

Supplementary Materials for

Constructive molecular configurations for surface-defect passivation of perovskite photovoltaics

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Materials and Methods

Materials

Unless stated otherwise, solvents and chemicals were obtained commercially and used without further purification. N, N-dimethylformamide (DMF) (anhydrous, 99.8%), dimethyl sulfoxide (DMSO) (anhydrous, \geq 99.9%), chlorobenzene (CB) (anhydrous, 99.8%), isopropanol (IPA) (anhydrous, 99.5%), water (ACS reagent), acetonitrile (ACN) (anhydrous, 99.8%), t-BP (99%), Li-TFSI (99.95% trace metals basis), theophylline (anhydrous, \geq 99%, powder), caffeine (anhydrous, 99%, FCC, FG), theobromine (\geq 98.0%), PbI₂ (99.999%, perovskite grade), silver (Ag) and gold (Au) were obtained from Sigma-Aldrich Inc. 4-Isopropyl-4'-methyldiphenyliodonium Tetrakis(pentafluorophenyl)borate (TPFB) (\geq 98.0%) was obtained from TCI Inc. FAI was obtained from Great Cell. MAC1 (99%) and MABr (99%) were obtained from Ai'an Polymer Light Technology Corp. Tin Oxide (SnO₂) nanoparticle (15 wt% in water) was obtained from Alfa-Aesar Inc.

Method

DFT Calculations. The VASP code is employed to carry out all first-principles calculations (29, 30). A revised Perdew-Burke-Ernzerhof generalized gradient approximation (PBEsol) (31, 32) was used for the exchange-correlation including a dispersion correction using Grimme's DFT-D3 scheme (33, 34). PBEsol functional has been introduced to improve the equilibrium properties of solids and surfaces (35). Valence-core interactions were described by projector-augmented-wave (PAW) pseudopotentials (36). Plane-wave expansions with kinetic energies up to 300 eV were chosen as the basis set for all geometry optimization calculations and then 500 eV were chosen for the single-point density-of-states (DOS) calculations based on these optimized geometries. Both atomic positions and cell dimensions were optimized using a conjugate gradient algorithm until all Hellman-Feynman forces are smaller than 0.02 eV/Å. All atomic positions are allowed to relax. 4x4x1-center k-point mesh was adopted for Brillouin-zone sampling for all cases. The surfaces were modeled by a slab consisting of 2x2 periodicity in the a-b plane and at least three atomic layers along the c axis, separated by 15-20 Å of vacuum in the surface normal direction.

All quantum chemical calculations were performed using Gaussian 16.1.(37) GaussView 6.0.16 was used to construct initial structures used in computations. For the initial structures, PbI₂ was positioned at various locations around the xanthine alkaloids and the geometry of each resulting PbI₂-small molecule geometry was optimized with the ω B97X-D density functional and the 6-311++G(2d,p) basis set for C, H, N and O atoms, and LANL2DZ basis set for Pb and I atoms. Optimized geometries were verified by frequency calculations as minima (zero imaginary frequencies) at the same level of theory as that used for geometry optimization. Interaction energies were computed using the same level of theory as that for geometry optimization using the following equation: $\Delta E_{int} = E(PbI_2 \cdot small \ molecule) - [E(PbI_2) + E(small \ molecule)]$. Molecular structures were visualized and rendered using CYLview.(38)

Device Fabrication. Perovskite solar cells were fabricated with the following structure: indium tin oxide (ITO)/SnO₂/(FAPbI₃)_x(MAPbBr₃)_{1-x}/Spiro-OMeTAD/Ag or Au. The ITO glass was precleaned in an ultrasonic bath of acetone and isopropanol and treated in ultraviolet-ozone for 20

min. A thin layer (ca. 30 nm) of SnO₂ was spin-coated onto the ITO glass and baked at 180 °C for 60 min. SnO₂ was diluted in water (2 mg mL⁻¹). After cooling to room temperature, the glass/ITO/SnO2 substrates were transferred into a nitrogen glove box. The PbI2 solution was prepared by dissolving 1.4 mM PbI2 into 1 mL DMF/DMSO mixed solvent (v/v 94/6). The FAI/MABr/MACl solution was prepared by dissolving 70 mg FAI, 4 mg MABr and 10 mg MACl into 1 mL IPA. The solutions should be stirring overnight before use. The PbI2 solution was spincoated on the substrate at 1500 rpm for 30 s and annealed at 70 °C for 1 min. And the FAI/MABr/MACl solution was spin-coated on the substrate at 1800 rpm for 30 s, then the film was annealed outside the glove box at 150 °C for 10 min with 40% humidity. And then the Theophylline/IPA:CB, Caffeine/IPA:CB or Theobromine/IPA:CB solutions was drop casted at 4000 rpm on the perovskite film, the volume ratio of IPA and CB is 1:1. The film was dried at 100 °C for 30 s. The Spiro-OMeTAD solution [60mg Spiro-OMeTAD in 700 µL CB with 25.5 µL t-BP, 15.5 µL Li-TFSI (520 mg/mL in ACN) and 12.5 µL FK209 (375 mg/mL in ACN)], or PTAA solution for stability test [40 mg/mL; in CB with 10% TPFB] was spun onto the perovskite film as a hole conductor. The devices were completed by evaporating 100-nm gold or silver in a vacuum chamber (base pressure, 5×10^{-4} Pa).

Device Characterization. J–V characteristics of photovoltaic cells were taken using a Keithley 2400 source measure unit under a simulated AM 1.5G spectrum, with an Oriel 9600 solar simulator. Typically, the devices were measured in reverse scan (1.2 V \rightarrow 0 V, step 0.02 V) and forward scan (0 V \rightarrow 1.2 V, step 0.02 V). All the devices were measured without pre-conditioning such as light-soaking and applied a bias voltage. Steady-state power conversion efficiency was calculated by measuring stabilized photocurrent density under a constant bias voltage. EQEs were measured using an integrated system (Enlitech, Taiwan) and a lock-in amplifier with a current preamplifier under short-circuits' condition. For transient photovoltage (TPV) and current (TPC) measurements, a pulsed red dye laser (Rhodamine 6G, 590 nm) pumped by a nitrogen laser (LSI VSL-337ND-S) was used as the perturbation source, with a pulse width of 4 ns and a repetition frequency of 10 Hz. The intensity of the perturbation laser pulse was controlled to maintain the amplitude of transient Voc below 5 mV so that the perturbation assumption of excitation light holds. The voltages under open circuit and currents under short circuit conditions were measured over a 1 M Ω and a 50 Ω resistor and were recorded on a digital oscilloscope (Tektronix DPO 4104B). The electron beam induced current (EBIC) data were collected using an FEI Scios Dual-Beam microscope with a Mighty EBIC 2.0 controller (Ephemeron Labs) equipped with a Femto DLPCA-200 pre-amplifier. During EBIC measurement, the electron-beam (e-beam) was rastered across a freshly prepared device cross-section. The device cross-section was prepared by mechanically cleaving the backside scribed sample. As e-beam reached and interacted with perovskite absorber, the generated carriers were collected via the front/back contacts, Ag and ITO. The same magnification 65000x and beam condition (1 kV and 6.3 pA) were used for collecting 2.5 x 2.5 μ m² EBIC map for samples with various treatments. A fixed dwell time of 17.5 μ s was used per pixel. The Mighty EBIC interface controlled/scanned FEI microscope externally, allowing scanning electron microscopy (SEM) images and EBIC data to be collected simultaneously. The dielectric spectra were tested by Precision Impedance Analyzer (Agilent 4294A).

Materials Characterization. UV-vis absorption spectra of the perovskite films were obtained using a U-4100 spectrophotometer (Hitachi) equipped with integrating sphere, in which monochromatic light was incident to the substrate side. XPS measurements were carried out on an

XPS AXIS Ultra DLD (Kratos Analytical). An Al Ka (1,486.6 eV) X-ray was used as the excitation source. Transmission Fourier transform infrared (FTIR) spectroscopic analysis was performed using FT/IR-6100 (Jasco). The chamber was purged with nitrogen gas during the measurement. Steady-state photoluminescence (PL) measurement was carried out using Horiba Jobin Yvon system, in which a 640 nm monochromatic laser was used as an excitation fluorescence source. Time-resolved PL decay profiles of the perovskite films were investigated by a Picoharp 300 with time-correlated single-photon counting capabilities. A 640 nm monochromatic pulsed laser with a repetition frequency of 100 kHz was generated from a picosecond laser diode head (PLD 800B, PicoQuant). The energy density of the excitation light was controlled to be ca. 1.4 nJ/cm². UPS measurements were carried out to determine the work function and the position of valence band maximum of materials. A He discharge lamp, emitting ultraviolet energy at 21.2 eV, was used for excitation. All UPS measurements were performed using standard procedures with a -9 V bias applied between the samples and detectors. Clean gold was used as a reference. Scanning Kelvin Probe Force Microscopy was performed on perovskite samples in ambient conditions using a Dimension Icon Scanning Probe Microscope (Bruker Nano, Inc.) in a single-pass frequency modulated (FM-KPFM) mode. FM detection maximizes spatial resolution by measuring the local electrostatic force gradient present solely at the apex of the AFM tip, thereby reducing contributions of the tip cone and cantilever present in more common amplitude modulated detection schemes. Application of an off-resonant AC voltage (~5 V, 2 kHz) between a conductive AFM probe (OSCM-Pt or PFQNE-AL, Bruker) and the grounded sample alters the effective spring constant of the cantilever and thus modulates its resonant frequency due to an induced electric force gradient. Spatial variations in the surface potential/work function were directly measured by nulling local electrostatic force gradient arising from contact potential differences between the AFM tip and the device surface through the use of a bias-controlled feedback loop. A minimum force setpoint was employed, as indicated by nominal phase contrast, in order to reduce potential artifacts in the surface potential images.

Supplementary Text S1. Density Functional Theory Characterization of surface defects and defect passivation

PbI₂ terminated (001) slab of FAPbI₃ is considered for all point defect calculations. The starting structure parameters are taken from the experimental unit cell of the cubic phase (39). We computationally described the defect formation based on the procedure by Yin *et al.* (18). We considered four different common perovskite intrinsic defects formed in bulk and/or surface (24, 40, 41): lead anti-site (Pb_I), iodine vacancy (V_I), lead vacancy (V_{Pb}) and iodine anti-site (I_{Pb}) defects. The surface structures of the optimized defects are shown in Fig. 1. For a defect *D* with a charge-state *q*, defect formation energies (DFE) over the slab surface is calculated from the following expression:

$$\Delta H_D(q) = E_D(q) - (E_{D=0} + n_I [\mu_I + E_{I_2}/2] + n_{Pb} [\mu_{Pb} + E_{Pb}]) + q(E_F + E_{VBM}) \text{ Eq. S1}$$

where $E_{D=0}$ is the total energy of the defect-free slab, μ_i are the chemical potentials E_{I_2} and E_{Pb} are corresponding electronic energies, n_i are the change in the number of atoms during the formation of the defect, E_F is the Fermi energy and E_{VBM} is the valence band maximum energy. The chemical potential, for the formation of FAPbI₃, should satisfy

$$\mu_{FA} + \mu_{Pb} + 3\mu_I = \Delta H(FAPbI_3)$$
 Eq. S2

under thermodynamic equilibrium growth conditions, where $\Delta H(FAPbI_3)$ is the formation enthalpy of *FAPbI*₃. Also, within the equilibrium conditions of *FAI* and *PbI*₂, the equations below should be satisfied:

$$\mu_{FA} + \mu_I \le \Delta H(FAI) \qquad \text{Eq. S3} \\ \mu_{Pb} + 2\mu_I \le \Delta H(PbI_2) \qquad \text{Eq. S4}$$

When the Pb-rich is considered (depending on the fabrication and other conditions), where $\mu_{Pb} = 0$, then $\mu_I = \Delta H (PbI_2)/2$ and $\mu_{FA} = \Delta H (FAI)$ conditions can be met. Therefore, in the case of neutral defects and a Pb-rich condition Eq. S1 is simplified as:

$$\Delta H_D = E_D - (E_{D=0} + n_I [\Delta H(PbI_2) + E_{I_2}]/2 + n_{Pb} E_{Pb})$$
 Eq. S5

Thermodynamic charge transition levels, *i.e.*, the Fermi level at which $\Delta H_D(q) = \Delta H_D(q')$ condition is satisfied, is calculated by

$$\epsilon(q/q') = [E_D(q) - E_D(q')]/(q - q') + E_{VBM}$$
 Eq. S6

Finally, the interaction energy between the molecule and the slab with defect D is found from

$$E_{int} = E_{D,X} - (E_D + E_X)$$
 Eq. S7

where, $E_{D,X}$ is the total energy of the slab+molecule complex (see Fig. 1), E_D is the energy of the free slab and E_X is the gas phase energy of the molecule, i.e., $X = \{\text{Theophylline, Caffeine, Theobromine}\}$.

Supplementary Text S2. Trap Density of States Analysis

The trap density of states (tDOS) can be deduced from the angular frequency dependent capacitance by the equation:

$$N_T E_{\omega} = -\frac{V_{bi} dC}{qW d\omega} \frac{\omega}{k_B T}$$
 Eq. S8

where $k_{\rm B}$ is the Boltzmann's constant, q is the elementary charge, T is the temperature, $V_{\rm bi}$ and W are obtained from the Mott-Schottky analysis, and the angular frequency ω is defined by the following relation:

$$E_{\omega} = k_B T \ln \frac{\omega_0}{\omega}$$
 Eq. S9

where ω_0 is the attempt-to-escape frequency. Combining the Eq S8 and Eq. S9, the *t*DOS level in different perovskite devices can be obtained.

Supplementary Text S3. Additional characterization of the role of defect passivation by theophylline.

To further investigate the role of defect passivation by theophylline on the enhanced device performance, we conducted X-Ray Diffraction (XRD) and ultraviolet-visible spectroscopy (UV-Vis) to study the effect of theophylline on the crystallinity and optical property of the perovskite film. From Fig. S8 and Fig. S9, there is no obvious difference observed on the perovskite films with and without theophylline treatment, which can further confirm that the enhancement of the photovoltaic performance is because of the reduced non-radiative recombination passivated by theophylline.

We also measured the transient photovoltage decay (TPV) under the open-circuit condition and transient photocurrent decay (TPC) under short-circuit condition to study the carrier dynamics on the perovskite solar cells with or without theophylline treatment. As shown in Fig. S10, we found that the charge-recombination lifetime (τ_r) of theophylline treated perovskite-based device was substantially longer than that of the device based on pure perovskite (2.34 ms versus 1.65 ms), consistent with the slower charge recombination in the theophylline treated perovskite-based film as concluded from the TRPL measurement. This indicates a passivation of the surface defects and hence superior electronic quality in the theophylline treated perovskite bulk film, consistent with the higher *V* oc of the corresponding devices. Meanwhile, from the TPC measurement (Fig. S11), the charge transfer lifetime (τ_t) of the theophylline treated perovskite decreased from 5.59 µs to 2.49 µs. The enhanced charge transfer might have resulted from the reduced interfacial defects of the theophylline treated perovskite film, consistent with the EBIC measurement.

Supplementary Text S4 XPS analysis

As shown in the XPS spectra (Fig. S13), the peaks of Pb 4f showed the largest shift to higher binding energy with theophylline treatment (143.38 eV for Pb 4f 5/2, 138.48 eV for Pb 4f 7/2), indicating the strongest interaction between C=O and Pb in perovskite. For the case of caffeine, a peak shift of Pb 4f was also observed but with a smaller shift value (143.20 eV for Pb 4f 5/2, 138.35 eV for Pb 4f 7/2). This suggested a less favorable interaction between caffeine and Pb in the absence of neighboring N-H. The peaks of Pb in the case of perovskite with theobromine showed an even less shift (143.20 eV for Pb 4f 5/2, 138.35 eV for Pb 4f 7/2), indicating the least favorable interaction between theobromine and Pb when the N-H group is so close to the C=O that N-H group cannot effectively assist with the interaction between C=O and Pb. The different values of XPS peak shifts was consistent with our DFT calculations, where the atomic distance between C=O and Pb was determined to be 3.06, 3.09, and 3.11 Å for the case of theophylline, caffeine and theobromine, respectively, suggesting a reducing interaction energy between Pb and C=O in perovskite with theophylline, caffeine and theobromine, respectively.



Fig. S1 XPS full scan of the reference perovskite film, Pb 4*f* and I 3*d* peaks were integrated to determine the surface composition.



Fig. S2 DFT-D3 predicted interaction energies between the molecule and slab complex for the $V_{\rm I}$ case.



Fig. S3 Top view of theoretical model of perovskite with the bromine surface passivation of Pb_I antisite.



Fig. S4 Theoretically Predicted tDOS of the surface Pb₁ antisite defect with or without small molecule treatment.



Fig. S5 Carrier extraction probability extracted from EBIC.



Fig. S6 EBIC distribution profiles of perovskite active layers with or without theophylline treatment.



Fig. S7 Evolution of power conversion efficiency (PCE) of perovskite solar cells with or without theophylline treatment. The devices were stored under dark with controlled humidity.



Fig. S8 XRD patterns of perovskite films with and without theophylline treatment.



Fig. S9 UV-Vis spectra of perovskite films with and without theophylline treatment.



Fig. S10 Transient Photovoltage of the perovskite solar cells with or without theophylline treatment.



Fig. S11 Transient Photocurrent of the perovskite solar cells with or without theophylline treatment.



Fig. S12 *J-V* curves of perovskite solar cells with theophylline treatment measured in Lawrence Berkeley National Laboratory (LBNL) under reverse scan (Voc = 1.19 V, $Jsc = 25.6 mA/cm^2$, FF = 0.75, PCE = 22.9%) and forward scan (Voc = 1.19 V, $Jsc = 25.6 mA/cm^2$, FF = 0.74, PCE = 22.5%). The device was sent to LBNL without any encapsulation.



Fig. S13. XPS data for Pb 4f 7/2 and Pb 4f 5/2 core level spectra in perovskite films with and without small molecules treatment.

Defect type	ΔH_{α} (eV) Surface	ΔH_{α} (eV) Bulk*
I_{Pb}	3.15	3.89
Pb _I	0.57	1.46
V_{I}	0.51	0.63
V_{Pb}	3.20	2.97

Table S1 ΔH_{α} , formation energy of neutral defects considered in this study. The energies are in eV. *from reference 12.

Type of Treatment	Voc (V)	J _{SC} (mA cm ⁻²)	FF	PCE (%)	
				average	best
Ref	1.153±0.02	24.19±0.35	0.73±0.07	20.36±0.53	21.02
Theophylline	1.187±0.01	24.74±0.46	0.77±0.02	22.61±0.58	23.48
Caffeine	1.168±0.02	24.63±0.39	0.75±0.01	21.58±0.69	22.32
Theobromine	1.151±0.02	24.36±0.43	0.70±0.03	19.63±0.65	20.24

Table S2 Photovoltaic parameters of average and the best perovskite solar cells with or without various types of surface treatments.

Type of Treatment	V _{OC} (V)	J _{SC} (mA cm ⁻²)	FF	РСЕ (%)
Reverse (Ref)	1.164	24.78	0.729	21.02
Forward (Ref)	1.159	24.19	0.693	19.43
Reverse (Theophylline)	1.191	25.24	0.781	23.48
Forward (Theophylline)	1.191	25.23	0.749	22.51

Table S3 Photovoltaic parameters of best perovskite solar cells under reverse or forward scan with or without theophylline treatment.

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