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Supporting Information

Heavy water additive in formamidinium: A novel approach to enhance the perovskite solar cell efficiency.

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(a)

(b)

Figure S1. (a) Cross sectional SEM image of the complete PCS device with 1 vol% D₂O (1 vol%). (b) J-V curves of the PSCs with 0.5, 2, and 4 vol% of D₂O measured under 1 sun illumination.

Figure S2. Statistical photovoltaic data for (a) V_{oc} , (b) J_{sc} , (c) FF and (d) PCE for the PSCs prepared with perovskite solution containing 0 (reference), 0.5, 1, 2, 4 vol% D₂O and 1 vol% H₂O. (e) Stability test under 1 Sun continuous illumination (devices were stored in N₂ glovebox without encapsulation during the stability test), (f) I - V hysteresis for the device prepared with 1 vol% H₂O additive (HI – 1.7) for comparison.

Figure S3. Atomic Force Microscopy (AFM) morphology images of thin films prepared with perovskite solution added with (a) 0%, (b) 0.5%, (c) 1% (d) 2% and (e) 4% D₂O concentration by volume.

Figure S4. UV-Vis absorption spectra of thin films prepared with the different concentrations of D₂O added perovskite solutions.

Figure S5. (a) X-ray diffraction patterns and (b) full width half maxima (fwhm) of thin films prepared with the different concentrations of D₂O added perovskite solutions.

Figure S6.(a) Photoluminescence (PL) spectra of perovskite film with 0 and 1, 4 % D_2O and 1% H_2O by vol. PL quenching by PCBM and PTAA layer on perovskite film with (b) 0, (c) 1, (d) 4 % D_2O and (e) 1 % H_2O added by vol. and (f) Time resolved PL lifetime of perovskite films: control (0%; black square), 1 vol% (blue circle), 4 vol% and (magenta triangle) D_2O concentration and 1% H_2O (purple inverted triangle)

Figure S7. Diffusion length measurements of the in the perovskite films with varying D₂O additive concentrations: (a) 0, (b) 1, (c) 4 vol% D₂O and (d) 1% H₂O with the respective quencher (black: bare film, red: PCBM layer, blue: PTAA layer) measured at a fluence of 0.5 $\mu\text{J cm}^{-2}$. Symbols are the data obtained from time resolved PL measurements while solid lines are exponential fits.

Figure S8: The optimized crystal structure of FAPbI₃ in the cubic phase.

Figure S9: The optimized crystal structures of MAPbI₃. (a) side-view (b) top-view

Figure S10: The calculated phonon dispersion of $(\text{CH}_3\text{NH}_3)\text{PbI}_3$ and $(\text{CH}_3\text{NH}_2\text{D})\text{PbI}_3$.

Figure S11: THz transmission spectra of perovskite films coated on z-cut quartz substrates.

Table S: Summary of TRPL lifetime and hole mobility in perovskite thin film with different D₂O concentrations. Lifetime was calculated through bi-exponential function fitting. Mobility was calculated using the equation $\mu = L^2 / \tau_d kT$, where μ, L and τ_d are the charge carrier mobility, hole diffusion length and lifetime respectively, while kT represents the room temperature energy.

Perovskite + D₂O additive conc.	A1	τ_1 (ns)	A2	τ_2 (ns)	Hole mobility ($\times 10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)
0%	0.29	8.2	0.2	71.5	12 ± 2
1% D₂O	0.28	8.8	0.17	178	72 ± 7
4% D₂O	0.29	8.4	0.2	94	48 ± 5

Supporting Notes

Supporting Note 1. UV- Absorption

UV-vis absorption measurements show a rise in photon absorption with the increase of D₂O concentration probably due to the extended grain size parallel to the substrate below the top surface, though it mainly occurs below 600 nm as shown in **Figure S4**. The onsets of the absorption edges of all the spectra nearly overlap at around 799 nm (or 1.55 eV). The bandgap of hybrid perovskite materials is mainly determined by the inorganic lead halide formulation by the dominant transition from I 5p to Pb 6p orbital.⁴⁻⁵ The close overlap of the absorption edges between the reference and D₂O added films is attributed to the steady band gap in these films. The incorporation of D₂O does not influence the bandgap nor the absorption edges.

Supporting Note 2. X-ray Diffraction Patterns

Figure S5 shows the XRD patterns of these films coated on glass substrates, consistent with the previous reports.^{1, 6} The presence of diffraction peaks at $2\theta = 13.0^\circ$ and 26.45° in standard perovskite film indicates the presence of hexagonal phase of PbI₂, affirm the use of excess PbI₂ as discussed in the methods section. The absence of these XRD peaks in D₂O added films confirm the incorporation of excess PbI₂ into black perovskite phase. Moreover, the resemblance of the XRD patterns of standard and D₂O added samples shows that D₂O does not influence the crystal structure and orientation of perovskite.

Supporting Note 3. NMR Spectroscopy

NMR Spectroscopy: The multinuclear solid state Magic Angle Spinning (MAS) NMR data were acquired at 14.1 T using a wide bore Bruker Avance III-600 spectrometer operating at the ¹H, ¹³C and ²H Larmor frequencies of 600.13, 150.93 and 92.13 MHz, respectively. The reference and deuterated powder samples of (FA_{0.83}MA_{0.12}CS_{0.05})Pb(I_{0.88}Br_{0.12}) were obtained by scraping thin-films and were center packed in 4 mm ZrO₂ rotors using Teflon tape as filler and capped with Kel-F caps. A Bruker 4 mm HX MAS probe was used to enable an MAS rate of 12 kHz for this study. A ‘non-selective’ (solution) ²H $\pi/2$ pulse length of 6.7 μ s was calibrated using D₂O from which a ‘selective’ (solids) $\pi/2$ pulse length of 4.47 μ s was derived

for the ^2H ($I = 1$) nucleus. All ^2H NMR data were measured using single pulse experiment using a $\pi/3$ pulse length of $3.13\ \mu\text{s}$ and a recycle delay of 10 s. A corresponding ^1H $\pi/2$ pulse length of $3.3\ \mu\text{s}$ was calibrated using solid adamantane, and all ^1H MAS NMR data were acquired using a single pulse experiment with a $\pi/2$ excitation pulse of $3.3\ \mu\text{s}$ and a recycle delay of 300 s. The ^2H and ^1H T_1 relaxation times were measured using the saturation recovery pulse experiment with the long recycle delay times ensuring that all MAS NMR data afforded a quantitative survey of the speciation in each case. The ^{13}C MAS NMR data were acquired using a cross-polarisation experiment which used an initial ^1H $\pi/2$ pulse time of $3\ \mu\text{s}$, a ^1H - ^{13}C Hartmann-Hahn contact period of 4 ms, high power ^1H decoupling of 80 kHz during data acquisition, and a recycle delay of 60 s. All ^1H and ^{13}C chemical shifts were calibrated against the IUPAC reference TMS ($\delta_{\text{iso}} = 0.0\ \text{ppm}$) via a secondary solid adamantane reference ($\delta_{\text{iso}} = 1.9\ \text{ppm}$ for ^1H ; $\delta_{\text{iso}} = 37.7\ \text{ppm}$ for ^{13}C).⁷ The resonances in ^1H MAS NMR spectra were integrated using Topspin 3.5 and deconvoluted using DMFit software packages.⁸ The integrated intensity in the region 2-5 ppm was assigned to the methyl group of MA and the region from 5-10 ppm was assigned to FA and NH_3 group of MA. The integrated intensities from the deuterated samples were corrected to account for the deuterated sites assuming that the isotope exchange reached equilibrium. The relative ratio of MA and FA was obtained using the following formula:

$$\text{Number of MA} = \frac{\text{Intensity from CH}_3}{3}$$

$$\text{Number of FA} = \frac{\text{Intensity from NH}_3, \text{FA} - \text{Intensity from NH}_3}{5}$$

DFT Calculations: Here, we employed the all-electron-like projector augmented wave (PAW) method¹ and the Perdew-Burke-Ernserhof (PBE) exchange-correlation potential⁹ as implemented in the VASP code¹⁰ *to calculate the phonon dispersion curves and IR spectra of cubic FAPbI₃*. The semicore of Pb atoms (5d orbital) was treated as valence electrons, *i.e.*, 14 valence electrons for Pb (5d¹⁰6s²6p²) atom. The cut-off energy for the plane wave expansion of the wave functions was 800 eV. The primitive cell was completely optimized, including its lattice vectors and atomic positions. The Hellman-Feynman forces were less than 1 meV/Å. The 6×6×6 Monkhorst-Pack grid of k-points¹¹ for Brillouin zone integration of MAPbI₃ was used in the optimization of crystal structure. The optimized lattice parameters are 6.532 Å and

the optimized crystal structure is shown in Figure S5. The phonon spectrum within the harmonic approximation was calculated using the PHONONPY code.¹² In the phonon calculations, we used a $2 \times 2 \times 2$ supercell to ensure that the boundary atoms were not affected by the atomic displacement. The force constants were constructed based on the density functional perturbation theory (DFPT) approaches.

*To calculate the phonon spectra of tetragonal $(\text{CH}_3\text{NH}_3)\text{PbI}_3$ and $(\text{CH}_3\text{NH}_2\text{D})\text{PbI}_3$, we employed the all-electron-like projector augmented wave (PAW) method¹ and the Perdew-Burke-Ernserhof revised for solids (PBE sol) exchange correlation potential² as implemented in the VASP code. The semicore of Pb atoms (5d orbital) was treated as valence electrons, *i.e.*, 14 valence electrons for Pb (5d¹⁰6s26p2) atom. The cut-off energy for the plane wave expansion of the wave functions was 800 eV. The primitive cell was completely optimized, including its lattice vectors and atomic positions. The Hellman-Feynman forces were less than of 1 meV/Å. The $5 \times 5 \times 3$ Monkhorst-Pack grid of k-points for Brillouin zone integration of MAPbI₃ was used in the calculations of structure optimization. The primitive unit cell of MAPbI₃ is tetragonal with space group I4/mcm (D_{4h}^{18}). Their optimized lattice parameters are as follows: $a_0 = 8.721$ Å, $b_0 = 8.694$ Å, $c_0 = 12.837$ Å, while the experimental values are 8.85, 8.85 and 12.64 Å respectively³. The optimized crystal structure is shown in Fig. S9. We used the Phonopy code⁶ to calculate the phonon spectrum within the harmonic approximation. A $2 \times 2 \times 1$ supercell was employed to ensure that the boundary atoms were not affected by the effects of the atomic displacement. The force constants were constructed based on the density functional perturbation theory approaches. The calculated phonon dispersion is shown in Fig. S10. We find that the deuterium atom does not affect the frequencies of phonons lower than 100 cm⁻¹. However, the influence of the deuterium atom to the LO phonons of the inorganic ions is quite small.*

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