Supporting information for:

The role of dimethylammonium in bandgap modulation for stable halide perovskites

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Materials and Methods

Perovskite precursor solutions

All perovskite precursor chemicals were used as received and stored inside a nitrogen glovebox. Perovskite solution preparation and film deposition was conducted in a nitrogen glovebox.

Wide gap perovskite precursor solutions were prepared by dissolving Formamidinium Iodide (Greatcell), Dimethylammonium iodide (Sigma), Cesium Iodide (Sigma Aldrich), Lead (II) Iodide (TCI), Lead (II) bromide and Lead (II) Chloride (Alfa Aesar) to produce a 1M solution of $FA_xCs_{1-x-y}DMA_yPbI_{2.4}Br_{0.6}Cl_{0.02}$ in DMF:DMSO with a ratio of 3:1 v/v. We note that the small amount of Cl added is in stoichiometric excess.

Different cation compositions were prepared by changing the ratios of FAI, CsI, MAI and DMAI in the precursor solution detailed above. Everything else was kept the same.

Device and film fabrication

ITO-coated glass substrates (Thin Film Devices) were initially cleaned by sonicating in acetone, propan-2-ol, and then UV ozone treating for 10min.

PolyTPD (Poly(N,N'-bis-4-butylphenyl-N,N'-bisphenyl)benzidine, 1-material) was coated by spin-coating from a 1mg/ml solution in anhydrous chlorobenzene, at 4000rpm for 30s, depositing the solution dynamically, and then annealed at 110°C for 10 mins.

PFN-Br (poly[(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)], 1material)) was coated as a wetting layer by spin-coating a 0.5mg/ml solution in anhydrous methanol, at 5000rpm for 20s, depositing the solution dynamically.

The perovskite was deposited by spin-coating the solution described above at 5000rpm for 60s, spreading the solution on the substrate before spinning, and depositing 120uL of anhydrous methyl acetate onto the spinning wet film at 25s into the spin cycle. This protocol is the same for all compositions with the exception of the pure MA composition, which was spin-coated for only 30s. After finishing spinning, the film was then annealed at 120°C for 20min.

Following deposition of the perovskite film, a thin (1nm) layer of lithium fluoride was deposited by thermal evaporation at a rate of 0.1Å/s. 30nm of C_{60} (Lumtec) was then deposited by thermal evaporation at a deposition rate of 0.2Å/s for the first 10nm and 0.5Å/s for the remaining 20nm.

A 6nm layer of bathocuproine (BCP, Sigma) and 100nm of gold or silver (gold for stability testing) were then deposited to finish the devices, (Kurt J. Lesker) both by thermal evaporation.

Perovskite films were deposited by following the above recipe for the perovskite film on UVO-cleaned glass.

Current-voltage characteristics measurement

Solar cells were tested on an Oriel Sol3A class AAA solar simulator from Newport inside a nitrogen glovebox, using a shadow mask with aperture area 0.058cm². Lamp intensity was calibrated using short-circuit current produced in a calibrated KG2-filtered silicon photodiode. A Keithley 2450 source unit was used to sweep voltage and measure current; devices were scanned at a rate of 0.4V/s.

X-ray measurements

High resolution X-ray diffraction data were collected at SSRL beamline 2-1 with an X-ray wavelength of 0.9913Å (12.5keV). Samples were measured under helium and the scattered X-rays detected by a Pilatus 100K detector at a distance of 700mm from the sample. Samples were measured in a grazing incidence geometry with an incidence angle of 3° to maximize the diffraction signal. As grazing incidence measurements project the X-ray beam footprint onto the detector, leading to a geometric peak broadening which increases at higher angles, data with less broadening due to geometric effects was collected under a nominal θ -2 θ geometry, with the sample angle at half of the scattering angle for the center of the detector to obtain more reliable peak shapes. The instrumental response was determined using diffraction collected from a sample of NIST SRM-1976b, a sintered plate of Al₂O₃. Lattice parameters were determined from a Rietveld refinement performed using TOPAS-Academic.¹ Structures were refined from the grazing incidence data.

All structures were refined in space group P_4/mbm . Structures included a single Pb atom with anisotrpic thermal parameters located at the origin and two different halide positions. The halides were modeled as iodine and bromine with fractional occupancies fixed at their nominal values and constrained to have the same fractional coordinates and thermal parameters for the iodine and bromine atoms. The A-site was modeled with Cs, FA, and DMA using fractional occupancies. The Cs atoms were modeled with an isotropic thermal parameter. Both the FA and DMA were modeled as z-matrices with internal degrees of freedom (bond lengths and angles) fixed at their nominal values. All atoms in either the FA or DMA molecule were refined with a common isotropic thermal parameter. Best fits required inclusion of a preferred orientation correction, modeled as spherical harmonics as well as the inclusion of a small sample displacement correction. Both of these corrections were found to have minimal influence on either the refined lattice parameters or the calculated octahedral tilt angles, defined as as 180° minus the Pb-I-Pb angle in the *ab* plane (the tilt system was assumed to be $a^0a^0c^+$, so that the only tilt is around the *c*-axis). Uncertainties were determined using a bootstrap approach as implemented in TOPAS-Academic.

¹H-NMR

NMR spectra were taken by dissolving perovskite material scraped off fabricated films in d6-DMSO. Spectra were recorded using a JEOL ECA-500 at 25 $^{\circ}$ C, and referenced to residual *d6*-DMSO solvent peak.

Density measurements

Density measurements were taken by Micromeritics Instrument Corp using gas pycnometry. This consists of determining the volume occupied by the powdered sample by measuring the gas pressure when filling a chamber of known volume with inert gas. It provides the 'true', or skeletal density, and is not affected by the porosity of the sample.

Stability measurements

For the elevated temperature thermal stability measurements, cells were placed on a covered aluminumtopped hotplate at 85°C in a nitrogen-filled glovebox and tested as per above at various intervals. The uniformity of the hotplate was measured and confirmed to hold the cells within ±5°C regardless of their position on it. 3-6 devices of each type were tested, and we have plotted the stability data for the champion devices in the main text. Averaged values are shown in the SI (Fig S8).

For the constant illumination stability measurements, solar cells were loaded into a custom-built degradation testing setup. In this study, devices were kept in a sealed flow chamber under N_2 flow, underneath a sulfur plasma lamp at ~0.8 suns and held under a resistive load of 510 Ohms. Every 30 minutes, the system removes the resistive load and takes a JV scan using a Keithley 2450 source-measure unit. JV curves are then analyzed to extract relevant parameters. Cell temperature was controlled using a chiller that flowed water through copper piping within the sealed chamber, thermally connected to the cells via the aluminum cell housing. We note that in the study here, the chiller temperature was set to 70°C, but the measured cell temperature (with a thermocouple) was at 60°C due to imperfect thermal contact with the devices.

Absorbance & PL measurements

UV-Vis absorbance was measured using a Varian UV-Vis spectrophotometer with an internally coupled integrating sphere.

Photoluminescence of films was measured using a supercontinuum fiber laser (NKT Photonics, Super K) operating at 5 MHz as the excitation source. Films were excited at 500 nm at a low fluence ($< 10^{15}$ s⁻¹) and a Hamamatsu C10910–04 streak camera was used to collect the spectra.

Supplementary Figures



Fig S1: Photoluminescence spectra for perovskite thin films of FA67Cs33, FA80Cs20, and DMA10FA60Cs30.



Fig S2: NMR spectrum for DMAI reference, including integrated peak intensities (blue).



Fig S3: Full NMR spectra for perovskites with (above) and without (below) DMA, including integrated peak intensities (blue). While the DMA methyl peak at 2.55 is observed, the NH2 peak at ~8.1 is not seen. We show below (Fig S4) that when adding more DMAI it becomes observable but weaker and more broadened than the neat DMAI, and is likely thus not observable in the spectrum above due to hydrogen bonding effects in solution. For DMA10FA60Cs30, ratioing the intensity of the dimethylamine methyl peak at 2.55 (6 H's) and the FA methyl peak at 7.84 (1 H) gives ~1:6 DMA:FA molecules in this film.



Fig S4: NMR spectra for DMA-containing perovskite plus DMAI spike. The NH peak becomes weakly observable (see inset) at 8.2 with high DMA content.



Fig S5: Microstrain determined by Williamson-hall analysis of the X-ray diffraction data for the strategy of adding both DMA and Cs into FA80Cs20 (DMA-SC, black), and of adding only DMA to FA67Cs33 (DMA-CR, red). Error bars are determined from the error in the linear fit to the Williamson-hall plot.



Fig S6: Williamson-hall plots for the XRD data analyzed above. We note that for this analysis X-ray data was converted into the 2theta equivalent for Cu K α radiation for easier comparison with literature data.



Fig S7: Absorbance spectra for hollow perovskites made using EN, as per Kanatzidis et al.



Fig S8: a) XRD of degraded FA67Cs33 and MA films, held at 85C for 700h in N_2 . b) zoom-in of the region around the delta phases, PbI_2 , and perovskite peaks.



Fig S9: Plots of bandgap versus octahedral tilt as extracted from literature sources.^{2–4} We have plotted only the data which exists for materials that do not undergo a phase transition.

Material systems are: ref 2 – 3D tin iodide based perovskites (experimental data); ref 3 – 2D lead iodide based perovskites (experimental data); ref 4 – 3D lead iodide perovskites (computationally determined).



Fig S10: PCE values for thermal aging data, averaged across all functioning devices of each type (3-6 in each case).

References

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