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Supplementary Information

In situ study on film formation mechanism of organic-inorganic hybrid perovskite solar cells: controlling the solvate phase by additive system

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Experimental

Material preparations. All additives and solvents were purchased from Sigma Aldrich and used without further purification. $PC_{61}BM$ (>99.5%) for ETLs was purchased from EM INDEX. PEDOT:PSS (Baytron P, AI 4083) was used for HTLs. The two precursor materials of CH_3NH_3I (Methylammonium iodide (MAI), Dyesol Ltd.) and PbI_2 (Lead (II) iodide, 99.9985% (metals basis), Alfa Aesar Co., Inc.) was used as received without further purification.

Fabrication of planar heterojunction PeSCs. Glass/ITO/PEDOT:PSS/$MAPbI_3$/$PC_{61}BM$/Al structured P-I-N PeSCs were fabricated in similar manner as our previous report[38]. First, Glass/ITO substrates (10 Ohm/sq, AMG Tech.) were cleaned with de-ionized water (10 min), acetone (10 min), and isopropyl alcohol (20 min) in a bath-type ultrasound. UV/O_3 treatment for 15 min was implemented after drying in an oven at 100 °C for 10 min. The PEDOT:PSS HTL (~40 nm) was spin-coated on the top of the cleaned ITO-coated glass substrates for 40 s at over 5,000 rpm and thermal annealing at 150 °C was implemented for 10 min in air. A 40 wt% perovskite solution composed of a 1:1 molar ratio of MAI:PbI_2 dissolved in DMF solvent in an N_2-filled glove box was used. For each additive, 60 µl was added to 1 ml of the 40 wt% DMF precursor solution and each additive/DMF mixed perovskite solution was deposited on top of a PEDOT:PSS layer at 5,000 rpm for 60 s with 3 s acceleration, followed by annealing at 100 °C for 5 min in an N_2-filled glove box. A PCBM solution (20 $mgml^{-1}$ dissolved in Chlorobenzene) was deposited on the prepared perovskite film as an ETL (~60 nm) at 700 rpm for 30 s and 2,000 rpm for 3 s without thermal annealing in an N_2-filled glove box. Finally, 100 nm-thick Al electrodes were deposited using a thermal evaporator at a 4 Å/s deposition rate and ~10^{-7} torr pressure.

Device measurement and characterization. The photovoltaic performances of PeSCs were evaluated by the current density–voltage (J–V) characteristics, which were measured under simulated AM 1.5 G conditions (100 mW/cm^2) with a Keithley 2400 instrument that had been calibrated with a Si reference cell (SRC-1000-TC-KG5-N, VLSI Standards. Inc.). The perovskite film images were obtained with an atomic force microscopy (AFM, Agilent 5400), scanning electron microscope (SEM, HITACHI S-4700), and optical microscopy (Nikon LV-100). *In situ* UV-Vis measurements under spin-coating conditions were obtained by F20-UVX spectrometer with a tungsten halogen light source (Filmetrics, Inc.) with an integration time of 0.5 s for each spectrum in an N_2-filled glove box. *In situ* UV-Vis is implemented exactly with the same spin-coating speed for device fabrications using 5000 rpm. *In situ* GIWAXS measurements were conducted at the Cornell High Energy Synchrotron Source (CHESS) on the D1 beam line. The measurements during spin-coating at 5,000 rpm were performed by customized spin-coating stage and controlled by the computer outside the hutch. Each 2 D GIWAXS data was obtained with a 0.2 s time interval until 300 s to observe the detailed information at room temperature. After dropping each precursor solution on the Glass/ITO/PEDOT:PSS substrate, *in situ* GIWAXS measurements started within 1 min. All *in situ* GIWAXS measurements were performed in an ambient atmosphere under > 20% relative humidity. The Lewis acid–base interaction between PbI_2 and solvents, and the Fourier Transform Infrared Spectroscopy (FT-IR, Bruker Tensor 27) of the attenuated total reflectance (ATR) mode was used to determine the wavenumber shift of the νC=O peaks. PbI_2 solutions with various additives were spin-coated on top of the glass substrate and scratched out through a blade to obtain the as-cast powder.

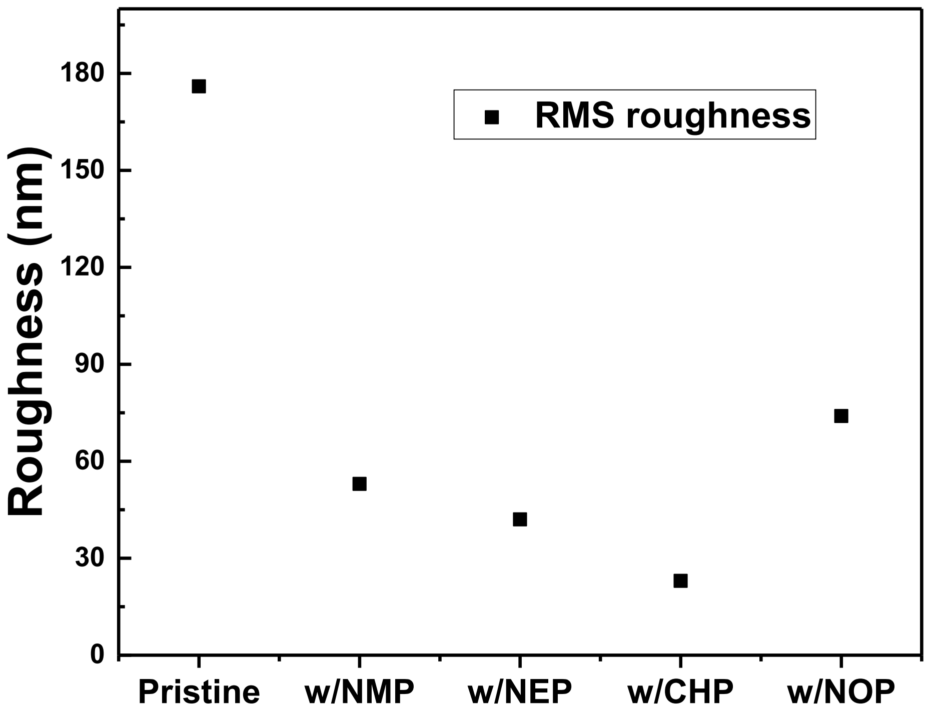

Figure S1 | RMS roughness graph of various perovskite films.

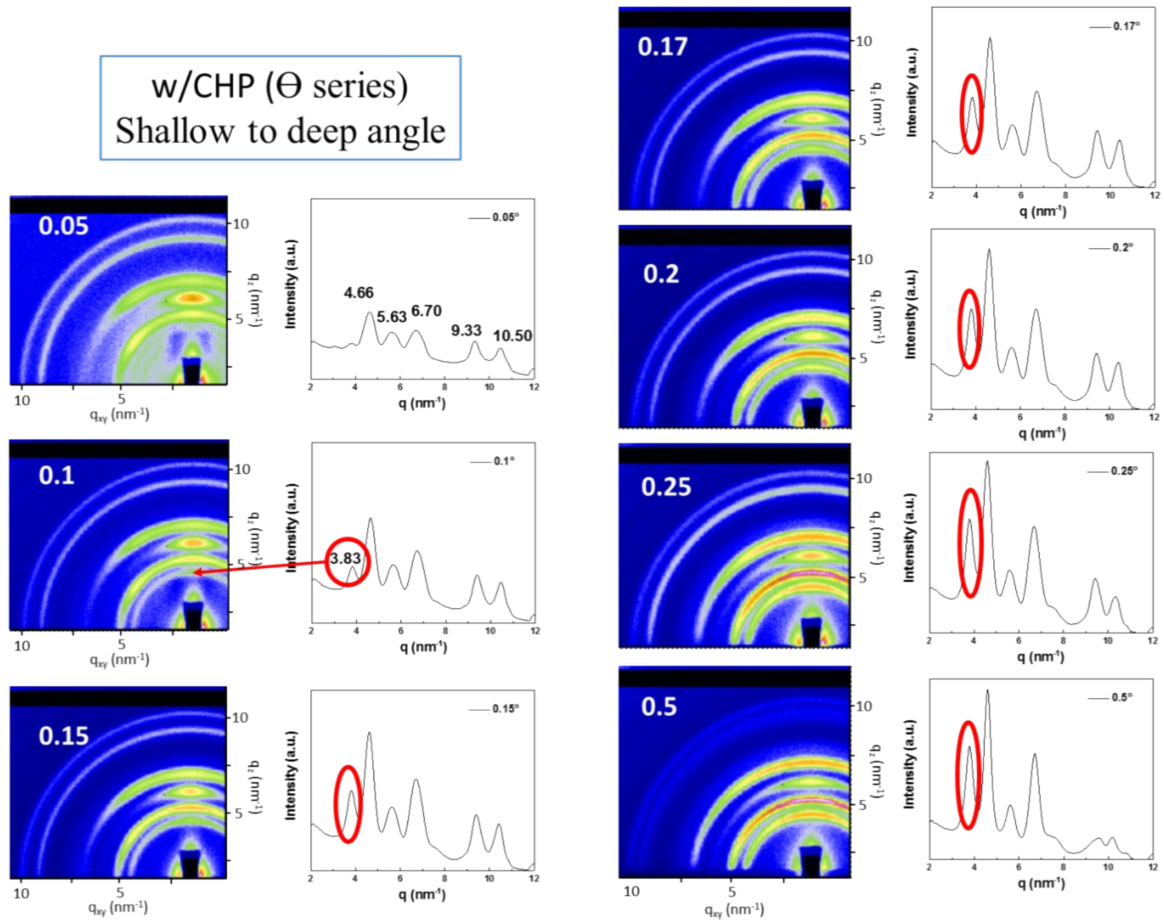

Figure S2 | w/CHP GIWAXS image and out of plane plot graph from shallow to deep incidence angle.

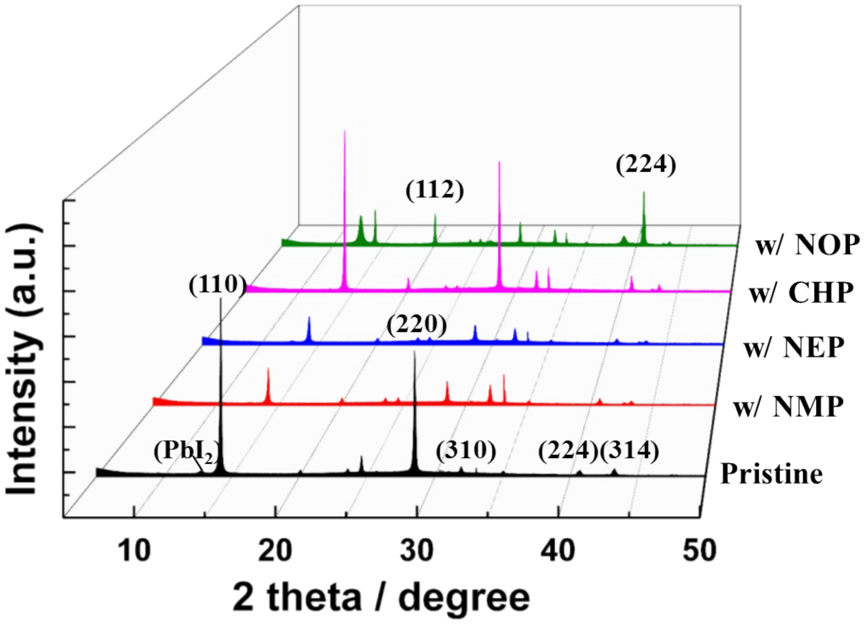

Figure S3 | *ex situ* XRD spectra of with and without additives.

XRD spectra were clearly showed that the residual PbI_2 peaks at 12.8 ° is observed in pristine and w/NOP samples. The orthorhombic lattice of (110) and (220) phase of representative perovskite peaks are also detected in 14.2 ° and 28.5 °, respectively. The w/CHP has a higher crystallinity among additive samples without residual PbI_2 crystal phase.

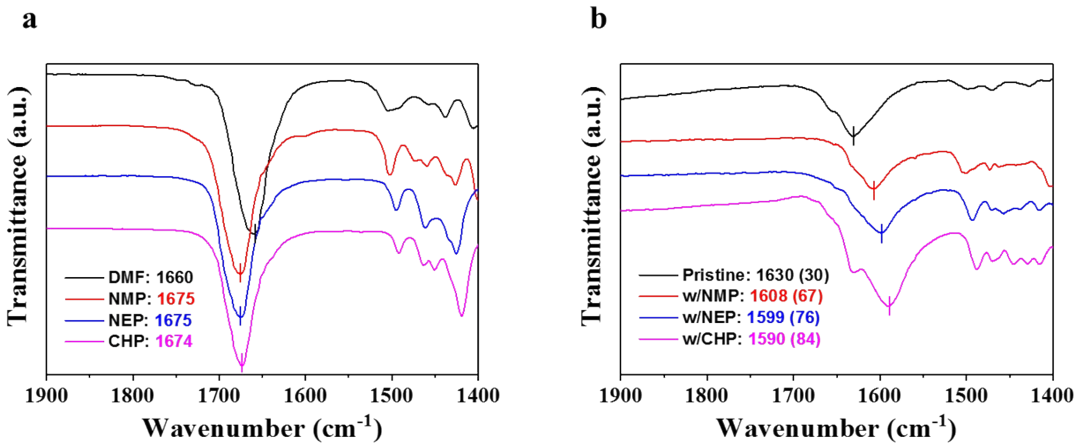

Figure S4 | FT-IR spectra of νC=O peaks in amide group. a, Various solvents, and **b,** As–cast PbI_2 films (degree of wavenumber shift in the brackets).

The interaction between solvents and PbI_2 molecules was evaluated by Fourier transform infrared spectroscopy (FT-IR) measurement. The FT-IR spectra of Fig. S4a indicated the νC=O of the amide functional group, which could have a Lewis base interaction with PbI_2 molecules[1] for all solvents. The FT-IR spectra of as-cast PbI_2 films (i.e., without thermal annealing) in Fig. 6b showed different degrees of wavenumber shifts toward lower wavenumber compared to the FT-IR spectra of the solvents. The intensity of the Lewis acid–base interaction with PbI_2 can be compared using the degree of wavenumber shift of the νC=O peak as displayed in the bracket of the Fig. S4b graph. The degree of wavenumber shifts for pristine, w/NMP, w/NEP, and w/CHP were 30, 67, 76, and 84 cm^{-1}, respectively. All additives showed at least a twice larger shift than pristine, which implies that the amide group in the pyrrolidone structure possesses the potential for strongly interacting with PbI_2 molecules. The largest wavenumber shift of w/CHP induced the state in which the CHP molecules were enough to interrupt the formation of PbI_2:DMF solvate phase due to the strong interaction between CHP and the PbI_2 molecules.

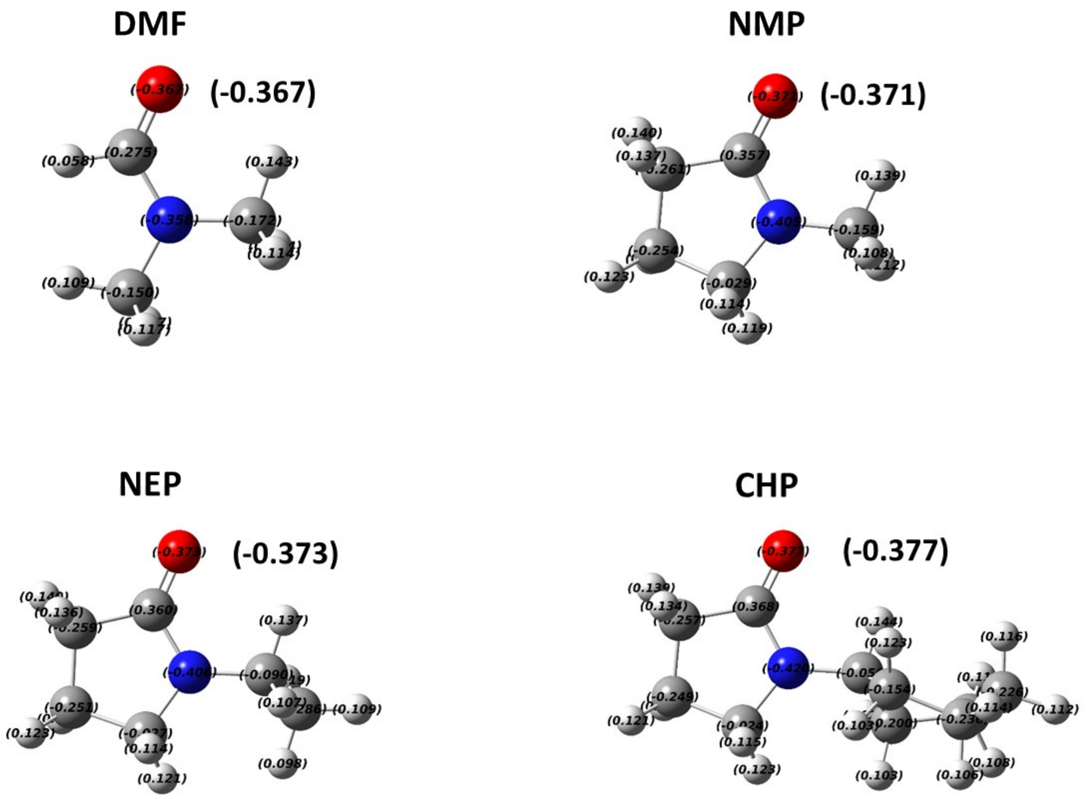

Figure S5 | DFT calculations of used solvents and partial charge value of oxygen in the brackets.

The results of FT-IR were supported by the density function theory (DFT) calculation, which was implemented for all solvents. As shown in Fig. S5, the partial charge of oxygen (red spheres) for DMF, NMP, NEP, and CHP were -0.367, -0.371, -0.373, and -0.377, respectively. CHP showed the most negative partial charge value, which well matched the FT-IR results, and the partial charge values of the other solvents were also observed as corresponding to the trend of the FT-IR results. Even though this partial charge difference is not large, this could be considered as one of the reasons why CHP most effectively suppressed DMF:PbI_2 solvate, however, other structural reasons may exist.

References

[1] N. Ahn, D. Y. Son, I. H. Jang, S. M. Kang, M. Choi, N. G. Park, *J. Am. Chem. Soc.* **2015**, *137*, 8696.