

Supporting Information

Deuterated N,N-dimethylformamide (DMF-d7) as An Additive to Enhance CsPbI₃ Solar Cell Efficiency

Youkui Xu^{1,#}, Yingtao Li^{1,#}, Yutian Lei¹, Qian Wang^{1,}, Huanhuan Yao¹, Xufeng Zhou², Qing Zhou^{3,*}, Zhipeng Ci^{1,*} and Zhiwen Jin¹*

[#]These authors contributed equally to this work

Dr. Y. Xu, Prof. Y. Li, Dr. Y. Lei, Prof. Q. Wang, Dr. H. Yao, Prof. Z. Ci, Prof. Z. Jin
¹School of Physical Science and Technology & School of Materials and Energy & Key Laboratory for Magnetism and Magnetic Materials of MoE, Lanzhou University, Lanzhou 730000, China

Dr. X. Zhou

²School of Material Science and Engineering, Liaocheng University, Liaocheng 252000, China

Dr. Q. Zhou

³School of Science, Minzu University of China, Beijing 100081, China

E-mail: qianwang@lzu.edu.cn, zhouqing86@iccas.ac.cn, cizhp@lzu.edu.cn

Keywords: Additive, CsPbI₃, DMF-d7, Hydrogen isotope effect

Experimental Section

Solution Preparation Section

Materials Preparation: lead (II) iodide (PbI_2 , >99.99%) and cesium iodide (CsI , $\geq 99.99\%$) were purchased from Xi'an Polymer Light Technology corporation. N,N-Dimethylformamide (DMF, 99%), N,N-Dimethylformamide-d7 (DMF-d7, $\geq 95\%$) were purchased from Alfa Aesar.

DMAI Synthesis: Hydriodic acid (HI 99%) and DMF were stirred in a 250 mL round bottom flask according to the molar ratio of 2:1 in an ice bath for 4 h. After stirring at 0 °C for 4 h, the resulting solution was evaporated by rotary evaporation at 65°C, then putting into a refrigerator for 2 hours to crystallize white crystals. The solid product was washed several times with diethyl ether and then was dissolved in ethanol, recrystallized from diethyl ether several times. Then, the solid product was dissolved in ethanol again and evaporated by rotary evaporation at 65°C and then vacuum-dried in 60°C. Finally, the solid product DMAI was obtained.

Precursor Solution Preparation: The CsPbI_3 precursor solution were formed by dissolving CsI (0.156 g), DMAI (1.1661 g) and PbI_2 (0.2766 g) in 1ml DMF solution under continuous stirring for 2 h.

HTL Solution Preparation: A solution was prepared by dissolving Spiro-OMeTAD (72 mg), a sulfonyl imide (Li-TFSI, 18 μL) solution (520 mg Li-TFSI in 1 mL acetonitrile) and tert-butylpyridine (TBP, 29 μL) in 1 mL of Chlorobenzene (CB) solution.

Device Fabrication Section

Preparation of TiO_2 -blocking layer: the purchased FTO glass (2.2 mm) was cleaned by acetone, isopropanol and ethyl alcohol with ultra-sonication for 30 min, then dried by the dry air and treated with O_2 plasma for 5 min. Afterwards, the FTO glasses were immersed in 200 ml TiCl_4 aqueous solution at 70°C for 60 min and washed with distilled water and ethanol. The compact TiO_2 film was formed after annealing at 200°C for 30 min.

Perovskite Film Fabrication: The perovskite precursor solution was coated on TiO_2 substrate by one-step spin-coating method at 1000 rpm for 10 s and 3000 rpm for 30 s, respectively. The final films were formed after annealing at 210°C for ~9 min.

Assembly of Solar Cells: The hole transport layer was coated on perovskite film by spin-coating at 5000 rpm for 30 s. Finally, MoO_3 (20 nm) and Ag (30 nm) were evaporated on prepared film.

Characterization Section:

SEM and Contact angle: The film surface morphology was characterized by FE-SEM

(Apreo S). Contact angle was measured via SZ-CAMB1.

Absorbance, PL, FTIR, TRPL, and Raman: Absorbance spectra was collected using a FLS920T. The PL spectra was measured using a PicoQuant Fluo Time 300. The source light was a xenon short arc lamp. FTIR spectra was measured using a NEXUS 670. The TRPL was measured using a PicoQuant FluoQuant 300. The Raman spectra was measured using a HR800.

XRD and XPS: XRD patterns of the samples were obtained using a Bruker D2 PHASER Diffractometer with the Cu K α line. The XPS measurements were performed in a Kratos AXIS Ultra DLD system with monochromatized Al K α radiation at a pressure of 5.0×10^{-7} Pa.

J-V and EQE: The J-V measurement was performed via the solar simulator (SS-F5-3A, Enlitech) along with AM 1.5G spectra whose intensity was calibrated by the certified standard silicon solar cell (SRC-2020, Enlitech) at 100 mV/cm². This used reverse scan mode (from V_{OC} to I_{SC}) and forward scan mode (from I_{SC} to V_{OC}) with a scan rate of 30 mV/s. The EQE data were obtained by using the solar-cell spectra-response measurement system (QE-R3011, Enlitech).

Calculation Section (Method and Model):

The density-functional theory (DFT) calculations were performed using the Vienna Ab initio Simulation Package (VASP). The projected augmented wave (PAW) method and the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) were employed to describe the interaction between ion-cores and valence electrons and the exchange-correlation effects, and an energy cut off of 500 eV was set for the plane-wave function's expansion. We build a supercell with 208 atoms for the relevant calculations with CsI as the crystal termination surface, and a supercell with 192 atoms for for the relevant calculations with PbI₂ as the crystal termination surface.

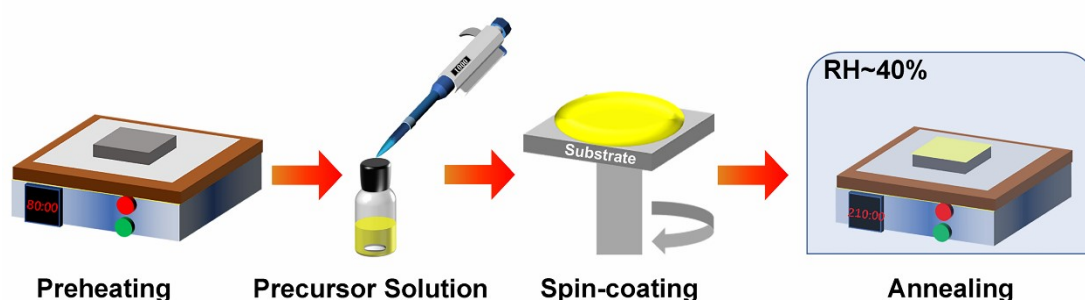


Figure S1. Schematic diagram of the preparation process of CsPbI₃ film.

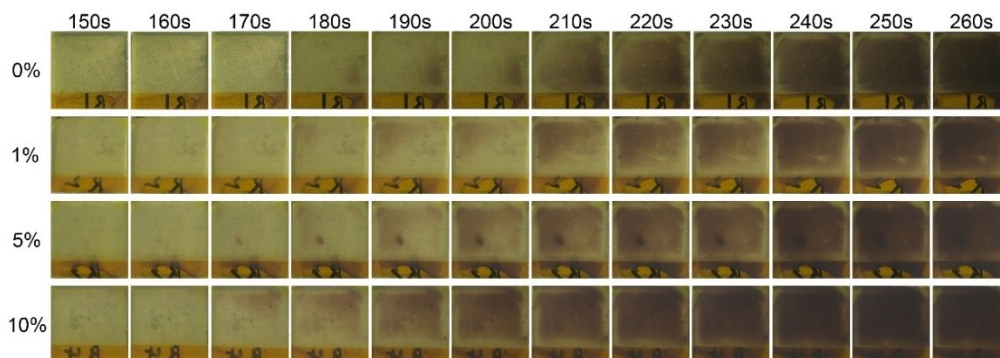


Figure S2. Color change of CsPbI₃ film with different DMF-d₇ concentration during annealing.

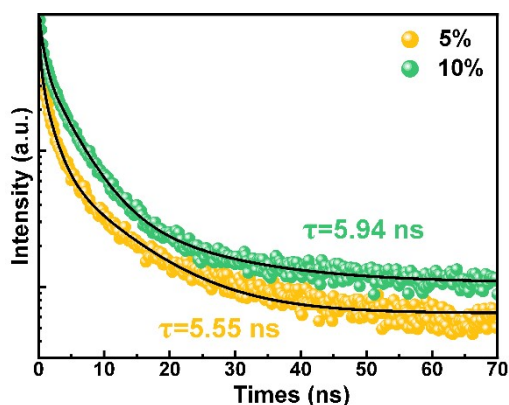


Figure S3. TRPL spectra with 5 and 10% DMF-d₇ addition.

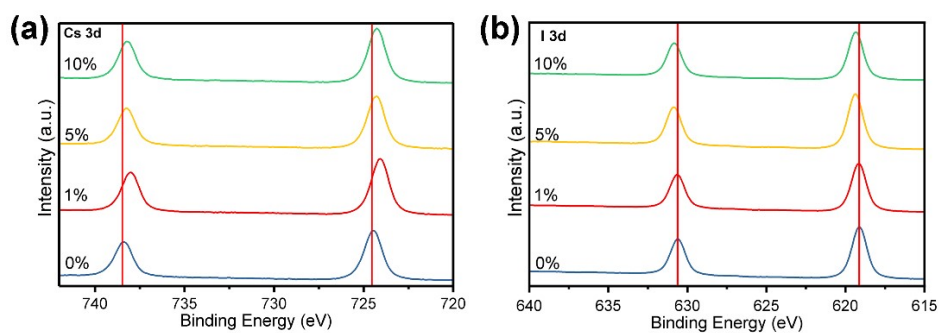


Figure S4. XPS spectra and high-resolution XPS spectra of (a) Cs 3d and (b) I 3d.

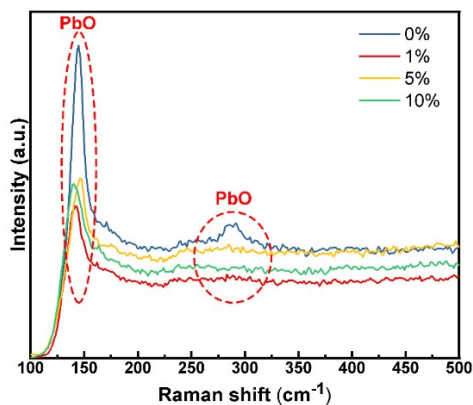


Figure S5. Raman spectra of the CsPbI₃ films with different DMF-d₇ concentration.

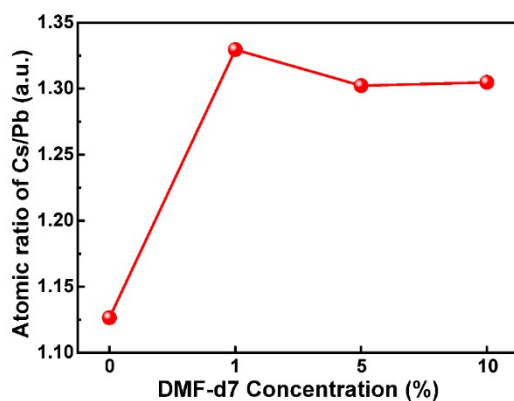


Figure S6. Atomic ratio of Cs to Pb (Cs/Pb) on the CsPbI₃ perovskite film surface with different DMF-d7 concentration.

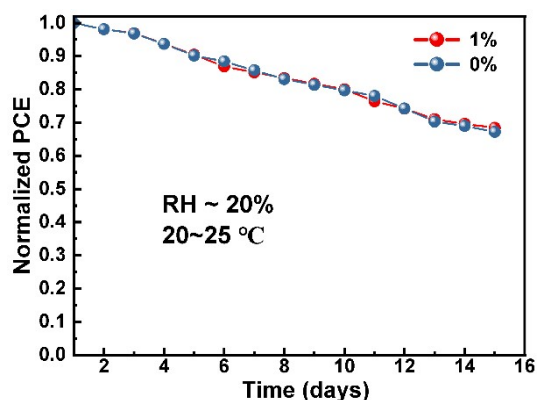


Figure S7. Normalized PCE of the pristine and optimal PSCs as a function of storage time in a dry box under $\sim 20\%$ RH and room temperature.

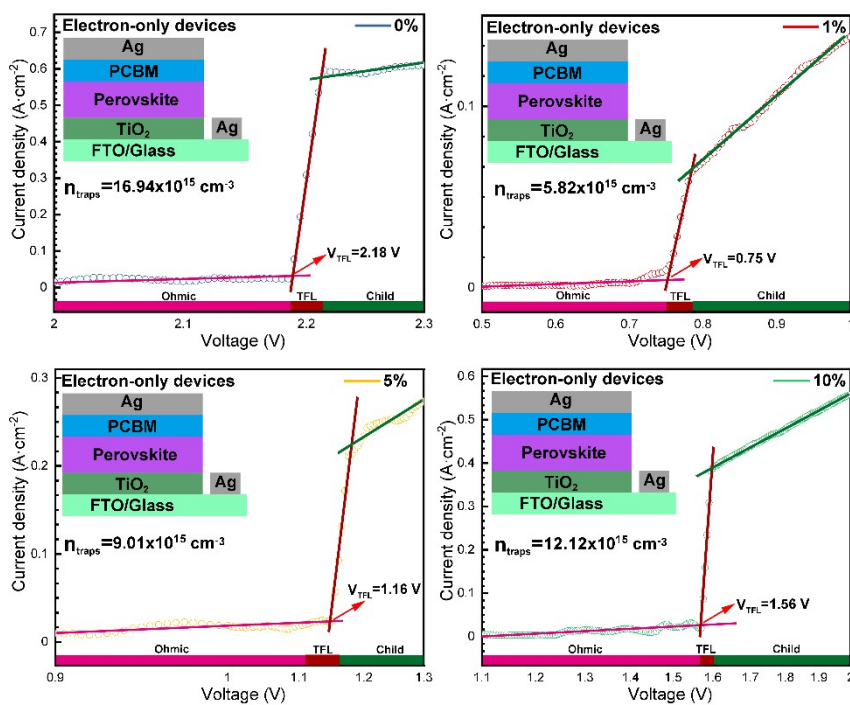


Figure S8. Electron-only device dark J–V measurements of the CsPbI₃ films with different DMF-d7 concentration.

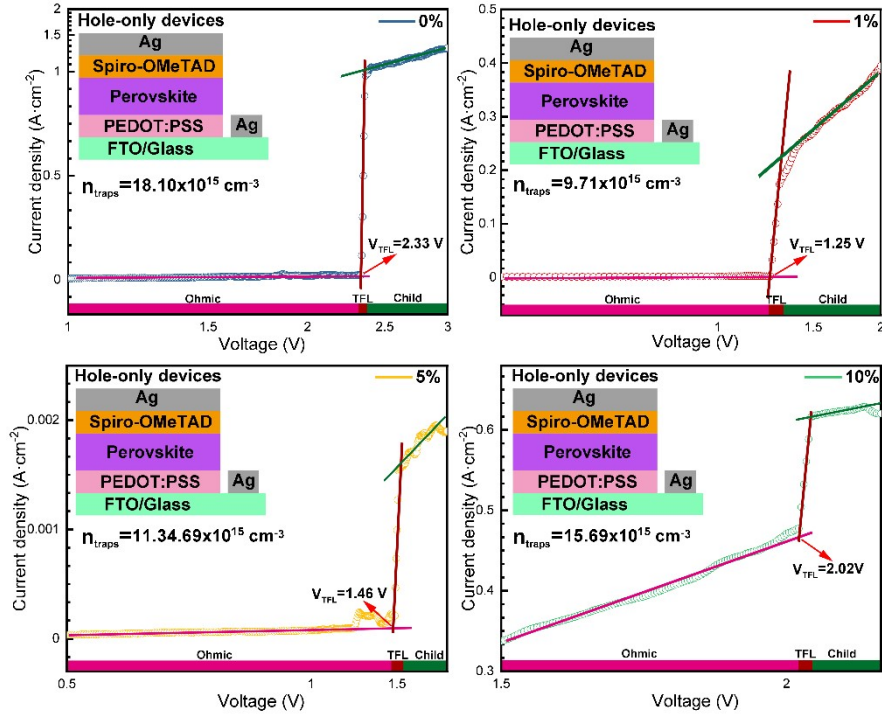


Figure S9. Hole-only device dark J-V measurements of the CsPbI₃ films with different DMF-d7 concentration.

Table S1. Key parameters of TRPL of the CsPbI₃ films with different DMF-d7 concentration (extracted from Figure 3c and S3)

Concentration	τ_1 (ns)	A1	τ_2 (ns)	A2	τ_3 (ns)	A3	τ_{ave} (ns)
0%	4.26	4490.54	14.00	463.69	1.47	5095.50	3.29
1%	4.63	3138.38	19.45	620.61	1.31	6051.77	3.52
5%	0.31	4202.01	1.68	2995.86	9.28	765.11	5.55
10%	0.65	5888.78	4.03	3979.44	14.89	383.84	5.94