Ferroelectric Graphene—Perovskite Interfaces

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ABSTRACT: Owing to their record-breaking energy conversion efficiencies, hybrid organometallic perovskites have emerged as the most promising light absorbers and ambipolar carrier transporters for solution-processable solar cells. Simultaneously, due to its exceptional electron mobility, graphene represents a prominent candidate for replacing transparent conducting oxides. Thus, it is possible that combining these wonder materials may propel the efficiency toward the Schokley–Queisser limit. Here, using first-principles calculations on graphene–CH₃NH₃PbI₃ interfaces, we find that graphene suppresses the octahedral tilt in the very first perovskite monolayer, leading to a nanoscale ferroelectric distortion with a permanent polarization of 3 mC/m². This interfacial ferroelectricity drives electron extraction from the perovskite and hinders electron–hole recombination by keeping the electrons and holes separated. The interfacial ferroelectricity identified here simply results from the interplay between graphene’s planar structure and CH₃NH₃PbI₃’s octahedral connectivity; therefore, this mechanism may be effective in a much broader class of perovskites, with potential applications in photovoltaics and photocatalysis.

Solution-processable solar cells represent an attractive photovoltaic (PV) technology due to low manufacturing costs, process scalability, and the compatibility with flexible substrates. Within this family of PV devices, hybrid organometallic perovskite solar cells have risen to prominence due to their record-breaking performance, which recently surpassed the 20% power conversion efficiency mark. The stunning performance of perovskite cells has been attributed to the efficient light absorption, the photoexcitation of free carriers as opposed to bound excitons, and the long electron and hole diffusion lengths.

While hybrid perovskites exhibit exceptional PV properties, in any optoelectronic device, the perovskite layer is sandwiched in a stack including ordinary electron- and hole-transport layers as well as the electrodes. Because charge extraction and collection are as critical as charge generation, it is paramount to optimize simultaneously all of the materials in the stack as well as their interfaces. The optimization of materials interfaces is especially urgent because the rate of charge extraction from perovskites is considerably lower than that in conventional dyesensitized cells, by up to 3 orders of magnitude.

A potential avenue for improving electron and hole transport toward the electrodes is to employ graphene in the place of the traditional TiO₂ and spiro-OMeTAD. The first application of graphene in perovskite PVs was in the form of graphene/TiO₂ nanocomposites. This combination was shown to selectively extract electrons from the perovskite layer, leading to a power conversion efficiency of 15.4%. In a subsequent work, graphene quantum dots were deposited between TiO₂ and the perovskite absorber, leading to a three-fold increase in the electron extraction rates. More recently, reduced graphene oxide was employed as a hole-transport material, leading to device efficiencies as high as 11.5% and 12.4%. Beyond PVs, graphene and methylammonium lead iodide (CH₃NH₃PbI₃, hereafter MAPbI₃) have also been combined to realize high-performance photodetectors. Despite these early successes, the structure and properties of the interface between these two materials and the origin of the efficient electron extraction are still unknown.

In this work, we employ first-principles calculations to probe for the first time the interfaces formed between MAPbI₃ and graphene. By investigating the structural and electronic properties of the most stable graphene–MAPbI₃ interfaces, we identify a graphene-induced ferroelectric distortion within MAPbI₃. Here, we fully characterize this novel effect and show that it results from the interplay between the planar structure of graphene and the octahedral connectivity of the perovskite. This ferroelectric distortion carries two consequences: (i) it favors selective electron transfer toward graphene, and (ii) it lifts the degeneracy of the valence band top in the perovskite, thereby pushing the hole wave functions away from the graphene sheet and suppressing electron–hole recombination.

MAPbI₃ crystallizes in an orthorhombic perovskite structure at low temperature (<160 K) and undergoes two phase transitions with increasing temperature to a tetragonal and a cubic structure. The unit cell of the high-temperature (>330 K) cubic structure has a lattice parameter of a = 6.312 Å and contains one MAPbI₃ formula unit. The unit cell of the tetragonal and of the orthorhombic structure contains four MAPbI₃ formula units, and corresponds to a \(\sqrt{2} \times \sqrt{2} \times 2\) supercell of the cubic cell, with the long axis along the [001] direction. X-ray diffraction measurements on MAPbI₃ crystals
exhibit strong peaks associated with the (110) and (001) reflections, suggesting that the crystallites are predominantly terminated by the (110) and (001) surfaces. This observation is supported by recent first-principles calculations. On the basis of these studies, we constructed graphene−MAPbI₃ interfaces with the perovskite exposing the (110) and (001) faces. For both surfaces, we considered the PbI₂ termination as the experiment indicates a slight iodine deficiency. Both surfaces are nonpolar, and the corresponding films can be seen as an alternation of MAI and PbI₂ layers, as if the structure was obtained via layer-by-layer deposition using the standard precursors. In both cases, the slab is terminated by truncated octahedra because this is the most stable non-defective termination. These models are shown in Figure 1a and b.

In order to form interfaces, we stacked graphene and MAPbI₃ in a planar geometry, as shown in Figure 1a and b. Strictly speaking, this model corresponds to a synthesis route whereby the perovskite is deposited layer-by-layer on CVD graphene or micromechanically exfoliated graphene. However, we expect our model to apply more generally to the case of bulk heterojunction blends with reduced graphene oxide. In fact, in this case, the oxygen functional groups are known to cluster, leaving islands of pristine graphene in direct contact with the perovskite layer.

We used large commensurate supercells in order to construct strain-free interfaces. In the case of the (110) interface, the supercell contains 168 atoms and corresponds to \( \sqrt{2} \times 1 \) perovskite unit cells along the [1\( \bar{1} \)0] and [001] directions. The lattice mismatch at the interface is less than 1.5%. The (001) interface model contains 164 atoms, and the supercell corresponds to \( 1 \times 2 \) MAPbI₃ unit cells along the [100] and [010] lattice vectors; here, the lattice mismatch is less than 3.5%. The optimized interface models for the (110) and the (001) MAPbI₃ surfaces are shown in Figure 1a and b, respectively, and a top view of the supercell is shown in Figure 1e. All of the calculations were performed using density functional theory in the local density approximation (LDA), and complete details on the methodology are provided in the Computational Methods section.

In the optimized interface models, the perovskite layers lie 3.4 Å above the graphene sheet (as measured from the Pb atoms to the C atoms), which is similar to the interlayer separation in graphite. We checked the stability of these interfaces by calculating the binding energy as the difference between the total energy of the combined system and the total energy of each component taken separately and optimized.
The Journal of Physical Chemistry Letters

Figure 3. Charge transfer at the graphene–MAPbI$_3$ interface. Difference between the electronic charge density of the interface and those of graphene and MAPbI$_3$, taken separately for (a) the (110) and (b) the (001) interfaces. (Isovalue = 0.003 Å$^{-3}$, and red/blue regions indicate electron accumulation/depletion.) (c) Schematic representation of the interface dipoles at the graphene–MAPbI$_3$ interface and the resulting potential step.

interface models considered yield a relatively strong binding, 0.38/0.27 eV per surface Pb atom in the case of the (001)/(110) surfaces, respectively. These values are comparable to the binding energy of ruthenium dyes$^{28}$ and quantum dot sensitizers$^{29}$ on TiO$_2$; therefore, we expect these configurations to be very stable. A further test using van der Waals density functionals yields even larger binding energies, thus reinforcing the validity of our models (see the Computational Methods section).

The most interesting structural change accompanying the formation of the graphene–perovskite interface is a suppression of the octahedral tilt in the first MAPbI$_3$ monolayer in contact with graphene, as shown in Figure 1e. At the atomic level, this distortion corresponds to a displacement of the first I sublattice (looking from graphene) away from the graphene layer by 0.3 Å and a displacement of the second I sublattice toward graphene by 0.2 Å. These sublattices are indicated by red and blue circles in Figure 1e, respectively. The shift of the center of mass is compensated for by a displacement of 0.1 Å of the first Pb sublattice toward graphene. At the level of PbI$_6$ octahedra, this distortion can be understood as a rotation of up to $8^\circ$ around the [110]/[001] axis in the case of the (110)/(001) interfaces, respectively, as shown in Figure 1c and d. The observed reduction of the octahedral tilt is substantial when compared to the apical and equatorial tilts of bulk MAPbI$_3$, 8.5 and 14.4$^\circ$, respectively.$^{19}$

The origin of the octahedral rotation can be understood as a consequence of the electronic charge transfer at the interface. Figure 2a and b show the electron charge density redistribution at the interface when the pristine MAPbI$_3$ slab is adsorbed on graphene, just before the structural relaxation. Here, the charge transfer at the interface leads to electron depletion underneath of the I atoms. According to the Hellmann–Feynman theorem, this should lead to a force oriented toward the MAPbI$_3$ slab. Furthermore, this force should be strengthened by the proximity of the C atoms. In the case of the Pb sublattice, we see instead an electron accumulation underneath of each atom, which indicates Hellman–Feynman forces oriented toward the graphene sheet. In line with these expectations, we calculate a strong force of 0.8 eV/Å acting on the I atoms closest to graphene, pushing toward the MAPbI$_3$ slab, while the Pb atoms experience a weaker force of 0.1 eV/Å toward graphene.

The observed charge redistribution at the interface can be interpreted as a simple consequence of the ionic character of MAPbI$_3$. Indeed, Pb$^{2+}$ ions at the interface tend to attract electrons in order to compensate for the missing halide atoms and restore local charge neutrality (this is clearly seen in Figure 2c). Conversely, I$^-$ ions tend to repel electrons. This simple mechanism suggests that a similar charge rearrangement can be expected for other graphene–ABX$_3$ interfaces. In fact, in the case of oxide perovskites such as CaTiO$_3$, the formal charges of the B-site cations and the X-site anion are even larger (B$^{4+}$ and X$^{2-}$, respectively); therefore, the effect observed here in the case of graphene–MAPbI$_3$ interfaces should be even more pronounced.

We now analyze the consequences of the charge transfer and octahedral rotations on the electronic structure of the interfaces, after performing complete structural optimizations. Figure 3a and b shows that the charge rearrangement is concentrated in the interstitial region between graphene and MAPbI$_3$, that there is a uniform electron-deficient layer just above graphene, and that electron accumulation is underneath of the first Pb sublattice (as noted above for the interfaces prior to structural optimization). We quantify the charge transfer at the interface using the planar average of the induced charge density, and we find that 0.18 electrons per C atom are transferred from graphene to MAPbI$_3$ for both (001) and (110) interfaces, respectively. This charge redistribution generates an electrostatic potential step at the interface, which can be determined by integrating the Poisson equation and corresponds to 0.34/0.31 eV for the two interfaces. Figure 3c shows that this potential step acts as to drive electrons from MAPbI$_3$ toward graphene and therefore favors charge extraction from the photovoltaic layer.

Interestingly, when we calculate the total shift of the vacuum level from below graphene to above MAPbI$_3$, we find a much larger potential step of 0.48/0.57 eV for the (110)/(001) interfaces (Figure 3c). A detailed analysis indicates that the additional potential step of 0.17/0.23 eV arises from the octahedral rotations discussed above (see the Computational Methods section). In fact, the suppression of the octahedral tilt destroys the centrosymmetric nature of MAPbI$_3$, thereby leading to a ferroelectric distortion that is confined within the first perovskite monolayer. By calculating the induced polarization of this layer and rescaling with the density of bulk tetragonal MAPbI$_3$, we obtain an equivalent bulk polarization of 2.4/2.9 mC/m$^2$ for the (110)/(001) interfaces, respectively. While these values are small on the scale of the best ferroelectric perovskites,$^{31}$ they are comparable to the largest polarization measured in bulk multiferroics.$^{32}$

We note that bulk ferroelectricity in inorganic perovskites is well-established,$^{33}$ and the potential role of ferroelectricity in organometallic perovskites has recently been highlighted by several groups.$^{33–35}$ However, to the best of our knowledge, this is the first report of interfacial ferroelectricity in MAPbI$_3$. The built-in potential arising from this interfacial ferroelectricity goes in the direction of further promoting the separation of
electron and holes and can be thought of as a “nanoscale” analogue of the band-bending effect found in standard metal–semiconductor heterojunctions. Given our results, it is plausible that the improved electron extraction rates from MAPbI$_3$ observed in the presence of graphene quantum dots$^{14}$ may be a consequence of the ferroelectricity identified in this work.

In addition to driving electron–hole separation, we are going to show that this interfacial ferroelectricity carries important implications on electron–hole recombination across the interface. Figure 4a and b shows the band structure of the interfaces within the LDA (black curves). For comparison, we superimposed the bands of pristine graphene (red curves) with the Dirac points aligned. In all cases considered here, the Dirac point falls well inside of the band gap of the perovskite layer; therefore, we have an atomic-scale Schottky junction. In order to determine the Schottky barrier heights, we performed relativistic LDA calculations (which are known to significantly underestimate the band gap of MAPbI$_3$)$^{36-39}$ and subsequently corrected the LDA energy levels by using GW quasiparticle corrections obtained for bulk MAPbI$_3$ using a self-consistent scissor.$^{40}$ This procedure is justified because the LDA band gap of the perovskite slab used here [1.58/1.47 eV for (110)/(001)] is very close to its bulk counterpart of 1.51 eV calculated within the same approximations.$^{37}$ In this procedure, we checked that the small relativistic LDA gaps did not lead to any pinning effects at the interface (see the Computational Methods section). The interfacial energy-level diagrams thus obtained are shown in Figure 4c.

From Figure 4c, we see that the p-type Schottky barrier height of the graphene–MAPbI$_3$ interface is as large as 1.1 eV and is sensitive to the termination of the perovskite layer. In an elementary analysis of the PV characteristics of a Schottky junction, this value would represent the maximum open-circuit voltage at which the cell can operate,$^{29,30}$ therefore, graphene–MAPbI$_3$ interfaces appear very promising for high-efficiency solar cells. This statement is further supported by the observation that the n-type barrier height is at least 0.7 eV. This value is well above the minimum overpotential of 0.3 eV, which is necessary to drive electrons from the donor (MAPbI$_3$) to the acceptor (graphene) side of the interface.$^{31,42}$

To complete the analysis of the interfacial electronic structure, we show in Figure 5a and b the electron wave functions corresponding to the valence band top of MAPbI$_3$. In both cases of the (001) and (110) interfaces, the wave functions are localized away from the graphene layer, and this effect is a direct consequence of the ferroelectric distortion described above. In order to show this, we calculated the same wave functions by removing the graphene layer, and by

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**Figure 4.** Band structures of (a) the (110) and (b) the (001) interfaces (solid black lines). For comparison, we superimposed the band structure of pristine graphene in the same computational cell (red lines). (The energy refers to the Dirac point of graphene, and small blue arrows indicate the band extrema of MAPbI$_3$.) (c) Schematic energy-level diagram obtained from relativistic calculations and after applying scissor-corrected (SS)-GW quasiparticle corrections.$^{37}$ (All energies are referred to vacuum, $\Phi$ is the work function of graphene, and VBM and CBM are the valence band maximum and conduction band minimum, respectively.)

**Figure 5.** Hole wave functions at the graphene–MAPbI$_3$ interface. Isosurface plot of the highest occupied electronic states at (a) the (110) and (b) the (001) interfaces. (The isovalue is chosen so as to capture more than 70% of the electron charge.) (c) Same as in (b), after removing the graphene sheet while keeping the geometry of MAPbI$_3$ unchanged. (d) Same as in (c), but this time MAPbI$_3$ is allowed to relax to its ground-state configuration.
considering two cases: (i) the perovskite layer maintains the same distorted configuration as in the interface (Figure 5d) and (ii) the perovskite is in its undistorted bulk geometry (Figure 5c). From this comparison, we see that the broken symmetry resulting from the ferroelectric distortion lifts the two-fold degeneracy of the highest occupied states in the perovskite layer and pushes the highest state away from graphene. The energy difference between this state and the next occupied MAPbI₃ state is 40/80 meV for the (110)/(001) interfaces, well above typical thermal energies. We checked that this effect persists even when considering more complex interface models including thicker MAPbI₃ layers (see the Computational Methods section).

The strict localization of holes away from the graphene layer implies that after electrons migrate from the perovskite to graphene, direct radiative electron–hole recombination is forbidden because the corresponding matrix element vanishes. Therefore, the graphene–MAPbI₃ interface appears to possess an optimal built-in mechanism to prevent recombination and should be able to operate without resorting to metal oxide barriers for keeping electrons and holes apart.⁴⁻⁵ We also note that the tendency of the holes to localize near the exposed surface of MAPbI₃ suggests that this configuration should lead to efficient hole extraction in the presence of a hole-transport layer.

In summary, we reported the first theoretical/computational study of the graphene–MAPbI₃ interface. Our study revealed that graphene tends to suppress the octahedral tilt in the perovskite layer by acting on the exposed Pb and I sublattices. This leads to a ferroelectric distortion that not only promotes electron extraction from the perovskite layer but also prevents direct electron–hole recombination across the interface by pushing the hole wave functions away from graphene. These findings, combined with the large Schottky barrier heights calculated here, establish that the graphene–MAPbI₃ interface represents a very promising platform for high-performance solar cells.

On the basis of our results, we propose that the fabrication of graphene–MAPbI₃ solar cells via layer-by-layer deposition of CH₃NH₃I and PbI₂ on CVD graphene could be a realistic pathway to simplified solar cell architectures where graphene acts as both a charge extraction layer and transparent electrode. This concept could be pushed even further by using graphene on both sides of the perovskite, after tailoring the work function via established covalent functionalization strategies.⁴⁴,⁴⁵ Proof-of-concept implementations of this proposal should be within reach by using vacuum deposition techniques.⁸,⁴⁶

More generally, the interfacial ferroelectricity identified in this work is likely to be found also in other graphene–ABX₃ interfaces because it is a direct result of the octahedral connectivity and the ionicity of the perovskite layer. This novel effect could be used to induce ferroelectricity in centrosymmetric perovskites⁴⁷ and may find application beyond PVs, for example, in nanoscale Nozik diodes for solar water splitting.⁴⁸

**COMPUTATIONAL METHODS**

All calculations were performed using density functional theory in the local density approximation (LDA)⁴⁹,⁵⁰ using the Quantum ESPRESSO distribution.⁵¹ The electronic wave functions and charge density were expanded in plane wave basis sets with kinetic energy cutoffs of 40 and 200 Ry, respectively. The ionic cores and the core–valence interactions were described using ultrasoft pseudopotentials⁵²,⁵³ including nonlinear core correction.⁵⁴ The Brillouin zone of MAPbI₃ was described using 6 × 6 × 6 and 6 × 6 × 1/6 × 3 × 1 grids for bulk and (110)/(001) interface calculations, respectively. The distance between periodic replicas of the graphene–MAPbI₃ bilayer was set to at least 10 Å, and the supercell dipole correction was employed throughout.⁵⁵ The convergence thresholds used for forces and total energy are 30 meV/Å and 1 meV, respectively. Structural optimizations were performed using scalar relativistic LDA.

In order to check the effect of van der Waals interactions on the structure and energetics of the interface, we repeated the calculations using the DFT-D2 method,⁶⁶,⁶⁷ as implemented in the Quantum ESPRESSO package.⁵⁸ In this case, the cutoff radius for dispersion interactions was set to 20 Å in order to avoid spurious interactions between periodic slab images. The binding energies obtained in this way are 0.58/0.63 eV/Pb atom for the (110)/(001) interfaces. These results indicate that the binding between graphene and MAPbI₃ should be even stronger than what we determined using standard LDA. Similarly, the dispersion-corrected calculations yield a more pronounced distortion of the first monolayer of MAPbI₃ upon interaction with graphene, with a decrease of the octahedral tilt by 6.5°. We also find that within the DFT-D2, the distance between the graphene plane and the plane defined by the Pb atoms at the first layer of the perovskite is slightly smaller (less than 3%), while the interlayer distances between adjacent PbI₂ layers within MAPbI₃ are slightly larger [less than 3% and 4% for the (110) and (001) interfaces, respectively]. Taken together, these results show that calculations including dispersion corrections support and even reinforce the main results of our work.

In order to check that the observed ferroelectricity is indeed an interfacial effect and is absent in the pristine MAPbI₃ layer, we calculated the electrostatic dipole across MAPbI₃, in the absence of graphene. In all configurations considered, no intrinsic dipole was found. We then repeated these calculations for the MAPbI₃ layers using the atomic coordinates from the complete interface calculation but without graphene. In this case, we obtained electrostatic potential steps of 0.16/0.22 eV for the (110)/(001) interfaces, in perfect agreement with the corresponding values discussed in the main text. This test unambiguously confirms that the ferroelectric distortion in MAPbI₃ results entirely from its interaction with the graphene sheet. Furthermore, in order to check the sensitivity of the ferroelectric polarization to the functionals and structural conformation used, we repeated these calculations for the (001) interface optimized within DFT-D2. In this case, the ferroelectric distortion is even more pronounced, leading to potential steps across the MAPbI₃ layer of 0.34 eV. This result provides additional support to our findings.

The calculation of the interfacial energy-level alignment in Figure 4c requires some care. The interface band structures reported in Figure 4a and b were obtained using LDA calculations, based on the observation that scalar-relativistic LDA band gaps of MAPbI₃ are close to experimental values.⁵⁹ However, it is well-established that spin–orbit coupling reduces the band gap of MAPbI₃ by almost 1 eV.⁶⁰ This underestimation can be corrected by using many-body perturbation theory within the GW approximation.⁵⁹,⁶¹ In particular, the use of a self-consistent scissor-corrected GW (SS-GW) approach leads to a quasiparticle band gap (for orthorhombic MAPbI₃) of 1.72 eV, in very good agreement with experiments.⁶²
In order to check that these effects do not alter the Schottky-type nature of the graphene–MAPbI$_3$ interface, we proceeded as follows. We computed the relativistic quasiparticle energy levels of the MAPbI$_3$ layer by first performing fully relativistic calculations in the absence of graphene and then adding the SS-GW corrections from separate calculations on bulk MAPbI$_3$. The SS-GW corrections are $-0.35$ eV and $+0.89$ eV for the valence band top and conduction band bottom, respectively. The resulting energy-level diagram is reported in Figure 4c. As an additional sanity check, we also performed fully relativistic calculations on the (001) interface model (including both graphene and MAPbI$_3$) and then added the same SS-GW corrections as above. This procedure yields essentially the same energy diagram as that in Figure 4c, within 0.03 eV.

Finally, we checked the sensitivity of our results to the thickness of the MAPbI$_3$ layer. To this aim, we studied the (001) interface model with four PbI$_2$ layers, corresponding to 212 atoms. All of the results described in the main text remained unchanged; in this case, the offset of the electrostatic potential at the interface is 0.29 eV, the potential step remained unchanged; in this case, the o 212 atoms. All of the results described in the main text.

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The research leading to these results has received funding from the European Union Seventh Framework Programme under Grant Agreement N° 604391, Graphene Flagship, from the Leverhulme Trust (Grant RL-2012-001), the UK Engineering and Physical Sciences Research Council (Grant No. EP/J009857/1), and the European Research Council (EU FP7/ ERC Grant No. 239578). This work used the ARCHER UK National Supercomputing Service via the “AMSEC” Leadership project and the Advanced Research Computing facility of the University of Oxford. Figures involving atomic structures were rendered using VESTA. 40

**REFERENCES**


(40) Filip, M. Personal communication, 2015.


