

Root-Toughened Molecular Interfaces Unlock Efficient and Air-Stable Blue Perovskite LEDs

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Abstract

Self-assembled monolayers (SAMs) is an important hole-transport layer widely adopted in perovskite optoelectronics, while is facing critical challenge on its environmental vulnerability of phosphonic acid root that undermines devices efficiency and durability. Herein, we present a root-toughening strategy by forming additional covalent bonds between ITO substrate and large amounts of unbonded phosphonic acid commonly existed in SAMs with high coverage. The interaction of dithiothreitol (DTT) and 2-(9H-Carbazol-9-yl)ethyl)phosphonic acid (Br-2PACz) suppresses the stacking of Br-2PACz in solution, as well as aligns the Br-2PACz conformation on ITO. Moreover, DTT simultaneously anchors on ITO and forms covalent bonds of P-O-C with Br-2PACz, creating a densely crosslinked and mechanically robust interfacial network with elevated energetic barrier for water-mediated nucleophilic degradation. As a proof of the achieved dense and robust SAMs layer, we explored its application in air-processed blue perovskite light-emitting diodes (PeLEDs). The champion air-processed blue PeLEDs exhibits external quantum efficiency (EQE) of 15.18% with emission area of 1.00 cm², representing a breakthrough in scalable, air-processed blue PeLEDs and among the highest efficiencies reported for large-area blue devices. These results establish root-toughened molecular interfaces as a powerful strategy for simultaneously addressing interfacial air instability, ambient and device scalability, opening a practical pathway toward next-generation perovskite displays and optical communication technologies.

Introduction

Carbazole-based self-assembled monolayers (SAMs) have emerged as hole transport layers (HTLs) for efficient perovskite solar cells and perovskite light-emitting diodes (PeLEDs), owing to their favorable interfacial band alignment, minimal parasitic absorption, and exceptional charge transport capability.^[1–5] However, upon the rapid spin-coating procedures, the SAMs molecules are physical absorbed or incomplete bonded on indium tin oxide (ITO) substrate.^[6, 7] Such thin film is vulnerable especially under external stresses of solvent scouring and thermal stimuli, which remarkably break interfacial structure, disturb perovskite deposition and ultimately undermine device durability.^[8, 9]

The SAMs stability is significantly determined by its chemical immobilization density, while the molecular stacking in solution and random molecular conformation during deposition compromise the chemical bonding density on the substrate.^[10–12] In order to address these limitations, a range of strategies including molecular structure engineering,^[13–16] cross-linking,^[17–20] binary or ternary SAMs deposition,^[21–24] increasing hydroxyl density on ITO substrate,^[6, 25] have been developed to suppress molecular aggregation, regulate molecular orientation, and enhance interfacial bonding density. However, the phosphonic chemical bonds are inherently insufficient tough especially exposing in air, because the hydrolysis reaction for chemical bond forming and breaking between SAMs and ITO substrate is reversible with catalysis of water, making the air-processed fabrication of stable SAMs and robust devices are challenge.^[26, 27]

The typical SAMs molecules consist of carbazole crown, carbon chain spacer and phosphonic acid root, the hydrolysis between phosphonic acid of SAMs and hydroxyl of ITO forms covalent bonds of P-O-In, which chemically immobilizes the SAMs on the substrate.^[28] However, the covalent bonds will be broken through nucleophilic attack of H₂O. As shown in Fig. 1a, H₂O attacks the phosphorus atoms of P = O, opens the double bond to form a transition state, the ionic oxygen atom re-bonds with phosphorus to break covalent bond of P-O-In, the SAMs molecule thus peel-off from ITO substrate.^[29, 30] Therefore, the structure of phosphonic acid root inherently determines its insufficient chemical bond strength, solely increasing the chemical bond density cannot eradicate the instability issue of SAMs layer. To achieve robust air-processed SAMs films and perovskite devices, a strategy of boosting chemical bond strength at root of SAMs molecules while preserving the electronic functionality of the SAM is urgently needed. Despite its importance, such root-level interfacial toughening remains largely unexplored.

Here, we present a root-toughened Br-2PACz SAMs layer that exhibited exceptional resistance to solvent rinsing and thermal stress. Dithiothreitol (DTT) serves as a molecular covalent linker, simultaneously anchoring to the ITO surface and forming robust P-O-C bonds with Br-2PACz, thereby reinforcing the phosphonic-acid anchoring motif and suppressing water-induced interfacial cleavage or attack. Density functional theory (DFT) calculations confirmed that the DTT involved SAM configuration exhibits substantially increased energy barrier for the nucleophilic hydrolysis reaction (Supplementary Fig. 1). As shown in Fig. 1b and Supplementary Fig. 2, in pristine SAMs film, SAMs molecules go through one step of nucleophilic reaction with Gibbs free energy change (ΔG) of 75.18 kJ mol⁻¹ between initial state and transition state, while in DTT involved SAMs film, two steps of nucleophilic reaction are needed in SAMs molecules, these related ΔG are 136.31 kJ mol⁻¹ for breaking P-O-In bond, and 200.48 kJ mol⁻¹ for breaking P-O-C bond, demonstrating substantially enhanced resistance to hydrolytic attack. Moreover, the interaction of DTT and Br-2PACz significantly suppressed the stacking of Br-2PACz in solution, thus improved homogeneity and regulation of SAMs on ITO substrate, which achieved a SAMs layer with high coverage and deep HOMO level for efficient hole injection at the interface of PeLEDs. The achieved champion air-processed blue PeLEDs exhibits external quantum efficiency (EQE) of 15.18% with emission area of 1.00 cm², representing the state-of-art efficiency for large-area blue PeLEDs. Furthermore, we demonstrate an air-processed segmented PeLEDs display with an active area of 900 mm², whose individual pixels retain robust electroluminescence (EL) during repeated on/off switching cycles, highlighting its strong potential for next-generation displays and optical communication technologies.

Results and Discussion

Stability and conformation of DTT involved Br-2PACz SAMs layer.

We conducted X-ray photoelectron spectroscopy (XPS) to investigate the chemical composition and bonding configuration of the SAM films. The characteristic signal of S 2p from DTT was clearly detected in the DTT mixed film, the covalent bonding of P-O-C between Br-2PACz and DTT was also detected,

which substantially consumed P-OH groups by comparing with that of pristine film (Supplementary Fig. 3). As shown in Fig. 2a-b, after rinsing with polar solvent of H₂O or DMSO, DTT mixed Br-2PACz SAMs film still exhibits strong P-O-C and PO₃²⁻ signal by comparing with pristine film (Supplementary Fig. 4 and Table 1), suggesting highly residual ratio of Br-2PACz molecules remains on the ITO substrate. The stability enhancement of DTT involved SAMs layer was also confirmed by ATR-FTIR experiments, stronger FTIR signal indicates higher residual ratio of Br-2PACz on the substrate, as shown in Supplementary Fig. 5. Furthermore, Joule heat in working PeLEDs will also break the bonding of Br-2PACz SAMs layer on the substrate, which significantly affects device operational stability. We employed conductive AFM to study the thermal stability of the SAMs films. As shown in Fig. 2c-d, after annealing at 70°C in ambient air, the DTT-modified Br-2PACz film retained highly uniform conductivity, whereas the pristine SAM exhibited a pronounced decrease in both conductivity and spatial homogeneity. These results further demonstrate that covalent bonding between DTT and Br-2PACz effectively reinforces the SAM/ITO interface, enabling the molecular layer to withstand both moisture-induced chemical attack and thermal stress.

The molecular conformation of SAMs in aspects of orientation and aggregation remarkably affect the interfaces stability and band structure alignment.^[31] We conducted the sum frequency generation (SFG) vibrational spectroscopy to investigate the molecular orientation of Br-2PACz on ITO with and without DTT. As shown in Fig. 2e, the C-H stretching vibration from methylene ($\nu_{ss} = 2849\text{ cm}^{-1}$, $\nu_{FR} = 2927\text{ cm}^{-1}$) and phenyl ($\nu_{20b} = 3022\text{ cm}^{-1}$, $\nu_2 = 3065\text{ cm}^{-1}$) of Br-2PACz were observed in ssp spectra, the resonance signal of methylene groups shifted to low frequency after adding DTT, indicated the bond interaction between Br-2PACz and DTT.^[32] Moreover, after mixing with DTT, the ν_2 vibrational mode of carbazole rings in Br-2PACz becomes stronger, suggesting the upward orientation of Br-2PACz (Supplementary Note 1).^[33] Such molecular orientation was also confirmed with related ppp spectrum (Supplementary Fig. 6). Because the carbazole moiety is intrinsically hydrophobic, its preferential exposure at the SAM surface increases the water contact angle (Supplementary Fig. 7), thereby reducing interfacial water accessibility and providing an additional barrier against moisture-induced degradation.^[34] To conclude, in addition to the covalent root toughening, DTT simultaneously regulates SAM molecular orientation to further reinforce the environmental stability of the Br-2PACz/ITO interface.

The Br-2PACz monomer has a deep and suitable HOMO level for hole injection in blue PeLEDs. In addition, the Br-2PACz stacking conformation governs the interfacial dipole moment, which plays a key role in carrier extraction at the interface.^[35, 36] We conducted DFT calculation to study the stack conformation dependent dipole moments and HOMO-LUMO levels of Br-2PACz, as shown in Fig. 2f. Involving DTT leads to parallel face-to-face conformation and random stack. The parallel face-to-face stack conformation exhibits largest dipole moment of 8.45 D, which is higher than that of both the monomer and the random stack (Supplementary Fig. 8 and Table 2). Meanwhile, Br-2PACz monomer exhibits HOMO level of $\sim -6.049\text{ eV}$ based on our calculation, which is consistent with literature.^[37] However, the HOMO levels are increased in the Br-2PACz dimers due to the electronic coupling of

conjugation structure, parallel face-to-face stack conformation shows HOMO level of ~ -5.909 eV and random angle stack conformation shows HOMO level of ~ -5.720 eV.^[38] Although Br-2PACz monomer exhibits deepest and suitable HOMO level, the optimal reality SAMs layer should be a dense layer with high coverage of stacked Br-2PACz rather than the individual monomers to avoid leakage current.^[39] Therefore, involving DTT regulates the molecular orientation, forming parallel face-to-face stack conformation of Br-2PACz on substrate, which give rises an interface with largest dipole moment and optimized deep HOMO level in reality, facilitates utmost hole extraction in the devices. The calculated band alignment is further supported by ultraviolet photoelectron spectroscopy (UPS) and cyclic voltammetry measurements (Supplementary Fig. 9), which show that DTT shifts the interfacial HOMO level from -5.79 to -5.88 eV, resulting in improved energetic alignment for hole extraction (Fig. 2g and Supplementary Fig. 10).

The assembly kinetics of DTT mixed Br-2PACz SAMs on ITO substrate.

The molecular dynamics simulation (MDs) was employed to study the self-assembly process of Br-2PACz on the ITO substrate (the MDs models with and without DTT are shown in Supplementary Fig. 11, the computational details can be found in the Method Section). The dispersion of Br-2PACz clusters near to substrate surface (with distance of ~ 6.0 nm) from 0 ns to 20 ns are shown in Fig. 3a-b, Br-2PACz molecules are always aggregated as clusters due to the intermolecular π - π stacking in solution, while mixing DTT remarkably reduces the intermolecular interaction (Supplementary Fig. 12), thus suppress the molecular aggregation to improve the mono-dispersion of Br-2PACz. The statistic of quantitatively dispersion of Br-2PACz was extracted and shown in Fig. 3c, where n represents to the number of Br-2PACz monomers in the related clusters. Before mixing with DTT, the dispersion of Br-2PACz in solution is dominated by monomers ($n = 1$) and large clusters ($n = 25$), while the presence of DTT significantly suppressed the formation of large clusters ($n = 25$), and the dispersion of Br-2PACz is dominated by monomers ($n = 1$) and dimers ($n = 2$) in solution. The cluster size variation was also characterized by dynamic light scattering (Supplementary Fig. 13), the size of Br-2PACz clusters decreased from ~ 396 nm to ~ 100 nm after adding DTT, further indicating the improved mono-dispersion of Br-2PACz in solution, which improves the homogeneity and coverage of Br-2PACz deposited on ITO substrate, leading to average mass density of Br-2PACz on the ITO surface increased from 286.24 kg/m³ to 295.11 kg/m³ after adding DTT (Supplementary Fig. 14). The atomic force microscopy-based infrared spectroscopy (AFM-IR) was employed to study the coverage of Br-2PACz. The characteristic P-O-C vibration (830 cm⁻¹) signal is also observed on the DTT mixed film, further confirming the formation of P-O-C covalent bonds (Supplementary Fig. 15). The mapping of the films based on the P = O stretching vibration (1180 cm⁻¹) are shown in Fig. 3d, the film with DTT exhibits enhanced intensity and improved homogeneity of P = O signal by comparing with control, indicating the superior mono-dispersion and increased coverage of Br-2PACz on the ITO substrate.

A simplified model based on Lambert-Beer's law was developed to calculate the coverage of Br-2PACz, the coverage of Br-2PACz with DTT is significantly increased from 55.86% to 96.14% in the model with

ideally dense Br-2PACz in face-to-face parallel conformation, see the details in Supplementary Note 2. We further validated the universal effect of DTT for improving the homogeneity and coverage of different SAMs molecules on ITO substrate (Supplementary Note 3). The images of atomic force microscopy (AFM) and kelvin probe force microscopy (KPFM) of those films with different SAMs molecules are shown in Supplementary Fig. 18–25, all DTT involved films exhibit reduced surface roughness and lower contact potential difference, indicating enhanced SAMs deposition uniformity and downshifted HOMO level by comparing with each control films, which are facilitated perovskite deposition and hole injection.

We proposed that the hydrogen bonds between SAMs molecules and DTT is responsible for suppressing intermolecular aggregation of SAMs, thereby improving the coverage uniformity of SAMs on ITO (Fig. 3e). The ^1H resonance signal at $\delta = 4.52$ ppm (2H) correspond to the -P-OH group of Br-2PACz, this peak shifts to 4.79 ppm after mixing with DTT (Fig. 3f and Supplementary Fig. 26), confirming the formation of hydrogen bond between Br-2PACz and DTT, which is also further confirmed by the FT-IR characterization (Supplementary Fig. 27). Furthermore, we found that the DTT has priority to deposit on ITO comparing with Br-2PACz because of the strong interaction between DTT and ITO (Fig. 3g). The interaction energy of DTT and ITO is ~ 21.19 KJ/mol which is approximately three times larger than that of Br-2PACz and ITO. The presence of DTT thereby enhances the interfacial bonding energy of Br-2PACz and ITO, increasing the energy from ~ 7.02 KJ/mol to ~ 21.52 KJ/mol. This strengthened anchoring enhances the stability of the SAMs and simultaneously regulates the molecular conformation of Br-2PACz on the ITO substrate.^[40]

Performance of air-processed perovskite films and blue PeLEDs

The perovskite films were prepared on these substrates by spin-coating and annealing under ambient conditions ($T \approx 21^\circ\text{C}$, $\text{RH} \approx 20\%$), the films show homogeneous blue light emission with similar PL spectra centered at ~ 485 nm (Fig. 4a). The perovskite film on DTT-modified substrate exhibits increased PL intensity, a higher PLQY (46.10%) and a longer PL lifetime compared with the control film (Supplementary Fig. 28 and Fig. 29), indicating reduced non-radiative recombination in the perovskite film. Transient-absorption (TA) was employed to probe the energy-transfer kinetics among different n-phases (Supplementary Note 4). As show in Fig. 4b and Supplementary Fig. 31, the TA data were globally fitted using a sequential $\text{S1} \rightarrow \text{S2} \rightarrow \text{S3}$ model, yielding evolution-associated spectra (EAS) with a common set of time constants across all probe wavelengths. The EAS3 spectra (Fig. 4b) represent the late-stage response following sequential evolution. After normalization to the $n = 2$ bleach at 433 nm, the target film shows a markedly stronger relative $n = 3$ bleach near 459 nm, with an $n = 3/n = 2$ amplitude ratio of 0.71 compared with 0.40 for the control film (Supplementary Table 5). The final-stage ratio is therefore 1.8-fold than that of the control film, supporting more effective energy funneling toward the $n = 3$ phases. Figure 4c shows the lifetime profiles analysis of the perovskite films at 433 and 459 nm. At the $n = 2$ bleach near 433 nm, both films exhibit an ultrafast component centered near 1 ps, whereas the pronounced tens-of-ps contribution centered near 30 ps in the control film shifts to around 20 ps and is

substantially suppressed in the DTT-modified film, indicating more rapid depletion of the photoexcited population in the $n = 2$ phases. Correspondingly, the formation-associated component of the $n = 3$ bleach near 459 nm shifts from 0.7 ps in the control film to 0.3 ps in the DTT-modified film, indicating a more than twofold acceleration in population buildup. The DTT-modified film also shows a more prominent long-lived contribution, revealing a more persistent population accumulation in the $n = 3$ phases. The correlated depletion of the $n = 2$ population and prompt establishment of the $n = 3$ response further support accelerated and more effective energy funneling from the $n = 2$ to the $n = 3$ phases.

The AFM images of perovskite films are shown in Supplementary Fig. 33, where the perovskite film deposited on DTT involved substrate exhibits reduced phase segregation and uniform surface even the relative humidity varied from 0% to 40%. Furthermore, the perovskite film on DTT involved substrate exhibits uniform PL intensity and uniform color even extending the scale from micrometers to centimeters (Supplementary Fig. 34–35), which benefits the fabrication of large-scale devices. We further characterized the surface potential of perovskite films, the results of KPFM are shown in Supplementary Fig. 36. The perovskite film on DTT involved substrate exhibits a uniform potential distribution and a lower surface potential, suggesting lower electrical barrier and homogeneous energy landscape in perovskite film. Grazing-incidence wide-angle X-ray scattering (GIWAXS) was performed to investigate the crystallinity of prepared perovskite films. As shown in Fig. 4d-e, the diffraction rings observed at $q = 0.82 \text{ \AA}^{-1}$ and $0.98 \text{ \AA}^{-1}$ in both films correspond to the (060) and (100) planes of quasi-2D perovskite, respectively. The perovskite film on DTT involved substrate exhibits stronger diffraction signal compared to control film, indicating improved perovskite crystallinity (Supplementary Fig. 37), due to the optimized n-phases crystallization kinetics (Supplementary Note 5).

The large-area blue PeLEDs (emission area is 1.00 cm^2) with architecture of glass/ITO/Br-2PACz with or without DTT /perovskite/TPBi/LiF/Al were fabricated in ambient air ($T \approx 21^\circ\text{C}$, $\text{RH} \approx 20\%$). The electroluminescence (EL) spectra of these devices are shown in Supplementary Fig. 40, all devices show color stable EL emission with peak wavelength of $\sim 485 \text{ nm}$ when increasing the applied voltage. The DTT involved blue PeLEDs shows reduced leakage current and enhanced luminance by comparing with control (Fig. 4f), suggesting decreased interfacial non-radiative recombination and improved hole injection efficiency due to the homogenous SAMs coverage and suitable band structure. As shown in Fig. 4g, the maximum luminance and peak EQE of champion device reach to $\sim 3815 \text{ cd m}^{-2}$ and $\sim 15.18\%$, respectively, which is much higher than that of control (max. luminance: $\sim 2120 \text{ cd m}^{-2}$, EQE: $\sim 6.43\%$). The blue PeLEDs also exhibit enhanced operational stability and outstanding reproducibility (Supplementary Fig. 41). Meanwhile, the current efficiency (CE) of PeLEDs on the DTT involved substrate reaches to $\sim 19.18 \text{ cd A}^{-1}$ (Supplementary Fig. 42), which is remarkably higher than that of the control devices ($\text{CE} = 8.15 \text{ cd A}^{-1}$). To evaluate the EL uniformity of those large-area PeLEDs, we further fabricated the PeLEDs with emitting area of 4.00 cm^2 under ambient air conditions. As shown in Fig. 4h-4i, the blue PeLEDs on DTT involved substrate displays identical EL intensities at 16 different positions, indicating their improved EL homogeneity (Supplementary Fig. 43). The 4.00 cm^2 PeLEDs show max. luminance of $\sim 324 \text{ cd m}^{-2}$, and peak EQE of $\sim 2.20\%$, these values should be lower than their reality

because of small incident window of the integrating sphere adopted in our measurement setup (Supplementary Figs. 44 and 45).

Consequently, the achieved new benchmark EQE of $\sim 15.18\%$ for air-processed large-area blue PeLEDs in this work (Fig. 4j and Supplementary Table 6), further supports the exploration in display applications. The segment digital display of air-processed blue PeLEDs was successfully achieved for the first time. The design and architecture of the device is schematically illustrated in Supplementary Fig. 46. The segment digital display consists of 13 pixels of individual PeLEDs with each emissive area of $4\text{ mm} \times 4\text{ mm}$ on a substrate ($30\text{ mm} \times 30\text{ mm}$). All pixel of individual PeLEDs exhibit same EL emission wavelength of $\sim 483\text{ nm}$ and same EL intensity under same operating voltage (Supplementary Fig. 47). By controlling the “on and off” states of these pixel PeLEDs, the digital numbers from 0 to 9 are displayed (Fig. 4k). These pixel PeLEDs show robust EL emission with switching their states between “on and off” for several cycles, the PeLEDs with label of 9, 11 and 13 could be light-up even undergoing maximum switching cycles over 10 (Fig. 4l), represents formidable potential in application of light communications.^[41, 42]

Conclusion

In summary, we introduce a root-toughened carbazole self-assembled monolayer for air-processed blue perovskite LEDs, enabled by dithiothreitol (DTT). DTT simultaneously anchors to ITO and forms dense P-O-C covalent bonds with Br-2PACz, transforming hydrolytically reversible phosphonic anchoring into a kinetically protected interface. This dual covalent coupling substantially elevates the energy barriers against water-mediated nucleophilic degradation and, at the same time, suppresses Br-2PACz aggregation while regulating its molecular orientation on the substrate. The resulting homogeneous, high-coverage SAM provides a well-aligned HOMO level and enhanced interfacial dipole moment, enabling efficient hole injection. Consequently, air-processed large-area blue PeLEDs (1.00 cm^2) achieve a record 15.18% EQE and enable robust operation of segmented pixelated displays, establishing a state-of-the-art performance benchmark for large-area blue PeLEDs.

Methods

Materials.

Cesium bromide (CsBr, 99.999%), lead bromide (PbBr_2 , 99.999%), dimethylsulfoxide (DMSO), Chlorobenzene (CB), 2-propanol (IPA), lithium fluoride (LiF, 99.999%), Triphenylphosphine oxide (TPPO) were purchased from Sigma-Aldrich. β -Alanine ($> 98\%$), (2-(3,6-Dibromo-9H-carbazol-9-yl)ethyl)phosphonic acid (Br-2PACz) was purchased from Tokyo Chemical Industry (TCI). 2, 2', 2''-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-Hbenzimidazole) (TBPI, 99.5%), Phenylethylammonium bromide (PEABr) was obtained from Xi'an Polymer Technology Corp. Dithiothreitol (DTT) were purchased from Macklin reagent. Diethyl ether, acetone and anhydrous ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. Deionized water fabricated in the laboratory. All the chemicals were used without

further purification. All of the ITO patterning glass substrates with a square resistance of 17 Ω/sq was purchased from Yingkou OPv Tech New EnergyCo., Ltd.

Hole transport layers (HTLs) fabrication

The ITO substrates were first washed with detergent and then sonicated with deionized water, acetone, and isopropanol subsequently for 15 min, and dried by N_2 . The cleaned substrates were treated with oxygen plasma for 20 min before used. Afterward, for the control samples, Br-2PACz (0.6 mg/ml in IPA) was spin-coating on the ITO substrates at 3000 r/min, 40 s and then annealed 10 min at 120 $^\circ\text{C}$. As for co-adsorption deposition, 1 mg/ml solutions of Br-2PACz and DTT were prepared in IPA, mixed the Br-2PACz and DTT solution precursor (3:2 v/v), and stirred for 20 min. Then, the obtained mixture was spin-coated onto ITO substrates at 3000 rpm for 40 s, and annealing at 100 $^\circ\text{C}$ for 10 min. It is noteworthy that all the precursor solution is spin-coated twice on the ITO substrate to form the HTL, effectively washing away the unbound SAM monomers on the ITO surface.

Perovskite light-emitting diodes (PeLEDs) fabrication

All of the perovskite devices are fabricated under glovebox and air conditions ($T \approx 21^\circ\text{C}$, $\text{RH} \approx 20\%$). The quasi-2D perovskite ($\text{PEA}_2(\text{CsPbBr}_3)_2\text{PbBr}_4$) precursor by disperse the CsBr (0.133 mmol), PbBr_2 (0.1 mmol), PEA Br (0.067 mmol) and β -Alanine (0.05 mmol) into 1 mL DMSO, and then stirred at 80 $^\circ\text{C}$ for 2 h. After filtered the precursor using 0.22 μm polytetrafluoroethylene filters, and dripping 40 μL precursor onto different SAMs HTL substrates, spin-coating at 3000 r/min for 70 s, and 300 mL of diethyl ether was dropped on the wet perovskite film after 40 s of spin-coating. The obtained perovskite films are immediately annealed at 70 $^\circ\text{C}$ for 4 min. TPPO was dissolved in CB solution (0.3 mg mL^{-1}) and spin-coated on perovskite film at 5000 r/min, 30 s, as passivation layer. Then, the films are transferred to the evaporation chamber, TPBi (40 nm), LiF (1 nm), and Al electrode (100 nm) were sequentially thermally deposited at 0.6, 0.1, and $>3.0 \text{ \AA s}^{-1}$, respectively. Finally, test the performance of prepared PLEDs devices, including current density-voltage curve, EL spectra, luminance, EQE, and operational lifetime.

Characterization.

The steady-state PL emission spectra were acquired using an Edinburgh (FLS 980) spectrometer (excitation wavelength: 365 nm). Absorption spectra were collected using the Perkin-Elmer Lambda 35 UV-vis-NIR spectrometer. Test time-resolved photoluminescence (TRPL) decay spectra of perovskite film using the HORIDA DeltaFlex lifetime system (400 nm blue LED excitation). Photoluminescence quantum yield (PLQY) tested by Hamamatsu's QY measurement system (C11347) with 365 nm ultraviolet excitation. Transient absorption (TA) spectroscopy was operated with a pump pulse of 410 nm, 1 kHz, and 356 uW with equipment from Light Conversion. The crystal structures of the samples were characterized by X-ray diffraction (XRD) using a Bruker D8 diffractometer (Cu K α radiation, $\lambda = 0.15418 \text{ nm}$). The morphologies of samples were observed using an Tescan Clara GMH scanning electron

microscopy (SEM) system. Transmission electron microscope (TEM) was performed by using an FEI Talos F200X equipped with a field emission gun (FEG) operated at 300 kV. All the surface roughness and KPFM potential distribution images tested by Bruker Dimension Icon atomic force microscopy (AFM) in ambient air. In-situ PL measurements were conducted using an Ocean Optics' spectrometer equipped with 365 nm UV exciter. Microscopic PL mappings were taken with a confocal spectroscopic system (South Port, Jade Mat), where a 400 nm continuous-wave laser was used as the excitation source. ^1H NMR spectra were recorded on a Bruker AVANCE 400 MHz system with the BBO probe. Fourier transform infrared (FTIR) spectra were measured with an attenuated total reflection (ATR) spectrometer (BRUKER TENSOR 27) from 4,000 to 400 cm^{-1} . Atomic force microscopy-infrared spectroscopy (AFM-IR) analyses were conducted with a nano-IR3 system from Bruker. GIWAXS measurements were conducted at the CMS beamline, NSLS II, to analyze perovskite films fabricated on different HTL substrates. SFG signals generated at the interface were detected using a CCD detector in a clean room ($T \approx 22.0\text{ }^\circ\text{C}$, $\text{RH} \approx 40\%$). The SFG signal in the CH stretching region was averaged for 2 min for each polarization combination, and the spectra were normalized against the spectra obtained from the surface of a gold film. XPS and UPS spectra were acquired using a PHI 5000 Versa Probe, where UPS using a VG Scienta R4000 analyzer and a monochromatic He I light source. Contact angles measurements were collected on a Data physics OCA-20 contact-angle system in ambient air. The performance of PeLEDs, including current density-voltage curve, EL spectra, luminance, EQE, and operational lifetime (T_{50}) was characterized using Keithley 2400 source meter equipped with a CDS2600 spectrometer (Labsphere Optics). The glue dispenser/spin coater (Brand-REESEEN, PvS-mini9) used in the lab are from Jiangyin J. Wanjia Technology Co., Ltd.

Computational details

DFT Calculations

All calculations were carried out with the Gaussian 16 software. Density functional theory (DFT) calculations were carried out with the B3LYP functional with the combination of the Grimme's D3BJ version of dispersion correction. The basis set of 6-311 + G(d, p) were adopted for the geometry optimization and frequency calculations. The geometries were fully optimized without any structural constraints. The implicit solvation model SMD with 2-propanol as the solvent was applied in the calculations. The harmonic frequency calculations were carried out at the same level of theory to verify that all structures have no imaginary frequency. The visualization of HOMO and LUMO were conducted with G view program, and the excited state from S_0 to S_1 states were calculated by time-dependent density functional theory (TD-DFT).

Molecular dynamics simulations

The assembly process of Br-2PACz and DTT on the ITO surface was performed through classical molecular dynamics simulations using the GROMACS 2021 software package. Based on the

concentration ratio of the SAMs precursors, two models of 26 Br-PACz, 1240 IPA molecules in the pure Br-2PACz system, and 26 Br-PACz, 52 DTT, and 1240 IPA molecules in the mixed DTT system were randomly inserted into a simulation box with dimensions $x = 6.8$ nm, $y = 6.8$ nm, $z = 10$ nm. The z -direction contained a 4 nm vacuum zone. The ITO substrate was fixed at the bottom during the MD simulations. The bonded and non-bonded interactions of Br-PACz, DTT and IPA structures were described with the GAFF force field, the charge used is RESP and the parameters for ITO were described with the UFF force field, obtained from the AuTo FF web server. The steepest descent method was applied to minimize the initial energy for each system with a force tolerance of $1 \text{ kJ mol}^{-1} \text{ nm}^{-1}$ and a maximum step size of 0.002 ps before MD calculations. In all the three directions, periodic boundary conditions were imposed. Leapfrog algorithm was used to integrate the Newtonian equation of motion. The MD simulation was processed in a canonical ensemble (NVT) and the simulation time is 20 ns and the temperature was maintained by the V-rescale thermostat at 373.15 K. The Particle-Mesh-Ewald (PME) with a fourth-order interpolation was used to evaluate the electrostatic interactions and whereas a cutoff of 3.0 nm was employed to calculate the short-range van der Waals interactions.

Data availability

The main data that support the findings of this study are available within the published article and its Supplementary Information and source data files. Additional data are available from the corresponding author on request.

Declarations

Competing interests

The authors declare no conflict of interest.

Additional information

Supplementary information for this article is given via a link at the end of the document.

Author contributions

J. W., and X. L. carried out the preparation and characterization of the perovskite films and devices. L. W. analyses the TA data. Y. B. and H. B. conducted the SFG measurements and data analyses. Y. Y., Y. S., and Z. K. helped films and devices fabrication. J. W. and H. L. designed the segment displays. J. W. and HY. W. wrote the manuscript and all authors contributed to the general discussion. OF. M., HY. W., and HQ. W. revised the manuscript.

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Figures

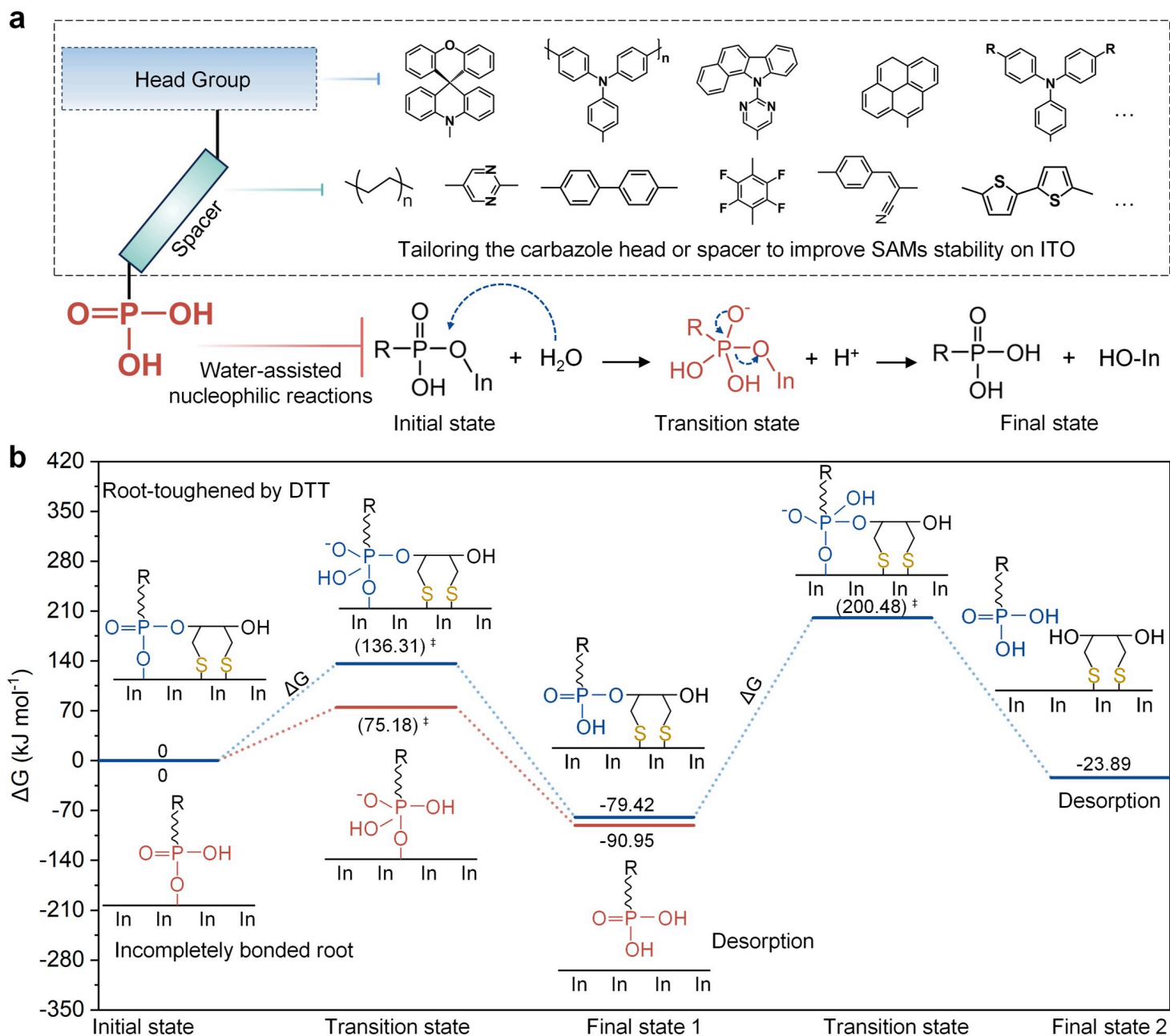


Figure 1

(a) The molecular structure of PACz SAMs and the nucleophilic reaction of phosphonic acid root. (b) The chemical desorption process of SAMs from the ITO substrate and corresponding Gibbs free energy for PACz with and without DTT.

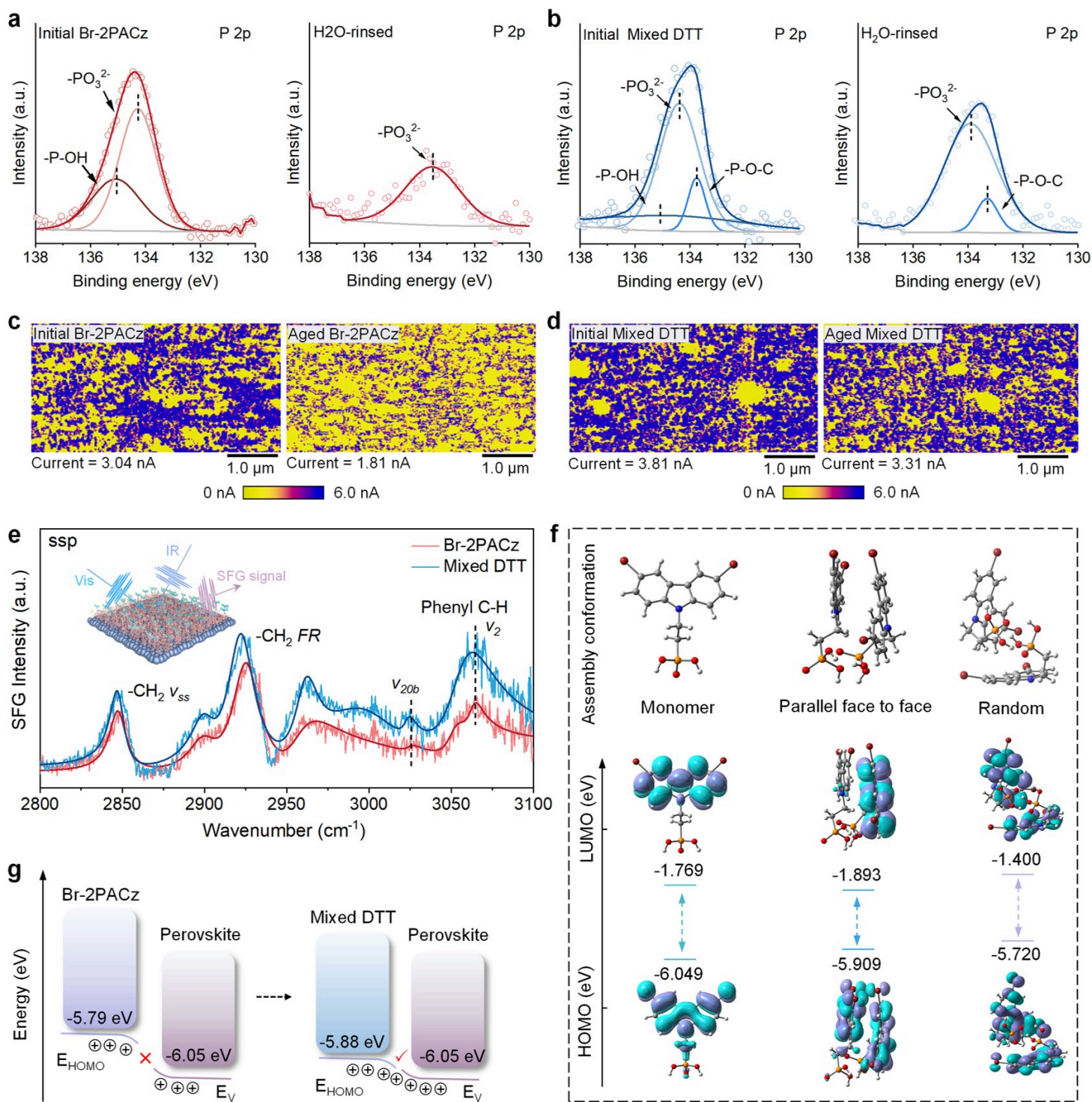


Figure 2

XPS P 2p spectrum of the initial and H_2O rinsed films for (a) Br-2APCz film and (b) mixed DTT film. C-AFM current maps (+2 V bias) of as-prepared SAMs before and after 200 hours of aging at 70°C in ambient air for (c) Br-2APCz and (d) mixed DTT films. (e) The ssp SFG spectra for the Br-2APCz and mixed DTT films. (f) HOMO-LUMO of Br-2APCz dimers with different stacking configurations. (g) Interfacial band structure of SAM layers.

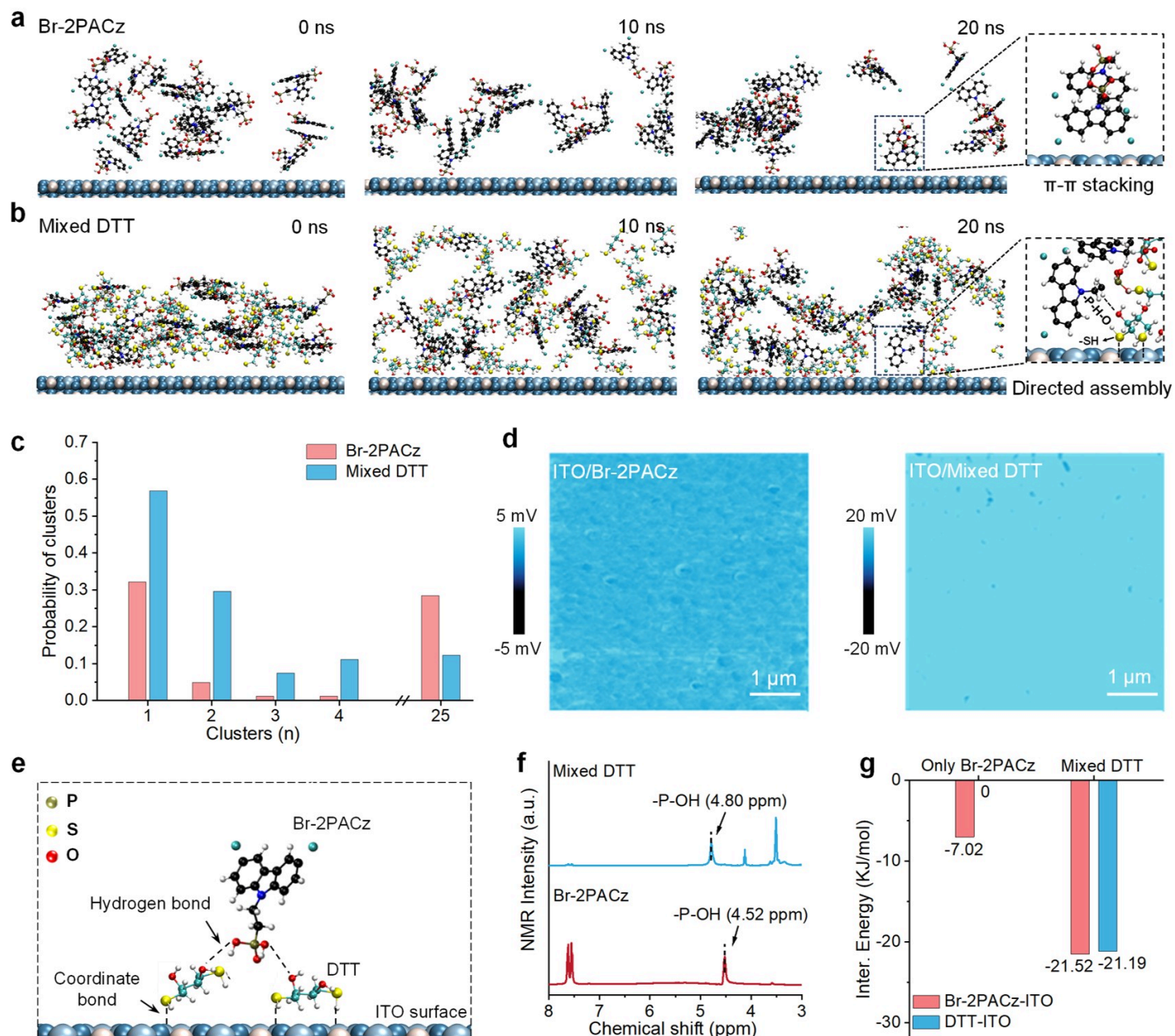


Figure 3

Sequential steps along the MD trajectory show the assemble process of (a) Br-2PACz and (b) mixed with DTT on ITO. (c) Types of Br-2PACz clusters formed at equilibrium in precursor solution. (d) AFM-IR absorption maps of P=O vibration (1180 cm^{-1}) on ITO surface. (e) Schematic illustration of the interaction between DTT and Br-2PACz assembly on ITO substrate. (f) ^1H NMR spectra of Br-2PACz and mixed with DTT. (g) The calculated interaction energy between Br-2PACz and ITO substrate with and without DTT.

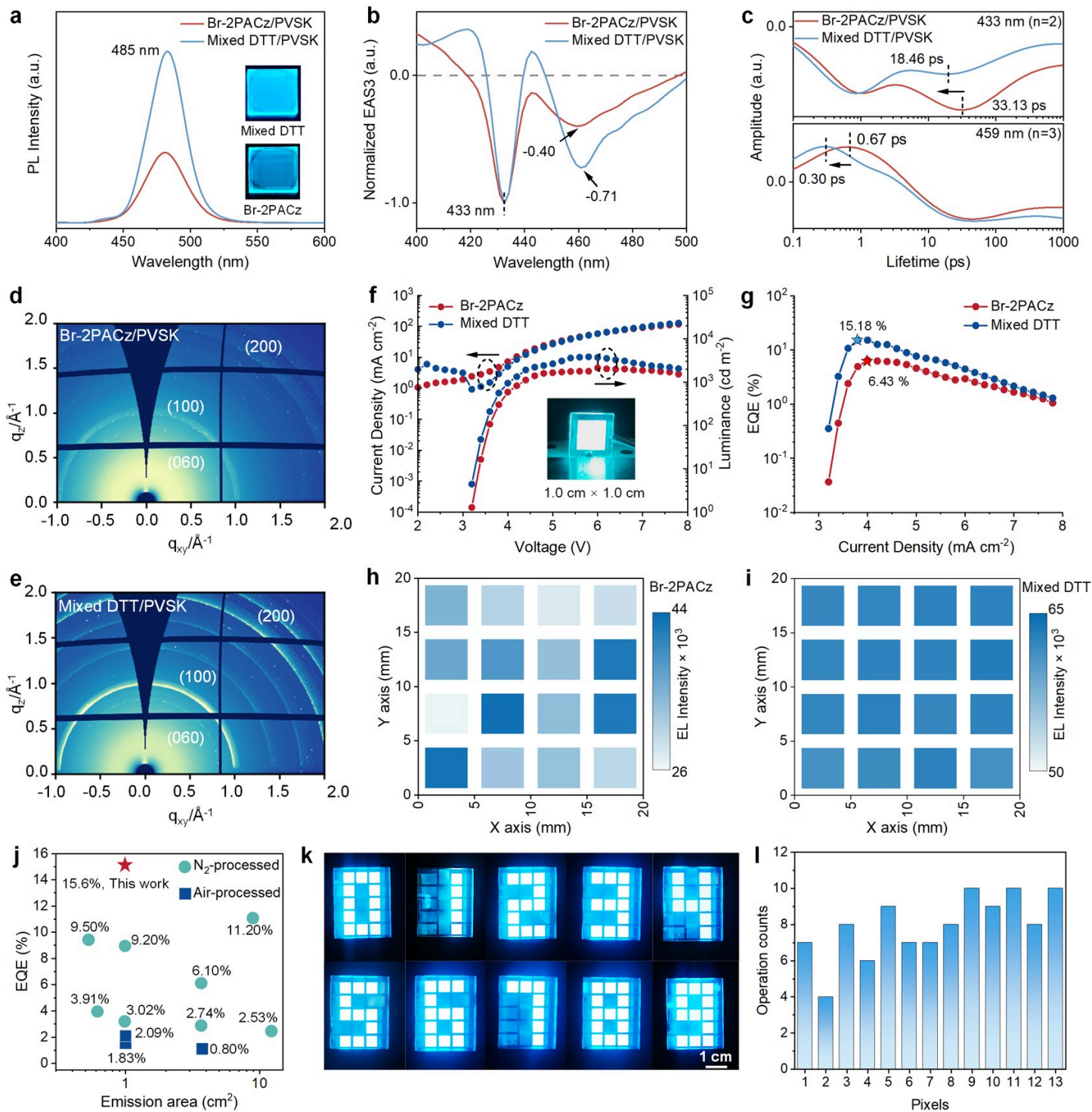


Figure 4

(a) PL spectra of air-processed perovskite films. (b) Late-stage evolution-associated spectra (EAS 3) obtained from global sequential analysis of the TA data. (c) Lifetime-density profiles of the perovskite films at 433 and 459 nm. 2D GIWAXS patterns of air-processed perovskite on (d) Br-2PACz and (e) mixed DTT substrates. (f) Current density-voltage-luminance curves and (g) EQE-current density curves of air-processed blue PeLEDs. The EL uniformity testing of air-processed large-area blue PeLEDs on (h) Br-2PACz and (i) mixed DTT substrates. (j) Performance comparison of large-area blue PeLEDs fabricated

in glovebox and ambient air. (k) Photographs of the air-processed segment PeLEDs display. (l) The statistics of operation times for corresponding pixels in segment PeLEDs display.

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