2$  which is mediated by the enhanced surface I-Pb-I tilting. Anyway, the Py2 CBM is slightly destabilized in energy by the larger localization of its wavefunction. Such a localization seems to be induced by the structural rearrangement associated with an agostic/anagostic-like interaction<sup>83,84</sup> of the Pb···H-C, a 3-center 2-electron bond, that seems to be effective for the case of  $Py_2$ . Fig. 7 shows the band edge wavefunctions for both the mechanisms. Fig. 7(d) in particular shows how the CBM wavefunction is spread on all but one (that involved in the mentioned  $Pb \cdots H$ -C interaction, Fig. 7(d)) of the Pb atoms.

We could speculate that  $\mathbf{Py_1}$  is the initial adduct structure, *i.e.* that which is immediately formed once Py approaches the MAPI surface, while  $\mathbf{Py_2}$  represents the evolution of the  $\mathbf{Py_1}$ structure towards the most thermodynamically stable structure. This speculation anyway would deserve more attention and we plan to investigate this issue in future studies.

Interestingly, evidence of the "perfect" dative bond formation in  $\mathbf{Py_1}$  is qualitatively provided by the charge analysis comparison between the bare molecule and the adduct. In particular, according to the Voronoi atomic charge distribution model,<sup>85</sup> the N in the Py molecule is initially -0.171e, in Py<sub>1</sub> the same charge becomes -0.110e. In a very symmetric way, the Pb involved in the Pb-N bond formation has a charge of 0.613e in the bare slab that becomes 0.585*e* in **Py**<sub>1</sub>. In **Py**<sub>2</sub>, at variance, the bent orientation of Py with respect to the surface plane has the effect of weakening the Pb-N bond (2.72 Å (2.80 Å at vdW-DF2) in Py2 vs. 2.57 Å (2.62 Å at vdW-DF2) in Py1) with a less effective dative bond formation, but with the energetic stabilization ascribed to the mentioned  $Pb \cdots$  (aromatic cycle) interactions at the surface. A fingerprint of the dative bond reduced character of  $Py_2$  is observed in the remaining amount of the lone pair, not used in the bond formation, that together with the high value of electronegativity of N ( $\chi_N$  = 3.04, according to Pauling<sup>86</sup>) localizes the carriers at the interface - both electron and hole are partly localized on N atoms - making the Py<sub>2</sub> adduct geometry a potential charge recombination centre (see Fig. 7(c) and (d)). Thus, despite the enhanced thermodynamic stability, the presence of residual Py molecules in the bent fashion seems to be detrimental for any light-induced conversion process.

On the experimental side, it is worth mentioning that  $\text{Snaith}^{41}$  reports the almost unchanged bandgap (see Fig. S5 (ESI<sup>†</sup>) in ref. 41) among the bare surface, the Py-passivated, and the thiophene (Lewis base here not investigated) passivated one (~1.5 eV). The co-existence of similar bandgaps for the mentioned structures seems to demonstrate that others apart from the most stable calculated adducts here are potentially preferred once the coverage increases. In particular, for the Py case, **Py**<sub>1</sub>, our less stable adduct, seems to be such a structure since the bare surface and **Py**<sub>1</sub> are characterized by a very similar bandgap (in the range 1.4–1.5 eV) also from our calculations. This could be consistent with a more ordered anchoring geometry.



Fig. 7 (a and b) Py1, and (c and d) Py2 DFT/PBE calculated VBM and CBM wavefunction distribution (isosurface level 0.02 eV Å<sup>-3</sup>).

To extend the analysis, we have then investigated the adducts formed by two aliphatic Lewis bases. The first one, and the first oxygen donor studied in the present work, is DMSO. Experimentally, in the passivation mechanism it is employed with both MAPI and FAPI.<sup>38,40</sup> We decided to investigate its anchoring mechanism in conjunction with MAPI in order to compare its behaviour with that of the previously investigated aromatic bases. The optimization of the two initial guesses has led to two adducts, DMSO<sub>1</sub> and DMSO<sub>2</sub>, that, according to eqn (2), are characterized by  $E_{ads}(DMSO_1) = 1.038$  eV per DMSO and  $E_{ads}$ (DMSO<sub>2</sub>) = 0.900 eV per DMSO (DFT/PBE), respectively. Their optimized structures are reported in Fig. 8, along with the PDOS analysis. The small difference in energy clearly is supported by the very similar geometry of the two anchorings, where the main geometrical features at the interface are retained, *i.e.* the Pb-O, O-S bond lengths and Pb-O-S angle are 2.47, 1.59 Å, and 111.0°, respectively. Because of the almost identical geometry of the two attacks we calculated the vdW-DF2 adsorption energy only for the **DMSO<sub>1</sub>** structure where  $E_{ads}$ (vdW-DF2) is 1.436 eV per DMSO, further testifying the increase of adsorption energy once the van der Waals interactions are included in the calculations.

The close similarity between the two systems – nothing changes but the S=O bond which is rotated by ~90° (see and compare Fig. 8(b and d)) on the *ab* plane – is accompanied by very similar bandgaps for **DMSO**<sub>1</sub> and **DMSO**<sub>2</sub> (1.624 and 1.547 eV, respectively,  $\Gamma$  point at the DFT/PBE level). Here the CBMs for **DMSO**<sub>1</sub> and **DMSO**<sub>2</sub> are identically upshifted (0.10 eV) with respect to the bare PbI<sub>2</sub>-rich flat (001) surface, while the **DMSO**<sub>1</sub> VBM is slightly more stabilized than **DMSO**<sub>2</sub> one.

Even if this latter difference is almost negligible, we tentatively try to relate such a stabilization to the geometry of the two structures observing a slightly enhanced Pb–I–Pb tilting at the surface of **DMSO**<sub>1</sub> and similarly MA cations of the very first sub-superficial layer oriented along the [001] direction that maximize the stabilizing Coulomb interactions confirming the trend we have observed for the previously analysed bases. Concerning the band edge wavefunction distribution, mainly electrons (VBM) but also holes (CBM) of the **DMSO**<sub>1</sub> structure reside on DMSO (see Fig. S3 in ESI<sup>†</sup>). This strong coupling between MAPI and DMSO is due to the strong electronegativity of oxygen and, not secondarily, to the presence of a second lone pair (O sp<sup>2</sup>) that enhances the electron density on the oxygen atom.

The presence of a second lone pair on the anchoring atom characterizes also the last Lewis base we analyse in the present work, *i.e.* thiourea (see Fig. 4(c)). As for some other cases here studied, we found that the two initial guesses have collapsed into the same identical structure, **Thu**<sub>1</sub> characterized by  $E_{ads} = 1.646$  eV per Thu at the vdW-DF2 level (1.293 eV per Thu at the DFT/PBE level) and a bandgap of 1.640 eV ( $\Gamma$  point, DFT/PBE). The structure, PDOS, and band alignment (anchored *vs.* free surface) for **Thu**<sub>1</sub> are reported in Fig. 9.

**Thu**<sub>1</sub> is the most stable MAPI·base adduct of all those here investigated, confirming somehow what is expected about the enhanced stability of the soft S-donor reacting with Pb(n).<sup>87</sup> Still in the case of **Thu**<sub>1</sub>, it is the I···H–N Coulomb interaction<sup>88,89</sup> that stabilizes the final adduct. There is indeed an almost symmetric arrangement between the MA aminic N–H···I Coulomb interactions due to the MA in the first layer and the I atom at the surface and the same distance between the aminic group of **Thu**<sub>1</sub> and the same surface I atom (both at ~ 2.60 Å at PBE/GGA).

Additionally, the appearance of a tetrel-like  $^{90,91}$  Pb $\cdots$ N–H interaction (here the N–H group is that belonging to the Thu molecule)



Fig. 8 Lateral (a and d) and top (b and e) view of the two DFT/PAO calculated mechanisms found in the case of DMSO, DMSO<sub>1</sub> and DMSO<sub>2</sub>, respectively. (c) PDOS of DMSO<sub>1</sub>. (f) VBM and CBM for the bare Pbl<sub>2</sub>-rich flat (001) surface (green), DMSO<sub>1</sub> (red) and DMSO<sub>2</sub> (blue) structure. The bare Pbl<sub>2</sub>-rich flat (001) surface VBM is used as energy zero.

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Fig. 9 Lateral (a) and top (c) view of Thu<sub>1</sub> DFT/PBE optimized geometry. (b) DFT/PBE calculated PDOS of Thu<sub>1</sub>. (d) VBM and CBM for the bare Pbl<sub>2</sub>-rich flat (001) surface (green) and Thu<sub>1</sub> (red) structure. The bare Pbl<sub>2</sub>-rich flat (001) surface VBM is used as energy zero.

seems to further favour the final adduct. This latter kind of interactions are reported for Group IV elements that behave as Lewis acids (as in our case). Even if no previous works have focused on such kind of interactions in OIHP chemistry, the close similarity between the chemical environment of the systems where tetrel interactions are initially reported (halogen terminated lead(II) organic-inorganic complexes<sup>90</sup>) and our one allows us to speculate on the existence of this non-covalent bonding feature in Thu<sub>1</sub>. Nitrogen electronegativity and accordingly Thu dipole moment are the further keys to focus on in order to understand the properties of the Thu<sub>1</sub> adduct. Overall the dipole moments we calculated for the Lewis bases here considered are in satisfactory good agreement with the experimentally reported ones,<sup>92–94</sup> and the value, regardless of the direction, reasonably correlates with the adsorption energy of the base on MAPI. One can observe from Fig. 4 that, due to the larger value of the electronegativity of N, the Thu dipole moment vector ( $\mu$  = 5.50 D) is oriented along the :S  $\rightarrow$  N direction, and not like in all other cases where the same vector points toward the donor atom  $(\rightarrow: O \text{ in DMSO and } \rightarrow: N \text{ in Pyr})$ . This has an influence on the

wavefunction distribution of **Thu**<sub>1</sub> mainly of VBM (reported in Fig. 10) which shows an extremely high localization of the electron on the Thu S and N atoms ( $\delta^-$  centres).

For the latter couple of bases (DMSO and Thu) recently Zhu *et al.*<sup>44</sup> studying the passivation of differently oriented perovskite layers have assembled devices characterized by low PCEs in the case of Thu (~3.93%) and high ones (~18.84%) in the case of DMSO. The authors<sup>44</sup> ascribe this noticeable difference to the possible residual presence of Thu in the perovskite film that can increase both the trap densities and recombination. The possible presence of residual Thu on the perovskite layer is further confirmed by our results, since we can clearly state that Thu binds MAPI stronger than DMSO does, thus showing the difficulty in washing out Thu from the MAPI surfaces.

Additionally, Park in his paper<sup>38,40</sup> reports that DMSO does not work properly for FAPI (OIHP here not investigated) but at the same time mentions Thu as a very good base for adduct formation still for FAPI, because of the chemical similarity between Thu and the formamidinium structure (HC-(NH<sub>2</sub>)<sub>2</sub>). Even if our analysis does not include FAPI, the results from



Fig. 10 DFT/PBE calculated (a) VBM and (b) CBM wavefunction distribution for Thu<sub>1</sub> (isosurface level 0.02 eV Å<sup>-3</sup>).



Fig. 11 Lateral views along the *x* direction (top) and the *y*-direction (bottom) (100) of the vdW-DF2 optimized structures for (a) bare (001) MAPI surface, (b) pyridine (**Py**<sub>1</sub>), (c) pyridine (**Py**<sub>2</sub>), (d) DMSO (**DMSO**<sub>1</sub>) and (e) thiourea (**Thu**<sub>1</sub>).

MAPI Thu are already sufficient to support Park findings<sup>38,40</sup> about the stability ascribed to the similar structure between Thu and the A-site organic cation. There is, in any case, no experimental comparison between the two bases for MAPI, for which only DMSO is reported. On the basis of thermodynamic analysis we can say that Thu appropriately works as a good passivating agent also for MAPI, at the same time care must be paid once washing it out from the surface because of the stronger anchoring it forms with the MAPI surface.

To better show the impact of the four bases considered on the MAPI surface in Fig. 11 we report the I–Pb–I tilting at the surface and at the subsurface region and the orientation of MA for the most stable anchoring attacks. The reader can in this way get an idea of the two main non-covalent interactions that stabilize the final attack, *i.e.* an intra (MAPI) interaction for the aromatic bases that induces large geometrical rearrangements in the MA orientation and in the I–Pb–I tilting in the superficial and sub-superficial layers, and an inter (MAPI-Lewis base) one for the aliphatic bases, mainly thiourea, whose highest stabilization is mediated by Thu···MAPI and Pb···(N–H)<sub>Thu</sub>. Further geometrical details of the adduct formation are available in the ESI† (Table S2 and Fig. S4, S5 in ESI†).

One last comparison among the Lewis bases we considered in the paper and the adducts they form with MAPI is based on the Hard and Soft Acid/Base Theory (HSAB).<sup>95,96</sup> As a consequence of size and charge, Pb( $\pi$ ) is considered a soft borderline acid. Following HSAB, soft acids are expected to better react with soft bases. We thus calculate<sup>76</sup> the hardness ( $\eta$ ) of the bases here considered following the equation:<sup>97</sup>

$$\eta = \frac{(\mathrm{IP} - \mathrm{AE})}{2} = \frac{E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}}{2} \tag{4}$$

where IP and AE are the base ionization potential and the electronic affinity, respectively. Their difference is approximated

to the Kohn–Sham bandgap, where  $E_{LUMO}$  ( $E_{HOMO}$ ) represents the eigenvalue of the Lowest Unoccupied (Highest Occupied) Molecular Orbital. For the investigated bases we get that Thu and DMSO are softer (2.47 and 2.39 eV) while Py (3.04 eV) is a slightly harder base. Even if the results previously shown and those here obtained with the HSAB theory do not perfectly match (DMSO is 0.08 eV softer than Thu, a difference which, in any case, is in the order of the accuracy of the calculation) still we have to mention that, even if of interest, the comparison is merely qualitative since the HSAB approach takes into account only the electronic features, i.e. the Lewis acid-base, nucleophilic-electrophilic reactivity and not any of the thermodynamic stabilizing surface-base interactions we have previously introduced and discussed. Interestingly, the same results obtained from eigenvalues calculations at the PAO/DFT/PBE48-51 level show that Thu is the softest base (1.28 eV), confirming it as the Lewis base with the highest affinity towards Pb(II).

It is worth stressing that our analysis at first aims to focus on the interactions between clean, non-defective, surfaces. At the same time, we are aware of the tendency of MAPI and other OIHP systems to easily form defects, most of them, in any case not active in the gap. Work to elucidate the interactions between defects and adduct stability/passivation is now in progress.

#### Conclusions

Motivated by the introduction of new experimental techniques based on the passivation of hybrid organic–inorganic halide perovskites with Lewis bases and on the adduct formation between MAI, PbI<sub>2</sub>, and the Lewis bases, we have here investigated the anchoring mechanism of some nucleophiles, both aliphatic and aromatic, on top of one of the most stable MAPI surfaces. In particular, we have performed the analysis of both stability (thermodynamics) and the electronic properties of the attack. Interestingly, we found that the aromatic adducts formed by pyridine can coexist giving rise to a larger number of stable adducts, while, globally, thiourea forms the most stable one. Such a stability is dominated by the non-covalent interactions present both at the interface (inter, MAPI-Lewis base) and in the MAPI surface (intra, MAPI surface), as also evidenced by the inclusion of the dispersion forces in the optimization procedure.

Concerning the electronic properties, saturating the surface with a single base molecule allows recovering the Pb bulk coordination, opening the gap of the final adduct. We have thus aligned the valence band maximum vs. the vacuum level finding a quite homogeneous scenario, where aromatic heterocycles and thiourea seem to be effective in lowering the valence band maximum compared to the bare surface. It is similarly important to mention that for some bases the most thermodynamically stable adduct does not necessarily correspond to the best arrangements for device assembly with the Pb–X bond acting as a possible recombination centre.

In other cases, the strong base adsorption energy could lead to the assembly of devices with poor performances due to the inherent difficulty in removing the passivating base from the MAPI surface.

The present investigation paves the way towards a more systematic analysis of larger coverages of Lewis bases on such perovskite surfaces, both with (001) and different orientations, in order to take into account the steric and inductive effects among passivating molecules that could impact on the energetic profile of such acid-base adducts. Also the thermal effect inclusion in the anchoring mechanism, an analysis now in progress, will be extremely useful to better investigate the features, both structural and electronic, that characterize the final adducts.

## Conflicts of interest

There are no conflicts to declare.

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