Support Information

Improving Stability and Efficiency of Perovskite Solar Cells by a Bidentate Anilinium Salt

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**Section 1. Experimental Procedures**

**1H nuclear magnetic resonance (NMR):** The spectra were collected in a Bruker Avance III 400 MHz (9.4 THz), with a 1H frequency of 400.13 MHz.

**Atomic force and Kelvin force probe microscopy measurements:** The morphology of the films was investigated using an NX10 atomic force microscope (AFM) from Prak Systems. Together with surface imaging, the surface potential was mapped using a Kelvin probe. A point probe-plus Silicon-SPM-Sensor (PPP-EFM-W) with a resistivity of 0.01–0.02 Ω cm produced by nanosensors was used for this purpose.

**Contact angle measurements:** Photographs of the drop of water on the perovskite film were acquired immediately after the dripping. Such measurements were performed using an Attension optical tensiometer, Theta model. The angle was measured in the software of the equipment.

**Device assembly:** FTO glass substrates were cleaned with Hellmanex (2%), deionized water, acetone, and isopropanol (IPA) for 20 min each in an ultrasonic bath. The FTO glasses were dried using nitrogen and treated in a UV-ozone chamber for 30 min. For the electron transport material (ETL) SnO\textsubscript{2} colloidal solution (15wt\%) was diluted in 1:3 (v:v) in deionized water, and this solution was spin-cast on the precleaned FTO glasses at 3000 rpm for 30 s, followed by annealing at 150°C for 30 minutes in the air. The substrates were then treated with UV-ozone for 30 min before transferring into the glovebox. For the fabrication of perovskite films, the gas quenching method was used. The perovskite Cs\textsubscript{0.05}FA\textsubscript{0.95}PbI\textsubscript{2.95}Br\textsubscript{0.05} (1.5 M, 6% excess of PbI\textsubscript{2}) solution was prepared by the dissolution of CsBr, formamidinium iodide (FAI), and PbI\textsubscript{2} in a mixture of DMF:NMP (4:1, v:v). The solution was stirred for 30 minutes at room temperature and then 40% of methylammonium chloride (MACl) was added. After an additional 30 min of stirring, the solution was spin-coated on SnO\textsubscript{2} films at 1000 rpm for 10 seconds, and then 4000 rpm for 25 s. After 5 seconds at 4000 rpm, a blow of nitrogen was used to remove the solvent. Immediately after the spin coating, the films were annealed at 100°C for 1 minute inside the glovebox. In sequence, all the films were removed to the air and thermally annealed at 100°C for 60-90 minutes in air ambient with a relative humidity of 30-40%. Following the films were placed again inside the glovebox.

The post-treatment of the perovskite was performed using a solution of the salt (FM-NH\textsubscript{3}X) or the neutral molecule (FM-NH\textsubscript{2}) in isopropanol or chlorobenzene,
respectively. For the deposition, 60 μL of the solution of the passivating molecule was dynamically spin-cast onto the perovskite using 3000 rpm for 30 s.

The preparation of the perovskite films used in the characterization was the same, with the exception that they were deposited onto a pre-cleaned glass substrate. To the hole transport layer (HTL), a solution of 97 mg of Spiro-OMeTAD, 42.4 μL of 4-tert-butyl pyridine, and 24.8 μL of Li-TFSI solution (520 mg mL⁻¹ in ACN), and 10.8 μL of FK209 (375 mg mL⁻¹ in ACN) in 1 mL chlorobenzene, was deposited on perovskite films at 4000 rpm for 20 s. Finally, 70 nm of Au was thermally evaporated as the electrode under a high vacuum using a thermal evaporator.

Device characterization: The current density vs. voltage (J–V) curves were characterized under simulated air mass (AM) 1.5 G illumination using a solar simulator (450 W xenon light source (Oriel), 100 mW cm⁻²) and a Keithley 2400 source meter. The light intensity was calibrated with a Si photodiode equipped with an IR-cutoff filter (KG3, Schott) and it was recorded during each measurement. The solar cells were measured under reverse scan (+1.2 V to 0 V) and forward scan (0 V to +1.2 V) with a step of 0.01 V and a delay time of 100 ms.

Fourier transform infrared (FTIR) spectroscopy: the data were acquired using a Cary 630 FTIR spectrometer. For the powder, the Attenuated Total Reflectance (ATR) acquisition mode was used. In the case of the films, they were deposited in a Si <100> substrate and the spectra were acquired in the transmission mode.

Scanning electron microscopy (SEM) measurements: A Thermo Fischer Scientific Quanta 250 FEG-SEM at 10 kV, under high vacuum (~10⁻⁴ Pa), the magnitude of 10⁻⁵, and with an Everhart-Thornley Detector (ETD) was used.

Single crystal X-ray diffraction (XRD): X-ray diffraction data collections on single crystals of FM-2Br and FM-NH₂ were performed with an Oxford-Diffraction GEMINI-Ultra using Mo-Kα radiations (0.71073 Å). Measurements were performed at 293 K. Data integration and scaling of the reflections for all compounds were performed with the CRYSALIS suite.¹ Final unit cell parameters were based on the fitting of all reflections positions. Analytical absorption corrections and the space group identification were performed using CRYSALIS suite.¹ The structures of the compound were solved by direct methods using the SUPERFLIP program.² The positions of all atoms could be unambiguously assigned on consecutive difference Fourier maps. Refinements were performed using SHELXL³ based on F² through a full-matrix least-square routine. All non-hydrogen atoms were refined with anisotropic atomic
displacement parameters. All hydrogen atoms were located in difference maps and included as fixed contributions according to the riding model. Values \( C-H = 0.97 \) Å and \( U_{iso}(H) = 1.2 \) \( U_{eq}(C/N) \) for the aromatic carbon atoms and amine groups.

**Stability upon aging of the devices:** To the stability test, the devices were stored at room temperature in a box filled with \( N_2 \), with humidity <30%, and protected from UV light. They were removed from the box to the electrical characterization and then stored again.

**Time-resolved photoluminescence (TRPL):** The decay curves were measured in an Edinburg Analytical Instruments FL 900 spectrofluorometer with an MCP-PMT (Hamamatsu R3809U-50; 50 ps). These measurements were carried out with a PicoQuant LDH-D-C-440 pulsed diode laser with \( \lambda_{exc} = 440 \) nm (bandwidth of 5 nm, pulse width = 80 ps, \( F = 9.7 \) nJ cm\(^{-2}\)). The decays were collected at 800 nm of each sample on a time scale of 10 \( \mu \)s.

**X-ray diffraction (XRD):** The diffractograms were obtained on a Shimadzu diffractometer, model XRD-6000 with Cu K\( \alpha \) radiation of 0.154 nm wavelength.

**X-ray photoelectron spectroscopy (XPS):** X-ray photoelectron spectroscopy (XPS) measurements were carried out using a monochromatic Al K\( \alpha \) source on a K-alpha spectrometer (Thermo Fisher Scientific) equipped with a 180° double-focusing hemispherical analyzer with 128-channel detector. Survey and selected atomic signals were obtained with a pass energy of 50 eV and a step of 0.02 eV. Casa XPS software package was used to analyze the obtained spectra and the peaks were fitted using a mixed Gauss-Lorentz function and Shirley background. All the measured spectra were corrected by setting the reference binding energy of carbon (C 1s) at 284.8 eV.
Section 2. Synthesis

The materials were purchased from Sigma-Aldrich and TCI chemicals and used as received. Tetrakistriphenylphosphine Pd (0) was synthesized according to the protocol described below. The synthetic route adopted is shown in Fig. S1.

2.1. Synthesis of 9-(dibromomethylene)-9H-fluorene (FM-2Br)

In the first step, 9-fluorenone (2.00 g, 11.1 mmol, 1 eq.) was mixed with carbon tetrabromide (CBr₄) (8.83 g, 26.6 mmol, 2.4 eq.), and triphenylphosphine (PPh₃) (13.01 g, 49.61 mmol, 4.5 eq.) in a round-bottom flask. The solids were dried under vacuum for 3 hours, purged with nitrogen, and 80 mL of anhydrous dichloromethane (DCM) was added. Then, the reaction was kept at 40 °C with vigorous stirring for 60 h. In sequence, it was cooled to room temperature, and the solvent evaporated. The product was extracted with CHCl₃ (3x 50 mL) and washed with brine (2x 50 mL). The organic phases were dried over Na₂SO₄ and the solvent evaporated. The crude product was purified in a chromatographic column using hexane as eluent, affording 3.00 g of FM-2Br (Fig. S1) with 80% yield. ¹H NMR (250 MHz, CDCl₃): δ 8.62 (d, J = 7.9 Hz, 2H), 7.69 (d, J = 7.3 Hz, 2H), 7.43 (t, J = 7.4 Hz, 2H), 7.32 (m, J = 11.1, 4.4 Hz, 2H). ¹³C NMR (250 MHz, CDCl₃): δ 140.45, 138.06, 131.13, 129.40, 127.34, 125.97, 119.55. CHN Calculated for C₁₄H₈Br₂: C, 50.04; H: 2.40; Br: 47.56. Found: C, 49.91; H, 2.03.

2.2. Synthesis of 3,3′-((9H-fluoren-9-ylidene)methylene) diaminine (FM-NH₂)

To a round-bottom flask, FM-2Br (500 mg, 1.48 mmol, 1 eq.), 3-aminobenzeneboronic acid (811 mg, 5.92 mmol, 4 eq.), and Pd(PPh₃)₄ (171 mg, 0.148 mmol, 10 mol%) were added. The solids were degassed and then an aqueous solution of sodium carbonate (4.5 mL from 2 mol L⁻¹), and 30 mL of dioxane were added under N₂. The reaction was heated with stirring at 90 °C for 60 h. In sequence, the product was extracted with ethyl acetate and washed with brine. Next, an acid-base extraction with HCl (1 mol L⁻¹) and NaOH (1 mol L⁻¹) was performed. The resultant organic product was extracted from the aqueous layer with ethyl acetate and concentrated. The final purification was performed in a chromatographic column using...
a mixture of ethyl acetate:hexane (1:1) as eluent, obtaining 430 mg of a yellow crystal FM-NH$_2$ (Fig. S1) with 75% yield. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.69 (d, $J = 7.5$ Hz, 2H), 7.26 – 7.13 (m, 4H), 6.96 (dd, $J = 11.2$, 4.0 Hz, 2H), 6.80 (m, $J = 6.7$ Hz, 4H), 6.71 (m, $J = 9.4$, 3.7 Hz, 4H), 3.69 (s, 4H). $^{13}$C NMR (500 MHz, CDCl$_3$): $\delta$ 146.74, 145.96, 143.91, 140.34, 138.73, 133.54, 129.70, 127.43, 126.44, 125.20, 119.75, 119.11, 115.79, 114.86. CHN Calculated for C$_{26}$H$_{20}$N$_2$: C, 86.64; H, 5.59; N, 7.77. Found: C, 85.21; H: 4.87; N: 7.58.

For the preparation of Pd(PPh$_3$)$_4$, PdCl$_2$ (178 mg, 1 mmol) and PPh$_3$ (1.310 g, 5 mmol) were added to a schlenk tube. The solids were degassed, and 12 mL of DMSO was added. The reaction was heated to 150 °C in an oil bath until the complete dissolution of the solids. Then, hydrazine monohydrate (0.200 mL, 4 mmol) was quickly added. The reaction was removed from the oil bath and slowly cooled to room temperature. The resultant solid was filtered under N$_2$, washed with ethanol (3x 20 mL) and diethyl ether (3x 20 mL), and dried over N$_2$ for 12 h before use.

### 2.3. Synthesis of 3,3'-(9H-fluoren-9-ylidene)methylene)dibenze-naminium (FM-NH$_3$X, X: Cl, Br, I)

To a round-bottom flask, 150 mg of FM-NH$_2$ (0.416 mmol, 1 eq.) and 5 mL of dioxane were added. Then, 2.2 equivalent of HCl (37 wt%), HBr (48 wt%), or HI (57wt%) were added dropwise for 10 minutes, and the reaction was kept at 27 °C for 6 h under N$_2$. The solvent was partially evaporated, toluene (20 mL) was poured into the solids, and the solvent was evaporated; this step was repeated 3x. Toluene helps to remove DMSO and water. In sequence, 10 mL of toluene was added and the suspension was heated with stirring until reflux and kept for 30 minutes. Following, it was cooled to room temperature, the solids were filtered and washed with diethyl ether (7x 20 mL). The product was dried in a vacuum oven at 80 °C for 12 h before use.

$^1$H NMR (250 MHz, CD$_3$OD): FM-NH$_3$Cl: $\delta$ 7.80 – 7.65 (m, 4H), 7.54 (dd, $J = 9.0$, 5.0 Hz, 6H), 7.31 (td, $J = 7.5$, 0.9 Hz, 2H), 7.00 – 6.88 (m, 2H), 6.56 (d, $J = 7.9$ Hz, 2H). FM-NH$_3$Br: 7.81 – 7.66 (m, 4H), 7.61 – 7.48 (m, 4H), 7.31 (t, $J = 7.5$ Hz, 2H), 6.95 (t, $J = 7.5$ Hz, 2H), 6.56 (d, $J = 7.9$ Hz, 2H). FM-NH$_3$I: $\delta$ 7.76 (d, $J = 7.6$ Hz, 2H),
7.71 (t, J = 6.7 Hz, 2H), 7.53 (d, J = 6.5 Hz, 6H), 7.30 (td, J = 7.5, 0.9 Hz, 2H), 6.98 – 6.90 (m, 2H), 6.54 (t, J = 7.1 Hz, 2H).

Carbon, Hydrogen, and Nitrogen (CHN): Calculated for: **FM-NH₂Cl**: C₂₆H₂₂Cl₂N₂: C, 72.06; H, 5.12; Cl, 16.36; N, 6.46. Found: C, 76.56; H, 4.76; N: 6.46. **FM-NH₂Br**: Calculated for: C₂₆H₂₂Br₂N₂: C, 59.79; H, 4.25; Br, 30.60; N, 5.36. Found: C, 55.63; H, 3.25; N, 4.24. **FM-NH₂I**: Calculated for: C₂₆H₂₂I₂N₂: C, 50.67; H, 3.60; I, 41.18; N, 4.55. Found: C, 50.65; H, 3.25; N, 4.24.

**Figure S1.** Synthetic route adopted for the FM-NH₂ and FM-NH₂X (X=Cl, Br, I).
Section 3. Characterization of the Molecules Synthesized

3.1. $^1$H Nuclear Magnetic Resonance

(a)

(b)
**Figure S2.** $^1$H NMR spectra of (a) FM-2Br, (b) FM-NH$_3^+$, (c) FM-NH$_3$Cl, (d) FM-NH$_3$Br, and (e) FM-NH$_3$I. (a) and (b) were obtained in CDCl$_3$ and (c), (d), and (e) in CD$_3$OD.
3.2. $^{13}$C Nuclear Magnetic Resonance

**Figure S3.** $^{13}$C NMR 500 MHz of (a) FM-2Br and (b) FM-NH$_2$ in CDCl$_3$. 

*Figure S3. $^{13}$C NMR 500 MHz of (a) FM-2Br and (b) FM-NH$_2$ in CDCl$_3$.***
3.3. **Attenuated Total Reflectance Infrared Spectroscopy**

*Figure S4.* ATR-IR of FM-NH$_2$ and its salts, FM-NH$_3$, with Cl$, Br$, and I$ as counteranion. The spectra were obtained for the powder of the materials in the ATR mode.
Section 4. Characterization of the Aggregation-Induced Emission Behavior of FM-NH$_2$

FM-NH$_2$ can be understood as a rigid fluorene core with two aniline groups attached. The aniline experienced a certain rotational degree of freedom around the fluorene, conferring to the molecule a flexible structure. An effect of this softness can be seen by the low photoluminescence (PL) emission intensity of the molecule in a solution of an aprotic solvent (such as ethyl acetate, EtOAc), as shown in Fig. S5a. This occurs because the energy of the absorbed light is thermally loosed due to the rotation of the aniline groups, thereby resulting in a poor emissive solution. Since the solvent cannot interact strongly with the solute via H-bonding interactions, for instance, nothing is precluding the rotation of the aniline rings.

In stark contrast, when thin films of FM-NH$_2$ were prepared we observed brightly yellowish emissions (Fig. S5a); the same is true for the solid-state emission. Probably, the increased emission of the thin films compared to the solution is due to the restriction of the intramolecular rotation of the aniline groups caused by physical hindrance. From Fig. S5b, we can see that the emission of the film is bathochromically shifted compared to the solution, which is related to an increase in the energy barrier for molecular motion, triggered by the steric hindrance between neighboring molecules.$^6$

The enhanced Stoke shift and the emission in the aggregated state suggest that FM-NH$_2$ presents the phenomenon of aggregation-induced emission (AIE).$^6$ To check our hypothesis, we force the restriction of the intramolecular rotation of the molecules in a solution with an aprotic solvent (EtOAc) by adding amounts of protic solvent (ethanol, EtOH). To each ethanol fraction added, we monitor the PL emission (Fig. S5c). Ethanol is expected to realize H-bonding interactions with the amine group of FM-NH$_2$, difficulting the rotation of the aniline groups, and decreasing the energy loss pathways, thereby resulting in increased emission intensity. Besides, ethanol solubilizes poorly FM-NH$_2$, triggering the formation of emissive aggregates in the solution. From Fig. S5c, we can see that PL emission intensity increases with the fraction of ethanol added. Concomitantly, the emission band becomes vibrationally structured, suggesting that the molecules were more rigid than when surrounded by EtOAc. This can be linked
to the H-bonding interaction between the amine groups in FM-NH$_2$ and the solvent EtOH, which helps to preclude the rotation of the aniline moieties.

We were also able to verify the effects of H-bonding in the PL emission spectra of FM-NH$_2$ in a solution of dimethylsulfoxide, DMSO, with the addition of EtOH (Fig. S5d). We note that the emission intensity in DMSO is more intense and structured compared to the EtOAc: an effect of the higher viscosity of the medium. As ethanol is added, the emission intensity increases, as a result of the H-bonding interaction between solute and solvent, and the poor solubility of the molecule in ethanol.

Such results evidenced that the FM-NH$_2$ is a typical example of AIE-luminogen. The soft molecular structure of this type of chromophore can be explored in the passivation of perovskite films, since it can penetrate better between the intergrain voids, passivating the grain boundaries. Also, the improved intermolecular interaction in the solid-state benefit the formation of a hydrophobic coating film that prevents the degradation of the perovskite.

Figure S5. (a) UV-Vis absorption and PL emission spectra of FM-NH$_2$ in EtOAc solution at C = 0.001 mg mL$^{-1}$ and as a thin film. PL emission of the FM-NH$_2$ in (b) EtOAc and (c) DMSO with the addition of EtOH. In (c) we can see the emission of the EtOAc solution of FM-NH$_2$. 

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Section 5. Density Functional Theory Calculations

5.1. Finite Size Systems

Theoretical Approach and Computational Details

All \textit{ab initio} total-energy calculations were based on spin-polarized DFT calculations within the screened exchange-correlation functional as proposed by Heyd-Scuseria-Ernzerhof (HSE06),\textsuperscript{7,8} using the Fritz-Haber Institute \textit{ab initio} molecular simulations package (FHI-aims),\textsuperscript{9,10} which employs numeric atom-centered basis functions (NAOs),\textsuperscript{9,10,11} whereas the second improvement level from a free-atom orbital minimal basis, \textit{i.e.}, \textit{light-tier2} (adopting FHI-aims terminology), was considered. The electrons were treated by the scalar-relativistic framework within the atomic zeroth-order relativistic approximation (atomic ZORA).\textsuperscript{12}

The self-consistent electronic density (SCF) for the \textbf{FM-NH\textsubscript{2}} and \textbf{FM-NH\textsubscript{3}} molecules was obtained once the following criteria were reached, \textit{i.e.}, 1.0 \times 10^{-6} \text{ eV} (total energy) and 1.0 \times 10^{-4} \text{ eV/Å} (atomic forces). The criteria of 1.0 \times 10^{-3} \text{ eV/Å} of the atomic forces were used to obtain the equilibrium geometries. Furthermore, for all total energy calculations, we employed a Gaussian broadening parameter of 10 meV to achieve the correct occupation of the electronic states.

The vibrational frequency calculations were performed upon the harmonic approximation and the finite-difference algorithm for all lowest energy configurations,
using $10^{-1}$ tighter parameter to calculate the Hessian Matrix, atomic displacements of 0.0025 Å were used. Finally, those molecules were verified as true local minima by the absence of negative eigenvalues in the Hessian matrix.

**Optimal SCF and Relaxation Parameter**

Using the Perdew-Burke-Ernzerhof (PBE) functional at light-tier2 level, we calculate the optimized structure of the FM-NH$_2$ and FM-NH$_3$, as well as the correspondent energy levels (HOMO and LUMO), and the energy gap ($E_g$) between HOMO-LUMO. We tested different criteria to obtain the SCF convergence: energy, density, and forces. We also compare the spin none and spin colinear configurations. The results are expressed in Table S1.

We started the geometry optimization using two different guesses: one with the aniline rings on the same plane of the fluorene, and the other with the aniline rings torsioned (’t’) regarding the fluorene. This strategy allows us to verify if the torsioned structure is in fact the most stable configuration. Our results demonstrate that regardless of the initial configuration the optimized structure always has the aniline rings torsioned.

**Table S1.** Initial tests at PBE/light-tier2 level for the optimal SCF and relaxation parameters for the optimization of FM-NH$_2$ and FM-NH$_3$, considering planar and torsional initial (-t) structures in relation to the aniline rings. $E_{tot}^{DFT}$ is the DFT total energy; $q^{n+}$ is the molecule total charge where n = 0-2; $\mu_{tot}$ is the total magnetic moment; $\varepsilon_{HOMO}$ and $\varepsilon_{LUMO}$ are the energies of HOMO and LUMO, respectively; and $E_g$ is the LUMO-HOMO energy gap.
### SCF and Relaxation Parameters

| Molecule       | \(E_{\text{tot}}^{\text{DFT}}\) (eV) | \(q^n\) (e) | \(m_{\text{tot}}\) (\(\mu_B\)) | \(\varepsilon_{\text{HOMO}}\) (eV) | \(\varepsilon_{\text{LUMO}}\) (eV) | \(E_g\) (eV) |
|----------------|-------------------------------------|-------------|---------------------------------|-----------------------------------|-----------------------------------|-------------|
| sc_accuracy_etot 2.5 \(10^{-5}\) | FM-NH\(_2\) | -30263.18730611 | 0 | 0 | -4.85 | -2.62 | 2.23 |
| sc_accuracy_rhoe 2.5 \(10^{-3}\) | FM-NH\(_3\) | -3280.17576643 | 0 | 0 | -9.85 | -8.13 | 1.72 |
| sc_accuracy_forces 2.5 \(10^{-3}\) | FM-NH\(_2\)-t | -30263.19395530 | 0 | 0 | -4.86 | -2.59 | 2.27 |
| relax_geometry trm 2.5 \(10^{-2}\) | FM-NH\(_2\)-t | -30280.17369400 | 2 | 0 | -9.85 | -8.13 | 1.72 |
| spin none | | | | | | |
| sc_accuracy_etot 1.0 \(10^{-6}\) | FM-NH\(_3\) | -30263.19068092 | 0 | 0 | -4.86 | -2.62 | 2.24 |
| sc_accuracy_rhoe 1.0 \(10^{-5}\) | FM-NH\(_3\) | -30280.17738725 | 2 | 0 | -9.84 | -8.12 | 1.72 |
| sc_accuracy_forces 1.0 \(10^{-4}\) | FM-NH\(_2\)-t | -30263.19489718 | 0 | 0 | -4.82 | -2.63 | 2.19 |
| relax_geometry trm 1.0 \(10^{-3}\) | FM-NH\(_2\)-t | -30280.17870829 | 2 | 0 | -9.84 | -8.11 | 1.73 |
| spin none | | | | | | |
| sc_accuracy_etot 1.0 \(10^{-6}\) | FM-NH\(_3\) | -30263.19061532 | 0 | 0 | -4.86 | -2.62 | 2.24 |
| sc_accuracy_rhoe 1.0 \(10^{-5}\) | FM-NH\(_3\) | -30280.17699360 | 2 | 0 | -9.85 | -8.13 | 1.72 |
| sc_accuracy_forces 1.0 \(10^{-4}\) | FM-NH\(_2\)-t | -30263.19489774 | 0 | 0 | -4.82 | -2.63 | 2.19 |
| relax_geometry trm 1.0 \(10^{-3}\) | FM-NH\(_2\)-t | -30280.17870778 | 2 | 0 | -9.84 | -8.11 | 1.73 |
| spin colinear | | | | | | |

We also tested another hybrid functional: the HSE06 with the same basis set level, i.e., light-tier2. Using this functional we performed two sets of calculations: In the first one, the geometry was optimized, and the energy was calculated using the HSE06 functional. In the second, we used the optimized geometry obtained from PBE/light-tier2 and we ran a single-point energy calculation. The results are shown in Table S2. Fig. S6 compares the optimized structure obtained from PBE vs. HSE06. We found that the geometry optimized by HSE06 presented a better match with the experimental results in what concerned the energy of the HOMO and LUMO (values signed with * in Table S2). Thus, due to the better accuracy, all structural, energetic, and electronic properties were obtained with the HSE06 optimized geometry.

Table S2. Energetic and electronic properties for the optimization of FM-NH\(_2\) and FM-NH\(_3\) at HSE06/light-tier2, considering the lowest energy configuration from the previous torsionated initial (-t) structures obtained at PBE/light-tier2 level. \(E_{\text{tot}}^{\text{DFT}}\) is the DFT total energy; \(q^n\) is the molecule total charge where \(n = 0-2\); \(m_{\text{tot}}\) is the total magnetic moment; \(\varepsilon_{\text{HOMO}}\) and \(\varepsilon_{\text{LUMO}}\) are the energies of HOMO and LUMO, respectively; and \(E_g\) is the LUMO-HOMO energy gap.
**Figure S6.** Optimized \textbf{FM-NH}_2 and \textbf{FM-NH}_3 structures at PBE/light-tier2 and HSE06/light-tier2 levels.

Going further, we compare in **Table S3** the bond lengths and dihedral angles obtained from the optimized geometry structure of \textbf{FM-NH}_2 and \textbf{FM-NH}_3 at both PBE and HSE06 levels. This comparison shows that, in both cases, the optimized structure is very similar to each other.

*The values in parenthesis were obtained experimentally from cyclic voltammetry and UV-Vis absorption spectroscopy.*
Table S3. Structural properties at PBE/light-tier2 for **FM-NH$_2$** and **FM-NH$_3$** molecules, where $d$ is the absolute bond length (in Å), $d_{av}$ is the average bond length (in Å ) and $\phi$ is the torsion angle (in º).

| Atom label | FM-NH$_2$ | FM-NH$_3$ |
|------------|-----------|-----------|
|            | PBE       | HSE06     | PBE       | HSE06     |
| dC2–C6     | 1.377     | 1.361     | 1.378     | 1.359     |
| dC6–C5     | 1.486     | 1.480     | 1.488     | 1.484     |
| dC6–C7     | 1.486     | 1.480     | 1.488     | 1.484     |
| dN1–C      | 1.395     | 1.385     | 1.499     | 1.484     |
| dN2–C      | 1.395     | 1.385     | 1.499     | 1.484     |
| $d_{av}$C–C,R1 | 1.403 | 1.393     | 1.402     | 1.392     |
| $d_{av}$C–C,R2 | 1.403 | 1.393     | 1.402     | 1.392     |
| $d_{av}$C–C,R3 | 1.403 | 1.392     | 1.400     | 1.389     |
| $d_{av}$C–C,R4 | 1.403 | 1.392     | 1.400     | 1.389     |
| $d_{av}$C–C,R5 | 1.454 | 1.446     | 1.456     | 1.448     |
| $\phi$C1–C2–C6–C5 | 21.89 | 21.21    | 18.64    | 15.71     |
| $\phi$C3–C2–C6–C7 | 21.72 | 21.00    | 18.50    | 15.44     |
| $\phi$C3–C2–C6–C5 | -158.28 | -159.18   | -161.80 | -163.88 |
| $\phi$C1–C2–C6–C7 | -158.12 | -158.61   | -161.06 | -164.97 |
| $\phi$C2–C6–C7–C8 | 49.91 | 50.09    | 56.32    | 59.68     |
| $\phi$C2–C6–C5–C4 | 50.35 | 50.48    | 57.59    | 62.28     |

*Isomers FM-NH$_2$ and FM-NH$_3$ Structures*
In both $\text{FM-NH}_2$ and $\text{FM-NH}_3$, the aniline/anilinium group can assume different conformations, yielding distinct isomers, as shown in Fig. S7. In this sense, we study from an energetic point of view the energy associated with them (Table S4). We observe that the isomers of $\text{FM-NH}_2$ are almost degenerate in energy, while for $\text{FM-NH}_3$, the energetic difference is slightly higher, ~100 meV. We can conclude that all configurations change their initial conformation, e.g., ring torsion angle, upon geometric optimization aiming to maximize the distance between the neighboring -NH$_2$ or -NH$_3$.

**Figure S7.** Optimized isomers of $\text{FM-NH}_2$ and $\text{FM-NH}_3$ structures at HSE06/light-tier2 level of
The experimental data evinces the preference of \( \text{NH}_2 \) at an up-down position which agrees with the DFT calculations. However, the electronic properties are not largely affected by the position of -\( \text{NH}_2 \) and -\( \text{NH}_3 \) groups, as observed in Table S4. For instance, the HOMO and LUMO are spread for both up and/or down isomers of FM-NH\(_2\), lying within an energy window of -5.3 to -5.4 eV (-2.1 to -2.2 eV).

We also calculated the projected density of states (PDOS) for FM-NH\(_2\) and FM-NH\(_3\). The results helped us understand the lower \( E_g \) of the salt compared to the neutral molecule. As can be seen from Fig. S8, the HOMO of FM-NH\(_2\) is composed of the coupling between C and N \( p \)-states. However, the HOMO orbitals of FM-NH\(_3\) (for up and/or down isomers) are localized at deeper energy levels, \textit{i.e.}, -10.3(5/6) eV, having a large contribution of C \( p \)-states, whereas the LUMO remains localized at -7.6(9) eV, with a large contribution of H- \( s \)-states. Those differences explain the smaller energy gap for the isomers of FM-NH\(_3\).  

**Table S4.** Energetic and electronic properties for the optimization of mono-/di-protonated FM-NH\(_2\) molecule at HSE06/light-tier2, considering the structural isomers where NH\(_2\) and/or NH\(_3\) groups are at up and/or down position. Whereas, \( E_{\text{tot}}^{\text{DFT}} \) is the DFT total energy.

| Molecule          | \( E_{\text{tot}}^{\text{DFT}} \) (eV) | \( q^{\text{e}^+} \) (e) | \( m_{\text{tot}} \) (\( \mu_B \)) | HOMO (eV) | LUMO (eV) | \( E_g \) (eV) |
|-------------------|----------------------------------------|---------------------------|---------------------------------|-----------|-----------|-----------|
| FM-NH\(_2\) up-up | -30268.136445794                      | 0                         | 0                               | -5.30     | -2.23     | 3.08      |
| FM-NH\(_2\) up-down | -30268.143836536                     | 0                         | 0                               | -5.38     | -2.19     | 3.19      |
| FM-NH\(_2\) down-down | -30268.136439811                    | 0                         | 0                               | -5.36     | -2.14     | 3.22      |
| FM-NH\(_3\) up-up | -30285.242140821                      | 2                         | 0                               | -10.29    | -7.60     | 2.69      |
| FM-NH\(_3\) up-down | -30285.347679144                    | 2                         | 0                               | -10.49    | -7.95     | 2.54      |
| FM-NH\(_3\) down-down | -30285.488467455                  | 2                         | 0                               | -10.59    | -7.94     | 2.65      |
**Figure S8.** Projected density of states (PDOS) per atom for the FM-NH$_2$ and FM-NH$_3$ up-up isomers at HSE06/light-tier2 level, taking vacuum as reference.

**Experimental vs Theoretical Structure**

We were able to obtain a single crystal of both FM-2Br and FM-NH$_2$ to ensure high purity and determine their crystal structures, in order to corroborate the chemical characterizations and bring light to the theoretical calculations performed for diaminine product. The single crystals were prepared by the slow-evaporation method from concentrated solutions of the compounds in hexane (case of FM-2Br) and ethyl acetate...
evaporated (case of \textbf{FM-NH}_2) at room temperature; for \textbf{FM-2Br} we obtained yellow needle-like crystals and for \textbf{FM-NH}_2, orange block crystals. It is worth mentioning that although \textbf{FM-2Br} has no chiral atoms, it crystallizes in the non-centrosymmetric space group P2\textsubscript{1}2\textsubscript{1}2\textsubscript{1}. It may be due to the slight concavity observed due to the central ring distortion, which prevents the molecule to have a specular counterpart. The final chirality of the structure could be determined by the Flack parameter, which at the end of the refinement has reached –0.018(12). The crystal structure of \textbf{FM-2Br} is presented in Fig. S9a. For \textbf{FM-NH}_2, the crystal structure determined by XRD is in agreement with the proposed from the chemical characterizations and crystallizes in centrosymmetric space group P2\textsubscript{1}/c. This molecule seems to have its three-ring fused system in the plane, with no concavity, and thus is achiral, as observed in its space group. During its refinement, we found that the aniline rings present structural disorder, being treated as double split positions. This is in line with the findings presented in the last section about the isomers having almost the same energy, which translates into solid state in disorder. Fig. S9b shows the representation of the crystal structure of \textbf{FM-NH}_2, focusing on only one of the possible for clarity. The main crystallographic information is summarized in Table S5. CCDC number for \textbf{FM-2Br} is 2156522 and for \textbf{FM-NH}_2 is 2156523, respectively.

We were able to obtain a single crystal of \textbf{FM-NH}_2 by the slow-evaporation method from a concentrated solution of the molecule in ethyl acetate. We then resolve the crystal structure of this molecule by XRD and found that the aniline rings present structural disorder, being treated as double split positions. Fig. S9b shows the representation of the molecular structure of \textbf{FM-NH}_2 obtained from the XRD experiment. The main crystallographic information is summarized in Table S5.
Figure S9. Representation of molecular structure of (a) FM-2Br, and (b) FM-NH₂ obtained by single-crystal X-ray experiments, with atomic labeling. Ellipsoids are presented at 50% of probability.

Table S5. Crystallographic data resume. \(^a\) \(R = \Sigma||F_o||−|F_c||/\Sigma|F_o||.\) \(^b\) \(wR = [\Sigma(|F_o|^2−|F_c|^2)^2/\Sigma|F_o|^2]^{1/2}\)

| Compound    | FMBr2C        | FMNH2A        |
|-------------|---------------|---------------|
| Formula     | C₁₄H₈Br₂      | C₂₆H₂₆N₂      |
| \(F_w\)     | 336.02        | 360.44        |
| \(T/ K\)    | 293(2)        | 293(2)        |
| \(\lambda/ \AA\) | 0.71073 | 0.71073 |
| Crystal system | Orthorhombic | Monoclinic    |
| Space group  | \(P2_12_12_1\) | \(P2_1/c\)    |
| \(a/ \AA\)  | 5.2523(4)     | 9.8328(5)     |
| \(b/ \AA\)  | 13.7411(10)   | 21.7615(15)   |
| \(c/ \AA\)  | 16.3685(9)    | 9.0522(5)     |
| \(\alpha/ ^\circ\) | 90           | 90            |
| \(\beta/ ^\circ\) | 90           | 91.749(5)     |
| \(\gamma/ ^\circ\) | 90           | 90            |
| \(V/ \AA^3\) | 1181.35(14)   | 1936.1(2)     |
| \(Z/Z'\)    | 4/1           | 4/1           |
| \(\rho/ \text{kg m}^{-3}\) | 1.889      | 1.237         |
| \(\mu/ \text{mm}^{-1}\) | 6.828     | 0.072         |
| \(F(000)\)  | 648           | 760           |
| Crystal size/ mm³ | 0.85×0.16×0.08 | 0.53×0.26×0.16 |
| Total reflections [\(R_{int}\)] | 8968 [0.043] | 14945 [0.0402] |
| \(R_a\), \(wR_b\) [\(I > 2\sigma(I)\)] | 0.0358; 0.0683 | 0.0546; 0.1095 |
| \(R_a\), \(wR_b\) (all data) | 0.0542; 0.0756 | 0.1050; 0.1330 |
| Larg. diff. peak and hole / e \(\AA^{-3}\) | 0.275; −0.490 | 0.102; −0.123 |
| Flack parameter | −0.018(12)  | ---           |

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To check the validity of our calculations in predicting the optimized structure of FM-NH$_2$ we compare in Table S6 the experimental and calculated bond lengths. We found an excellent correlation between theoretical and experimental results, evidencing the validity of our DFT calculations.

**Table S6.** Comparison between the experimental (X-ray) and theoretical bond lengths (HS06/light-tier2) for the up-down isomer of FM-NH$_2$. The theoretical values are shown in italic.

| Atom 1 | Atom 2 | Length (Å)   |
|--------|--------|--------------|
| C1     | C13    | 1.493(2)     |
|        |        | 1.480        |
| C1     | C14    | 1.340(3)     |
|        |        | 1.359        |
| C1     | C2     | 1.489(2)     |
|        |        | 1.480        |
| C10    | H10    | 0.930(3)     |
|        |        | 1.083        |
| C10    | C11    | 1.374(4)     |
|        |        | 1.392        |
| C11    | H11    | 0.930(2)     |
C12  H12  1.083
     0.930(2)
     1.081
C12  C11  1.386(3)
     1.388
C13  C12  1.388(3)
     1.392
C14  C21  1.461(5)
     1.480
C14  C15  1.481(5)
     1.481
C15  C16  1.390(8)
     1.397
C15  C20  1.390(8)
     1.392
C16  H16  0.930(5)
     1.082
C16  C17  1.390(6)
     1.386
C17  H17  0.930(4)
     1.083
C17  C18  1.391(7)
     1.385
C18  H18  0.930(4)
     1.085
C18  C19  1.390(6)
     1.397
C19  C20  1.389(6)
     1.395
C2  C3  1.385(3)
     1.392
C20  H20  0.929(5)
     1.084
C21  C22  1.391(6)
C21  C26  1.389(6)
     1.392
C22  H22  0.930(4)
     1.085
|     |     |     |     |     |     |     |     |
|-----|-----|-----|-----|-----|-----|-----|-----|
| C22 | C23 | 1.390(6) |     | 1.394 |
| C23 | C24 | 1.391(6) |     | 1.398 |
| C24 | H24 | 0.930(4)  |     | 1.084 |
| C24 | C25 | 1.390(6) |     | 1.385 |
| C25 | H25 | 0.930(4)  |     | 1.083 |
| C25 | C26 | 1.390(6) |     | 1.386 |
| C26 | H26 | 0.930(4)  |     | 1.082 |
| C3  | H3  | 0.930(2)  |     | 1.081 |
| C4  | H4  | 0.930(2)  |     | 1.083 |
| C4  | C3  | 1.386(3) |     | 1.388 |
| C5  | H5  | 0.930(3)  |     | 1.083 |
| C5  | C4  | 1.378(4) |     | 1.392 |
| C6  | H6  | 0.930(2)  |     | 1.083 |
| C6  | C5  | 1.370(4) |     | 1.387 |
| C7  | C2  | 1.406(3) |     | 1.409 |
| C7  | C6  | 1.383(3) |     | 1.387 |
| C8  | C7  | 1.458(3) |     | 1.456 |
| C8  | C13 | 1.404(2) |     | 1.409 |
| C8  | C9  | 1.386(3) |     | 1.388 |
| C9  | H9  | 0.930(3) |     |       |
Theoretical Absorption Spectra

The TDDFT calculations\textsuperscript{13,14} were performed with ORCA program package v4.2.1\textsuperscript{15,16} at B3LYP/def2-TVP level with def2/j auxiliary basis set\textsuperscript{17} Thus, a Tight SCF Convergence criteria and Normal criteria for Optimization (those values reported in ORCA’s manual) were used along with the Conductor-like Polarizable Continuum Model (CPCM)\textsuperscript{18} for implicit solvent representation. The results are shown in \textbf{Fig. S10}.

From the time-dependent (TD)-DFT analysis, \textit{i.e.}, natural transition orbitals, the singlet excitations that occur at \(~356\) nm have a larger contribution from HOMO \(\rightarrow\) LUMO (experimentally, this transition appears at \(330\) nm), while the transitions at \(~227.7\) nm both HOMO-1 \(\rightarrow\) LUMO+1 and HOMO \(\rightarrow\) LUMO contribute almost equally for the \textbf{FM-NH\textsubscript{2} up-up} isomer. The character of those singlets excitations remains the same for all investigated solvents, with only minor changes in the energy associated with each transition.
Energy Level Distribution and Charge Analysis

We calculated the energy level distribution and performed Hirshfeld charges analysis using the HSE06/light-tier2 level. For the case of the neutral molecule, FM-NH$_2$, we found that the aniline groups were twisted about 20° about the plane of the fluorene. In the case of the salt, FM-NH$_3$, the torsion angle between the anilinium groups and the fluorene decreases to ~16°. Changes can also be seen in the distribution of the energy levels over the molecule (Fig. S11a). Whereas in the neutral molecule both HOMO and LUMO are spread out over the entire backbone, in the protonated the
HOMO is mainly concentrated on the fluorene moiety, while the LUMO experiences a similar distribution found for \textbf{FM-NH}_2. This is an indication that an internal charge transfer from the fluorene to the anilinium groups could be occurring in the case of the salt. In addition, the charge distribution is significantly affected by protonation (Fig. S11b): the charge on the nitrogen atoms changes from -0.192 to +0.027. Also, the carbon atom attached directly to the N becomes more positively charged upon protonation.

\textbf{Figure S11.} (a) HOMO and LUMO distribution in FM-NH\textsubscript{2} and FM-NH\textsubscript{3} up-up isomers at HSE06/light-tier2 level. Isosurface value: 0.0025. (b) Hirshfeld charges analysis for the FM-NH\textsubscript{2} and FM-NH\textsubscript{3}\textsuperscript{+} molecules at HSE06/light-tier2.
6.1. Description of the Models

To better understand the interaction between FM-NH$_2$ and FM-NH$_3$ with the perovskite surface, we developed different models for each. To maintain the charge neutrality of the system and avoid the formation of dipoles, the perovskite surfaces were built to cancel the charge of the molecules interacting with it. Thus, to interact with the neutral FM-NH$_2$ molecule, the perovskite surface was configured to be neutral, and to interact with the positively charged FM-NH$_3$, the perovskite surface must be negatively charged, ensuring charge neutrality. Thus, the following models were created:

- Two FM-NH$_2$ molecules were distributed on a 2x2x3 FAPbI$_3$ surface where the FAI salt was removed (keeping the neutrality of the system), thus the molecules interacted with Pb and I.
- Two FM-NH$_3$ molecules were distributed on a 2x2x3 FAPbI$_3$ surface where only the FA molecules were removed (thus, being positively charged), allowing the protonated sites of FM-NH$_3$ to effectively replace the FA molecules.

For each model, we considered two possible configurations for the adsorbed molecule (up-up / down-down), which are differentiated by the rotation angle between the aniline/anilinium group and the fluorene. The geometry of these structures was previously determined and is shown in Section 5. These arrangements will affect the interaction between the molecules and the perovskite surface.

Additionally, we evaluated two different possible positions the molecules can occupy on the perovskite surface, to evaluate if some arrangement was preferential. To summarize, considering the two molecules, two models, the two possible molecule configurations, and the two possible molecule positions, we have eight models to study.

6.2. Total Energy Calculations

Our theoretical calculations were based on DFT, within the semilocal Perdew–Burke–Ernzerhof (PBE)$^{19}$ formulation for the exchange–correlation energy functional, as implemented in the Vienna ab initio Simulation Package (VASP),$^{20,21}$ version 5.4.1. The semiempirical vdW D3 correction proposed by Grimme et al.$^{22}$ was
included to improve the deficient description of interlayer vdW interactions by the PBE functional, which is key in the description of hybrid organic-inorganic perovskites. The Kohn–Sham (KS) equations are solved using the all-electron projector augmented-wave (PAW) method, where the KS orbitals are expanded in plane-wave basis sets.

The equilibrium structures were obtained using a conjugate gradient algorithm minimization of the stress-tensor (in-plane, xy) and/or atomic forces on each atom to less than 0.05 eV Å, employing plane-wave cutoff energy of 466 eV. It is 12.5% greater than the largest default cutoff energy for the employed PAW projectors (Pb, I, C, H, N), due to the slower convergence of the stress-tensor as a function of the number of plane waves. A total energy convergence criterion of $1 \times 10^{-5}$ eV was employed, and a vacuum thickness of 20 Å was added in the z-direction to all configurations to avoid spurious interactions between the heterostructures and their images. For the Brillouin zone integration, we sampled only the $\Gamma$ point due to the large size of the systems.

### 6.3. Analyses

To quantify the interaction between molecules and surface, we calculated two properties: (i) the interaction energy, $E_i$, which is the difference between the energy of the equilibrium geometry of the perovskite+molecule system and the sum of the energy of the respective parts, separated and frozen; (ii) the adsorption energy, $E_a$, which is the difference between the energy of the equilibrium geometry of the perovskite+molecule system and the sum of the energy of the respective parts, separated but optimized. This allows the understanding of the role of the distortions in the adsorption process, and the energy associated with these distortions, $E_d$, can be used to correlate the adsorption and interaction energies via $E_a = E_i + E_d$. Additionally, we evaluated the dispersion energy of the different systems and their respective components, as well as the dispersion energy associated only with the interaction between the molecules and the perovskite slab, $\Delta E_{\text{disp}}$, which can be defined as $\Delta E_{\text{disp}} = E_{\text{disp}}^{\text{A+B}} - E_{\text{disp}}^{\text{A}} - E_{\text{disp}}^{\text{B}}$.

### 6.4. Results

The eight models constructed are illustrated in Figure S12. Following the structural optimization, their resulting configurations are illustrated in Figure S13, and the energy results are summarized in Tables S7 and S8.
Figure S12. Atomic configurations of the proposed models where (a) FM-NH$_2$ interacts with a neutral perovskite surface and (b) where FM-NH$_3$ interacts with a negatively charged perovskite slab.
**Figure S13.** Equilibrium atomic configurations obtained after stress-tensor calculations, of the proposed models where (a) FM-NH$_2$ interacts with a neutral perovskite surface and (b) where FM-NH$_3$ interacts with a negatively charged perovskite slab.

**Table S7.** Lattice parameters ($a_0$, $b_0$), relative energy ($\Delta E$), interaction energy ($E_i$), adsorption energy ($E_a$), and distortion energy ($E_d$) of the different systems studied.

|          | $a_0$ (Å) | $b_0$ (Å) | $\Delta E$ (meV/atom) | $E_i$ (eV/mol) | $E_a$ (meV/Å$^2$) | $E_d$ (eV/mol) | $E_d$ (meV/Å$^2$) |
|----------|-----------|-----------|------------------------|----------------|-------------------|----------------|-------------------|
| FAPbI$_3$ + FM-NH$_2$ (1) | 11.71     | 13.56     | 0.00                   | -1.15          | -14.54            | -1.02          | -12.81            |
| FAPbI$_3$ + FM-NH$_2$ (2) | 11.55     | 13.56     | 1.01                   | -1.07          | -13.65            | -0.85          | -10.85            |
| FAPbI$_3$ + FM-NH$_3$ (3) | 11.83     | 13.35     | 1.26                   | -1.36          | -17.18            | -1.13          | -14.33            |
| FAPbI$_3$ + FM-NH$_3$ (4) | 11.68     | 13.55     | 1.79                   | -1.29          | -16.32            | -0.99          | -12.47            |

|          | $a_0$ (Å) | $b_0$ (Å) | $\Delta E$ (meV/atom) | $E_i$ (eV/mol) | $E_a$ (meV/Å$^2$) | $E_d$ (eV/mol) | $E_d$ (meV/Å$^2$) |
|----------|-----------|-----------|------------------------|----------------|-------------------|----------------|-------------------|
| FAPbI$_3$ + FM-NH$_2$ (1) | 11.83     | 13.98     | 0.00                   | -8.88          | -107.34           | -7.49          | -90.54            |
| FAPbI$_3$ + FM-NH$_2$ (2) | 11.13     | 14.08     | 2.33                   | -9.00          | -114.80           | -7.03          | -89.66            |
| FAPbI$_3$ + FM-NH$_3$ (3) | 11.80     | 13.92     | 3.35                   | -8.68          | -105.68           | -7.51          | -91.47            |
| FAPbI$_3$ + FM-NH$_3$ (4) | 11.41     | 13.99     | 2.30                   | -9.18          | -115.11           | -7.64          | -95.75            |

**Table S8.** Dispersion energy of the different components of each system, as well as the dispersion energy associated with the interaction of the molecules and the perovskite slab.

|          | Edisp A+B (eV) | Edisp A (eV) | Edisp B (eV) | $\Delta$Edisp (eV) |
|----------|----------------|-------------|-------------|---------------------|
| FAPbI$_3$ + FM-NH$_2$ (1) | -16.74        | -12.68      | -2.62       | -1.44               |
| FAPbI$_3$ + FM-NH$_2$ (2) | -16.80        | -12.64      | -2.73       | -1.42               |
| FAPbI$_3$ + FM-NH$_3$ (3) | -16.72        | -12.69      | -2.29       | -1.74               |
| FAPbI$_3$ + FM-NH$_3$ (4) | -16.53        | -12.74      | -2.27       | -1.52               |
| FAPbI$_3$ + FM-NH$_3$ (1) | -18.61        | -13.22      | -2.69       | -2.70               |
| FAPbI$_3$ + FM-NH$_3$ (2) | -18.32        | -13.45      | -2.69       | -2.19               |
| FAPbI$_3$ + FM-NH$_3$ (3) | -17.51        | -12.96      | -2.21       | -2.34               |
| FAPbI$_3$ + FM-NH$_3$ (4) | -17.58        | -13.05      | -2.29       | -2.25               |
Section 7. Scanning Electron Microscopy Images of the Perovskite Films Passivated with FM-NH$_2$

Figure S14. SEM images of the perovskite film modified with FM-NH$_2$ using (a) 4, (b) 8, (c) 12, (c) 16 mM solutions.
Section 8. Effects of FM-NH$_2$ on the Perovskite Solar Cell Efficiency and Contact Angle Measurements

(a)

![Box plots of solar cell parameters](image)

(b)

![Contact angle images](image)

**Figure S15.** (a) Statistics of the solar cell parameters and (b) contact angle measurements for the perovskite film modified with FM-NH$_2$ at various concentrations.
Section 9. Device Performance with the Post-Treatment with FM-NH$_3$X (X=Cl, Br, I)

Table S9. Summary of the parameters obtained for the stabilized devices. The star (*) represents the best efficiency devices.

| Direction | V$_{oc}$ (V) | J$_{sc}$ (mA cm$^{-2}$) | FF (%) | Efficiency (%) |
|-----------|--------------|-------------------------|--------|----------------|
| Control   |              |                         |        |                |
| Reverse*  | 1.03         | 23.52                   | 74.22  | 18.09          |
| Forward*  | 1.03         | 23.40                   | 76.04  | 17.84          |
| Reverse   | 1.023 ± 0.008| 23.15 ± 0.24            | 72.40 ± 2.43 | 17.16 ± 0.79   |
| Forward   | 1.017 ± 0.007| 23.17 ± 0.22            | 71.96 ± 2.48 | 16.95 ± 0.61   |
| FM-NH$_3$Cl |          |                         |        |                |
| Reverse*  | 1.05         | 23.47                   | 76.34  | 18.6           |
| Forward*  | 1.04         | 23.56                   | 76.69  | 18.68          |
| Reverse   | 1.040 ± 0.005| 23.13 ± 0.31            | 74.42 ± 1.54 | 17.91 ± 0.59   |
| Forward   | 1.023 ± 0.008| 23.12 ± 0.35            | 74.16 ± 1.79 | 17.55 ± 0.68   |
| FM-NH$_3$Br |          |                         |        |                |
| Reverse*  | 1.06         | 23.31                   | 74.60  | 18.35          |
| Forward*  | 1.05         | 23.39                   | 74.77  | 17.97          |
| Reverse   | 1.050 ± 0.009| 22.98 ± 0.25            | 71.99 ± 1.38 | 17.32 ± 0.57   |
| Forward   | 1.037 ± 0.009| 22.98 ± 0.25            | 72.11 ± 1.61 | 17.17 ± 0.56   |
| FM-NH$_3$I |          |                         |        |                |
| Reverse*  | 1.07         | 23.51                   | 77.82  | 19.35          |
| Forward*  | 1.05         | 23.58                   | 78.75  | 19.14          |
| Reverse   | 1.054 ± 0.012| 23.28 ± 0.13            | 74.80 ± 2.18 | 18.36 ± 0.72   |
| Forward   | 1.041 ± 0.011| 23.28 ± 0.17            | 73.94 ± 3.63 | 17.93 ± 0.99   |
Section 10. X-ray Diffraction of the Perovskite Film modified with FM-NH$_3$X Salts

Figure S16. XRD of the perovskite film modified with FM-NH$_3$X (X=Cl, Br, I) salts.
Section 11. Fourier Transform Infrared Spectroscopy of the Perovskite Films Modified with FM-NH$_3$X Salts

Figure S17. FTIR spectra of the perovskite film modified with the FM-NH$_3$X (X=Cl, Br, I) salts.
Section 12. X-ray Photoelectron Spectroscopy of the N 1s, C 1s, and Pb 4f Core Levels of Perovskite Films Modified with FM-NH$_3$X Salts

Figure S18. High-resolution XPS spectra of (a) N 1s, (b) C 1s, and (c) Pb 4f core levels of the perovskite films modified with FM-NH$_3$X (X = Cl, Br, I). In (c) it is also showed the XPS spectra of the perovskite
modified with FM-NH₂.
Section 13. Discussion About the Kelvin Probe Force Microscopy Measurements

In Kelvin probe force microscopy (KFPM), a voltage is applied to an AFM tip to nullify the charges on the surface. The samples were placed in a resistor and connected by metallic contact (silver ink) (Fig. S19), allowing the electrons to flow between one sample and another. In this sense, KFPM will provide information about the local changes in contact potential difference \( V_{\text{CPD}} \) in the sample, measured between the sample and the tip. Interestingly, for metals and semiconductors, it is possible to relate the \( V_{\text{CPD}} \) with the Fermi energy \( E_F \) of the materials: \( V_{\text{CPD}} \propto E_{F, \text{sample}} - E_{F, \text{tip}} \). Note that we used a proportionality signal and not equality. This is because \( V_{\text{CPD}} \) is affected by the electrostatic charges adsorbed on the surface, contamination, and degradation of the sample. These parameters will influence the value measured, making it slightly different from the real \( E_F \).

In this sense, we only can probe the trends on the \( E_F \) of the surface and not the absolute value. To do so, we must use the same tip to run all the measurements, avoiding changes in the \( E_{F, \text{tip}} \), which otherwise will affect the comparison between the \( E_F \) of the samples in a given batch of the experiment. We minimize the interfering parameters cited above using this strategy while keeping the same \( E_{F, \text{tip}} \). As a result, since the samples are in short-circuit, the electrons of the lower \( E_F \) material will flow to the higher ones. When the equilibrium is reached, the \( E_F \) will be equalized, and the higher \( E_F \) material becomes negatively charged, whereas the lower \( E_F \), is positively charged. Consequently, the tip-applied potential necessary to nullify the charges on the former will be lower compared to the latter. In this sense, the measured \( V_{\text{CPD}} \) of the sample with the higher \( E_F \) will be lower compared to the lower \( E_F \) material. Thus, we can monitor the variation on the \( E_F \) position from sample to sample.

Figure S19. Scheme of the sample preparation for the KPFM measurements. The samples were placed onto a steel dis, and silver ink was used to electrically connect them and allow electron flux.
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