

Energy Band Alignment and Interfaces in FAPbI₃ Perovskite Solar Cells: A Hard X-ray Photoelectron Spectroscopy Investigation

Rahul Mahavir Varma, Bhavya Rakheja, Karen Radetzky, Evelyn Johannesson, Stefania Riva, Alberto García-Fernández, Roberto Félix, Adam Hultqvist, Soham Mukherjee, Ute B. Cappel, Tobias Törndahl, and Håkan Rensmo*



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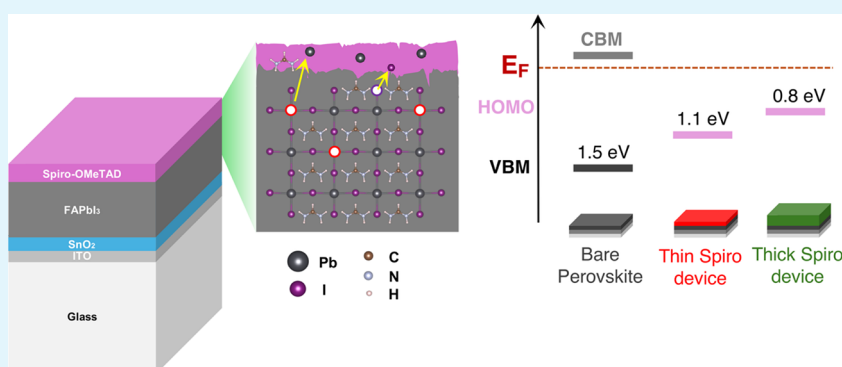
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ABSTRACT: Interfacial phenomena critically influence both the performance and long-term stability of perovskite solar cells; hence, optimizing interfaces remains a key challenge for their commercialization. In this study, we investigate the chemical interactions and electronic structure of the buried interface between the FAPbI₃ perovskite absorber and spiro-OMeTAD-based hole transport layer (HTL) in an ITO/SnO₂/FAPbI₃/HTL device using hard X-ray photoelectron spectroscopy. Our results indicate Pb and I ion incorporation in the spiro-OMeTAD HTL. The Pb 4f core level spectra show the formation of new nonperovskite Pb species, and the N 1s spectra exhibit an additional peak, indicating chemical modifications induced by the deposition of spiro-OMeTAD on the perovskite layer. Moreover, the spiro-OMeTAD N 1s peak exhibits a systematic shift toward lower binding energies with increasing HTL thickness, indicating a downward band bending in the spiro-OMeTAD HTL. Overall, these findings provide direct insight into the chemical and electronic interactions near the FAPbI₃/HTL interface and emphasize the importance of optimizing transport layer thickness to achieve favorable energy level alignment and improved device performance.

KEYWORDS: FAPbI₃, spiro-OMeTAD, perovskite solar cells, interfaces, HAXPES

INTRODUCTION

Perovskite solar cells (PSCs) have rapidly emerged as front runners in next-generation photovoltaics owing to their exceptional optical and electronic properties.^{1–4} Continuous advances in material design and device engineering have propelled their power conversion efficiency (PCE) beyond 26%^{5,6} within a rather short time frame, surpassing that of established thin film technologies such as copper indium gallium selenide (CIGS) and cadmium telluride (CdTe). The field gained momentum in 2009 when Kojima and co-workers first demonstrated a PCE of 3.81% using methylammonium lead iodide (MAPbI₃) as the light absorbing layer.⁵ Since then, extensive efforts have been devoted to improving both the performance and the stability of MAPbI₃ based PSCs.^{7–10} However, MAPbI₃ suffers from poor thermal stability, decomposing above 85 °C due to

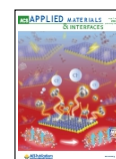
volatilization of methylammonium (MA) cations in the organic–inorganic hybrid lattice.¹¹ These limitations restrict its long-term operational reliability. In contrast, formamidinium lead iodide (FAPbI₃) offers enhanced thermal stability¹² and a narrower band gap (~1.48 eV)¹³ compared to MAPbI₃ (~1.57 eV),¹³ making it a more suitable absorber. While the development of more thermally robust absorbers such as FAPbI₃ has mitigated intrinsic instability issues to some extent,

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the overall device stability of PSCs remains critically dependent on the quality of the interfaces within the device stack.

Among these, the interface between the perovskite absorber and the hole transport layer (HTL) strongly influences charge extraction and recombination dynamics, thereby affecting photovoltage, photocurrent, and long-term durability. In conventional n-i-p architectures, 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD) has been the most widely adopted HTL.^{14–18} However, pristine spiro-OMeTAD exhibits low intrinsic conductivity and typically requires chemical doping to achieve efficient hole transport and favorable energy level alignment with the perovskite absorber.^{19–21} Although such dopants improve the device performance, they also introduce chemical instabilities and enhance moisture sensitivity, leading to rapid material degradation due to their hygroscopic nature.^{22–24} Consequently, a fundamental understanding of the chemical nature and electronic interactions at the perovskite/spiro-OMeTAD interface, and their impact on long-term stability, remains essential for developing efficient PSCs.

To probe such buried interfaces, various advanced characterization techniques have been employed. Methods like Kelvin probe force microscopy (KPFM) and electron beam induced current (EBIC) imaging provide some insights into local potential distributions across a solar cell cross section. For instance, Bergmann et al.²⁵ visualized the built-in potential in a p-i-n architecture using KPFM, while Cai et al.²⁶ demonstrated that tuning the PbI₂ to MAI ratio in the precursor solution modulates the internal potential drop within MAPbI₃, effectively shifting its doping profile. Similarly, EBIC measurements by Edri et al.²⁷ revealed a characteristic two peak feature near both selective contacts, attributed to enhanced charge separation at the p-i and i-n junctions due to built-in electric fields. Despite these advances, KPFM and EBIC focus more on cross-sectional imaging and such techniques lack chemical specificity.

Photoemission spectroscopy (PES) offers a nondestructive, complementary approach, enabling direct access to the chemical states and electronic properties of PSCs.^{28–30} In the past, PES has been extensively utilized to study interfacial chemical reactions, energy band alignment, and degradation-induced chemical changes such as the formation of PbI₂ or other secondary phases in PSCs.^{31–34} While conventional in-house PES using soft X-rays (<1500 eV) is more surface sensitive, synchrotron-based hard X-ray photoelectron spectroscopy (HAXPES) increases the probing depth by employing higher photon energies (>1500 eV) and generally utilizes a higher photon flux. Previously, Maheu et al.³⁵ investigated the spiro-OMeTAD/MAPbI₃ interface by thermally co-evaporating LiTFSI and spiro-OMeTAD onto MAPbI₃. They reported a surface photovoltage of 0.65 eV under illumination and a systematic shift toward lower binding energy in the HTL core levels, i.e., N 1s, F 1s, and C 1s, with increasing HTL thickness, indicative of interfacial band bending. Das et al.³⁶ studied [(FAPbI₃)_{0.85}(MAPbBr₃)_{0.15}]-based PSCs using tapered cross-sectional photoelectron spectroscopy (TCS-PES) and found increased iodine concentration at the spiro-OMeTAD/perovskite interface, with the perovskite showing n-type character and forming a p-n-n structure. Such an investigation aimed toward understanding the interfacial chemistry and energetics of the FAPbI₃/spiro-OMeTAD system, which is central to PSC performance, remains poorly explored.

In this paper, we investigate the FAPbI₃/spiro-OMeTAD interface in a device with ITO/SnO₂/FAPbI₃/spiro-OMeTAD architecture with two different HTL thicknesses. In the

conventional PSC devices, the spiro-OMeTAD thickness (~150–200 nm) exceeds the effective probing depth of HAXPES. Therefore, we fabricated modified devices with reduced spiro-OMeTAD HTL thickness (~10–50 nm) while maintaining device functionality, thereby enabling interfacial study with HAXPES. Our results provide direct evidence of chemical and electronic modifications happening near the perovskite/spiro-OMeTAD interface. These modifications are sensitive to the HTL thicknesses and highlight the crucial role of material mixing and tuning interfacial energetics. Such insights help optimize the design of more stable interfaces integral to PSC architectures that minimize interfacial recombination losses, which is essential for developing efficient PSCs.

■ EXPERIMENTAL SECTION

Materials

Lead Iodide (PbI₂, 99.99% trace metal basis) was acquired from TCI Chemicals. Methylammonium chloride (MACl, 99.99%) and formamminium iodide (FAI, 99.9%) were purchased from Greatcell Solar Materials. Tin oxide (15% in H₂O colloidal dispersion) was obtained from Alfa Aesar. Spiro-OMeTAD (sublimed grade, 99.8%) was purchased from Borun Material Tech. Lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI), 4-*tert*-butylpyridine (TBP), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), deionized water (DIW), chlorobenzene, and acetonitrile were provided by Sigma Aldrich. Diethyl ether was obtained from VWR Chemicals and FK-209 was purchased from Dyenamo AB.

Device Fabrication

Indium tin oxide (ITO) coated glass substrates were cleaned by ultrasonication for 30 min in a 1% Hellmanex solution, followed by sequential rinsing in deionized water, acetone, and ethanol. The substrates were then dried with a N₂ gun and treated in a UV-O₃ cleaner for 30 min. The as-received SnO₂ colloidal solution was diluted by mixing one part of stock solution with four parts deionized water. This diluted solution was deposited onto freshly cleaned ITO substrates by spin coating at 3000 rpm for 30 s in ambient conditions, and the films were immediately transferred to a hot plate and annealed at 150 °C for 30 min, as described in ref.³⁷ Prior to perovskite deposition, the SnO₂ coated substrates were subjected to a UV-O₃ treatment for 30 min. A 1.8 M FAPbI₃ precursor solution was prepared by dissolving 829.8 mg PbI₂, 309.5 mg FAI, and 42.5 mg MACl in 0.2 mL of DMSO and 0.8 mL of DMF. The solution was stirred at room temperature inside an N₂-filled glovebox until fully dissolved and then filtered through a 0.45 μm PTFE filter. The perovskite films were deposited by static spin coating at 6000 rpm for 50 s in ambient conditions, with diethyl ether (DEE) used as the antisolvent and dispensed 15 s after the start of the program. The resulting films were annealed at 150 °C for 10 min to form crystalline α -FAPbI₃.³⁸ One bare perovskite film was used as a reference. For the HTL deposition, 91.5 mg spiro-OMeTAD was dissolved in 1 mL of chlorobenzene inside an N₂-filled glovebox, followed by addition of 35.5 μL of TBP, 20.3 μL of LiTFSI solution (0.516 g mL⁻¹ in acetonitrile), and 8.8 μL of FK209 solution (0.375 g mL⁻¹ in acetonitrile). This final additive spiro-OMeTAD solution mixture was filtered through a 0.45 μm PTFE filter and spin coated under ambient conditions at 4000 rpm for 20 s to yield the regular devices, and in this paper, it is referred to as a “thick spiro device”. The solution with the same concentration was also spin coated directly onto ITO substrates for spiro-OMeTAD reference samples, expected to have comparable thickness of the spiro-OMeTAD layer to that of the thick spiro device described above. In order to reduce the thickness of the spiro-OMeTAD layer, the original solution was diluted 4 times with chlorobenzene, followed by spin coating on top of the perovskite layer, resulting in a thinner layer of

spiro-OMeTAD, and hence, this device is referred to as a “thin spiro device”. Throughout this article, we refer to the devices containing standard HTL thickness as “thick spiro devices” and reduced HTL thickness as “thin spiro devices”. Finally, 80 nm of Au electrode was thermally deposited onto the spiro-OMeTAD layer to complete the device stack for photovoltaic characterization.

X-ray Diffraction

The phase purity of bare FAPbI₃ sample was checked by recording an X-ray diffraction (XRD) pattern, which is presented in Figure S1. The XRD pattern was acquired using a Panalytical Empyrean system comprising a Cu K α X-ray source with a focusing X-ray mirror on the primary side and a d-core 0.27° collimator with a PIXcel detector on the secondary side. The measurements were performed in grazing incident mode with an incidence angle of 1°. The XRD pattern was recorded in the range of 5°–50° with a step size of 0.03°.

Scanning Electron Microscopy

To estimate the thickness of spiro-OMeTAD layer in both thin and thick devices, scanning electron microscopy (SEM) was utilized. The SEM micrographs were obtained using a Zeiss LEO 1530/1550 system. The micrographs were acquired with an in-lens detector and by utilizing an acceleration voltage of 4 kV. Further, all the samples were grounded using an aluminum tape, and the beam's aperture size was set to 10 μ m to minimize any surface charging.

Solar Cell Measurements

The current density–voltage (J – V) characteristics were acquired using an LED-based WAVELABS SINUS-70 solar simulator under an AM1.5G spectrum with an irradiance of 100 mW/cm². The illumination area was defined using a shadow mask of an opening of area 0.0688 cm². Measurements were performed by scanning devices from –0.2 to 1.5 V (forward scan) and from 1.5 to –0.2 V (reverse scan) with a voltage settle time of 50 ms and a step size of 0.02 V.

HAXPES Measurements

Hard X-ray photoelectron spectroscopy (HAXPES) experiments were conducted at the high kinetic energy electron spectroscopy (HIKE) endstation, located at the KMC-1 bending magnet beamline of Helmholtz–Zentrum Berlin.^{39,40} The beamline is equipped with a high-resolution double crystal monochromator (DCM) featuring three selectable crystal sets: Si(111), Si(311), and Si(422). Electrons were analyzed using a VG Scienta R4000 hemispherical analyzer. All measurements were performed under ultrahigh vacuum conditions, with a base pressure below 5×10^{-8} mbar. All core level and survey spectra were measured with a photon energy of 2200 eV. Measurements were performed at a grazing incidence angle to minimize intensity per unit area and enhance photoemission intensity. It is noted that for this configuration the absolute intensity is rather sensitive and may vary slightly between the samples. Core level spectra were acquired with a pass energy of 200 eV, and overview scans with 500 eV. The total energy resolution given by spectrometer and beamline is approximately 0.25 eV³⁹ at 2200 eV photon energy for 200 eV pass energy. Survey scans were recorded with a 0.5 eV step size, while high-resolution core level and valence band (VB) spectra were acquired using a 0.1 eV step size. Energy calibration of all spectra was performed using the Au 4f_{7/2} peak as a reference at 84.0 eV. To mitigate potential X-ray-induced damage, a beryllium filter was employed to reduce the incident photon flux during measurements. X-ray induced damage and charging effects were carefully monitored by tracking any changes in spectral shape and peak position over a period of time as shown in Figure S2. No significant changes in spectral line shapes were observed, and peak shifts remained below 0.1 eV across all measurements, indicating no or negligible X-ray damage. To further ensure data reliability, measurements were conducted in looped sequences, including the I 3d, Pb 4f, N 1s, C 1s, O 1s, and F 1s core levels and the VB. This approach allowed

for continuous monitoring of potential spectral drift or damage. Data from the first five loops showing minimal or no change in spectral line and shape were selected for analysis. The peak fitting of all the spectra was performed using a pseudo-Voigt peak function with linear background, except for Pb 4f and I 3d peaks of the bare perovskite sample where a pseudo-Tougaard (Herrera–Gomez) background was used to better fit the region between the two spin–orbit coupled (SOC) peaks, using the XPST program package available in the Igor Pro suite.⁴¹ The intensity ratios of the spin–orbit components were fixed at 4:3 for Pb 4f_{7/2}:Pb 4f_{5/2} and 3:2 for I 3d_{5/2}:I 3d_{3/2}. The energy separations between spin–orbit pairs were allowed to vary, with final converged values of 4.86 eV for Pb 4f and 11.50 eV for I 3d for perovskite signals, consistent with previously reported literature values.^{32,38,42}

RESULTS AND DISCUSSION

Figure 1a,b shows the cross-sectional scanning electron microscopy (SEM) images of both thin and thick spiro devices (ITO/SnO₂/FAPbI₃/spiro-OMeTAD/Au), respectively. The SEM images reveal a clear reduction in the spiro-OMeTAD layer thickness for the thin spiro device compared to the thick spiro device. As expected for spin coated films, the spiro-OMeTAD layer exhibits nonuniform thickness across the device. In the thin spiro device, localized regions with thicknesses up to $\sim$ 100 nm are observed with some areas that are clearly much thinner, while in the thick spiro device, some areas reach thicknesses as high as $\sim$ 300 nm. Despite these local variations, the overall thickness distribution confirms a successful reduction of the HTL thickness while maintaining full device functionality, as evidenced by the current density–voltage (J – V) characteristics shown in Figure 1c. The observed spiro-OMeTAD layer thickness ranges from approximately 10 nm but also with regions that are closer to 50 nm for the thin spiro device (Figure 1a). In contrast, the spiro-OMeTAD layer for the thick spiro device is clearly thicker varying from 150 to 200 nm (Figure 1b). On top of the spiro-OMeTAD HTL, an 80 nm Au electrode was deposited for solar cell characterization.

The J – V characteristics corresponding to the two devices are compared in Figure 1c. The best performing devices exhibited power conversion efficiency (PCE) of 12.63% and 18.15% for the thin and thick spiro device configurations, respectively. The PCE values of multiple devices are summarized in a box plot (Figure S3) and demonstrate good reproducibility for thick spiro devices. However, thin spiro devices exhibited a wider range of PCE values, which is possibly linked to nonuniform deposition of the spiro-OMeTAD layer. The J – V curve shows a decrease in open-circuit voltage (V_{OC}) from 0.96 V in the thick spiro device (in green) to 0.80 V in the thin spiro device (in red). This reduction in V_{OC} for thin spiro device may be attributed to differences in interfacial energetics and/or kinetics, thus highlighting the importance of investigating the interface. The SEM images (Figure 1a,b) reveal that the perovskite layer exhibits some lateral nonuniformity. As a consequence, in the thin spiro device, there are regions where the thickness of the spiro-OMeTAD HTL is possibly 10 nm or lower, as marked in Figure S4. In such areas, the reduced thickness increases the likelihood of local defects or pinholes, which could potentially allow direct contact between the Au electrode and the FAPbI₃ absorber. If extensive metal–perovskite contact were present, a significant increase in leakage current would be expected, leading to deterioration of the diode characteristics. However, the device J – V characteristics do not show signatures

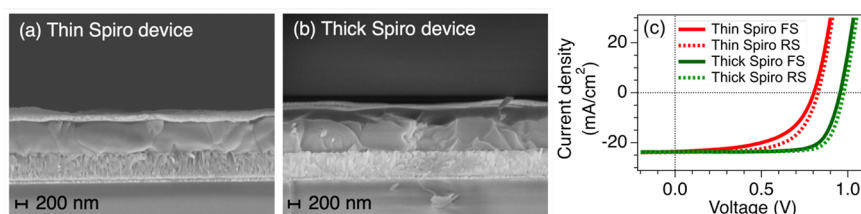


Figure 1. SEM cross-sectional view of the (a) thin spiro device and (b) thick spiro device, with ITO/SnO₂/FAPbI₃/Spiro-OMeTAD/Au device architecture. (c) *J*–*V* characteristics curve for thin and thick spiro devices with both forward (FS) and reverse scans (RS).

of severe shunting. This suggests that any pinholes, if present, occupy only a small fraction of the total device area and that the decrease in V_{OC} is likely to be affected by other origins. Additionally, both devices exhibit *J*–*V* hysteresis between the forward scan (FS, solid lines) and reverse scan (RS, dotted lines), which is commonly associated with ion migration occurring near the interface.^{43–46} Given the acceptable performance of thin spiro-OMeTAD based devices, they were further utilized for probing the buried perovskite/spiro-OMeTAD interface.

Interfacial Chemistry

To substantiate the chemical effects between the perovskite and spiro-OMeTAD interface, HAXPES measurements were performed on four samples with the following architectures shown in Figure 2a: ITO/SnO₂/FAPbI₃ (bare perovskite; black), ITO/SnO₂/FAPbI₃/~10–50 nm spiro-OMeTAD HTL (thin spiro device; red), ITO/SnO₂/FAPbI₃/~150–200 nm spiro-OMeTAD HTL (thick spiro device; green), and ITO/~150–200 nm spiro-OMeTAD HTL (spiro reference; blue). It is important to note that both thin and thick spiro devices used for HAXPES investigation were prepared via identical synthesis procedure but without Au on top of the spiro-OMeTAD layer, which was used in the complete device configuration for *J*–*V* characterization.

We first acquired survey spectra for all the four samples shown in Figure 2b, following the same color code as described in Figure 2a. For the bare perovskite sample, all visible core level peaks are identified and labeled. The perovskite shows

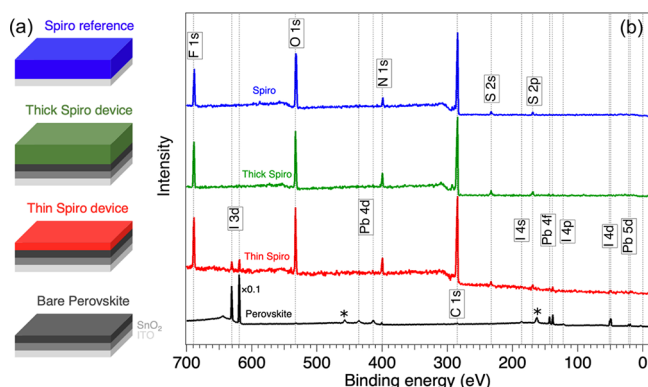


Figure 2. (a) Device architectures, (b) survey spectra of all four samples shown in (a), measured at 2200 eV with all the core levels identified and labeled. The intensity of the spectrum of the bare perovskite sample is shown multiplied by a factor of 0.1 for better comparison. The two peaks highlighted by two black asterisk symbols are the 3rd order peaks of I 2p_{3/2} (seen at ~163 eV) and I 2p_{1/2} (seen at ~457 eV).

signals stemming from Pb, I, N and C, as expected. Two additional peaks observed at ~163 and ~457 eV (marked by black asterisks) exhibit higher binding energy values (~4557 and ~4852 eV) and correspond to I 2p_{3/2} and I 2p_{1/2} core levels, respectively, excited by X-ray photons from the third order monochromator harmonic (6600 eV). Survey spectra of the thin spiro device, the thick spiro device, and the spiro reference exhibit all characteristic peaks of the elements present in spiro-OMeTAD and its additives. These include O 1s, C 1s, and N 1s which can originate from spiro-OMeTAD, LiTFSI, and FK209, while the additional F 1s, S 2s, and S 2p peaks originate from TFSI. The spectrum of the thin spiro device (red solid line) contains weaker signals of I 3d and Pb 4f from the underlying perovskite layer. This attenuation is expected due to the presence of the thin spiro-OMeTAD HTL on top of the perovskite, as can be further seen in the high-resolution core level spectra presented in Figure 3. In the thick spiro device, these peaks are barely visible. The bare perovskite and spiro-OMeTAD reference (~150–200 nm spiro-OMeTAD thickness) samples serve as the reference points for accurate peak assignment, and following the variations in peak intensities, widths, and positions while comparing thin and thick perovskite/spiro-OMeTAD interfaces.

Figure 3a–f shows the high-resolution core level spectra of Pb 4f, I 3d, N 1s, C 1s, F 1s, and O 1s. The Pb 4f and I 3d spectra reveal the effect of varying spiro-OMeTAD thickness (Figure 3a,b). A pronounced decrease in both Pb 4f and I 3d peak intensities is observed on going from the bare perovskite to the thin spiro device, consistent with attenuation of the perovskite signal by the HTL. The detection of perovskite signals in the thin spiro device confirms that HAXPES using 2200 eV photon energy allows us to probe through the spiro-OMeTAD layer, thus making it possible to investigate the interfacial chemistry at the perovskite/spiro-OMeTAD interface. In the thick spiro device, both Pb and I peaks decrease further and are only visible in the intensity normalized spectra, with a decreased signal-to-noise ratio as shown in Figure S5. The thick spiro device with ~150–200 nm spiro-OMeTAD thickness is sufficiently thick to block the photoelectron generated in the perovskite layer to reach the analyzer. However, we still observe minor amounts of Pb and I, which can possibly be attributed to both Pb and I ion incorporation in the spiro-OMeTAD layer, as will be discussed in more detail in the following paragraph.

Figure 3c compares the N 1s spectral region of all four samples, showing contributions from the bare perovskite, spiro-OMeTAD, and its additives. The N 1s spectrum of the bare perovskite exhibits a single intense peak, as expected from the formamidine cation.⁴⁷ Upon deposition of the thin spiro-OMeTAD-based HTL, a new intense N 1s structure characteristic of spiro-OMeTAD and additives emerges. The line shape

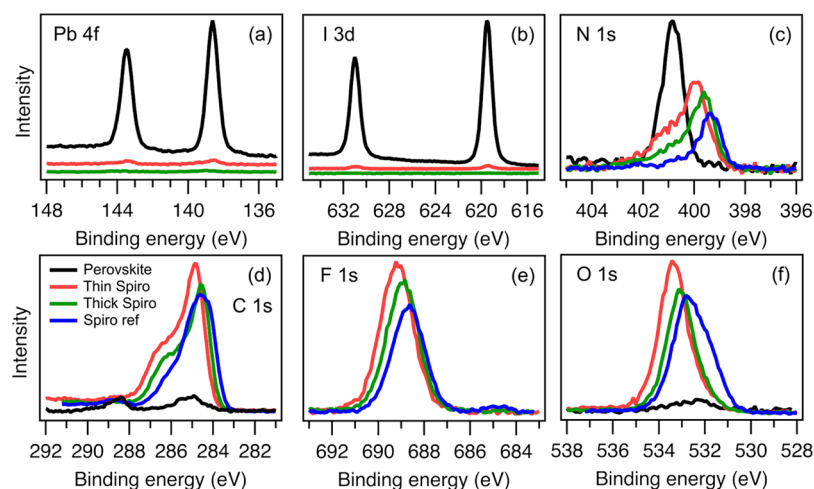


Figure 3. Raw core level spectra of (a) I 3d, (b) Pb 4f, (c) N 1s, (d) C 1s, (e) F 1s, and (f) O 1s measured on bare perovskite, thin and thick device, and spiro-OMeTAD reference sample at 2200 eV photon energy. In panels (a) and (b), spectra are offset vertically for better visibility.

of N 1s core level spectra is discussed in detail in [Energy Band Alignment](#). Also, the C 1s, F 1s, and O 1s related to the spiro-OMeTAD based layer become evident, as shown in [Figure 3d–f](#), respectively. In the F 1s spectrum of the spiro-OMeTAD reference sample, a weak additional low binding energy peak (~ 685 eV) is detected, which may be attributed to the minor decomposition of LiTFSI to LiF formation.⁴⁸ Notably, the spiro-related N 1s structure originating from spiro-OMeTAD and its additives generally shifts to lower binding energy when going from the thin spiro to the thick spiro device, i.e., the HTL thickness increased. Similar shifts are also observed in the C 1s, F 1s, and O 1s core level peaks related to the spiro-OMeTAD-based layer with increasing thickness.

To gain deeper insight into the chemistry of the FAPbI₃/spiro-OMeTAD interface, detailed curve fitting of the Pb 4f and I 3d spectra was performed as described in the [Experimental Section](#), and the results are shown in the [Figure 4](#). The Pb 4f and I 3d spectra of the bare perovskite, in [Figure 4a,b](#), each exhibit single species of Pb²⁺ and I[−] in FAPbI₃, thereby substantiating the purity of the perovskite layer. No substantial sign of metallic Pb or secondary phases is observable that may arise from perovskite degradation. The peak positions and peak widths obtained from fitting of Pb 4f and I 3d core level spectra are tabulated in [Table S1](#). The fitting of Pb 4f level of the thin spiro device shown in [Figure 4c](#), revealing a new slightly broader component appearing at a high binding energy peak (light yellow shaded) at 139.5 eV, shifted by 1.0 eV from the main perovskite Pb peak (gray shaded peak at 138.5 eV). The presence of a new peak signifies the formation of a new Pb species (nonperovskite Pb), suggesting that the perovskite and spiro-OMeTAD layer react chemically at the interface region. In contrast, the I 3d spectrum of the thin spiro device shown in [Figure 4d](#) does not require an additional component to describe the I 3d signal or show any visible peak broadening. This is highlighted by comparing the intensity normalized spectra of I 3d_{5/2} peak of bare perovskite and thin spiro device, in [Figure S5](#). We also note that the binding energy positions of the perovskite core levels (both Pb 4f and I 3d) remain similar and shift less than 0.1 eV, upon spin coating thin spiro layer on top of perovskite.

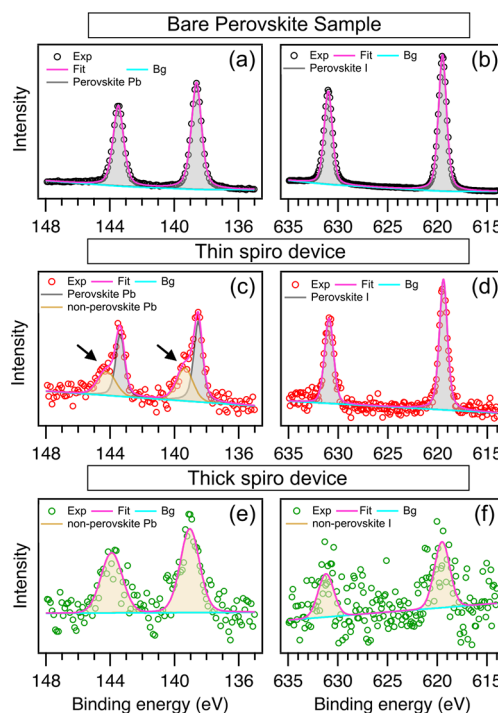


Figure 4. Fitting of the Pb 4f and I 3d core level spectra of bare perovskite (a, b), thin spiro device (c, d), and thick spiro device (e, f), respectively.

For the thick spiro device ([Figure 4e,f](#)), Pb 4f fitting shows a single doublet with a significantly broader peak compared to the perovskite peaks. The peak width of the Pb 4f_{7/2} peak is 1.4 eV, and that of I 3d_{5/2} is 1.8 eV for the thick spiro device, which increased from 0.7 eV (Pb 4f_{7/2}) to 1.0 eV (I 3d_{5/2}) for the bare perovskite. This observation indicates that both the Pb and I signals seen in the thick spiro device do not originate from the perovskite phase but are nonperovskite Pb and I incorporated into the spiro-OMeTAD HTL. The corresponding Pb 4f and I 3d signals in the thick spiro device are considerably weaker as evident from the low signal-to-noise ratio. However,

the fitting parameters still provide valuable insight while following the systematic changes. The I/Pb ratio of the various samples, calculated from the core level areas and the relative peak positions, is summarized in Table 1.

In Figure 5a,b, we compared the Pb 4f and I 3d spectra normalized to the total Pb 4f peak area to track any changes in the I/Pb ratio among the samples. In the presence of spiro-OMeTAD, the I 3d intensity decreases relative to the Pb 4f intensity compared to the bare perovskite reference, suggesting preferential migration of Pb ions into the spiro-OMeTAD layer. This conclusion is further supported by a quantitative analysis of the elemental ratios summarized in Table 1. Elemental ratios were estimated from the integrated peak areas corrected for the photoionization cross section.⁴⁹ For the bare FAPbI₃ sample, the calculated Pb/I ratio is 0.30, which is close to the stoichiometric value of 0.33 expected for an ideal perovskite. In the case of the thin spiro device, we observed two Pb peaks: one perovskite Pb and another nonperovskite Pb peak. For the perovskite Pb peak, the Pb/I ratio is estimated to be 0.34 which is similar to the bare perovskite sample. For the nonperovskite, the Pb peak Pb/I ratio comes to 0.22 the making total Pb/I ratio to 0.56 for the thin spiro device, which is higher compared to the bare perovskite. This suggests the presence of more Pb per I content. This Pb/I ratio further increases significantly to 1.5 in the case of the thick spiro device.

From Figure 4c,d, it is evident that both perovskite and nonperovskite related signals are detected through the spiro-OMeTAD HTL. Therefore, it is important to evaluate whether the probing depth of the measurement allows detection of the underlying perovskite layer. Using the TPP-2 M equation,⁵⁰ we estimated the probing depth for X-ray photon energy of 2200 eV for photoelectrons originating from the perovskite layer and passing through the spiro-OMeTAD HTL. The resulting information depths are 15.2 nm for Pb 4f and 12.2 nm for I 3d photoelectrons. All initial parameters used in the IMFP calculation are listed in Table S4. Given that the probing depths for Pb 4f and I 3d are on the order of 12–15 nm, it is therefore highly plausible that photoelectrons originating from the underlying perovskite layer can escape through these thinner regions of the HTL and be detected in the HAXPES measurements. Clearly, this scenario is not possible for the thick spiro device, where the spiro-OMeTAD layer thickness is in the range of 150–200 nm. At such thicknesses, the probing depth is insufficient to detect signals from the underlying perovskite layer. Consequently, no perovskite-related Pb or I signal is observed. The weak Pb 4f and I 3d signals detected in this case, therefore, must originate from nonperovskite Pb and I species that have migrated into the spiro-OMeTAD HTL.

To further examine the compound integrity of the perovskite phase, we compared the binding energy difference between the I 3d_{5/2} and Pb 4f_{7/2} peaks [$\Delta E = E(I3d_{5/2}) - E(Pb4f_{7/2})$],

which is material specific and is expected to be constant for a bulk perovskite. For bare FAPbI₃, we determined this difference in binding energy to be $\Delta E = 480.9$ eV, consistent with our previous report.⁴² The thin spiro device shows an identical value of 480.9 eV for the perovskite Pb peak, confirming that the perovskite structure close to the interfaces remains intact, while the ΔE value for the nonperovskite Pb peak appears to be 479.9 eV. In contrast, for the thick spiro device, ΔE decreases to 480.5 eV. Combining both observations, i.e., the increased Pb/I ratio and lowered ΔE for the thick spiro device, we conclude that the detected Pb and I signals in thick spiro device no longer originate from the perovskite lattice but rather from a different chemical (nonperovskite phase) within or near the surface of the spiro-OMeTAD layer. This finding provides compelling evidence for the incorporation of perovskite ions in the spiro-OMeTAD phase. This could be due to intermixing upon the spiro-OMeTAD layer formation or due to migration of both Pb and I ions into the spiro-OMeTAD HTL.

Since both Pb and I are observed to migrate into the spiro-OMeTAD HTL, it is reasonable to initially consider the possible formation of PbI₂. For the thin spiro device, the Pb 4f core level spectra show a clear contribution from perovskite-Pb in addition to a nonperovskite-Pb component. In contrast, for iodine, no additional peak or noticeable peak broadening is observed, making it difficult to directly distinguish between perovskite and nonperovskite contributions. Therefore, the relative contributions were evaluated using the ratios $Pb_{\text{perovskite}}/I_{\text{total}}$ and $Pb_{\text{nonperovskite}}/I_{\text{total}}$. For the thick spiro device, no perovskite-Pb or I components are detected. Thus, the measured Pb and I signal originates exclusively from nonperovskite species that have migrated into the spiro-OMeTAD layer. In the absence of a perovskite contribution, the Pb/I ratio reflects only the relative extent of Pb and I migration into the HTL. The observed increase in the Pb/I ratio indicates that Pb species migrate more readily into the spiro HTL than iodine species. If Pb and I were migrating into the spiro-OMeTAD layer and reacting together to form PbI₂, the resulting Pb/I ratio would be 0.5. However, the experimentally observed ratios are 0.22 and ~1.5 for thin and thick devices, respectively. Such a strong deviation from the expected value indicates that the migrated Pb and I species are not present as PbI₂. This conclusion is further supported by our binding energy analysis. In PbI₂, the energy separation between the Pb and I core levels is comparable to that in FAPbI₃.⁴⁷ In contrast, the present measurements show a reduced separation of ~1.0 eV for the thin spiro device and ~0.4 eV for the thick spiro device. Taken together, these observations indicate that Pb and I do not form PbI₂ within the spiro-OMeTAD layer. Another possibility is that the Pb ions migrating into the spiro-OMeTAD HTL form coordination complexes with the pyridine nitrogen of the TBP additive. Previous reports have suggested

Table 1. Estimated Elemental Ratio (Pb/I) and ΔBE (I 3d_{5/2} – Pb 4f_{7/2}) Binding Energy Difference in eV Units for Bare Perovskite, Thin, and Thick Reference Samples^a

	Pb/I ratio		binding energy difference (eV)	
	$\frac{Pb_{\text{perovskite}}}{I_{\text{total}}}$	$\frac{Pb_{\text{non-perovskite}}}{I_{\text{total}}}$	$(I\ 3d_{5/2})-(Pb\ 4f_{7/2})_{\text{perovskite}}$	$(I\ 3d_{5/2})-(Pb\ 4f_{7/2})_{\text{nonperovskite}}$
bare perovskite	0.30		480.9	
thin spiro device	0.34	0.22	480.9	479.9
thick spiro device		~1.5		~480.5

^aWe note that for the thick spiro device, the signal-to-noise ratio of the Pb 4f and I 3d spectra is significantly lower.

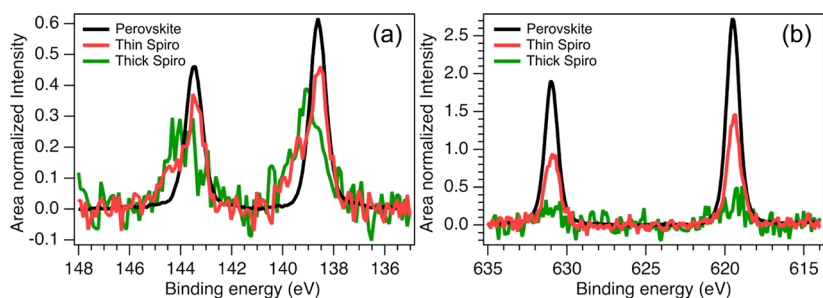


Figure 5. Comparison of (a) Pb 4f and (b) I 3d core level spectra normalized against the integrated area of the corresponding Pb 4f levels.

the formation of I-Pb-N(pyridine)TBP or $[\text{PbI}_2-(\text{TBP})_x]$ complexes.^{51–54} While such scenarios are chemically plausible, we currently do not have direct experimental evidence to conclusively identify such complexes. Instead, the migrated species likely exist in a different chemical environment, although the exact phase or compound formed by Pb and I in the HTL cannot be identified at present.

Energy Band Alignment

To investigate the interfacial energetics of the perovskite/spiro-OMeTAD interface, we focus on the N 1s core level spectra, as nitrogen is present in both the perovskite and the spiro-OMeTAD based HTL. Figure 6 presents the fitting of N 1s core level spectra for the bare perovskite, the thin spiro device, the thick spiro device, and the spiro reference going from bottom to top. The bare FAPbI₃ sample exhibits a single N 1s component, characteristic of the formamidinium cation appearing at 400.8 eV, as obtained from the fitting and matches well with our previous result.⁴⁷ The N 1s core level spectra of the additive

spiro-OMeTAD mixture reference sample indicate the presence of at least three components of nitrogen. As shown in the fitting, the intense low binding energy peak (blue solid line, called "HTL_N1") at 399.3 eV comes from the spiro-OMeTAD compound, and the two high binding energy peaks at 400.4 eV (yellow solid line, called "HTL_N2") and 402.2 eV (brown solid line, called "HTL_N3") originate from the Li-TFSI and FK 209 additives used in the spiro-OMeTAD solution, as detailed in the Experimental Section. This asymmetric peak shape matches well with our previous report measured with a comparable photon energy of 2010 eV.⁵⁵ We note that the peak widths of these components reflect chemical inhomogeneity of the compounds in the final spiro-OMeTAD additive film arising from the Li-TFSI and FK 209 additives.

In the case of thin and thick spiro devices, the overall N 1s spectra show large similarities. However, a closer look indicates some smaller differences in the electronic structure that may suggest some variation in compositions as well as properties (e.g., doping levels). For fitting the N 1s spectra of the thin and thick spiro devices, the profile of the spiro-OMeTAD-based film including the additives was set to be constant, that is, the binding energy separations between the three related components, as well as the area ratios (HTL_N1/ HTL_N2) and (HTL_N1/ HTL_N3), were fixed to the values obtained from the spiro-OMeTAD reference sample. Based on such a procedure, accurate fitting of the thin and thick spiro device requires an extra N 1s component (dark yellow dotted line), in addition to the three spiro-OMeTAD-related peaks, referred to as "Interface N 1s". The appearance of this extra component indicates the formation of new mixing compounds having different nitrogen chemical environments, likely associated with interfacial species at the perovskite/spiro-OMeTAD interface and/or chemical modification within the HTL upon deposition on the perovskite layer.

This interfacial contribution becomes even more pronounced in the thin spiro device, where a significantly larger intensity of the additional component is required to reproduce the experimental spectrum. Notably, the convolution of this chemistry is difficult to determine. We note that when using a single peak, the width of this new component exceeds 2 eV, suggesting that it arises from nitrogen atoms experiencing multiple local chemical environments. This feature could also originate from different compounds, leading to variations in screening, i.e., the chemical shift resulting in a broader distribution of binding energies. The peak area of this interfacial component in the thin spiro device is approximately twice that observed for the thick spiro device, indicating that this species is more prominent closer to the perovskite/spiro-OMeTAD interface. However, the presence of the "interface N 1s" component even in the

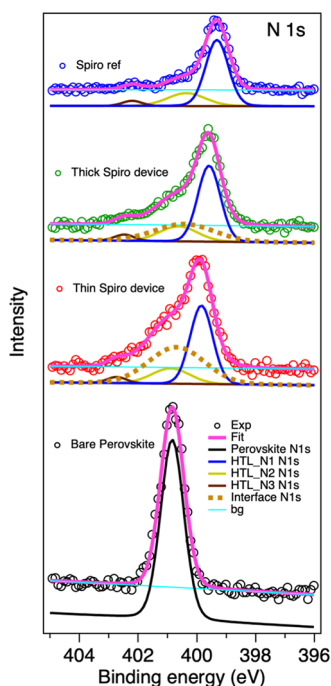


Figure 6. Fitting of the N 1s core level spectra of bare perovskite (black open circle), thin spiro device (red open circle), thick spiro device (green open circle), and spiro reference (blue open circle). Individual fitted components are vertically offset to lower intensities for better visibility of each peak.

thick spiro device indicates that these modified nitrogen species are not confined strictly to the buried interface but are likely partly migrated and distributed within the spiro-OMeTAD HTL. It is important to consider that the N 1s spectra with its pronounced "interface N 1s" signal observed in the thin spiro device could partly reflect nonuniform HTL coverage or possible minor Li-TFSI redistribution within the HTL upon dilution. However, Figure S7 shows that the overall N 1s spectra of the thin and thick spiro-OMeTAD reference films (deposited on the ITO substrate) are very similar, indicating that the dopant-related N 1s components (HTL_N2 and HTL_N3) remain largely unchanged with film thickness. This suggests that the "interface N 1s" feature cannot be explained by mere variations in dopant concentration or morphology but indeed reflects chemical modifications originating from interfacial reactions at the perovskite/spiro-OMeTAD interface.

In addition to the emergence of this new component, all three spiro-OMeTAD-related N 1s peaks (HTL_N1, HTL_N2, and HTL_N3), as well as the interfacial component, shift uniformly toward a lower binding energy by 0.26 eV in the thin spiro device compared to the thick spiro device. The extracted binding energy positions and corresponding peak widths for all N 1s components are summarized in Table S2. Importantly, although Pb 4f and I 3d features from the perovskite are still detectable in the thin spiro device, a significant contribution from the FA cation to the N 1s spectra is not expected due to strong attenuation of the perovskite signal by the overlying spiro-OMeTAD layer, as shown in Figure 3c.

To summarize, the thin and thick spiro devices require one additional peak to accurately fit the N 1s spectrum compared to spiro reference, where three nitrogen components are clearly visible. This indicates that the extra peak (yellow solid line) is an additional component stemming from a different environment originating from some decomposition or dissolution of perovskite layer beneath. We note that the increased intensity of this feature in the thin spiro device compared to the thick spiro device suggests that this new nitrogen component originates specifically from the perovskite/spiro-OMeTAD interface region. This is likely due to the accumulation of FA cations at the interface, appearing at a lower binding energy position compared to perovskite FA nitrogen peak position, when detached from the perovskite lattice and are no longer in its original perovskite structure.^{56,57} The broad "interface N 1s" feature with a peak width of >2 eV indicates that it does not originate from a single chemical species, but rather represents a convolution of multiple components. Since the precise origin of the individual contributions cannot be unambiguously resolved, it is more appropriate to treat this feature as a single broad peak, as implemented in the present analysis. Several factors may contribute to the broadening of the "interface N 1s" signal: (1) At the perovskite/spiro-OMeTAD interface, chemical interactions or structural modifications may lead to the formation of new nitrogen-containing species. (2) A fraction of FA⁺ ions near the interface may become structurally distorted or partially detached from the FAPbI₃ lattice. Such FA-related species in a modified chemical environment could contribute to higher binding energy components. (3) The coexistence of perovskite related and nonperovskite nitrogen species within a potential gradient induced by the spiro-OMeTAD overlayer may also contribute to spectral broadening. This local potential variation can lead to additional shifts, causing a wider distribution in the N 1s binding energy. Overall, a reliable deconvolution and

definitive chemical assignment of the individual nitrogen species at the perovskite/spiro interface is not feasible.

To evaluate the potential gradient across the spiro-OMeTAD overlayer, we modeled the gradual energy shift as described in the Supporting Information and showed the simulated spectra in Figure S8. The simulation indeed produces a slight asymmetry toward a higher binding energy but still could not fully reproduce the experimental spectrum. The "interface N 1s" component is thus interpreted as multiple components arising due to interfacial chemical modification at the perovskite/spiro-OMeTAD interface.

We now discuss the general shift of the HTL peaks as observed in Figure 6. The shifts in all three HTL_N1, HTL_N2, and HTL_N3 peaks toward lower binding energy with increasing spiro-OMeTAD thickness provide clear evidence of charge distribution at the interface and that this depends on the HTL thickness. This may be modeled as downward band bending that occurs in the spiro-OMeTAD HTL near the perovskite/spiro-OMeTAD interface. This interpretation is further supported by the analogous shift observed in F 1s and O 1s spectra (Table S3), reinforcing that the observed variations originate from a general shift of all core levels in the spiro-OMeTAD-based layer. To verify the origin of this shift, reference "thick" and "thin" spiro-OMeTAD films were prepared directly on ITO substrates, using the same additive concentrations as in the perovskite-based devices. As shown in Figure S7, the N 1s and F 1s core level peaks of the thick and thin spiro films deposited on ITO align with each other. This indicates that electronic structure of spiro-OMeTAD remains essentially unchanged despite variations in film thickness or solution concentration. Therefore, the binding energy shifts observed in the N 1s and F 1s spectra of spiro-OMeTAD in the complete devices cannot be attributed to variations in spiro-OMeTAD layer. Instead, they originate solely from electronic interactions between spiro-OMeTAD and the underlying perovskite absorber, which induce band bending at the perovskite/spiro-OMeTAD interface. Similar trends were reported in our previous work on the perovskite/TIPS-pentacene interface,⁵⁸ where the Si 2p and C 1s peak arising from TIPS-pentacene shifted systematically to higher binding energies as the organic overlayer thickness was increased. We note here that the direction of the shift is opposite in the TIPS-pentacene system, and it is expected that such a charge distribution or band bending depends strongly on the choice of perovskite/HTL heterojunction. Moreover, the results highlight the pronounced influence of transport layer thickness on the overall energy level band diagram of PSCs.

Using the binding energy values along with the energy position of the valence band maximum (VBM), we constructed the energy band diagram for ITO/SnO₂/FAPbI₃/spiro-OMeTAD device. To do so, the position of the VBM of FAPbI₃ was determined using linear extrapolation on the outermost edge of the valence band. This gives the VBM position at 1.5 eV relative to the Fermi level for the bare perovskite, as shown in the top panel of Figure 7a. By using the optical band gap of 1.54 eV, obtained from the photoluminescence measurements as shown in Figure S6, the conduction band maximum (CBM) position can be estimated to be at 0.04 eV above the Fermi level. This indicates that the surface is more n-doped, possibly due to the formation of the undesired hexagonal δ -FAPbI₃ phase (visible in the XRD, Figure S1), resulting in n-type self-doping.^{59–61} While the presence of the δ -phase in FAPbI₃ can affect the

VBM position of the perovskite,⁶² in our case, the δ -phase is rather minor, which makes it unlikely to significantly affect the interfacial energetics or the overall trend of the band bending diagram presented in Figure 7b. Using the VBM position value, we calculated the energy difference between the perovskite N 1s level and VBM, which is 399.3 eV. Similarly, we can estimate the highest occupied molecular orbital (HOMO) position for the spiro-OMeTAD reference sample. However, at 2200 eV photon energy, we could not resolve any signal in the VB region for spiro-OMeTAD reference sample due to the low-photoionization cross section of lighter elements (C and N) at high X-ray photon energies. Therefore, we measured the binding energy difference of the VB and N 1s core level spectra of the spiro-OMeTAD reference sample using a 758 eV soft X-ray photon energy at the FlexPES beamline⁶³ (MAX IV, Lund, Sweden); corresponding experimental details are provided in the Supporting Information. Using linear extrapolation, we estimate the HOMO position at 0.8 eV below the Fermi level, while the N 1s peak position is at 399.6 eV, shown in the bottom of Figure 7b. The energy difference between the N 1s core level and the HOMO position comes out at 398.8 eV. With the assumption of a rigid band model, this Δ BE value, the separation between the N 1s core level peak and the HOMO does not change for a given material. Therefore, the Δ BE = 398.8 eV value was used to estimate the HOMO positions from the known N 1s peak position for the thin and thick spiro devices.

Based on the B.E. shifts of the N 1s peaks and the VBM, a schematic energy level diagram was constructed to follow how the frontier energy levels corresponding to the FAPbI₃/spiro-OMeTAD interface evolve with increasing HTL thickness. As shown in Figure 7b, the spiro-OMeTAD HOMO level shifts toward the perovskite VBM as the HTL thickness decreases, i.e., going from the thick spiro device to the thin spiro device. These findings were obtained on a functional interface with material compositions prepared by spin coating and yielding efficient thin film configuration. However, the results are consistent with previous studies on the MAPbI₃/spiro-OMeTAD interface. Maheu et al.³⁵ investigated this interface by depositing spiro-OMeTAD via thermal evaporation, where both spiro-OMeTAD and LiTFSI were co-evaporated. They observed a similar shift toward lower binding energy in the N 1s, C 1s, and F 1s core levels as the spiro-OMeTAD layer thickness increased. In another study, Das et al.³⁶ employed tapered cross-sectional photoelectron spectroscopy, performing line-scan PES measurements along the tapered cross section of PSCs. Their results also revealed a similar lower binding energy shift in the N 1s and C 1s core level spectra when going from the Au/spiro-OMeTAD interface to the [(FAPbI₃)_{0.85}(MAPbBr₃)_{0.15}] and spiro-OMeTAD interface. The observed shift in the spiro-OMeTAD HOMO energy levels near the surface, that is, the areas that will form an interface with Au in the device structure when comparing the thin and thick spiro devices, is expected to affect device performance. While the energy matching at the perovskite/spiro interface may stay the same, it indicates that the HOMO level in this region of thin spiro device is 0.4 eV closer to the perovskite VBM (see Figure 7b). This reduced energy offset may constrain the achievable photovoltage. This interpretation is consistent with the experimentally observed 0.16 V lower V_{OC} in the thin spiro device compared to the thick spiro device. Moreover, reducing the HTL thickness likely increases charge recombination due to spiro-OMeTAD HTL

nonuniformity in the thin spiro device. Such nonuniform coverage adversely affects both device performance and reproducibility, as evidenced by the larger spread in PCE values observed for the thin spiro devices (Figure S3). Additionally, it is important to note that the band diagram presented here was derived for the ITO/SnO₂/FAPbI₃/spiro-OMeTAD device architecture without the top Au electrode. A similar interfacial trend is expected in a complete device containing the Au contact, although the magnitude may be affected by possible charge redistribution arising from the HTL/Au interface. This can be deduced based on previous investigations,³⁵ which revealed no such effects and that no additional photovoltage is generated at the spiro-OMeTAD/Au interface, highlighting the crucial role of the perovskite/spiro-OMeTAD junction in determining device energetics. Therefore, while the absolute energy level alignment may differ slightly in the fully fabricated device, the experimentally observed trend of downward band bending within the spiro-OMeTAD HTL is expected to remain valid.

CONCLUSIONS

We investigated the interfacial chemistry and energy band alignment within the buried FAPbI₃/spiro-OMeTAD interface in PSCs. Our HAXPES measurements on two devices with different spiro-OMeTAD thicknesses reveal substantial incorporation of both Pb and I ions into the spiro-OMeTAD HTL from the perovskite layer. Additionally, we observe a new high binding energy nonperovskite Pb component in the Pb 4f spectra of the thin spiro device, while the I 3d signal showed no notable shifts. In the case of the thick spiro device, we see both Pb and I peaks originating from the nonperovskite phase. From the decreased binding energy difference between the Pb and I peaks and the lower I/Pb ratio for the thick spiro device compared to the bare perovskite sample, we conclude that both Pb and I ions are present near the surface of the spiro-OMeTAD HTL. Moreover, the higher contribution of a new feature in the N 1s core level spectrum in the thin spiro device compared to the thick spiro devices suggests that nonperovskite FA⁺ cations accumulate at the perovskite/spiro-OMeTAD interface region.

Using the energy difference between the N 1s core level peak and the HOMO level, we constructed the energy level diagrams. The N 1s level of the spiro-OMeTAD based hole transport layer shifts toward a lower binding energy with increasing HTL thickness. Assuming a rigid band model, such a shift reveals the spiro-OMeTAD based HOMO level shifts away from the perovskite VBM as the HTL becomes thicker, confirming downward band bending within the spiro-OMeTAD layer, with no distinct band realignment observed within the perovskite layer near the interface. Although a thinner HTL improves energetic alignment, nonuniform spiro-OMeTAD coverage may also introduce additional recombination pathways, thereby contributing to the observed V_{OC} loss.

Overall, these results provide direct spectroscopic evidence of band bending behavior and interfacial chemical modification near the perovskite/spiro-OMeTAD interface. They highlight the need for effective interfacial passivation strategies to suppress undesirable chemical reactions, as well as the importance of carefully optimizing the HTL thickness to achieve favorable energy level alignment and minimize recombination losses in high-efficiency PSCs.

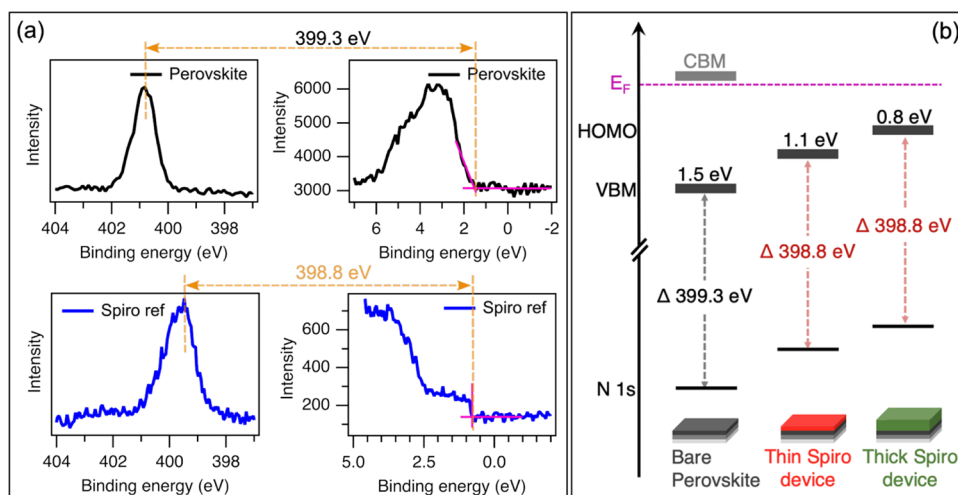


Figure 7. (a) Δ BE between the N 1s level and valence band maxima (VBM) for the perovskite measured at 2200 eV in top and spiro HTL measured at 758 eV at the bottom. (b) Energy band alignment for all the devices obtained by drawing the highest occupied molecular orbital (HOMO) level for thin and thick spiro devices by keeping the Δ BE fixed, obtained from the spiro reference device.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.6c08990>.

Figure S1: X-ray diffraction pattern recorded on bare FAPbI₃ perovskite thin film, Figure S2: X-ray damage test procedure, Figure S3: statistical distributions of power conversion efficiencies for devices with different spiro-OMeTAD thicknesses, Figure S4: SEM image of a thin spiro-OMeTAD device with highlighted regions, Figure S5: intensity normalized comparisons of Pb 4f and I 3d core levels, Figure S6: photoluminescence spectra of FAPbI₃, Figure S7: (a) N 1s and (b) F 1s core level spectra measured for ITO/thick-spiro and ITO/thin-spiro films, Figure S8: modeling of the N 1s spectral asymmetry considering potential gradient within the spiro-OMeTAD layer, Tables S1–S3: parameters extracted from curve fitting analyses for Pb 4f and I 3d, N 1s, and O 1s and F 1s core levels, respectively, and Table S4: estimated IMFP and probing depth of Pb 4f and I 3d signals (DOCX)

■ AUTHOR INFORMATION

Corresponding Author

Håkan Rensmo – Condensed Matter Physics of Energy Materials, Division of X-ray Photon Science, Department of Physics and Astronomy, Uppsala University, Box 516, Uppsala SE-75120, Sweden; Wallenberg Initiative Materials Science for Sustainability, Department of Physics and Astronomy, Uppsala University, 75120 Uppsala, Sweden; orcid.org/0000-0001-5949-0997; Email: hakan.rensmo@physics.uu.se

Authors

Rahul Mahavir Varma – Condensed Matter Physics of Energy Materials, Division of X-ray Photon Science, Department of Physics and Astronomy, Uppsala University, Box 516,

Uppsala SE-75120, Sweden; orcid.org/0000-0001-9826-7958

Bhavya Rakheja – Department of Materials Science and Engineering; Solar Cell Technology, Uppsala University, Box 35, Uppsala SE-751 03, Sweden; orcid.org/0009-0000-8411-124X

Karen Radetzky – Condensed Matter Physics of Energy Materials, Division of X-ray Photon Science, Department of Physics and Astronomy, Uppsala University, Box 516, Uppsala SE-75120, Sweden; Wallenberg Initiative Materials Science for Sustainability, Department of Physics and Astronomy, Uppsala University, 75120 Uppsala, Sweden; orcid.org/0009-0007-0221-890X

Evelyn Johannesson – Condensed Matter Physics of Energy Materials, Division of X-ray Photon Science, Department of Physics and Astronomy, Uppsala University, Box 516, Uppsala SE-75120, Sweden

Stefania Riva – Condensed Matter Physics of Energy Materials, Division of X-ray Photon Science, Department of Physics and Astronomy, Uppsala University, Box 516, Uppsala SE-75120, Sweden; orcid.org/0000-0001-8449-1166

Alberto García-Fernández – Condensed Matter Physics of Energy Materials, Division of X-ray Photon Science, Department of Physics and Astronomy, Uppsala University, Box 516, Uppsala SE-75120, Sweden; CICA (Interdisciplinary Center for Chemistry and Biology), Department of Chemistry, Faculty of Science, Universidade da Coruña, As Carballeiras, s/n, Campus de Elviña, A Coruña 15071, Spain; orcid.org/0000-0003-1671-9979

Roberto Félix – Department Interface Design, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH (HZB), Berlin 12489, Germany; orcid.org/0000-0002-3620-9899

Adam Hultqvist – Department of Materials Science and Engineering; Solar Cell Technology, Uppsala University, Box 35, Uppsala SE-751 03, Sweden; orcid.org/0000-0002-2402-5427

Soham Mukherjee – Condensed Matter Physics of Energy Materials, Division of X-ray Photon Science, Department of

Physics and Astronomy, Uppsala University, Box 516, Uppsala SE-75120, Sweden; orcid.org/0000-0002-3656-7207

Ute B. Cappel – Condensed Matter Physics of Energy Materials, Division of X-ray Photon Science, Department of Physics and Astronomy, Uppsala University, Box 516, Uppsala SE-75120, Sweden; Wallenberg Initiative Materials Science for Sustainability, Department of Physics and Astronomy, Uppsala University, 75120 Uppsala, Sweden; orcid.org/0000-0002-9432-3112

Tobias Törndahl – Department of Materials Science and Engineering; Solar Cell Technology, Uppsala University, Box 35, Uppsala SE-751 03, Sweden; orcid.org/0000-0001-7757-5847

Complete contact information is available at:

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

thin spiro device	ITO/SnO ₂ /FAPbI ₃ /~10–50nm spiro-OMeTAD HTL
thin spiro device	ITO/SnO ₂ /FAPbI ₃ /~150–200nm spiro-OMeTAD HTL
HAXPES	hard X-ray photoelectron spectroscopy
PES	photoelectron spectroscopy
XPS	X-ray photoelectron spectroscopy
J–V	current density–voltage
SEM	scanning electron microscopy
XRD	X-ray diffraction

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