Atomic Scale Investigation of the CuPc–MAPbX₃ Interface and the Effect of Non-Stoichiometric Perovskite Films on Interfacial Structures

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ABSTRACT: Metal halide perovskites (MHPs) have become a major topic of research in thin film photovoltaics due to their advantageous optoelectronic properties. These devices typically have the MHP absorber layer sandwiched between two charge selective layers (CSLS). The interfaces between the perovskite layer and these CSLs are potential areas of higher charge recombination. Understanding the nature of these interfaces is key for device improvement. Additionally, non-stoichiometric perovskite films are expected to strongly impact the interfacial properties. In this study, the interface between CH₃NH₃PbI₃ (MAPbI₃) and copper phthalocyanine (CuPc), a hole transport layer (HTL), is studied at the atomic scale. We use scanning tunneling microscopy (STM) combined with density functional theory (DFT) predictions to show that CuPc deposited on MAPbX₃ (X = I, Br) forms a self-assembled layer consistent with the α-polymorph of CuPc. Additionally, STM images show a distinctly different adsorption orientation for CuPc on non-perovskite domains of the thin film samples. These findings highlight the effect of non-stoichiometric films on the relative orientation at the MHP/HTL interface, which may affect interfacial charge transport in a device. Our work provides an atomic scale view of the MHP/CuPc interface and underscores the importance of understanding interfacial structures and the effect that the film stoichiometry can have on interfacial properties.

KEYWORDS: metal halide perovskite, scanning tunneling microscopy, density functional theory, copper phthalocyanine, interfacial properties

Metal halide perovskites (MHPs) have proven to be highly capable photovoltaic materials, with MHP-based solar cells reaching an impressive record power conversion efficiency (PCE) of 25.5%.¹ In these devices, electrons and holes separated in the MHP absorber layer are selectively conducted by an electron transport layer (ETL) and a hole transport layer (HTL), respectively. The interfaces between adjacent layers in MHP-based solar cells are possible areas of increased charge recombination.²,³ Interfacial engineering via passivation of the perovskite surface has proven a viable strategy for improving device performance.⁴–⁶ Additionally, reports have found that non-stoichiometric precursor ratios, achieved during the perovskite film preparation⁷ or via postannealing treatment,⁸ can significantly affect performance. Such non-stoichiometric ratios in the perovskite material are expected to strongly impact the interfacial properties. Using thin interlayers of MAI at the perovskite interface was shown to be a useful method for tuning energy level alignment.⁹ Proper engineering of these interfaces can also result in increased stability.⁴,¹⁰ Obtaining a clear understanding of the perovskite/charge selective layer (CSL) interface is crucial for rational interface engineering and further device improvement.
The transition metal phthalocyanines (TMPcs) have been identified as viable HTLs that feature a higher thermal stability than spiro-MeOTAD.11–15 TMPcs have also been utilized as additives in HTLs.16 Undoped copper phthalocyanine (CuPc) derivatives have been shown to enable a high PCE in MHP-based solar cells.17 CuPc itself has shown excellent compatibility with low-cost carbon electrodes as well, both as a distinct HTL18 and as an additive in the carbon electrode,19 resulting in performance increases. Furthermore, the relatively hydrophobic nature of CuPc enables it to act as a blocking layer from moisture in the environment, delivering impressive stability for unencapsulated devices.11,13,18

Scanning tunneling microscopy (STM) has been shown to be an excellent tool for studying both perovskite surfaces20–25 and CuPc molecular and interfacial properties.26–28 STM studies of perovskites have determined the surface reconstructions of MAPbI3, MAPbBr3, and CsPbBr3 perovskites20,21,25 and the effect of illumination on the surface structure.22 In addition, STM investigations have shown how surface defects and halide substitution can affect interfacial properties and material stability.23,24 Here, utilizing two materials well-suited for STM study, we investigate an MHP/HTL interface by examining submonolayer CuPc deposited on MAPbX3 (X = I, Br) thin films. We reveal that CuPc forms a self-assembled layer on MAPbI3 and that it behaves differently on non-perovskite domains that may exist in non-stoichiometric perovskite films. This differing behavior has important consequences for interfacial properties and charge transfer in devices.

RESULTS AND DISCUSSION

MAPbI3 thin films were obtained by the co-deposition of PbI3 and MAI precursor materials onto an Au(111) substrate in a UHV chamber, using methods analogous to those previously reported.20 Following this, CuPc was sublimated onto the MAPbI3/Au(111) sample, resulting in submonolayer coverage (see Methods and Figure S1 for details).

First, we will examine the behavior of a single, isolated CuPc adsorbed on the MAPbI3 surface (Figure 1a). A zoomed-in filled-state image of the CuPc (Figure 1b) shows eight round outer orbitals, which surround eight smaller, inner orbitals. This intramolecular contrast is indicative of the highest occupied molecular orbital (HOMO) of CuPc, as well as a flat-lying, or “face-on”, adsorption orientation.28 This image also shows the face-on CuPc adsorbed so that its pairs of outer orbitals are aligned along the same [10 ± 1] directions as the Γ’ pairs of the MAPbI3 substrate (solid white and yellow lines).

It was also observed that a single, isolated CuPc molecule can adsorb 45° rotated relative to the halide pairs (Figure S2). The molecular dimensions of CuPc are such that periodic overlap between the CuPc orbitals and the Γ’ lattice sites is difficult, as discussed later. Additionally, it was found that the face-on adsorbed CuPc molecule was easily moved by the STM tip (Figure S3), suggesting a relatively weak molecule–substrate interaction between MAPbI3 and CuPc.

The face-on adsorbed CuPc molecule was a rare observation, and it was found that CuPc preferentially formed a self-assembled (SA) layer on top of the MAPbI3 film. In Figure 2a, there are multiple MAPbI3 grains exhibiting the previously reported paired surface reconstruction.20 In the middle of the image, there is a brighter, striped domain, which is attributed to an SA layer of CuPc molecules. A zoomed-in image of one of these domains (Figure 2b) reveals alternating rows of brighter and darker protrusions. The direction perpendicular to these rows will be referred to as the c-axis of the SA layer. The direction parallel to the bright and dark rows will be referred to as the b-axis. Periodicities of 4.4 ± 0.2 Å along the b-axis and 1.14 ± 0.04 nm along the c-axis were obtained from an average of 17 different SA layers. To interpret these images, it is important to note that CuPc is polymorphic in nature. These polymorphs are characterized...
both by intermolecular spacings and the so-called stacking angle. Here, the convention used for the stacking angle is the angle (\(\phi\)) between the CuPc molecular plane and the b-axis of the CuPc SA layer (Figure 2c). The \(\alpha\)-polymorph of CuPc (\(\alpha\)-CuPc) features a b-axis periodicity of 3.8 Å and a stacking angle of approximately 63°. The CuPc SA layers measured on MAPbI₃ exhibit periodicity along an angle of 61 ± 2° (red line, Figure 2b), which is consistent with the \(\alpha\)-phase CuPc stacking angle, suggesting that CuPc molecules may also stack at this angle in the observed SA layer. The measured value of 1.14 ± 0.04 nm for the c-axis spacing is slightly lower than but nearly consistent with the value of 1.2 nm reported in the literature for \(\alpha\)-CuPc. It should also be noted that a wide range of c-axis spacings (1.18–1.69 nm) have been reported for CuPc SA layers on other substrates. Notably, both the c-axis and b-axis periodicities observed here match well the values for a CuPc layer on Bi₂Se₃. Importantly, the b-axis periodicity in these studies is larger than the expected 3.8 Å spacing of \(\alpha\)-CuPc; therefore, the exact stacking structure may be due to some modification of the \(\alpha\)-CuPc structure.

To further evaluate the possible structure and orientation of the CuPc SA layer, simulated STM images were generated via DFT for various crystal plane surfaces of \(\alpha\)-CuPc. Additionally, the surface energy for each crystal plane surface was calculated using the following equation:

\[
E_{\text{surf}} = \frac{E_s - E_0}{2 \times S}
\]

where \(E_s\) and \(E_0\) are the energies of the CuPc molecule structure with and without the surface and \(S\) is the area of the surface. The surface area is multiplied by a factor of 2 because two symmetric surfaces are introduced due to periodic boundary conditions. The (100) surface of \(\alpha\)-CuPc (Figure 2d) is found to be the most favorable, with a surface energy of 19.09 mJ/mm². All other surfaces have energies over twice as high. Additionally, the low isosurface density value simulated STM image of the (100) surface (Figure 2e) well-reproduces the pattern of alternating rows of bright and dark protrusions observed in the experimental STM images. Also, both the experimental and simulated STM images for the (100) surface show periodicity along a stacking angle of 61°–62°, which is consistent with the literature values for \(\alpha\)-CuPc. The high isosurface density value simulated STM image of the (100) surface shows clearer features of individual atoms in the CuPc molecule and demonstrates how CuPc molecules correspond to the bright and dark protrusions in the experimental image (inset, Figure 2b). The 1.21 nm periodicity along the c-axis in the simulated image of the (100) \(\alpha\)-CuPc is nearly consistent with that measured in the experiment (1.14 ± 0.04 nm). It should also be noted that the (001) and (110) surfaces also qualitatively reproduce the bright-dark alternating rows of protrusions but exhibit much higher surface energies. The surface energies and simulated STM images for the four different crystal planes considered are summarized in Figure S4. Although the analysis here is based on STM images taken at a negative bias (filled states), an image of the CuPc SA layer taken at positive bias (empty states) has been included for reference (Figure S5).

The fact that multiple crystal planes provide a qualitative match to the experiment strongly corroborates the hypothesis that an \(\alpha\)-CuPc type structure gives rise to the alternating bright and dark rows of protrusions seen in the STM images. A detailed comparison of the simulated STM images with different isosurface density values shows how CuPc stacking can give rise to the bright-dark pattern seen in the experiment (Figure S6). High isosurface density value images show a surface with a high electron density, closer to the individual atomic cores, whereas low isosurface density value images...
show a surface with a low electron density, indicative of overall molecular size or shape. The (100) α-CuPc surface is the most promising candidate, but the exact orientation of the CuPc molecules is not discernible from these results since the simulation and experiment are not an exact match. Periodicity along a 62° angle relative to the b-axis in the simulated image of the (100) surface matches the experimental data well and is consistent with the expected stacking angle for α-CuPc. However, in the simulated image, the c-axis (green line, Figure 2e) intersects the bright protrusions, in a different fashion than in the experimental image (green line, Figure 2b). Thus, the exact stacking structure likely differs slightly from the structures determined via simulation. Testing alternate accounting for the MAPbI3 substrate. Thus, it is possible the relative to the MAPbI3 value does represent the true physical height of the SA layer obtained. In both cases, the height value is significantly less than the measured molecular width of CuPc (Figure S8), which gives a first approximation of the apparent step height expected if CuPc molecules are adsorbed edge-on.25,32 The measured SA layer height is also less than the measured molecular width of CuPc (Figure S8), which gives a first approximation of the apparent step height of the SA layer if the molecule was adsorbed edge-on. This implies two possibilities: (1) the CuPc molecules are adsorbed edge-on, but the measured apparent height is strongly influenced by electronic effects or (2) the measured value does represent the true physical height of the SA layer but the CuPc molecules are adsorbed at some tilt angle, θ, relative to the MAPbI3 film. Here, θ can be approximated using the STM measured values and basic trigonometric relations (see Figure S7c for details), and an estimated tilt angle of 24° was found. Some non-zero tilt angle relative to the substrate could also potentially explain the deviation of the b-axis spacing we observed with respect to the literature values for stand-alone α-CuPc.

Further hints of the stacking structure were gleaned from the zigzag shape of the SA layer’s supramolecular structure, which features bends of 121° ± 2° (Figure 3a). There is no apparent threshold width or length of the SA layer above which these bends occur. It is worth noting that deposition trials of CuPc on MAPbBr3 were performed and qualitatively similar results were obtained (Figure S9), suggesting that the halide in the X position of the perovskite is not of critical importance to the CuPc adsorption behavior. Similar bends have also been previously reported for CuPc on Bi(111), but it is not clear what triggers these bends to occur. However, the fact that the angle of the bend is approximately twice the stacking angle of α-phase CuPc suggests that the bend occurs due to the border of two domains of α-CuPc.

Evidence supporting this hypothesis was found by looking at defects in the SA layer near one of these bends (Figure 3b). The defects occur as pairs of depressions, with one depression in a bright row (dashed yellow circles) and an accompanying depression in the adjacent darker row (dashed green circles). However, the orientation of these pairs is different on each side of the bend. On the top right side of the bend, the accompanying depressions in the darker row are positioned above and to the left of the depressions in the bright row. In contrast, on the lower left side of the bend, the relative position of the paired defects, which are being tentatively interpreted as a missing CuPc molecule, is flipped. We propose that the bend depicted in Figure 3 is observed when two α-CuPc domains meet in an offset fashion at the bend itself (white/brown two-tone rectangles, Figure 3b).

Additionally, if the two bends shown in Figure 3a, b are compared closely, it is evident that there is a different arrangement occurring at each bend. In Figure 3b, the bright and dark rows on each side of the bend line up with each other, whereas in Figure 3a, they are offset from each other. For that offset row case, the CuPc arrangement is similar to Figure 3b, except the relative position of the molecules on each side of the bend are shifted by half of a molecule.

The SA layers were found to follow a Volmer–Weber, or “island”, growth pattern, in which the second layer begins to grow before a complete first layer is formed (Figure S10). The second layer shows the same bright-dark alternating row structure as the first layer. This suggests that the structure adopted by the first layer is not strongly affected by the underlying MAPbI3 film, providing evidence of a weak CuPc SA layer-MAPbI3 interaction. This idea is further supported by the observation that CuPc SA layers can cross unperturbed over MAPbI3 grain boundaries (Figure S11). Additionally, a survey of STM images reveals that numerous relative angles between the CuPc SA layer and the MAPbI3 are possible, further indicating a weak interaction (Figure S12).
To evaluate the CuPc-MAPbI₃ interaction and better understand CuPc SA layer formation from a theoretical perspective, DFT calculations of a CuPc molecule on top of MAPbI₃ were performed (Figure 4). It should be noted that the CuPc for these calculations is forced to match the periodicity of the MAPbI₃ to reduce computational costs. Thus, these do not reflect the α-CuPc structures but are used as a basic model to gain insight into molecule–substrate interactions. Two different edge-on adsorption scenarios, single and double isoindole group adsorption, were modeled and compared with the system energy of a face-on adsorption. For each case, δE values for the CuPc-MAPbI₃ systems were calculated using the formula:

\[ \delta E = E - E_{\text{bulk}}(\text{CuPc}) - E_{\text{surf}}(\text{MAPbI}_3) \]

where \( E \) is the total system energy, \( E_{\text{bulk}}(\text{CuPc}) \) is the energy of bulk α-CuPc, and \( E_{\text{surf}}(\text{MAPbI}_3) \) is the energy of the \( \sqrt{2} \times \sqrt{2} \) MAPbI₃ supercell (Figure 4). Physically, \( \delta E \) represents the energy gain or loss when putting CuPc in contact with the MAPbI₃ perovskite surface. The first important result is that the face-on adsorption is lower in energy than both the single and double isoindole edge-on adsorption cases. This is consistent with a previously reported calculation \(^{17}\) and also agrees with the experimental STM images reported here showing that a single, isolated CuPc molecule adsorbs on MAPbI₃ in a face-on orientation (Figure 1). The higher energy for the edge-on CuPc simulations is somewhat surprising considering that the predominant SA layers seen in the experimental STM images show characteristics of edge-on adsorption. This can be explained by the fact that the CuPc in the computations is forced to match MAPbI₃ periodicity. This
results in CuPc molecules that are much further away from each other than they would be in \(\alpha\)-phase CuPc (e.g., neighboring CuPc can be considered as weakly- or non-interacting). Consequently, the energetically beneficial \(\pi\text{-}\pi\) orbital stacking present in \(\alpha\)-CuPc is not accurately taken into account in these calculations, providing a rationale for the lower \(\Delta E\) energy estimated here for the face-on configuration with respect to the edge-on configuration. The models of Figure 4 suggest that molecule–molecule interaction must be considered to explain the formation of the CuPc SA layer depicted earlier, where molecules were placed in the edge-on configuration. A particular stacking angle of the CuPc that maximizes intermolecular interaction is necessary to compensate for the lower stability calculated for isolated (e.g., non-interacting) edge-on CuPc with respect to a face-on molecule. The combined experimental and theoretical results suggest that the CuPc intermolecular forces are stronger than the CuPc–MAPbI\(_3\) interaction. It is important to reiterate that the simulated STM images, which match the experimental images of the SA layer, are for \(\alpha\)-CuPc in the gas phase. Thus, CuPc on MAPbI\(_3\) largely resembles \(\alpha\)-CuPc on its own, implying a very weak effect from the perovskite substrate. Considering this weak interaction in the extreme case, the energy of the CuPc SA layer–MAPbI\(_3\) system could be approximated by the sum of the energy of the two separated systems. The fact that the \(\Delta E\) values are positive for every case means that the simulated interface is higher in energy than the sum of the bulk \(\alpha\)-CuPc and MAPbI\(_3\) reference state (Figure 4). Using the approximation proposed above, the positive \(\Delta E\) values mean that the CuPc SA layer–MAPbI\(_3\) system is more energetically favorable than the simulated scenarios, further supporting the importance of intermolecular interaction in the stabilization of the SA layer recorded in the STM experiment.

The MAPbI\(_3\) thin film samples featured some domains of non-perovskite material, and it was observed that CuPc behaves differently on these non-perovskite domains. In Figure 5a, an image of the MAPbI\(_3\) surface shows the expected perovskite surface reconstruction except for a small area where no apparent corrugation is observed (blue square). A closer look at this area in Figure 5b reveals atomic corrugation with a hexagonal pattern and a lattice constant of 4.3 Å. The right side of Figure 5c shows how CuPc interacts with the unknown, non-MAPbI\(_3\) surface. In stark contrast to MAPbI\(_3\), on the non-perovskite domains there are numerous CuPc molecules face-on adsorbed in a disordered fashion and in close proximity to each other. A zoomed-in image shows the HOMO of an individual CuPc on this unknown material, as evidenced by the eight outer orbital lobes (Figure 5d). The fact that CuPc molecules in close proximity are able to maintain a flat-lying orientation without clear ordering, rather than forming an SA layer, indicates that the molecule–substrate interaction with the non-perovskite material is stronger than with MAPbI\(_3\) and can compete with SA layer formation. This behavior is particularly striking considering that there is an SA layer extremely close to the individual CuPc molecules. It is also worth noting that the MAPbI\(_3\) surface in Figure 5c is completely devoid of individual, face-on CuPc molecules. This difference in behavior has important implications for the perovskite–HTL interface in devices that have a non-stoichiometric perovskite film. Different adsorption geometries would have a dramatic effect on the orbital overlap between CuPc and MAPbI\(_3\). Additionally, reports have shown orientation dependent changes in the ionization potential and interfacial energy level alignment for CuPc, attributed to the C–H surface dipole present in an edge-on orientation.\(^{34}\) Such changes in the CuPc HOMO level (Figure 5e) would affect energy level alignment at the interface of an MHP-based device and can be expected to significantly alter interfacial charge transfer and overall device performance.

The identity of the non-perovskite domain cannot be completely determined from the STM images alone, but some candidates can be identified on the basis of the lattice structure and spacing. A reasonable hypothesis is that these non-perovskite domains are excess precursor material, either PbI\(_2\) or MAI. The literature shows that PbI\(_2\) forms a hexagonal lattice with the nearest neighbor spacing ranging from 4.5 to 4.6 Å.\(^{35,36}\) The hexagonal structure on the non-perovskite domains was 4.3 Å, consistent with the literature within STM measurement uncertainty. Therefore, PbI\(_2\) is considered to be a viable candidate for the non-perovskite domain. For the other precursor, MAI, a tetragonal unit cell is expected,\(^{37}\) which is not consistent with the hexagonal lattice of the non-perovskite domain. On the basis of this interpretation, MAI was eliminated as a candidate for the non-MAPbI\(_3\) domains observed. She et al. reported a hexagonal pattern after the deposition of MAI on Au(111) and explained the result as iodine atoms left over after MAI dissociate upon reacting with the metal Au(111) surface.\(^{38}\) This explanation is also feasible for the result obtained in this study. Evidence supporting this hypothesis was found in STM images of a non-optimized MAPbI\(_3\) deposition trial, in which only approximately 30% of the sample surface was perovskite. The non-perovskite domain featured a hexagonal superstructure with a spacing of 2.61 nm that was rotated 90° relative to the 4.3 Å atomic hexagonal lattice (Figure S13). The superstructure spacing is somewhat larger than previous reports, but the atomic lattice spacing and relative degree of rotation match well with previous reports of iodine adlayers.\(^{38,39}\) On the basis of this, the non-perovskite domain could potentially be an iodine adlayer. Overall, evidence was found supporting both PbI\(_2\) and an iodine adlayer as the identity of the non-perovskite domains. Pb and bare Au(111) were also considered and eliminated as possibilities. The rationale for these eliminations is described in the Supporting Information.

The utilization of excess precursor has been reported in the literature as having a strong influence on perovskite film quality, device performance, and stability. For example, excess PbI\(_2\) has been shown to be beneficial in small amounts but detrimental above a threshold value.\(^{40}\) Our study highlights a complication that can occur even with small, nanometer scale domains of non-perovskite material. Namely, changes in the composition of the perovskite film can cause secondary effects on the adsorption geometry and continuity of organic thin film HTLs. This change in interfacial orientation affects energy level alignment, charge transfer, and, ultimately, device performance. As can be seen in Figure 5d, a nanometer scale domain of non-perovskite material can cause a disruption in the ordered formation of the HTL. Although the results of this study were obtained at low temperatures, we have observed the same perovskite surface reconstruction via STM in the tetragonal and cubic phase temperature ranges in which perovskite solar cells are typically characterized and operated. Additionally, the \(\alpha\)-CuPc phase used as the basis of the DFT simulations has been characterized in the literature using X-ray diffraction (XRD) and transmission electron diffraction (TED) measurements taken at room temperature.\(^{40}\) Therefore, the
CuPc/perovskite interfacial behavior observed here is also expected to hold for the devices. Understanding how, even at the currently recommended low levels of excess PbI₂, these non-perovskite domains in non-stoichiometric perovskite films interact with potential HTL layers is essential for accurately predicting interfacial properties. The confounding effects such discontinuity at the interface has on charge transfer, performance, and stability is of prime importance for optimizing the use of excess precursor to further improve perovskite device technology.

CONCLUSION

Utilizing a combined STM and DFT study, we shine a light on the atomic structure of the CuPc/MAPbI₃ interface. The CuPc/MAPbI₃ film was used as a model system for understanding how non-stoichiometric perovskite films could affect the perovskite/HTL interface structure and potentially its electronic properties. Scanning tunneling microscopy reveals that the first interfacial layer of CuPc does not adsorb face-on to MAPbI₃ but instead forms a self-assembled layer that features a structure similar to the α-polymorph of CuPc. A similar result was found for CuPc on MAPbBr₃, suggesting that changing the halide in the X position does not significantly alter the CuPc–MAPbX₃ interfacial structure. In contrast, CuPc behaved differently on non-perovskite domains in the film, adsorbing in a face-on orientation. The orientation of the CuPc molecule has been shown to affect interface energetics; thus, this behavior shows how non-stoichiometric ratios in perovskite films can affect interface structure and charge transfer at the HTL/MHP interface in MHP-based devices. This work underscores the importance of understanding the exact structure of interfaces in MHP devices to properly predict device performance and rationally design perovskite devices.

METHODS

Surface Characterization. Optimized MAPbI₃ films were prepared in UHV by the coevaporation of PbI₂ and MAI at 513 and 378 K, respectively, for 5 min onto a cleaned Au(111) substrate held at 130 K. Two Knudsen cells (K-cells) containing the respective precursor materials, PbI₂, and MAI, were gradually heated from room temperature to the desired deposition temperature over a period of approximately 120−180 min. Power applied to the K-cells was manually adjusted until the thermocouples on the K-cells had stable readouts of the desired deposition temperatures for at least 5 min. The sample was then introduced into the deposition chamber. Once the sample was in position, the shutters of the K-cells were opened to allow the sample composition and determine necessary adjustments to the power of the K-cells filled with MAI. The I/Pb peak height ratio, as well as the presence and height of C and N peaks were used as guides for adjusting the MAI K-cell's power for the next deposition. A higher MAI temperature during deposition led to the non-stoichiometric films with larger non-perovskite domains, possibly due to MAI decomposition during deposition. The preparation of these non-optimized films was carried out using the same protocols as the optimized films except using deposition temperatures of T_PbI₂ = 521 K and T_MA = 397 K. Samples were annealed at room temperature for at least 3 h before being transferred into the STM setup. After the success of the perovskite deposition was confirmed via STM imaging, the sample was transferred in UHV to a preparation chamber where CuPc was deposited onto the perovskite sample. The commercial CuPc powder (Sigma-Aldrich, triple sublimated grade) was further purified by vacuum sublimation in situ before performing any depositions. CuPc was deposited via vacuum sublimation using a K-cell at 638 K for an initial duration of 30 s. Additional CuPc (up to 190 s of cumulative deposition) was incrementally deposited to explore higher coverages. The perovskite/Au(111) substrate was held at room temperature during this deposition, and the sample was transferred to the STM chamber without any further treatment. During CuPc deposition, the chamber pressure was 6 × 10⁻⁸ Torr. Narrow-mouthed crucibles were used, and a shutter was used to prevent unintended deposition onto the sample during transfer within the preparation chamber. To prevent a blocking layer of recondensed CuPc near the top of the crucible, CuPc was filled almost to the top of the crucible. Additionally, the K-cell shutter was left open during temperature ramping so that any material sublimated during temperature ramping would not collect near the mouth of the crucible. The shutter was only closed for the 2−3 min immediately before deposition, while the sample was being transferred into the deposition chamber. All STM imaging was performed at 4.5 K. For MAPbBr₃ films, PbBr₂ and MABr were coevaporated at 533 and 376 K, respectively, for 4 min onto a cooled Au(111) substrate held at 150 K, followed by post-annealing at room temperature for 2 hours.

Density Functional Theory. In this study, the DFT calculations were performed using the Vienna ab Initio simulation package (VASP). The projector augmented wave approach was employed using a plane wave basis set with an energy cutoff of 500 eV. The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional was used to evaluate the exchange-correlation energy. In all calculations, the total energy of the system was converged within 10⁻⁶ eV. In CuPc bulk calculations, a cell containing one molecule of CuPc was used, and for MAPbI₃ calculations, a supercell containing four molecules of MAPbI₃ was used. Brillouin zone sampling was done using 3 × 9 × 3 and 4 × 4 × 4 Monkhorst–Pack k-point grids centered at the γ point in the CuPc and MAPbI₃ bulk crystal calculations, respectively. For CuPc crystal surface calculations, a 3 × 9 × 1 Monkhorst–Pack k-point grid was used and a vacuum region of 12 Å was added in the direction normal to the surface. Slab cells were used to model CuPc stacking on top of the MAPbI₃ substrate, with a vacuum region of 26 Å in the direction normal to the stacking plane to minimize the effect of periodic images. A Monkhorst-Pack k-point grid of 3 × 3 × 1 was used for these slab models. All the structures were fully relaxed until the residual force acting on each atom was lower than 0.01 eV Å⁻¹.

ASSOCIATED CONTENT

# Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.1c04867.

Figures of sample deposition method, alternate adsorption orientation, mobility of a face-on CuPc on MAPbI₃, STM images, energies of various α-CuPc crystal planes, height profiles, and schematic for estimation of tilt angle and discussion of elimination of Pb and Au(111) as candidates for non-MAPbI₃ domains (PDF)

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Notes

The authors declare no competing financial interest.

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