Supplementary Information for

Interface Energetics in Organo-Metal Halide Perovskite-based Photovoltaic Cells

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Experimental

MAPbX film preparation

F-doped tin oxide- (FTO-) covered glass substrates were cut and cleaned by sequential 15 min sonication in warm aqueous alconox solution, deionized water, acetone and ethanol, followed by drying in a N_2 stream. A compact ca. 100 nm thin TiO_2 was then applied to the clean substrate by spray pyrolysis of 20 mM titanium diisopropoxide bis(acetylacetonate) solution in isopropanol using air as carrier gas on a hot plate set to 350˚C, followed by annealing at 500˚C for 1 h in air.

A MAPbX solution was prepared as described elsewhere.[22] In short, CH_3NH_3X was prepared by mixing methyl amine (40% in methanol) with concentrated HX acid (CAUTION: exothermic reaction) in a 1:1 molar ratio under continuous stirring at 0˚C for 2 hr. CH_3NH_3X was then crystallized in a rotary evaporator, washed in diethyl ether and filtered. The crystals were then dried overnight *in vacuo* at 60˚C.

Single step method - A 40% wt solution of MAPbX was prepared by mixing PbX_2 and CH_3NH_3X in an equimolar ratio in anhydrous dimethyl formamide (DMF). For $CH_3NH_3PbI_{3-x}Cl_x$ a similar procedure was followed as described in ref. 2. The solution was then spin casted on the substrate and heated on a hot plate at 100°C ($MAPbX_3$) or 120°C ($MAPbI_{3-x}Cl_x$) for 45 min.

Two step method - MAPbX was prepared by the two-step procedure as described in ref. 7, a 1M PbX_2 in DMF solution was prepare and spin casted at 70°C on the substrate. After drying on a hot plate for 20 min at 70°C the substrate was dipped for 20 sec in CH_3NH_3X propanol solution ($10 mg\cdot mL^{-1}$), rinsed and then dried on a hot plate for another 20 min.

Both methods gave similar results, but the two-step procedure resulted in a more uniform layer and was preferred when possible. All MAPbX samples were prepared in inert gas atmosphere and transferred to the UHV chamber for analysis and HTL film growth without exposure to ambient. Measurements were repeated on three MAPbI3, three MAPbBr3 and two MAPbIxCl3-x films grown independently, and on several spots of each of these surfaces. Film preparation and measurements were found to be highly reproducible, i.e. resulted in similar spectra with the same offsets in repeated sample production runs and for different spots on the sample, indicative of good homogeneity across the film. Devices build with these films yield power conversion efficiencies comparable to well-performing cells reported in the literature and showed a good reproducibility.

HTL layer preparation

Spiro-MeOTAD and PTCDI-C1 were purchased from Sigma Aldrich and used without further purification. Layers were evaporated from a Knudsen cell in a vacuum chamber operated at a pressure of 5 x 10^{-9} mbar. A constant rate of 2 Å/min was verified by a quartz crystal microbalance. After growth samples were transferred in-situ to the analysis chamber in the same UHV system.

Direct and inverse photoemission spectroscopy

Direct and inverse photoemission experiments were performed in a custom built UHV chamber described elsewhere.[23] UPS spectra were acquired from He I (21.22 eV) and He II (40.8 eV) excitation lines at a nominal experimental resolution below 150 meV, while XPS spectra were taken employing Al Ka radiation (1486.7 eV) at a resolution of 800 meV. IPES spectra were recorded in isochromat mode at a nominal resolution of 400 meV. All experiments were calibrated to the Fermi edge of an atomically clean gold surface. Note that the current study focuses entirely on the determination of band edges and photoemission cut-offs, which are determined with higher accuracy. Error bars for band edge positions and energy gaps are given in the text.

22 A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, *J. Am. Chem. Soc., 2009,* **131,** 6050
23 C. I.Wu, Y. Hirose, H. Sirringhaus, A. Kahn, *Chem. Phys. Lett., 1997* **272,** 43

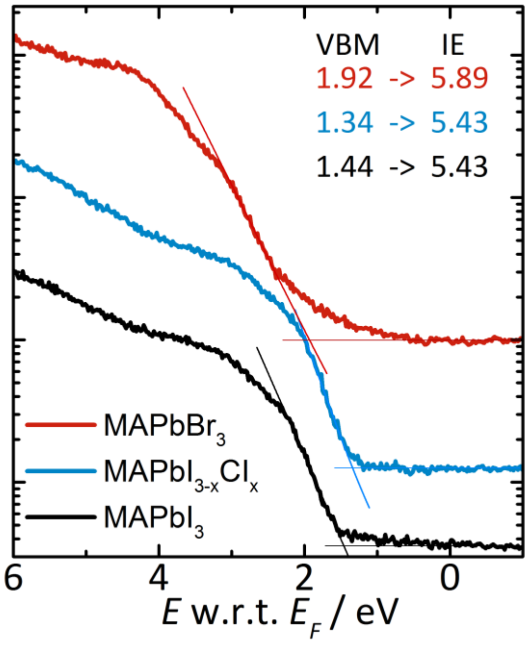

Figure S1: UPS spectra (He I) of the bare perovskite layers on TiO_2, taken with proportional gain in log scale that allows a precise location of the VBM position. In the $MAPbBr_3$ case, a significant density of tail states is observed in the gap of the material.

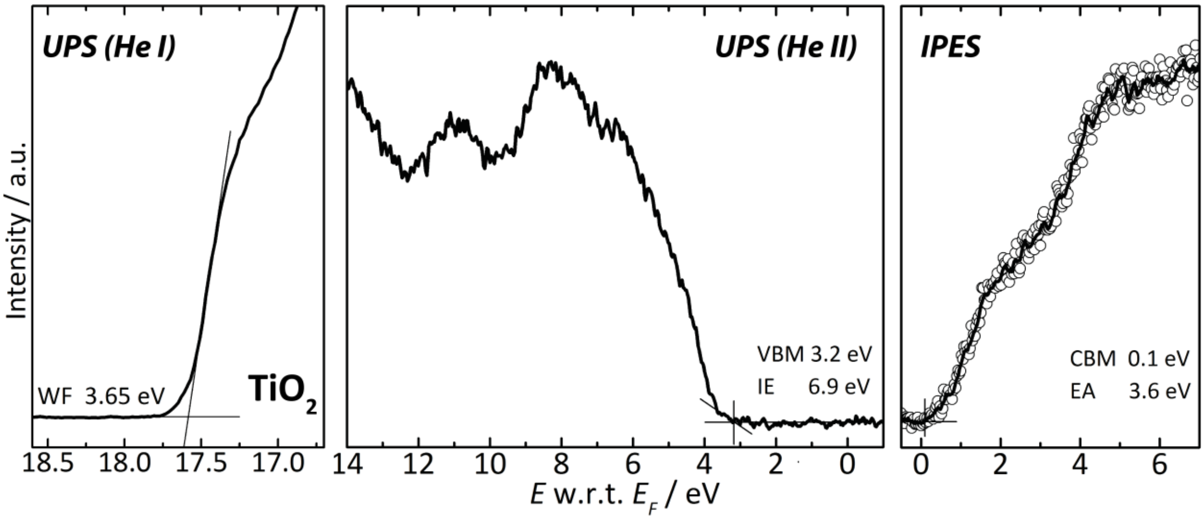

Figure S2: UPS/IPES spectra of TiO_2 on FTO. UPS and IPES measurements were performed on dense TiO_2 layers from spray pyrolysis after annealing and without any further treatment or cleaning step, to capture the electronic properties of the film as used before the preparation of the subsequent perovskite layer.

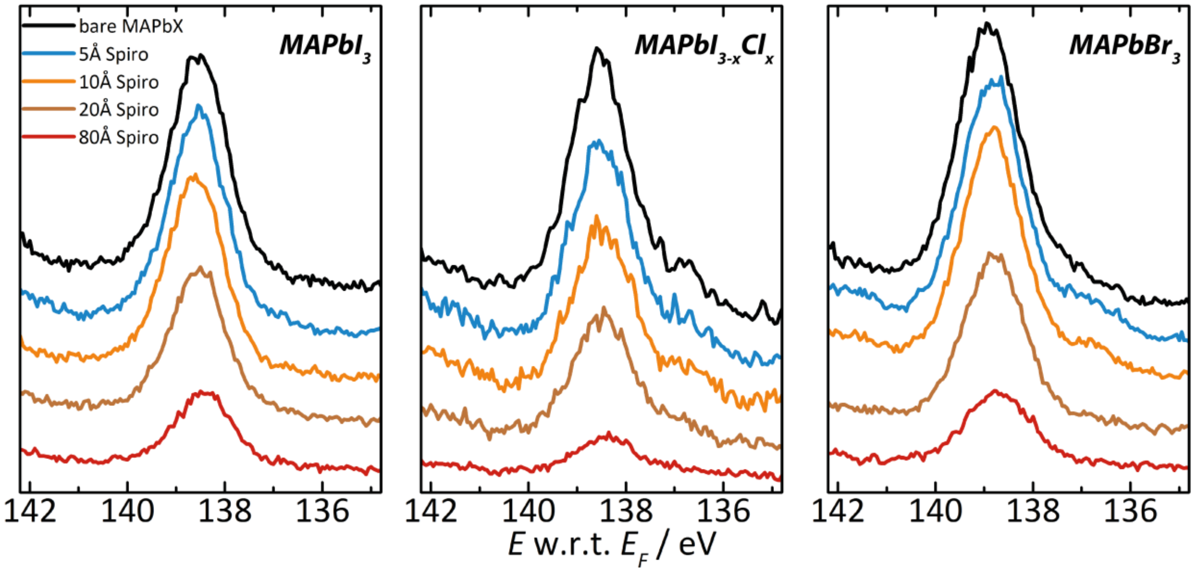

Figure S3: XPS spectra of the Pb $4f_{7/2}$ core level for $MAPbI_3$, $MAPbI_{3-x}Cl_x$ and $MAPbBr_3$, bare and with increasing thicknesses of spiro-MeOTAD. The decrease of the Pb $4f_{7/2}$ signal intensity reflects the increasing thickness of the organic film, while the fixed peak position gives clear evidence for the absence of band bending within the perovskite layer.

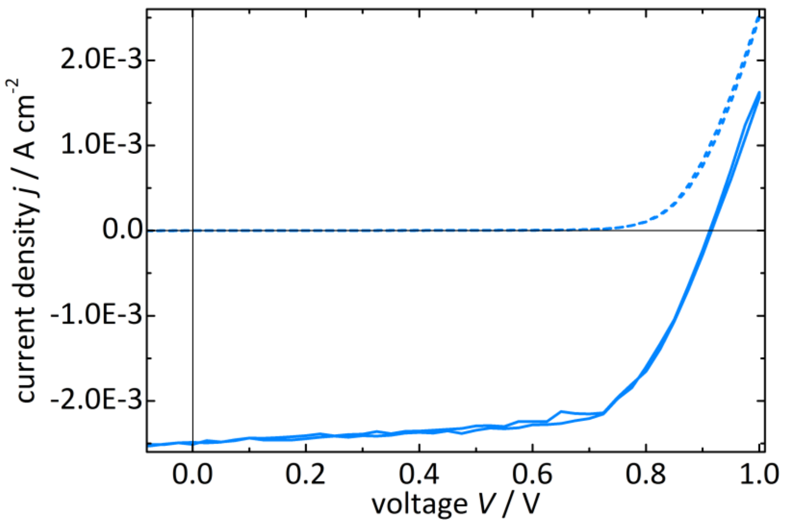

Figure S4: j-V characteristics (dashed: dark, solid: illuminated) of a solar cell comprising a FTO/TiO_2/$MAPbBr_3$/spiro-MeOTAD/Ag layer stack. We find V_{OC} values at 0.9 V which is in the limits that are given by the alignment of the HOMO level of the HTM with respect to the VBM of the perovskite.

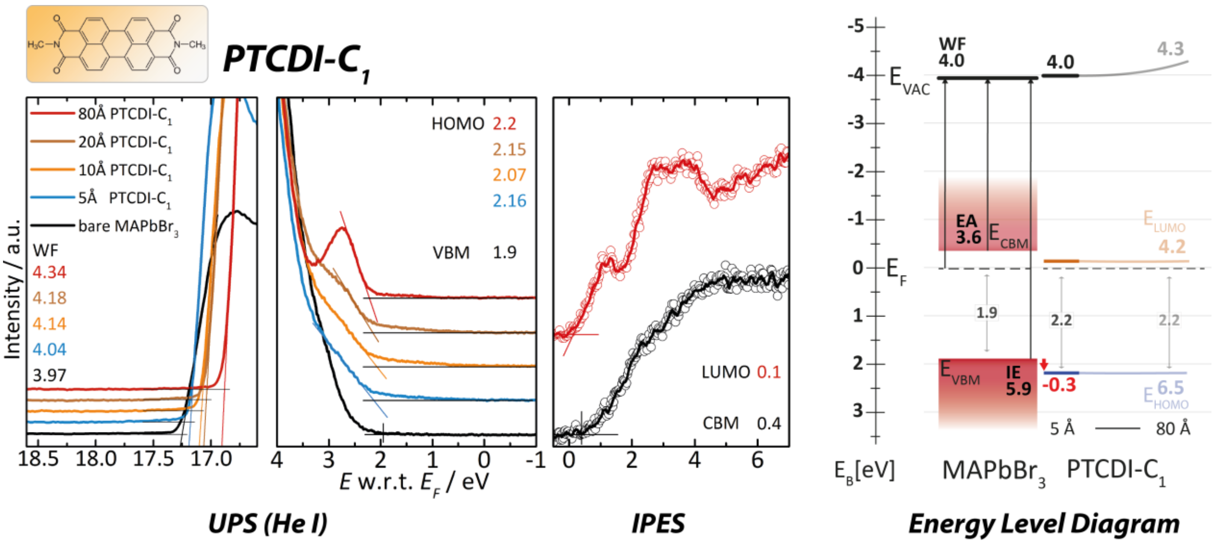

Figure S5: UPS/IPES spectra of N,N'-Dimethyl-3,4,9,10-perylenedicarboximide (PTCDI- C_1) on top of $MAPbBr_3$ on TiO_2. No significant interface dipole is observed. The emergence of the molecular levels is clearly monitored in the photoemission spectra. The Fermi level is pinned to the LUMO of the acceptor-type molecule. This defines the offset between the PTCDI-C_1 HOMO and the perovskite VBM. No band bending is seen throughout the organic layer, but the vacuum level gradually shifts upwards, with the IE and EA of the molecular film reaching their equilibrium value at a thickness of 8 nm. In contrast to the case of spiro-MeOTAD HTL on $MAPbBr_3$ the position of the HOMO level at the PTCDI-C_1 / perovskite interface does not constrain the maximum attainable built-in potential. However, the small hole extraction barrier (0.3 eV) and absence of an electron-blocking barrier between the perovskite CBM and the organic LUMO likely lead to losses in V_{OC} and J_{SC}.