

ADVANCED MATERIALS

Supporting Information

for *Adv. Mater.*, DOI: 10.1002/adma.202100791

Multifunctional Conjugated Ligand Engineering for Stable
and Efficient Perovskite Solar Cells

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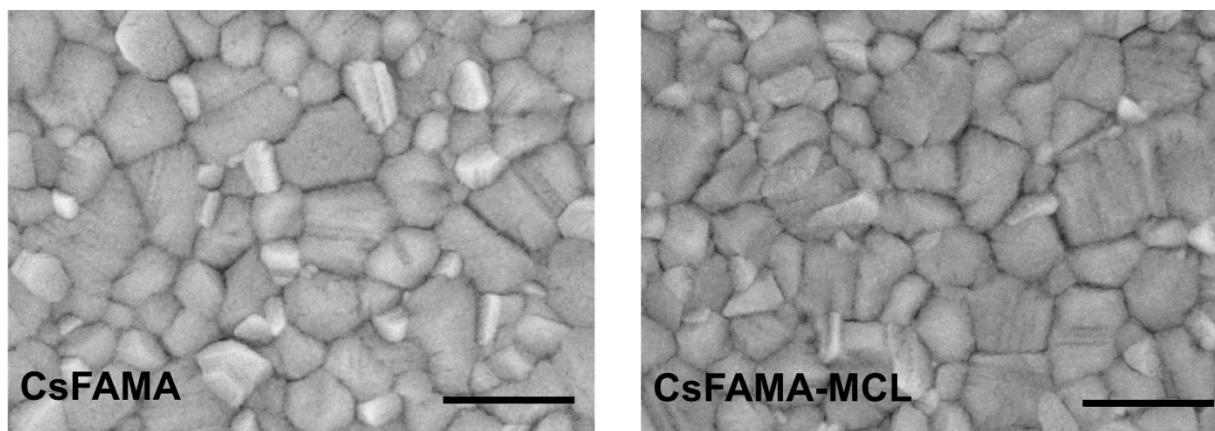


Figure S1. Top-view SEM images of CsFAMA pristine film and CsFAMA-MCL film. No obvious differences on surface morphology can be observed after 4Tm modification. Scale bar: 500 nm.

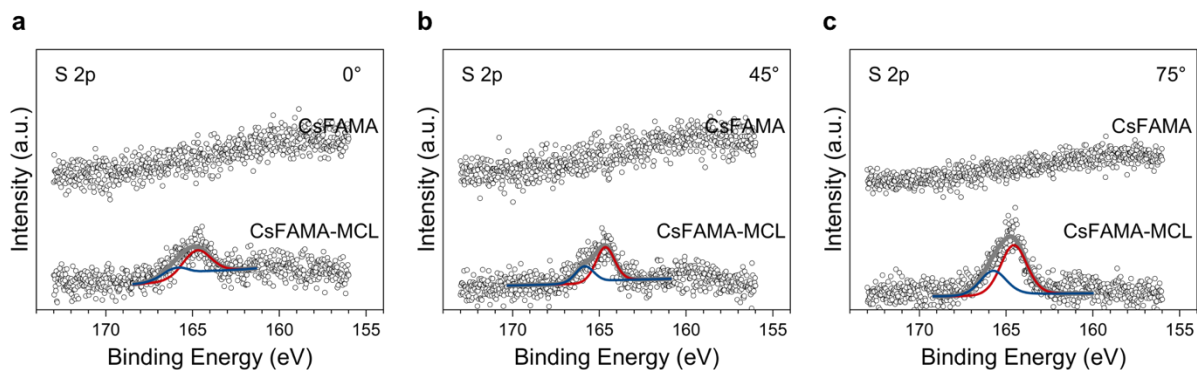


Figure S2. XPS spectra of S 2p region of the CsFAMA film and CsFAMA-MCL film deposited on ITO glass substrate. Various angles, including (a) 0°, (b) 45°, and (c) 75°, between samples and detector were applied to probe different depth. 0° is correlated with a probing depth of 6-8 nm, while 75° is correlated with a probing depth of 2-3 nm. The increase in the S 2p peak intensity with the decrease of probing angles indicates that the MCL is mainly localized on film surface.

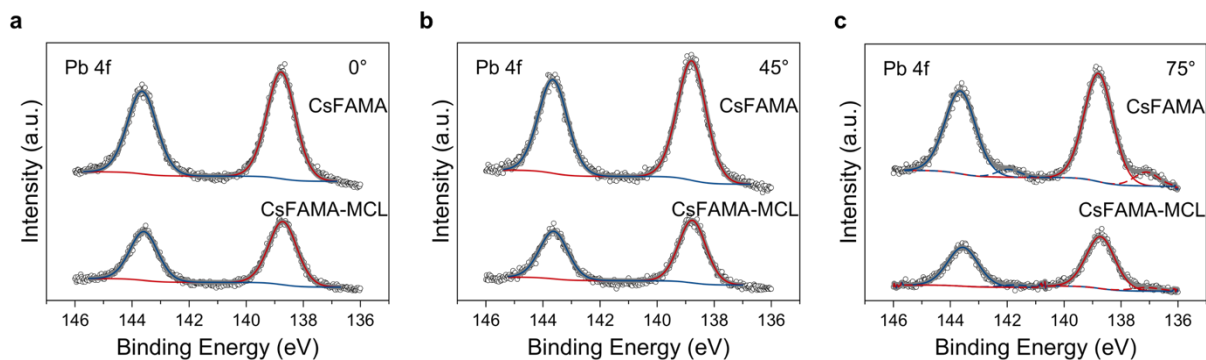


Figure S3. XPS spectra of Pb 4f for the CsFAMA film and CsFAMA-MCL film at probing angles of (a) 0°, (b) 45°, and (c) 75°. The two main peaks located at 138.6 eV and 143.5 eV are attributed to $4f_{7/2}$ and $4f_{5/2}$, respectively. The slight shift of these two peaks toward lower energy by *ca.* 0.1 eV indicates the decreased work function of the CsFAMA-MCL surface. The peaks at 137.2 eV and 142.0 eV, attributed to Pb^0 , are suppressed in CsFAMA-MCL sample, indicating the improved stability and reduced Pb^0 defect after MCL modification.

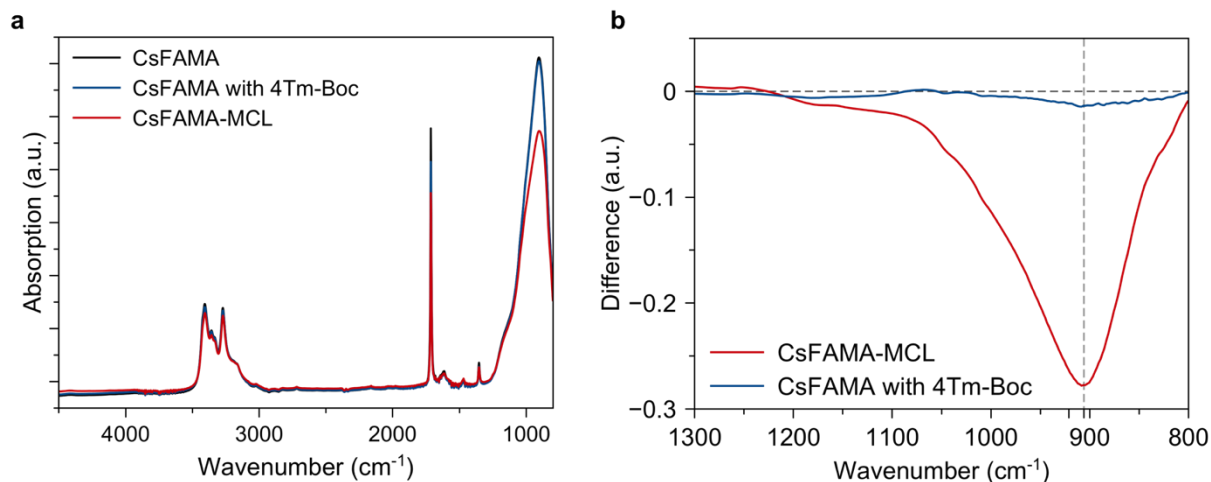


Figure S4. FTIR spectra of CsFAMA coated with 4Tm halide salt ligand or 4Tm-Boc ligand. (a) The original FTIR spectra. The IR spectra of films with or without ligand exhibit similar shapes due to the thin layer of ligand coating, and large amount of amine groups in the pristine CsFAMA film. (b) The difference in FTIR spectrum with the spectrum of neat CsFAMA as background. The peak at 905 cm^{-1} is ascribed to the out-of-plane wagging of N-H bond. The significant decrease in absorption in CsFAMA-MCL sample indicates different binding mode comparing with 4Tm-Boc coated film.

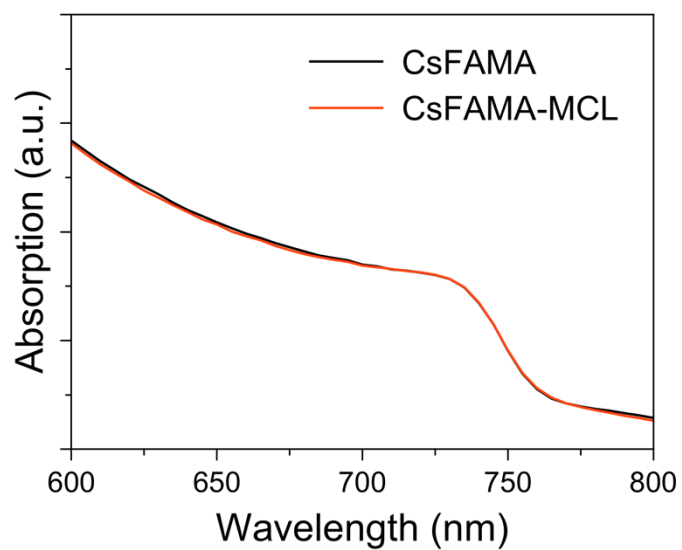


Figure S5. UV-vis absorption spectra of CsFAMA films without and with MCL. No detectable differences between the CsFAMA control film and the MCL modified film can be observed in the UV-vis absorption spectra.

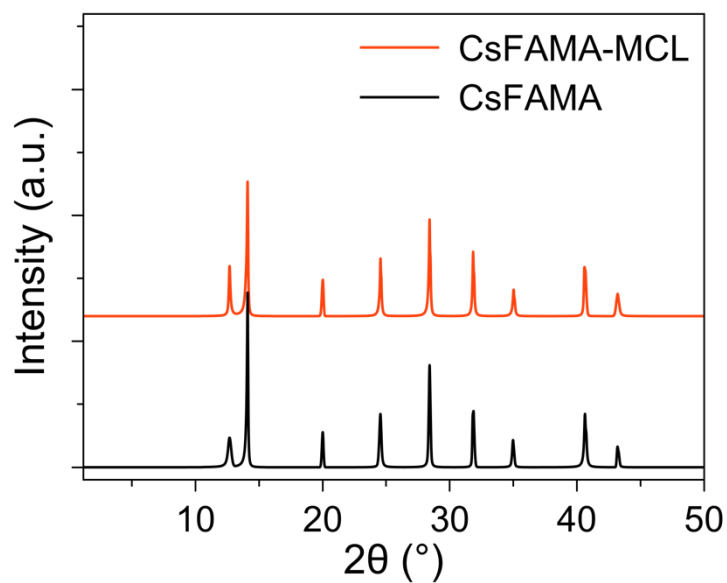


Figure S6. XRD patterns of CsFAMA films without and with MCL. No obvious difference in these XRD patterns can be observed. Specifically, the orientation of the CsFAMA film maintained the same, and no 2D XRD peaks appear at low angle region after MCL modification.

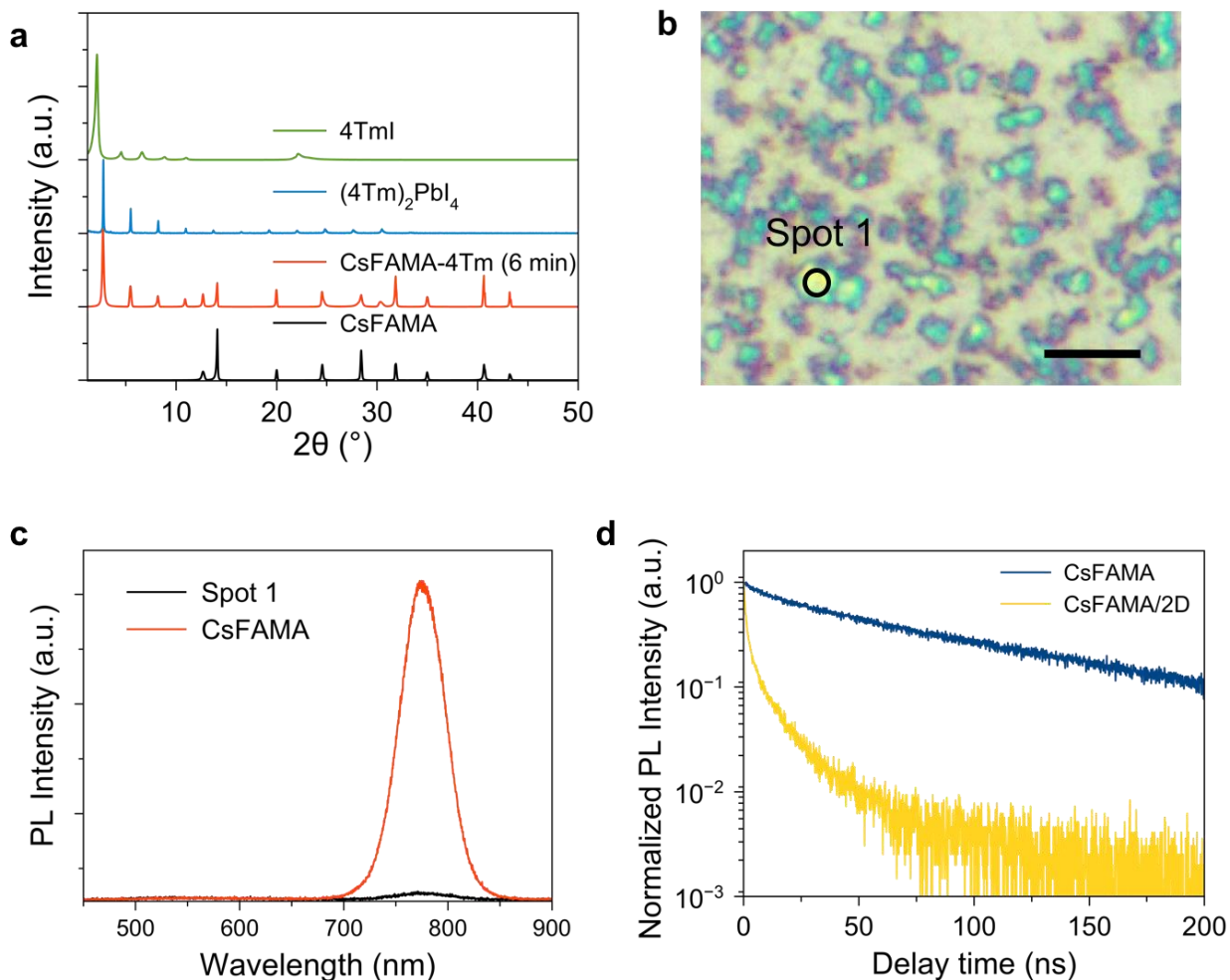


Figure S7. Thick (4Tm)₂PbI₄ 2D layer formation on CsFAMA surface through extended reaction time. (a) XRD patterns of pristine CsFAMA, CsFAMA film dipped in 4Tm solution for 6min, (4Tm)₂PbI₄ 2D perovskite, and 4TmI ligand film, respectively. The distinct (4Tm)₂PbI₄ 2D perovskite peaks at low angle region appear in the CsFAMA film that is dipped in 4Tm solution for 6 min, implying long time treatment of CsFAMA surface with 4Tm can form discernable 2D perovskite on surface. The 2D XRD peaks can be observed without thermal annealing after 4Tm treatment, indicating the strong interactions between 4Tm ligand and perovskite lattice can introduce 2D layers at room temperature. (b)-(d) Optical image of discontinuous 2D capping layer on CsFAMA surface (b), the corresponding PL spectra of 2D

spot indicating the PL quenching (c), and the TRPL from pristine CsFAMA and CsFAMA covered with 2D layer as indicated in spot 1 (d). The PL quenching effect and bi-exponential PL decay indicate efficient charge transfer from 3D perovskite to 2D perovskite, and a potential type-II interface is formed.

4Tm initially absorbs on perovskite surface and bond with perovskite through ionic and hydrogen bonding. The formation of 2D perovskite layer is due to the intercalation of 4Tm into the 3D perovskite lattice and replacing the small cations during the solution processed method. The molecule absorbing and 2D layer formation cannot be disentangled owing to the fast process and low energy required. By extending the reaction time and providing more 4Tm ligand in the solution phase, the equilibrium of dissolving small cations and incorporating 4Tm into perovskite lattice moved further toward the formation of 2D perovskite. Therefore, thicker 2D layer can be observed.

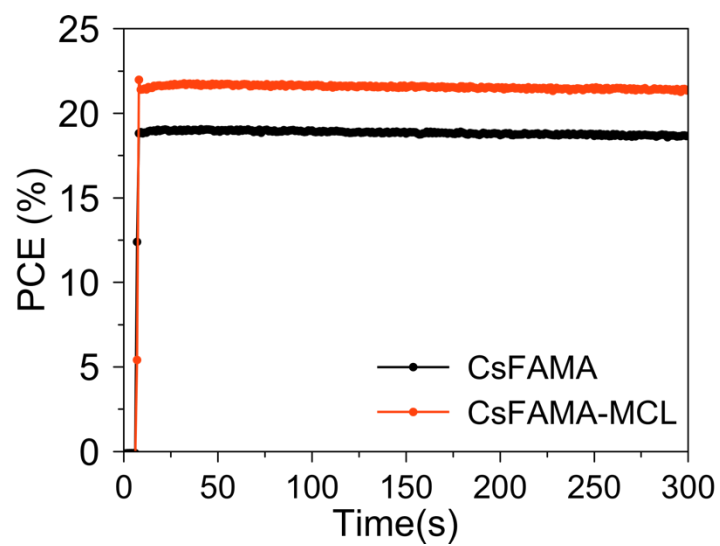


Figure S8. Maximum power point (MPP) tracking of perovskite devices without and with MCL.

The stabilized PCE of CsFAMA-MCL sample is 21.43% with a voltage of 1 V, while the stabilized PCE of CsFAMA control sample is 18.65% with a voltage of 0.9 V.

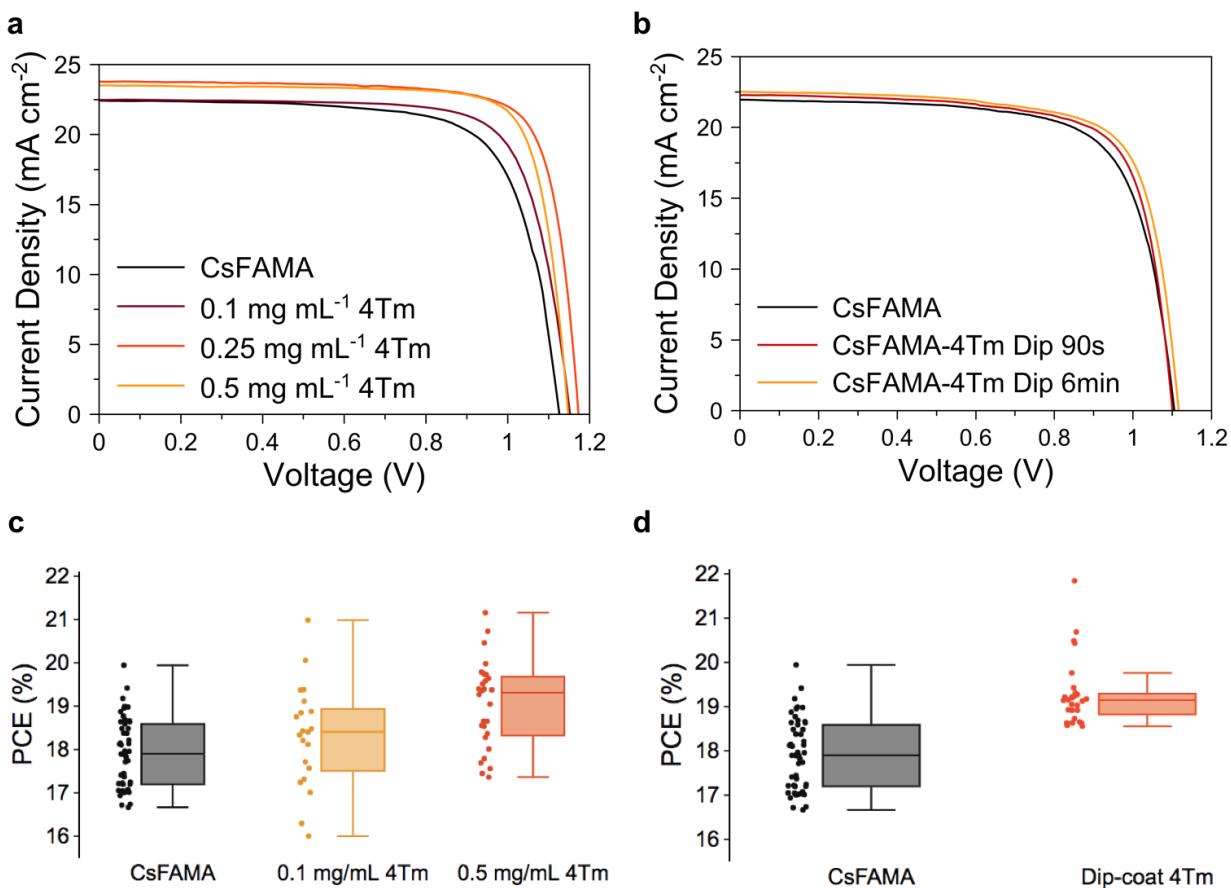


Figure S9. *J-V* characteristics of perovskite devices base on CsFAMA solar cells with different modification condition. *J-V* characteristics of perovskite devices base on CsFAMA modified by 4Tm solution with (a) different concentration and (b) different reaction time. (c), (d) PCE distribution of CsFAMA coated with 4Tm under different conditions. The surface modifications in devices with different 4Tm concentration were all achieved through spin coating methods. Different reaction times between 4Tm and CsFAMA surface were acquired from dipping CsFAMA film into 4Tm solution for different amounts of time, to avoid the influence of solvent evaporation during 4Tm coating process. We observe the minimal improvement in performance when the 4Tm concentration is low. However, the solubility of 4Tm ligand in non-polar solvents restricts the application of 4Tm at high concentration to achieve consistent results. Thus, the

optimized concentration of 4Tm solution is 0.25 mg mL^{-1} . Through increasing the reaction time, thick 2D layer can be formed on CsFAMA surface, which does not further introduce the charge transfer barrier. Improvement in device performance can still be observed in devices with long reaction time.

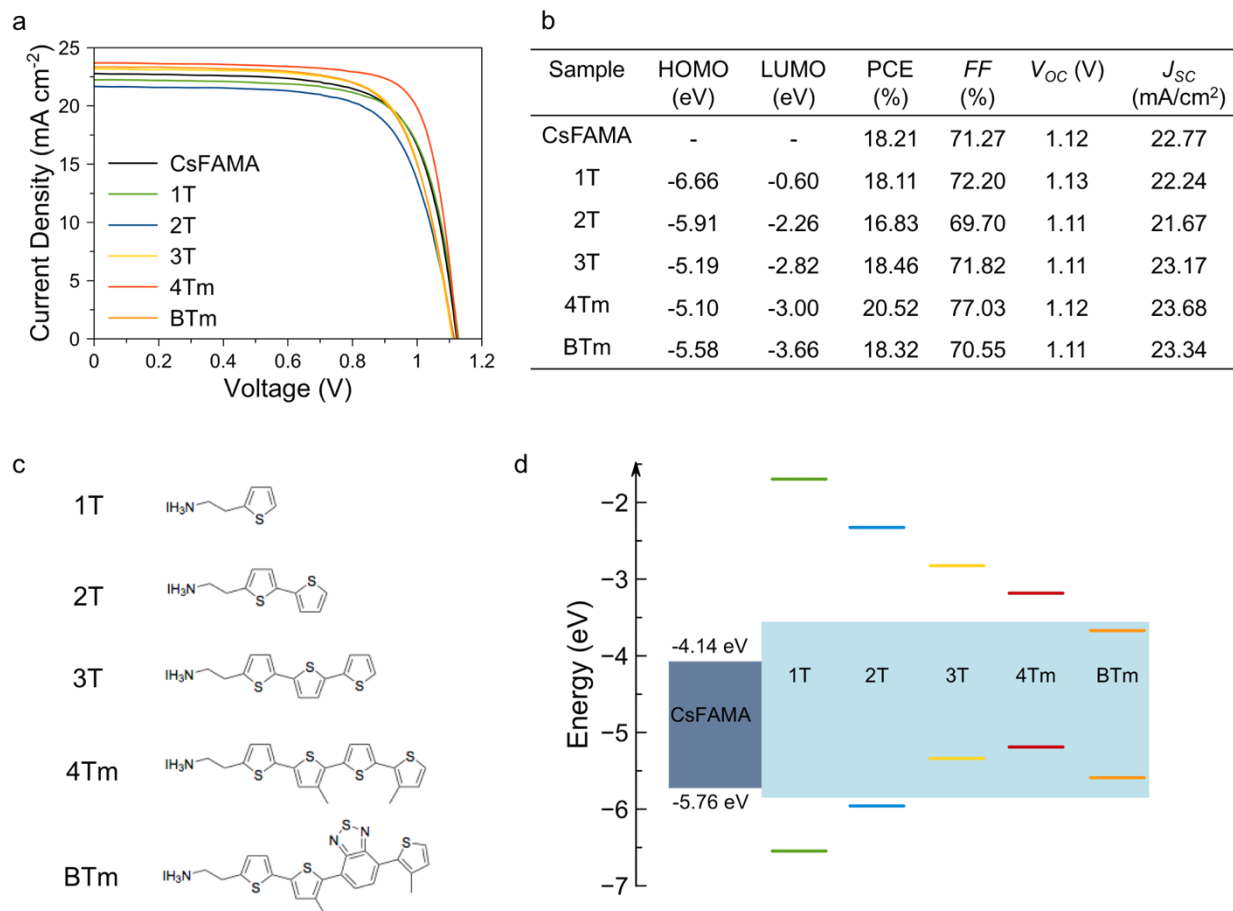


Figure S10. *J-V* characteristics of perovskite devices base on CsFAMA solar cells modification with different ligands. (a) *J-V* curves of devices modified with different semiconducting organic molecules. (b) Summary of energy level of different ligands and photovoltaic parameters obtained from corresponding *J-V* curves. (c) Chemical structures of applied semiconducting organic molecules. (d) Energy level diagram of CsFAMA and different semiconducting organic molecules. The light blue area indicates the valence band and conduction band of inorganic slab in 2D perovskite. The relative energy levels of 1T and 3T are calculated from the current-voltage curve and the absorption spectra. Due to the misalignment of energy levels, 1T, 2T, and BTm ligands are not able to efficiently facilitate hole transfer between perovskite and HTL as 4Tm. 3T ligand suffers from greater solubility issue, therefore it unable to generate reliable results.

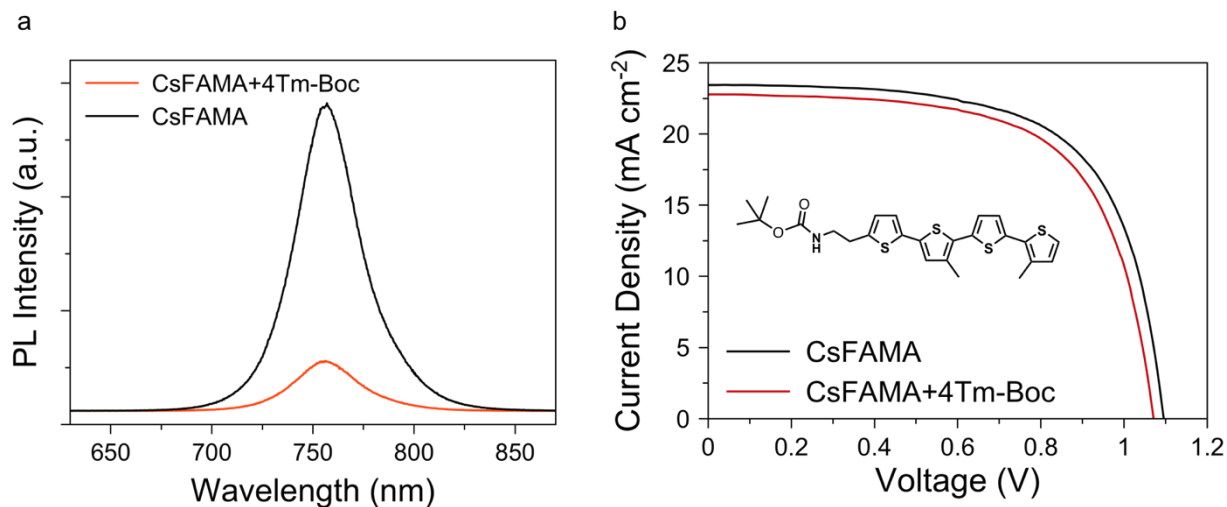


Figure S11. Devices characterization of CsFAMA modified with 4Tm-Boc. (a) The steady-state PL spectrum of CsFAMA films before and after 4Tm-Boc coating. The PL quenching effect after 4Tm-Boc coating indicates the hole extraction process from perovskite to 4Tm-Boc. (b) The J - V curve of 4Tm-Boc modified CsFAMA solar cell devices. inset, chemical structure of 4Tm-Boc. Without ammonium functional group, 4Tm-Boc is not able to anchor on perovskite lattice and packs into well-organized molecular layer. Even though the holes can be extracted from perovskite to 4Tm-Boc, the thick ligand layer is not beneficial in charge transfer between perovskite and HTL, thus decreased efficiency after 4Tm-Boc coating is observed.

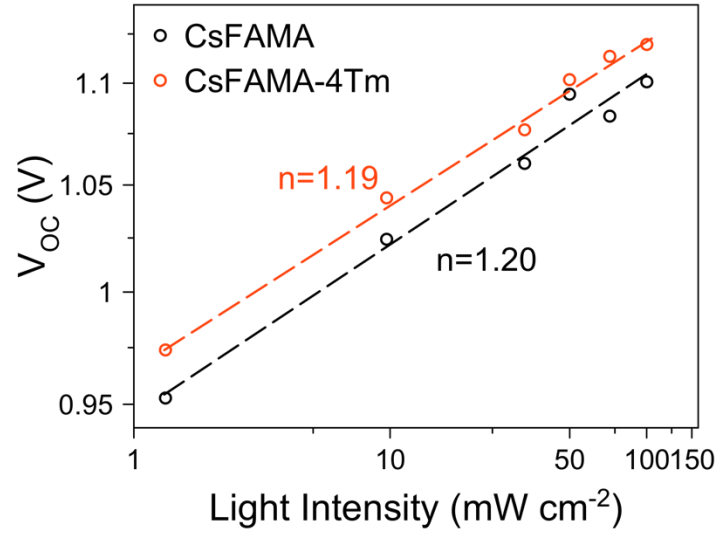


Figure S12. Light-intensity dependent J - V characteristics. Light intensity dependent V_{OC} of CsFAMA device and CsFAMA-MCL device. The relation $V_{OC} \propto (k_B T/q) \ln \phi$ is used to calculate the ideality factor, where k_B is Boltzmann's constant, T is Kelvin temperature, and q is the elementary charge. The ideality factor of 4Tm modified device is closer to 1, indicating less trap-assisted recombination in this device.

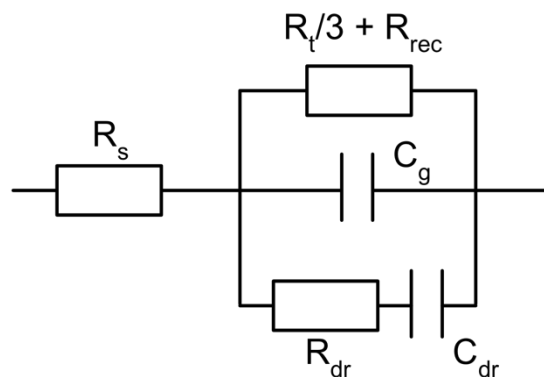


Figure S13. Equivalent circuit of EIS measurements. C_g , geometric capacitance, the classical electrostatic capacitance produced by the electrical field between two plates. C_{dr} , dielectric relaxation capacitance. R_s , series resistance. R_{dr} , dielectric relaxation resistance. R_t , charge transport resistance. R_{rec} , recombination resistance. In high-performance PSCs, it can be considered that R_t is far smaller than R_{rec} . Therefore, R_{rec} can be simply obtained by combining high and low frequency.

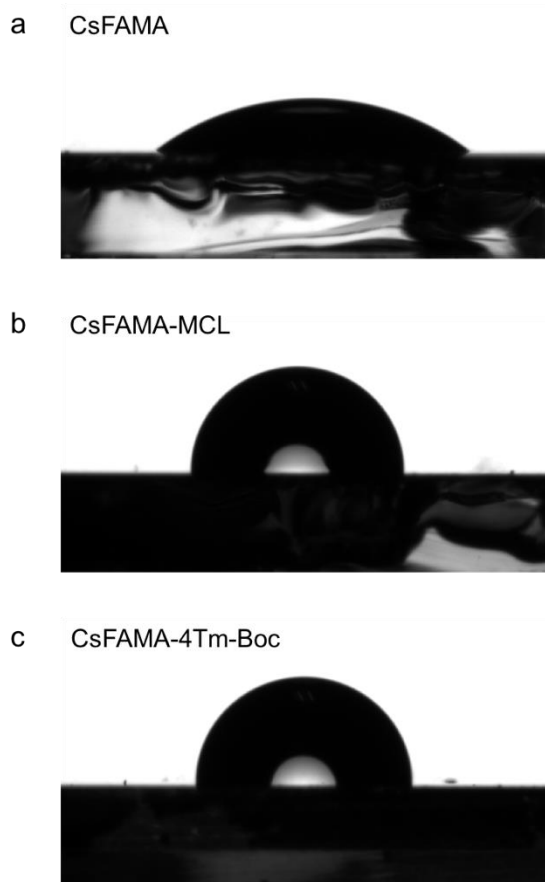


Figure S14. Water contact angle measurements. Water contact angle of (a) pristine CsFAMA film, (b) CsFAMA-MCL film and (c) CsFAMA film capped with 4Tm-Boc. The water contact angles were measured around 1 s after the water drop. The pristine CsFAMA film exhibits a more hydrophilic surface with a contact angle of 41° , while the CsFAMA-MCL and CsFAMA-4Tm-Boc surface show dramatic increase in contact angle, both with a number of 90° . The hydrophobic tail of 4Tm ligand contribute to this large contact angle.

The 2D perovskites formed with 4Tm ligands have shown extraordinary water stability in early reports^{1,2}. Here, the CsFAMA-MCL films also exhibit significant improvement in moisture stability in air comparing with pristine CsFAMA films. No observable decomposition can be seen after the films being left in air for weeks.

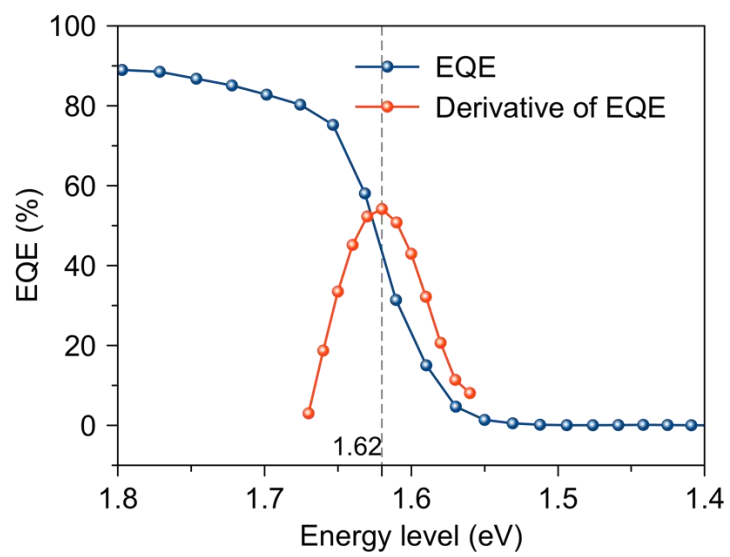


Figure S15. EQE spectra and the derivative of EQE used for the calculation of perovskite bandgap.

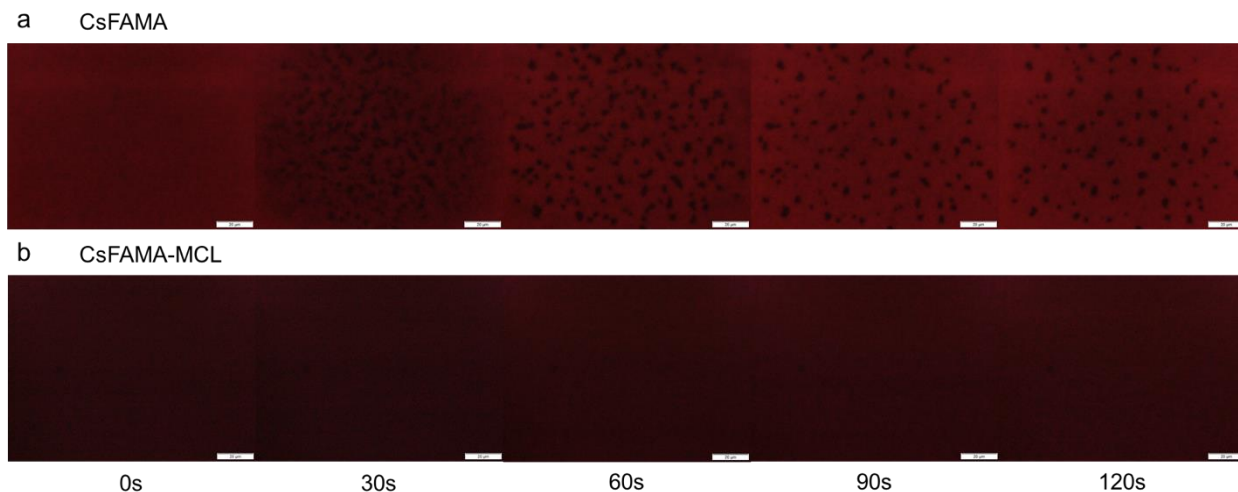


Figure S16. PL images of CsFAMA films under light. Evolution PL images of (a) CsFAMA and (b) CsFAMA-MCL films irradiated in air under LED light with 1-sun intensity over 120s. Scale bars: 20 μm . The LED light spectrum possess large portion of UV light which can accelerate the phase segregation in air. The LED light coupled with the microscope is used for the irradiation, which allows us to observe the PL image evolution of the same area without moving the samples. The PL images of CsFAMA film exhibit heterogeneity within 30 s after irradiation. The quenched regions are referred to the formation of Br-rich domains, which have wider bandgap and transfer the photogenerated electrons and holes to the I-rich domains. The initially separated small domains merge into larger domains after 30 s. Due to the composition of the CsFAMA film, which contains more I^- than Br^- , the quenched regions only take small portion of the PL images. In the PL images of CsFAMA-MCL film, lower PL intensity can be observed due to the 4Tm quenching effect. Homogeneity of the PL images is well-maintained during the irradiation time, indicating the suppressed phase segregation with MCL modification.

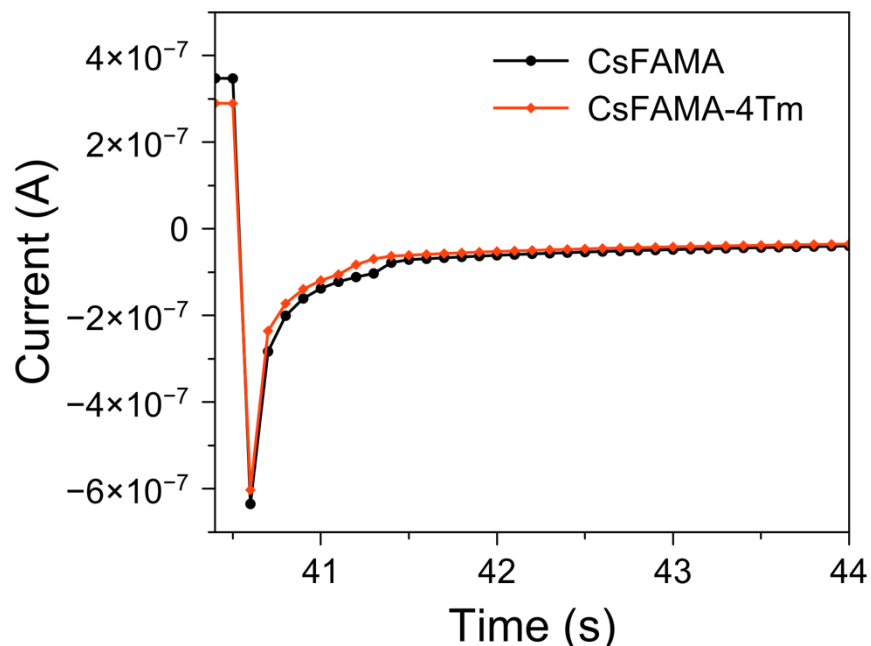


Figure S17. Charge-discharge experiments on CsFAMA device and CsFAMA-MCL device. The ions were driven by an external bias to the interface in the devices, after which the external bias was abruptly removed. The concentration gradient will drive a backward movement of ions and results in a negative current. The decay rate of the negative current reflects the recovery time of the ion distribution, thus indicates the ion migration. CsFAMA-MCL devices possess slightly shorter recovery time, and indicating less ion migration occurred at a faster rate.

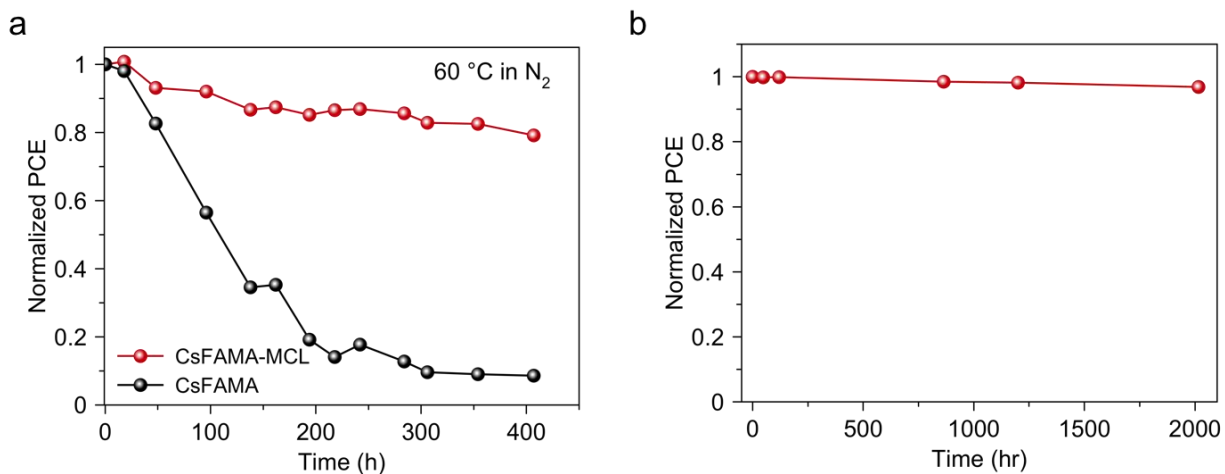


Figure S18. Device long-term stability test. (a) Thermal stability test performed at 60 °C in N₂ environment without encapsulation. The fast decay of CsFAMA control device is attributed to the ion migration in the device and evaporation of organic cations. The improved thermal stability of device with MCL is expected due to the suppressed ion migration and decomposition of perovskite. (b) Long-term storage stability of unencapsulated device in ambient environment in the dark. Over 96% of initial PCE was maintained after 2000 hr of storage.

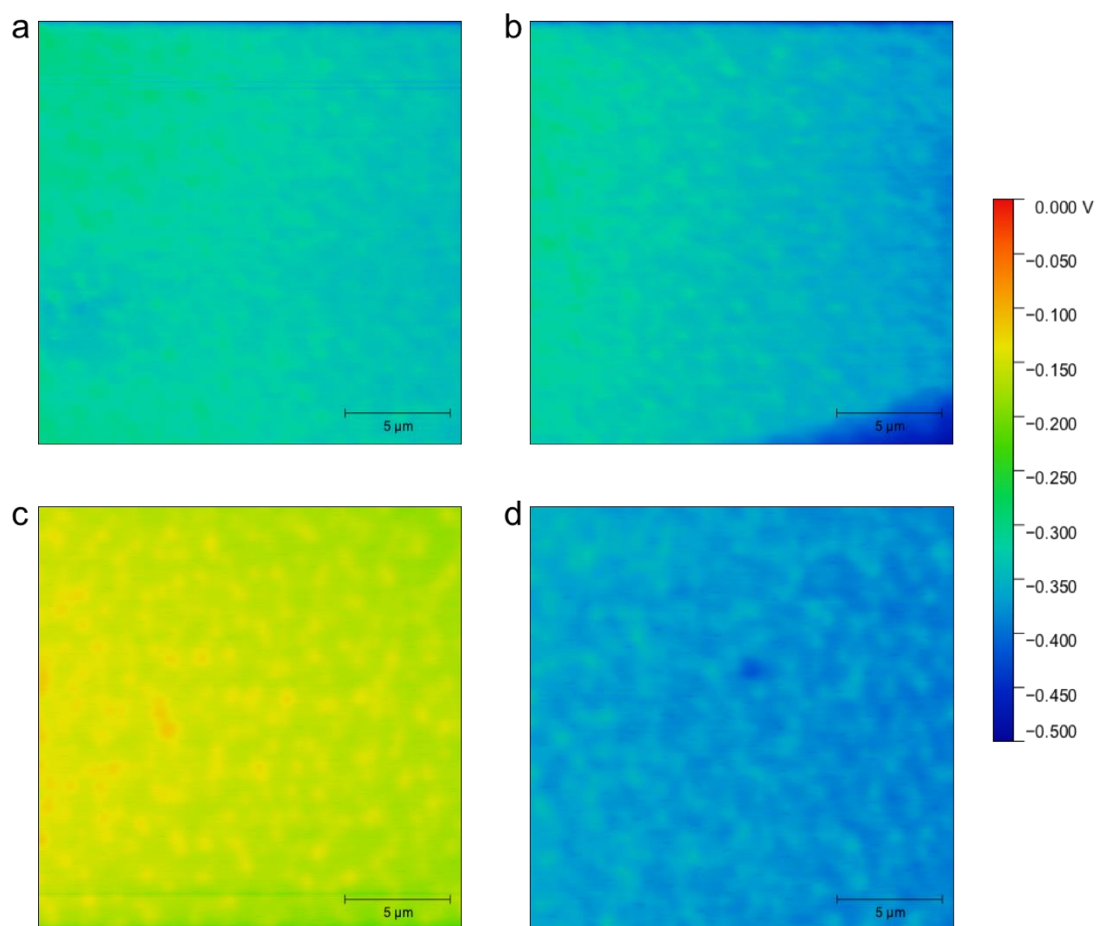


Figure S19. Surface potential mapping images of Spiro-OMeTAD coated on (a, c) CsFAMA and (b, d) CsFAMA-MCL before (a, b) and after (c, d) thermal aging at 60 °C for 72 hr in N₂ environment. The surface potential is probed by KPFM. The surface potential of Spiro before thermal aging is -0.33 mV, and no obvious difference is observed between CsFAMA and CsFAMA-MCL samples. However, the surface potential of Spiro increased to -0.16 mV when it's coated on pristine CsFAMA, indicating the changed p-type property of aged Spiro. However, the surface potential of Spiro maintained around -0.37 mV when it's coated on CsFAMA-MCL. The thermal stability of CsFAMA-MCL/Spiro heterojunction is owing to the suppressed ion migration (dopant in Spiro) across the interface.

	Take off angle	Pb	I	Br	Halide / Pb
CsFAMA	0	13.83	35.89	3.74	2.87
	45	12.38	31.5	3.01	2.79
	75 without Pb ⁰	11.37	30.29	4.41	3.05
CsFAMA-MCL	0	7.52	18.79	3.37	2.95
	45	6.69	16.68	4.57	3.18
	75 without Pb ⁰	3.43	8.83	1.85	3.11

Table S1. Atomic ratio for elements from XPS. The halide/Pb ratios were calculated by the integrated area of corresponding peaks, based on different measurement angles. Comparing with pristine CsFAMA, the slightly increased halide/Pb ratio in CsFAMA-MCL sample indicates the formation of a reduced dimensionality phase on CsFAMA surface, which matches with the GIWAXS results.

	τ_1 (ns)	A_1	τ_2 (ns)	A_2
CsFAMA	20.83±0.56	0.31±0.01	128.92±1.78	0.65±0.00
CsFAMA-MCL	2.16±0.02	0.75±0.00	39.24±0.42	0.19±0.00
CsFAMA/HTL	4.11±0.24	0.23±0.02	11.75±0.12	0.76±0.02
CsFAMA-MCL/HTL	1.57±0.02	0.77±0.00	33.87±0.44	0.16±0.00

CsFAMA-MCL	τ_1 (ns)	A_1	τ_2 (ns)	A_2
1.7nW	1.65±0.09	0.67±0.02	55.21±4.25	0.11±0.01
3.6nW	1.34±0.05	0.73±0.02	38.32±1.55	0.15±0.00
8.2nW	1.58±0.03	0.75±0.02	43.69±0.78	0.17±0.00
13.2nW	2.27±0.03	0.71±0.01	57.88±0.78	0.20±0.00
18.7nW	2.56±0.03	0.66±0.01	63.7±0.69	0.24±0.00
26.3nW	2.93±0.04	0.60±0.01	72.67±0.71	0.27±0.00

CsFAMA	τ_1 (ns)	A_1	τ_2 (ns)	A_2
1.6nW	16.91±0.89	0.33±0.01	122.3±3.27	0.60±0.01
12.3nW	17.91±0.38	0.32±0.00	119.99±1.14	0.68±0.00
22.2nW	18.79±0.26	0.38±0.00	115.60±0.93	0.61±0.00

Table S2. The fitted lifetime and parameters deduced from the bi-exponential decay kinetic of CsFAMA films coated with different top layers (top), and measured under different excitation powers (middle and bottom).

Supplemental Reference:

1. Gao, Y. *et al.* Molecular engineering of organic–inorganic hybrid perovskites quantum wells. *Nat. Chem.* **11**, 1151–1157 (2019).
2. Gao, Y. *et al.* Highly Stable Lead-Free Perovskite Field-Effect Transistors Incorporating Linear π -Conjugated Organic Ligands. *J. Am. Chem. Soc.* **141**, 15577–15585 (2019).
3. Prasanna, R. *et al.* Design of low bandgap tin–lead halide perovskite solar cells to achieve thermal, atmospheric and operational stability. *Nat. Energy* **4**, 939–947 (2019).