Supporting Information for

Solvent Gaming Chemistry to Control the Quality of Halide Perovskite Thin Films for Photovoltaics

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Methods

Precursor materials. All chemicals and reagents were used without any further purification. Lead iodide (PbI₂) and Cesium iodide (CsI) were purchased from TCI (Tokyo Chemical Industry Co., Ltd.); Formamidinium iodide (FAI) from Greatcell. Lead chloride (PbCl₂), phenylethylamine iodide (PEAI), 4-tert-butylpyridine (tBP), lithium bis (trifluoromethanesulfonyl) imide (Li-TFSI) and 2,2',7,7-tetrakis (N,N-di-p-methoxyphenylamine)-9,9’-spirobifluorene (Spiro-OMeTAD) from Xi’an Polymer Light Technology Corp.; 4-Fluorophenol and 4-Fluoroanisole from Aladdin; 2-methoxyethanol (2ME) and all other solvents from Sinopharm Chemical Regent Co., Ltd.

Growth of Crystals. PbI₂-OXR: 461 mg of PbI₂ powders (or 172 mg of FAI and 461 mg of PbI₂ powders, or 633 mg of FAPbI₃ powders) were dissolved by solvents such as DMSO (dimethyl sulfoxide), DMPU (N,N-dimethylpropyleneurea) or DESO (diethyl sulfoxide) under 100 °C heating and stirring. Then ethyl acetate, chlorobenzene or chloroform was slowly diffused into these filtered solutions in a closed container at room temperature. After two or three days, the crystals crystallized from above solutions. CCDC numbers: 2104894, (PbI₂-2DESO); 2104895, (PbI₂-DMPU); 2104896, (PbI₂-2DMSO).

(FA···OXR)PbI₃: 172 mg of FAI and 461 mg of PbI₂ powders (or 633 mg of FAPbI₃ powders) were dissolved by solvents such as DMF (N,N-dimethylformamide), PDI (2-pyrrolidinone), TMSO (tetramethylene sulfoxide), NMP (N-methylpyrrolidone), DMI (1,3-dimethyl-2-imidazolidinone), DMA (N,N-dimethylacetamide), HMPA (hexamethyl phosphoryl triamide) or TPPO (tris(N,N-tetramethylene)phosphoric acid triamide) under 100 °C heating and stirring. Then ethyl acetate, chlorobenzene or chloroform was slowly diffused into these filtered solutions in a closed container at room temperature. After two to three days, the crystals crystallized from above solutions. CCDC numbers: 2104899, [(FA···0.5DMA)PbI₃]; 2104890, [(FA···2DMF)PbI₃]; 2104891, [(FA···2.5DMI)PbI₃]; 2104892, [(FA···HMPA)PbI₃]; 2104893, [(FA···NMP)PbI₃].

Precursor preparation. Precursor preparation of perovskite layers. 729 mg of (FA···NMP)PbI₃, or 603 mg of PbI₂-2DMSO and 172 mg of FAI powders were dispersed by 600 μL of 2ME solvent to obtain clear precursors. For additive-contained precursor, 60 μL of CsI/2ME solution (130 mg/mL) and 2.78 mg of PbCl₂ were added into above precursors before using.

Solution preparation of hole-transition layers. The Spiro-OMeTAD/chlorobenzene (72 mg/mL) solution was doped with the additives containing 17.5 μL of Li-TFSI/ACN (520 mg/mL) and 28.8
μL of tBP. The synthetic nickel phthalocyanine powders were dissolved by chloroform (10 mg/mL) without any additives.

**Solar cell and module fabrication.** FTO glasses (NSG, 7 Ω per square) in sizes of 2 × 2 cm² or 6 × 6 cm² were ultrasonically cleaned with distilled water, acetone, and 2-propanol. After drying with N₂, the substrate was treated with ozone for 15 min and a compact ZnTiO₃ layer was deposited by spray pyrolysis at 450 °C. After cooling to room temperature, an ethanol solution (1 M) of thiourea was span coating on the above ZnTiO₃ substrate at 3000 rpm for 30 s, followed by 450 °C heating for 30 min. A 150 nm-thickness mesoporous TiO₂ film was deposited on the as-prepared ZnTiO₃ substrate with ethanol solution (1:5, mass ratio) of TiO₂ paste (Dyesol DSL 18NR-T), which was followed by heating at 450 °C for 60 min. The preparation of perovskite film was conducted as following: a dose of perovskite precursor (typically 3 μL for 2 × 2 cm² substrate and 30 μL for 6 × 6 cm²) was dipped into the gap (~200 μm) between the blade and as-prepared substrate, followed by the automatically moving at a speed of ~1000 mm·s⁻¹. Then the wet thin film was quickly transferred into a homemade vacuum chamber to undergo the vacuum-flash process, which could be pumped to ~10⁻¹ Pa within 10 s, and then the as-prepared substrate was annealed at different temperatures for 30 min. After preparation of the perovskite layer, a PEAI/2-propanol solution (3 mg/mL) was span onto the perovskite film at 5000 rpm for 30 s. Then the hole transport layer solution was coated dynamically at 3000 rpm for 30 s. Finally, 80 nm-thickness Au counter electrode was deposited by thermal evaporation under a reduced pressure of 2 × 10⁻⁷ Torr. All the above processes were manufactured in ambient air at ~30% RH.

Module fabrication. To fabricate the perovskite solar modules, the FTO electrode / ZnTiO₃ / Perovskite / HTL / Au electrode layers were laser-scribed sequentially to form a P1-P4-P2-P3 pattern as shown in Figure S19b. The active area of small-scale device and large-scale module were 0.12 cm² and 18 cm², respectively.

Module encapsulation. The redundant edge of perovskite film was etched by laser scribe firstly. Encapsulant PIB (polyisobutylene) and glass were successively put onto the module at N₂ atmosphere, then the as-prepared sample was transferred to a hot-press machine for combination of module and glass, the process was maintained at 100 °C for 5 min.

**Characterizations.** The diffraction data of PbI₂-OXR and (FA···OXR) PbI₃ crystals were collected on an Agilent Technologies SuperNova system and the data were processed using CrysAlis. The structure was solved and refined using full-matrix least-squares based on \( F^2 \) with
program SHELXS-97 and SHELXL-97 within Olex2. Raman spectra were recorded on a Confocal in-situ Raman Spectroscope. \textsuperscript{1}H NMR and in-situ \textsuperscript{1}H NMR spectra were recorded on a AVANCE NEO 500 MHz Digital FT-NMR Spectrometer. TG and DSC data were collected by 449F5 and DSC214 from NETZSCH-Gerätebau GmbHand, respectively. Surface morphologies and surface potentials were recorded on a SEM-4800 field-mission scanning electron microscope and Oxford Instruments Asylum Research Cypher ES, respectively. XRD patterns were analyzed on an X-ray diffractometer (Rigaku, RINT-2500) with a Cu K\textalpha radiation source. XPS data were measured by Thermo Scientific ESCALAB Xi\textsuperscript{+}. The time-resolved photoluminescence spectra were measured on an Edinburgh Instruments FLS980 spectrometer, and the data were fitted with biexponential functions $\tau = A + B_1 \exp(-t/\tau_1) + B_2 \exp(-t/\tau_2)$. For Mott-Schottky analysis, capacitance-voltage measurements were performed at fixed frequency (1 kHz) and the calculation formula was $1/C^2 = 2/[(e\varepsilon_0 \varepsilon N)(V-V_{bi}-(k_B T)/e)]$, where $e$ is the elementary charge, $\varepsilon$ is the dielectric constant of perovskite, $\varepsilon_0$ is the permittivity of vacuum, $N$ is the carrier density, $V_{bi}$ is the flat band potential, $k_B$ is the Boltzmann constant and $T$ is the absolute temperature. Current-velocity characterizations were recorded on a solar simulator equipped with a Keithley 2400 source meter and a 300-W collimated xenon lamp (Newport) calibrated with a light intensity to 100 mW cm\textsuperscript{-2} at AM 1.5 G solar light. The dark current density of devices was recorded on the same Keithley 2400 Source Meter in dark condition. IPCE values were measured on a computer-controlled IPCE system (Newport) containing a xenon lamp, a monochromator, and a Keithley multimeter and collected at DC mode. The stabilized power output of the PSCs/modules was measured using the Keithley 2400 source meter under AM 1.5 simulated solar irradiation, and a bias at the corresponding maximum power point (MPP) was applied.

**DFT calculation.** All the DFT calculations were performed by the Vienna ab initio simulation package (VASP).\textsuperscript{2,3} The electron-core interactions were described by the projected augmented wave (PAW)\textsuperscript{4} method and electron exchange–correlation was expressed at the general gradient-approximation (GGA) level by the Perdew–Burke–Ernzerhof (PBE) functional.\textsuperscript{5} A cutoff energy of 500 eV was adopted for the plane-wave basis set. All calculations were performed with spin polarization. For structural optimization, a convergence threshold of 0.02 eV Å\textsuperscript{-1} was set in force and the total energy converged to within 10\textsuperscript{-5} eV. To better evaluate the van der Waals’ interaction, Grimme’s method (DFT-D3) was included during the surface adsorption. For integration over the reciprocal space, we used a $3 \times 3 \times 1$ k-point mesh with horizontal shifts. Ab initio molecular
dynamics (AIMD) were performed under temperature of 363 K. At each AIMD time step (2 fs for modeling dynamics in all simulations), the total energy is evaluated to an accuracy of $10^{-5}$ eV per atom employing a plane-wave energy cutoff of 400 eV and a $3 \times 3 \times 1$ k-point mesh. VESTA was used to draw the molecular structure.\(^6\)

Classical MD simulations were performed with the Gromacs 5.1.4 MD software package.\(^7\) L-J parameters with partial charges of Pb\(^{2+}\) and I\(^-\) were used to simulate phase transition process of FAPbI\(_3\).\(^8\) In the simulations, the resulting systems were subject to 100000 steps of steepest descent minimization. The periodic boundary condition was applied in the simulation. The cut-off radius for the Lennard Jones and electrostatic interactions were set to be 10 Å. For accurate evaluation of the long-range Coulomb interactions, Particle Mesh Ewald (PME) summation method is used for electrostatic interactions beyond the cut-off. The system was heated to 363 K in 100 ps by using a v-rescale\(^9\) thermostat for the canonical ensemble (NVT) simulations. During this process, the Linear Constraint Solver (LINCS) algorithm\(^10\) was used to constrain all the bond lengths. The isothermal isobaric ensemble (NPT) was used in the subsequent simulations, with the pressure set to 1 bar in 100 ps, controlled using a v-rescale thermostat and Parrinello-Rahman barostat. Thereafter, the systems were simulated for 100 ns under 363 K. Three repeated MD simulations with different initial velocities were also performed. Throughout the simulations a time step of 2.0 fs was used.

**Supplementary Text**

**Basicity of solvents**

The testing mechanisms and objects of donor number (DN) and Kamlet-Taft $\beta$ values were different. O atom of solvent molecules could attack the SbCl\(_5\) to form Sb-O bonds, and DN value was based on the reaction heat from the solvents dissolved in CH\(_2\)ClCH\(_2\)Cl and SbCl\(_5\). Hence, the DN value of solvent can reflect coordination strengthen of solvents with Lewis basic species; the higher DN, the stronger coordination. By contrast, Kamlet-Taft $\beta$ was defined as the difference in the maximum absorbance of two dyes (4-nitroaniline and N,N-diethyl-4-nitroaniline), resulting from that one dye had an acidic proton. To a certain degree, the $\beta$ value can reflect the formation capacity of hydrogen bonds between solvents and Lewis basic species. The higher $\beta$, the stronger hydrogen bonds.

**Measurement of DN and Kamlet-Taft $\beta$ values**

S4
Measurement of DN: $^{23}\text{Na}$ NMR was used to estimate the DN values of solvents. Here we exploited the linear trend of DN values against $^{23}\text{Na}$ NMR shifts and extracted the DN values of solvents from this trend,\textsuperscript{11-14} and $^{23}\text{Na}$ NMR test was carried out in a 0.2-M solution of NaClO$_4$.

Using these data, the DN values of PDI and TMSO were estimated to be 24.4 and 28.0 kcal/mol, respectively.

Measurement of Kamlet-Taft $\beta$: $^{19}\text{F}$ NMR was used to estimate the $\beta$ values of solvents.\textsuperscript{15-18} NMR measurements were conducted by 4-fluorophenol (less than 0.01 mol/L) and 4-fluoroanisole (less than 0.1 mol/L) solutions. The NMR tube contained an inserted capillary of hexafluorobenzene/CDCl$_3$ solution (v./v. varying from 0.05\% to 0.5\%) as an external standard, and the chemical shifts were reported relative to $\delta\left[^{19}\text{F}\left(C_6\text{F}_6\right)\right] = -162.2$ ppm. Hydrogen-bonds induced chemical shifts could be calculated by

$$\Delta\{-\delta[^{19}\text{F}\text{ (OH - OMe)}]\} = -\delta[^{19}\text{F}\text{ (OH)}] - \{-1.009\delta[^{19}\text{F}\text{ (OMe)}] - 1.257\}$$

The $\beta$ values were calculated by $\beta = \Delta\{-\delta[^{19}\text{F}\text{ (OH - OMe)}]\}/3.395$.

![Figure S1](image)

**Figure S1.** Plot of $^{23}\text{Na}$ NMR shifts versus DN values from corresponding solvents. The fitted line was $Y=29.77 + 2.39X$. X represented the $^{23}\text{Na}$ NMR shifts and Y represented the DN values. The DN values of used solvents are listed in Table S1.
Figure S2. (a-c) XRD patterns of crystals grown from different solutions in the case of $\beta < \text{DN}^*$: (a) PbI$_2$/DESO and FAI/PbI$_2$/DESO, (b) PbI$_2$/DMPU and FAI/PbI$_2$/DMPU, (c) PbI$_2$/DMSO and FAI/PbI$_2$/DMSO. The same XRD results from PbI$_2$/OXRs and FAI/PbI$_2$/OXRs demonstrated the Pb-O coordination within PbI$_2$-OXR structures. (d-k) XRD patterns of crystals grown from different solutions in the case of $\beta \geq \text{DN}^*$: (d) PbI$_2$/TPPO and FAI/PbI$_2$/TPPO, (e) PbI$_2$/HMPA and FAI/PbI$_2$/HMPA, (f) PbI$_2$/DMI and FAI/PbI$_2$/DMI, (g) PbI$_2$/NMP and FAI/PbI$_2$/NMP, (h) PbI$_2$/DMA and FAI/PbI$_2$/DMA, (i) PbI$_2$/TMSO and FAI/PbI$_2$/TMSO, (j) PbI$_2$/PDI and FAI/PbI$_2$/PDI, (k) PbI$_2$/DMF and FAI/PbI$_2$/DMF. The different results from PbI$_2$/OXRs and FAI/PbI$_2$/OXRs indicated the formation of OXRs-intercalation (FA$\cdots$OXR)PbI$_3$ structures from FAI/PbI$_2$/OXRs solutions.
Figure S3. (a,b) $^{16}$O and (c,d) $^1$H NMR spectra of FAI and PbI$_2$ precursors in solvents. CDCl$_3$ was used as an external reference for NMR measurements.
**Figure S4.** Single crystal structures of PbI$_2$-OXR crystals (see Table S4). Both PbI$_2$-2DMSO and PbI$_2$-2DESO structures exhibit a single-chain type of edge-shared PbI$_4$O$_2$ octahedra, and the PbI$_2$-DMPU structure exhibits a double-chain type of edge-shared PbI$_5$O octahedra. CCDC numbers were shown in the parenthesis. Color legend: pink, I; green, Pb; red, O; yellow, S; grey, C; blue, N; white, H.
Figure S5. Single crystal structures of (FA···OXR)PbI₃ crystals (see Table S5). All (FA···OXR)PbI₃ structures display a face-shared PbI₆ octahedra with different stoichiometric ratio of OXRs and FA⁺ counter ions. CCDC numbers were shown in the parenthesis. Color legend: pink, I; green, Pb; red, O; grey, C; orange, P; blue, N; white, H.
Figure S6. (a) I-Pb-I bond angles of different PbI₆ octahedral species and corresponding crystal parameters (FA⁺ cations and NMP molecules are omitted here). (b) Raman spectra of α-FAPbI₃, (FA···NMP)PbI₃ and δ-FAPbI₃ crystals. The similar Pb-I vibration of δ-FAPbI₃ and (FA···NMP)PbI₃ demonstrated the similar connection mode of PbI₆ octahedra, different from that of α-FAPbI₃ with corner-shared PbI₆ octahedra. (c) UV-vis absorption spectra of δ-FAPbI₃ and (FA···NMP)PbI₃ crystals.
**Figure S7.** (a,b) ATR-FTIR of (FA···NMP)PbI$_3$, δ-FAPbI$_3$ and NMP. (c,d) $^1$H NMR spectra of δ-FAPbI$_3$, FAI, (FA···NMP)PbI$_3$ and NMP tested at room temperature. (e) $^1$H NMR spectrum of (FA···NMP)PbI$_3$ crystals from Figure S7d. The integrated area of two splitting peaks among 8.5–9.5 ppm was equal. *In-situ* $^1$H NMR spectra of (f) δ-FAPbI$_3$ and (g) (FA···NMP)PbI$_3$ crystals tested from 20 to 50 °C. DMSO-d$_6$ was chose as deuterated reagent.

ATR-FTIR characterizations (Figure S7a) display an obvious blue shift of -C=N stretching vibration (FA$^+$ cations) for (FA···NMP)PbI$_3$, compared to δ-FAPbI$_3$, due to the formation of hydrogen bonds between FA$^+$ and NMP. Correspondingly, the -C=O peak of NMP in (FA···NMP)PbI$_3$ shows a red shift, compared to pristine NMP. Not only the C=O (from NMP molecule) and C=N (from FA$^+$) signals but also the change of -N-H signal from (FA···NMP)PbI$_3$ were observed (Figure S7b). Room-temperature $^1$H NMR spectra (Figure S7c) show that the same broad peaks at 8.83 ppm from FAI and δ-FAPbI$_3$ are assigned to -N-H resonance of FA$^+$ cations. However, upon the formation of (FA···NMP)PbI$_3$, this single peak is split into two symmetric peaks at 9.00 and 8.66 ppm (Figure S7d,e). Temperature-dependent $^1$H NMR spectra show that these two split peaks of -N-H in (FA···NMP)PbI$_3$ experienced a gradually merging process from 20 to 50 °C, but little influence on the -N-H single peak of δ-FAPbI$_3$ (Figure S7f,g). The higher temperature, the weaker hydrogen bonds between FA$^+$ and NMP. Consequently, above results demonstrate the stable intercalation of NMP into (FA···NMP)PbI$_3$ lattice by FA···NMP hydrogen bonds.
Figure S8. Raman spectra of (a) (FA···NMP)PbI$_3$ and (b) PbI$_2$-2DMSO + FAI (grinding mixture) from Figure 2b,c. (c) In-situ temperature-dependent Raman spectra of δ-FAPbI$_3$ crystals. (d) XRD patterns of PbI$_2$-2DMSO and PbI$_2$-2DMSO + FAI (grinding mixture) crystals.
Figure S9. Photographs of (a) PbI$_2$-2DMSO, (b) FAI, and (c) PbI$_2$-2DMSO + FAI (grinding mixture) crystals subjected to heating at 100 °C.
Figure S10. DSC curves of (a) PbI$_2$-2DMSO + FAI (grinding), (b) PbI$_2$-2DMSO + FAI (without grinding) and (c) PbI$_2$-2DMSO powders. Peak I: the low-temperature peak. Peak II: the high-temperature peak. (d) Thermogravimetric analysis and (e) in-situ ATR-FTIR characterization of (FA···NMP)PbI$_3$ crystals during heating under N$_2$. (f) In-situ pool of ATR-FTIR measurement. The gradual shifts of -C=N signal and the disappearance of -C=O signal with increasing temperatures recorded the NMP removing process from (FA···NMP)PbI$_3$ lattice, and the formation of black powders within in-situ pool indicated the α-FAPbI$_3$ formation.
**Figure S11.** (a) *In-situ* single crystal XRD patterns of a single (FA···NMP)PbI₃ crystal. (b) Photographs of (FA···NMP)PbI₃ crystals subjected to heating at 90 °C. Photographs of δ-FAPbI₃ crystals subjected to heating at (c) 100 °C and (d) 150 °C.
**Figure S12.** (a) I-Pb-I bond angles of metastable phase and corresponding crystal parameters (FA$^+$ cations and NMP molecules are omitted here), demonstrating the deformation of PbI$_6$ octahedral framework of metastable phase. (b) AIMD simulated transforming path of metastable phase at 363 K. At the beginning, the adjacent isolated octahedral polytypes connected with neighboring octahedra by I-vertexes. The crowded polytypes moved and produced more corner-shared PbI$_6$ octahedra during time scale, exhibiting the favourable conversion trend towards α-FAPbI$_3$ at 363 K.
Figure S13. DSC curves of (a) PbI$_2$-OXR + FAI (grinding mixture) and (b) (FA⋯OXR)PbI$_3$ powders. (c) Single crystal analysis of the (FA⋯2DMF)PbI$_3$ structure. (d) $^1$H NMR and (e) in-situ $^1$H NMR spectra of (FA⋯2DMF)PbI$_3$ crystals. The peak of -N-H from (FA⋯2DMF)PbI$_3$ had a splitting phenomenon at room temperature but underwent gradual merging with increasing temperatures, due to the hydrogen bonds between FA$^+$ and DMF molecules. (f) Photographs of (FA⋯2DMF)PbI$_3$ crystals subjected to heating at 90 °C.
Figure S14. (a) Photographs of (FA···NMP)PbI$_3$ crystals before and after ethyl acetate treatment. (b) XRD pattern of black powders from Figure S14a. The pale-yellow crystals turned black after introducing ethyl acetate, indicating the α-FAPbI$_3$ formation at room temperature. The coexistence of δ-FAPbI$_3$ and α-FAPbI$_3$ might be due to incomplete transformation or the self-instability characteristics of α-FAPbI$_3$ after exposing to the atmosphere during XRD measurement. Photographs of (c) (FA···2DMF)PbI$_3$ and (d) PbI$_2$-2DMSO + FAI powders (grinding mixture) before and after ethyl acetate treatment.
Figure S15. (a) Scheme showing the vacuum-flash assisted blade-coating technology. The residual solvents within wet film are extracted to form intermediate film in the vacuum-flash step. (b, c) SEM images and (d, e) XRD patterns of intermediate films made from (FA···NMP)PbI₃ and PbI₂-2DMSO (with FAI addition) powders in 2ME solution. SEM images of (f) (FA···NMP)PbI₃ intermediate film by annealing at 90 °C and (g) PbI₂-2DMSO (with FAI addition) intermediate film by annealing at 100 °C. XRD patterns of FAPbI₃ films obtained from (h) (FA···NMP)PbI₃ intermediate film by annealing at 90 °C or treating with ethyl acetate, and (i) PbI₂-2DMSO (with FAI addition) intermediate film by annealing at 100 °C or treating with ethyl acetate at room temperature.
Figure S16. Cross-sectional SEM images of (a) pure FAPbI$_3$ film and (b) FAPbI$_3$-based film (with Cs$^+$ and PbCl$_2$ additives) obtained from (FA···NMP)PbI$_3$ intermediates by 90 °C annealing. The scale bar is 500 nm. Atomic force microscope (AFM) and kelvin probe force microscope (KPFM) images of (c,e) NMP-film and (d,f) DMSO-film. The NMP-film had a lower roughness of 15.80 nm compared with the DMSO-film (22.42 nm). High-resolution XPS spectra of (g) Pb and (h) I in the surface of the NMP-film and DMSO-film. XPS by integrating the spectra with respect to the Pb 4f and I 3d peaks was used to investigate the difference of I/Pb composition. (i) UV-vis and (j) PL spectra of the NMP-film and DMSO-film.
Figure S17. (a) XRD patterns of as-prepared FAPbI$_3$ films transferred from δ-FAPbI$_3$ before and after annealing at 150 °C. (b) Top-view SEM image of as-annealed α-FAPbI$_3$ film and (c) J-V curves of the resembled device from corresponding film. The precursor was prepared by dissolving the FAI and PbI$_2$ powders in 2ME without OXR$s$, as same as abovementioned precursor preparation. The α-FAPbI$_3$ film by annealing at 150 °C accompanied with undesirable δ-FAPbI$_3$ and PbI$_2$, and the resembled device exhibited PCE of 15.81% in reverse scan and 15.16% in forward scan.
Figure S18. (a) Space charge limited current (SCLC) measurements for the devices (FTO/ZnTiO$_3$/Perovskite/PCBM/Au). (b) Dark current densities, (c) IPCE measurements, and (d) operational stability of the NMP-PSC and DMSO-PSC. (e) Statistics of PCE and $V_{OC}$ analyzed on 20 individual PSCs. (f) $J$-$V$ curves of (FA$\cdots$OXR)PbI$_3$ based devices. The precursors with additives were prepared as same as abovementioned precursor preparation, and the mole ratio of OXRs relative to FAPbI$_3$ was 2:1, 0.5:1 and 2.5:1 for DMF, DMA and DMI-based precursors, respectively. The as-prepared films after vacuum flashing were annealed at 100 °C. The PSCs from the DMF-film, DMA-film and DMI-film displayed PCEs of 21.08%, 21.57% and 20.98%, respectively.
Figure S19. (a) SEM images of $6 \times 6 \text{ cm}^2$ NMP-film. The scale bar is 500 nm. (b) Diagrammatic sketch of a module, including P1, P2, P3 and P4. (c) Maximum power point tracking of encapsulated modules under harsh hydrothermal condition (85 °C and 50% RH%). While both modules lost lot of PCE at the beginning, the NMP-module recovered partial current and maintained stable over 40 hours. By contrast, the DMSO-module dropped 53.9% of initial PCE after 3 hours.
**Table S1.** DN values of solvents and corresponding $^{23}$Na NMR shifts of NaClO$_4$ dissolved in them.

| Solvent | $^{23}$Na NMR shift (ppm) | DN (kcal/mol) | DN* (DN/38.8) |
|---------|---------------------------|---------------|---------------|
| ACN     | -6.65                     | 14.4          | 0.37          |
| 2ME     | -3.78                     | 19.8          | 0.51          |
| PDI     | -2.25                     | 24.4          | 0.63          |
| TMSO    | -0.75                     | 28.0          | 0.72          |
| DMPU    | 1.30                      | 33.0          | 0.85          |
| HMPA    | 3.85                      | 38.8          | 1.00          |

**Table S2.** Kamlet-Taft β values calculated by $^{19}$F NMR shifts.

| Solvent | $\delta^{(19F)}$(OH) | $\delta^{(19F)}$(OMe) | $\Delta_1[-\delta^{(19F)}$(OH-OMe)] | β   |
|---------|----------------------|----------------------|-------------------------------------|-----|
| 2ME     | 127.56               | 125.79               | 1.89                                | 0.62|
| DMF     | 127.73               | 125.77               | 2.10                                | 0.69|
| DMI     | 127.76               | 125.67               | 2.21                                | 0.73|
| DESO    | 126.70               | 124.50               | 2.35                                | 0.77|
| TPPO    | 129.10               | 125.94               | 3.30                                | 1.09|
Table S3. Basicity parameters of solvents.

| Solvent | DN (kcal/mol) | DN* (DN/38.8) | Kamlet-Taft β |
|---------|---------------|----------------|---------------|
| ACN     | 14.4          | 0.37           | 0.37          |
| 2ME     | 19.8          | 0.51           | 0.62          |
| PDI     | 24.4          | 0.63           | 0.72          |
| DMF     | 26.6          | 0.68           | 0.69          |
| NMP     | 27.3          | 0.70           | 0.77          |
| DMI     | 27.7          | 0.71           | 0.73          |
| DMA     | 27.8          | 0.72           | 0.75          |
| TMSO    | 28.0          | 0.72           | 0.74          |
| DMSO    | 29.8          | 0.77           | 0.71          |
| DMPU    | 33.0          | 0.85           | 0.75          |
| DESO    | 33.2          | 0.85           | 0.77          |
| HMPA    | 38.8          | 1.00           | 1.00          |
| TPPO    | 40.9          | 1.05           | 1.09          |
Table S4. Crystal data and structure refinement of PbI$_2$-OXR.

| Complex          | PbI$_2$-2DESO   | PbI$_2$-DMPU    | PbI$_2$-2DMSO   |
|------------------|----------------|----------------|----------------|
| Empirical formula| C$_8$H$_{20}$I$_2$O$_2$PbS$_2$ | C$_6$H$_{12}$I$_2$N$_2$OPb | C$_4$H$_{12}$I$_2$O$_2$PbS$_2$ |
| Formula weight   | 673.35         | 589.17         | 617.25         |
| Temperature/K    | 100.01(10)     | 193.0          | 100.00(10)     |
| Crystal system   | orthorhombic   | monoclinic     | orthorhombic   |
| Space group      | Fdd2           | P2$_1$/a       | Pccn           |
| a/Å              | 28.8096(17)    | 15.5062(15)    | 13.6992(4)     |
| b/Å              | 26.4452(15)    | 4.5372(4)      | 10.8620(4)     |
| c/Å              | 4.5530(3)      | 18.2167(18)    | 8.7610(2)      |
| α/°              | 90             | 90             | 90             |
| β/°              | 90             | 107.874(5)     | 90             |
| γ/°              | 90             | 90             | 90             |
| Volume/Å$^3$     | 3468.8(4)      | 1219.8(2)      | 1303.64(7)     |
| Z                | 8              | 4              | 4              |
| ρ calcg / cm$^{-3}$ | 2.579          | 3.208          | 3.145          |
| μ/mm$^{-1}$      | 49.003         | 45.210         | 17.963         |
| F(000)           | 2432.0         | 1032.0         | 1088.0         |
| Crystal size/mm$^3$ | 0.01x0.01x0.01 | 0.12x0.1x0.1   | 0.02x0.01x0.01 |
| Radiation        | Cu Kα ($λ$ = 1.54184) | Ga Kα ($λ$ = 1.34139) | Mo Kα ($λ$ = 0.71073) |
| 2θ range for data collection/° | 9.078 to 148.11 | 8.874 to 121.298 | 7.504 to 61.002 |
| Index ranges     | -33 ≤ h ≤ 35,  | -19 ≤ h ≤ 19,  | -17 ≤ h ≤ 18,  |
|                  | -30 ≤ k ≤ 32,  | 0 ≤ k ≤ 5,    | -10 ≤ k ≤ 15,  |
|                  | -5 ≤ l ≤ 5     | 0 ≤ l ≤ 23    | -7 ≤ l ≤ 12    |
| Reflections collected | 5417          | 2790          | 4898          |
| Independent reflections | 1610 [Rint = 0.0833, Rsigma = 0.0541] | 2790 [Rsigma = 0.0484] | 1766 [Rint = 0.0373, Rsigma = 0.0478] |
| Data/restraints/parameters | 1610/26/81      | 2790/36/112    | 1766/0/53      |
| Goodness-of-fit on F$^2$ | 1.150          | 1.143          | 1.017          |
| Final R indexes [I>2σ (I)] | R$_1$ = 0.0552, wR$_2$ = 0.1491 | R$_1$ = 0.0610, wR$_2$ = 0.1801 | R$_1$ = 0.0318, wR$_2$ = 0.0622 |
| Final R indexes [all data] | R$_1$ = 0.0605, wR$_2$ = 0.1657 | R$_1$ = 0.0743, wR$_2$ = 0.1921 | R$_1$ = 0.0448, wR$_2$ = 0.0702 |
| Largest diff. peak/hole / e Å$^{-3}$ | 3.16/-3.07     | 3.23/-2.39     | 1.28/-3.55     |
Table S5. Crystal data and structure refinement of (FA···OXR)PbI₃.

| Complex | (FA···HMPA)PbI₃ | (FA···0.5DMA)PbI₃ | (FA···2.5DMF)PbI₃ | (FA···NMP)PbI₃ | (FA···2DMF)PbI₃ |
|---------|-----------------|------------------|------------------|-----------------|-----------------|
| **Empirical formula** | C₅H₁₀N₂OPb | C₆H₁₁N₂O₄Pb | C₇H₁₂N₂O₆Pb | C₈H₁₄N₂O₇Pb | C₉H₁₅N₃O₇Pb |
| **Formula weight** | 812.16 | 1353.04 | 1836.67 | 1464.18 | 779.15 |
| **Temperature/K** | 193(2) | 193.0 | 99.98(10) | 100.00(10) | 100.01(10) |
| **Crystal system** | monoclinic | orthorhombic | triclinic | triclinic | monoclinic |
| **Space group** | P2₁/c | Cmcm | P-1 | P-1 | C2/c |
| **a/Å** | 27.765(2) Å | 7.9664(5) | 7.9996(4) | 7.9126(5) | 19.6503(10) |
| **b/Å** | 28.963(2) Å | 22.5622(13) | 13.7838(7) | 10.8044(6) | 7.8643(3) |
| **c/Å** | 8.0928(6) | 20.0737(11) | 24.1633(6) | 24.6600(14) | 24.6496(13) |
| **α/°** | 90° | 90 | 89.953(3) | 95.248(5) | 90° |
| **β/°** | 98.216(4) | 90 | 83.608(3) | 91.925(5) | 99.613(5) |
| **γ/°** | 90° | 90 | 82.455(4) | 109.633(6) | 90° |
| **Volume/Å³** | 6441.2(9) | 3608.0(4) | 2624.6(2) | 1972.6(2) | 3755.8(3) |
| **Z** | 8 | 4 | 2 | 2 | 8 |
| **ρ│e/a³** | 1.675 | 2.491 | 2324 | 2.465 | 2.756 |
| **μ/mm⁻¹** | 22.676 | 39.779 | 9.980 | 53.385 | 13.915 |
| **F(000)** | 2942 | 2320.0 | 1684.0 | 1280.0 | 2768.0 |
| **Crystal size/mm³** | 0.02×0.01×0.01 | 0.12×0.1×0.1 | 0.02x0.01x0.01 | 0.05x0.01x0.01 | 0.02x0.01x0.01 |
| **Radiation** | Mo Kα (λ=0.71073) | Ga Kα (λ=1.34139) | Mo Kα (λ=0.71073) | Cu Kα (λ=1.54184) | Mo Kα (λ=0.71073) |
| **2θ range for data collection/°** | 1.399 to 54.222 | 6.816 to 126.836 | 6.788 to 66.06 | 7.216 to 133.19 | 7.282 to 60.744 |
| **Index ranges** | -33 ≤ h ≤ 23, -34 ≤ k ≤ 35, -9 ≤ l ≤ 9 | -10 ≤ h ≤ 10, -30 ≤ k ≤ 24, -18 ≤ l ≤ 26 | -12 ≤ h ≤ 10, -20 ≤ k ≤ 21, -35 ≤ l ≤ 36 | -9 ≤ h ≤ 9, -12 ≤ k ≤ 11, -29 ≤ l ≤ 29 | -26 ≤ h ≤ 15, -10 ≤ k ≤ 10, -32 ≤ l ≤ 33 |
| **Reflections collected** | 44997 | 13698 | 31977 | 12731 | 9652 |
| **Independent reflections** | 11804 [Rin = 0.0812] | 2424 [Rin = 0.0666, Rsigma = 0.0499] | 17507 [Rin = 0.0669, Rsigma = 0.1678] | 6952 [Rin = 0.0996, Rsigma = 0.1289] | 4891 [Rin = 0.0446, Rsigma = 0.0668] |
| **Data/restraints/parameters** | 11804/313/327 | 2424/82/108 | 17507/495/497 | 6952/155/231 | 4891/75/160 |
| **Goodness-of-fit on F²** | 1.039 | 1.089 | 0.997 | 1.048 | 1.046 |
| **Final R indexes** [I＞2σ(I)] | R₁ = 0.1291, wR₂ = 0.3072 | R₁ = 0.0702, wR₂ = 0.1992 | R₁ = 0.0630, wR₂ = 0.1008 | R₁ = 0.1056, wR₂ = 0.2069 | R₁ = 0.0535, wR₂ = 0.1292 |
| **Final R indexes [all data]** | R₁ = 0.2140, wR₂ = 0.3474 | R₁ = 0.0719, wR₂ = 0.2015 | R₁ = 0.1771, wR₂ = 0.1436 | R₁ = 0.1293, wR₂ = 0.2845 | R₁ = 0.0782, wR₂ = 0.1497 |
| **Largest diff. peak/hole / e Å⁻³** | 4.019/-3.191 | 3.58/-2.91 | 2.49/-1.85 | 6.03/-4.97 | 6.88/2.53 |
Table S6. Energies of monomer structure of (FA···NMP)PbI₃, metastable phase (removing all the NMP molecules from (FA···NMP)PbI₃), NMP, PbI₂-2DMSO, FAI, DMSO and α-FAPbI₃.

| Structure              | Energy (eV)  |
|------------------------|-------------|
| (FA···NMP)PbI₃         | -151.495990 |
| Metastable phase       | -56.425487  |
| NMP                    | -94.340007  |
| PbI₂-2DMSO             | -111.660952 |
| FAI                    | -47.629667  |
| DMSO                   | -101.803510 |
| α-FAPbI₃               | -56.607627  |

Table S7. Detailed parameters of small-scale devices.

| 0.12-cm²   | Voltage (V) | J (mA cm⁻²) | FF (%) | PCE (%) |
|------------|-------------|-------------|--------|---------|
| RS:NMP     | 1.18        | 24.68       | 80.46  | 23.43   |
| FS:NMP     | 1.17        | 24.59       | 78.09  | 22.47   |
| RS:DMSO    | 1.08        | 24.28       | 78.46  | 20.57   |
| FS:DMSO    | 1.05        | 24.29       | 76.09  | 19.41   |

Table S8. Detail parameters of large-scale devices.

| 18-cm²     | Voltage (V) | J (mA cm⁻²) | FF (%) | PCE (%) |
|------------|-------------|-------------|--------|---------|
| RS:NMP     | 8.42        | 3.00        | 73.45  | 18.55   |
| FS:NMP     | 8.40        | 2.96        | 73.33  | 18.23   |
| RS:DMSO    | 8.03        | 3.00        | 70.31  | 16.94   |
| FS:DMSO    | 7.86        | 3.01        | 65.52  | 15.50   |
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