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Supramolecular bridging strategy enables high performance and stable organic–inorganic halide perovskite solar cells

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ABSTRACT

The manipulation of grain boundaries in polycrystalline perovskites is an indispensable consideration for the photovoltaic performance and environmental stability of solar cells, because perovskite films obtained by solution process will inevitably introduce many defects in the grain boundaries. Although additives based on small molecules have proven to be effective defect passivators, their high volatility and diffusibility cannot satisfy the stability requirements of perovskite films. As an upgraded approach, herein, we introduced a supramolecular bridging strategy with 2,5-diaminobenzotrifluoride (DTF) molecular binder as the repeating unit to form a supramolecular-perovskite composite. The supramolecular binder plays a role of bridging the perovskite crystal grains, passivating the trap states of the perovskite films and producing excellent environmental stability, which is superior to the conventional additive engineering. As a result, the power conversion efficiency of the MAPbI₃ solar cell has been significantly increased from 18.8% to 21.0 %. The perovskite solar cells with S-DTF maintaining 93% of their original efficiency for over 30 days (~70% humidity) in air ambient without encapsulation, exhibiting an excellent long-term stability. This will inspire a wider range of ideas beyond the regular additive engineering for improving the performance of polycrystalline perovskite-based photoelectronic devices.

1. Introduction

Organic-inorganic hybrid perovskites have been used in various optoelectronic applications, such as photodetectors [1], light-emitting diodes [2–3], and solar cells [4–6] because of their high absorption coefficient [7], long-distance charge diffusion length [8–9], and high photoluminescence quantum yield [2]. Since the perovskite solar cell was reported in 2009 [10], a large number of experiments have been conducted to understand the photophysical properties of perovskite and improve the photovoltaic performance of perovskite-based solar cells. Recent improvements through composition [11–12], morphology [13–14], and interface engineering [15] have led to a rapid increase in the power conversion efficiency (PCE) of perovskite solar cells.

Since the organic–inorganic hybrid perovskite film is prepared by

solution process and is crystallized during the annealing process, there are many structural defects exist along the grain boundaries of polycrystalline perovskite films. [16–17] Grain boundaries that have uncoordinated Pb²⁺ can provide migration paths for ions and can become charge trap centers and cause non-radiative recombination, which significantly effects on the photophysical properties of the perovskite film. [18–19] Furthermore, defective grain boundaries are more vulnerable to moisture degradation which propagates inwards into the grain interiors from the boundaries to induce the degradation of individual grains, thus reducing device performance. [20] Therefore, to improve photovoltaic performance and stability, it is necessary for polycrystalline perovskite films to achieve the following goals: (a) Improving the crystallization to minimize the grain boundaries and obtain high-quality thin films; (b) Effective passivation for the defects at

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the boundaries and the bulk of the grains; (c) Suppressing ions migration and improving the hydrophobicity of the perovskite, so that the device has higher moisture-tolerance.[21–23].

Small molecule-based defect passivating agents that have lone pair electrons on oxygen, sulfur, or nitrogen (e.g., pyridine, thiophene, and fullerenes) have been used to improve the photophysical properties of perovskites by coordinating with defect sites at grain boundaries.[24–25] However, the high degree of volatility and high diffusion coefficients of small molecules likely pose difficulties in incorporating them into practical devices operated under harsh environments, such as high temperature or high humidity.[26–27] Moreover, since most of the reported additive molecules only have modest conductivity, their independent distribution within the perovskite films will raise the resistance of the whole film, which is disadvantage to charge transportation.[28–29].

For solving these problems, connecting these additives through polymerization may be an effective way to encapsulate the perovskite surface but without increasing the films resistance. For example, polythiophene polymer and indacenodithiophene perylene diimide (IDTTPDI) polymer have successfully used to modify the perovskite surface to improve device performance and long-term stability under severe conditions.[30] Besides, supramolecular, which usually refers to the combination of two or more molecules by intermolecular interaction to form complex and organized aggregates, is also a new type of modifier.[31] The size of supramolecular is usually smaller than polymer molecular, which makes it can be easily decorated on the grain boundary and avoids the local aggregation of polymer conformation. Moreover, the supramolecular has a wealth of functional ligands for selection, which gives the possible to terminating the trap state, forming a moisture-barrier, thereby improving the performance and stability of the device.

Accordingly, herein, we propose a novel supramolecular-bridging strategy, induced by using the 2,5-diaminobenzotrifluoride (DTF) as a repeating unit, for achieving high performance and stable device. The supramolecular DTF (S-DTF) network, which is constructed by the electrostatic interaction of trifluoromethyl ($-CF_3$) and benzene rings, can bind with perovskite precursor to form an intermediate adduct and retard the perovskite crystallization, hence enlarging the grain size and minimizing the grain boundaries. Moreover, the S-DTF network is much denser than the independent DTF additives, which is facilitating to reduce the resistivity of the films. As an extra benefit, the $-CF_3$ network of the S-DTF could increase the hydrophobicity of the perovskite surface to further improve moisture-tolerance of the perovskite solar cells. The combination of the above effects resulted in a significantly increased PCE from 18.8% to 21.0%. The perovskite solar cells with S-DTF

maintaining 93% of their original efficiency for over 30 days ($\sim 70\%$ humidity) in air ambient without device encapsulation, exhibiting a high long-term stability.

2. And discussion

We first give a glimpse of the structure and the surface electrostatic potential of the DTF molecules. The DTF is composed with one $-CF_3$ and two $-NH_2$ groups chemically bridged by benzene rings. From the electrostatic potential, it can be clearly seen that the amino group has electron-donating properties, and the $-CF_3$ group has strong electro-negativity (Fig. 1a). According to previous reports, dipole interaction of organic ions promotes the ordering of benzene rings; and the supramolecular electrostatic interaction between electron-deficient F atoms with neighbor benzene rings makes them connected and beneficial charge transfer.[32] The supramolecular interactions are expected to serve as an anchor to crosslink the bulky organic cations of the perovskite, block the ions migration paths, improve the crystal stability, and increase the overlap of electron clouds to change the corresponding optoelectronic properties.[33] Here, in order to confirm the supramolecular electrostatic interaction, we performed the Fourier transform infrared (FTIR) (Fig. 1b) spectra and the liquid ^{19}F magnetic resonance measurement (NMR) (Fig. 1c) tests on DTF and S-DTF, respectively. [34] We observed C-F vibration in the FTIR from 1306 cm^{-1} (DTF) redshift to 1315 cm^{-1} (S-DTF); and compared with DTF in NMR, S-DTF shifts to a small direction. These phenomena confirmed the electrostatic interaction between the C-F of the DTF and the benzene ring of another DTF to form a supramolecular (Fig. 1d). Moreover, compared with DTF, S-DTF has higher absorption, which is attributed to its denser molecular system (Fig. S1). This denser structure of S-DTF is also beneficial to improve its hydrophobicity. This property is proved by the water contact angle tests (Fig. 1e). The contact angle of the S-DTF film is 80° , which is much larger than the contact angle of the DTF film (55°). Therefore, the S-DTF can be expected to serve as a perovskite binder network, reduce internal perovskite defects, and improve crystal and device stability (Fig. S2).

Based on above analyses, we then fabricated the planar heterojunction perovskite solar cells with ITO/ SnO_2 /perovskite ($MAPbI_3$ in this work)/Spiro-OMeTAD/Ag structure (Fig. 2a top). The cross-sectional SEM image shows that the large crystal grains are perpendicularly oriented to the substrate (Fig. 2a bottom). The characteristic element F in the cross-sectional energy dispersion spectrum (EDS) further proves low-volatility S-DTF exists in the perovskite absorption layer (Fig. S3). The Fig. 2b shows the current density–voltage (J - V) curve of the control and Perovskite-S-DTF device. The corresponding performance parameters of the device are listed in Table 1. The control device

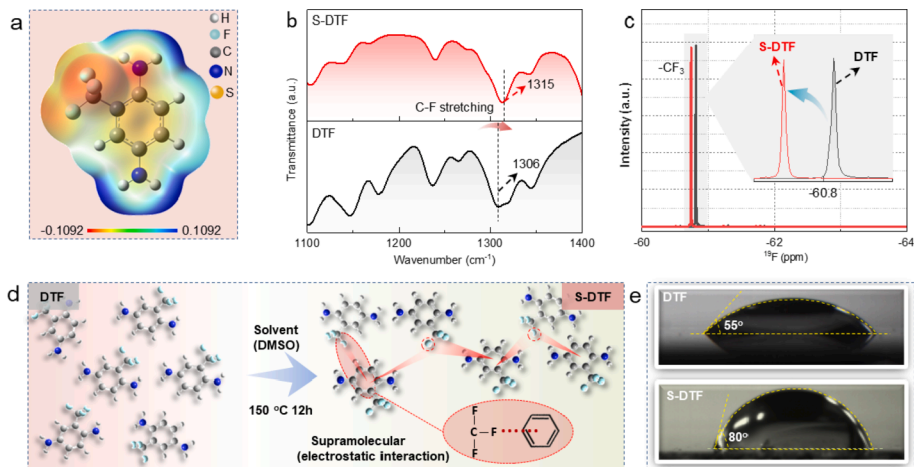


Fig. 1. Formation mechanism of S-DTF. (a) Molecular structure and surface potential of the DTF. (b) FTIR of DTF and S-DTF. (c) The liquid-state ^{19}F magnetic resonance measurements of S-DTF and DTF. (d) Formation process of S-DTF (e) Water contact angle of DTF and S-DTF film.

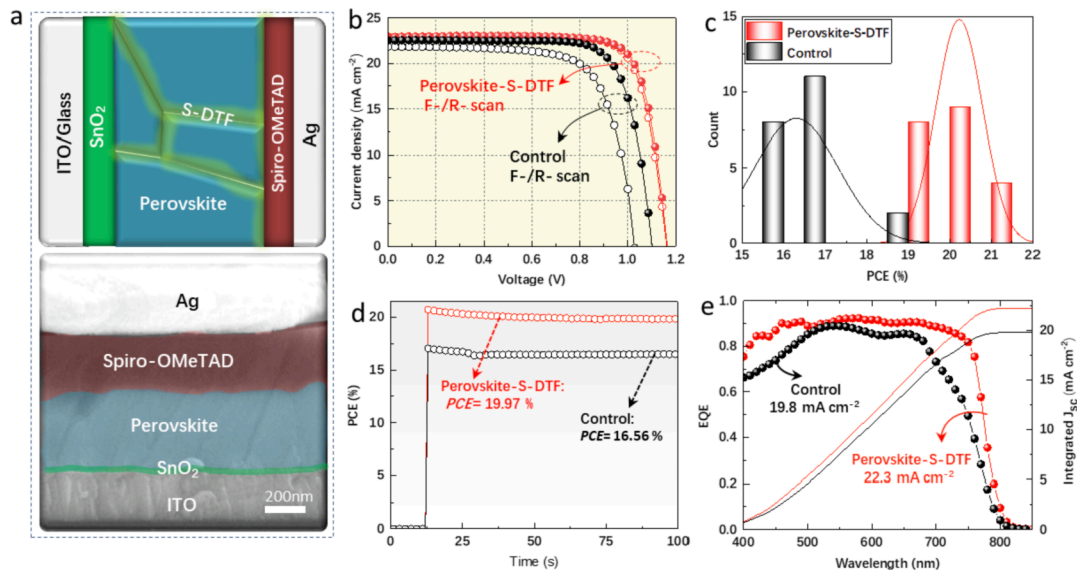


Fig. 2. Cell structure and performance. (a) Top: Schematic of the device structure. Bottom: Cross-sectional SEM image of the device. (b) J - V curves of the perovskite solar cells based on control and Perovskite-S-DTF layer. (c) Reproducibility analysis of the device efficiency of the control and Perovskite-S-DTF cells (21 devices for each branch). (d) PCE measured at V_{mpp} of perovskite solar cells. (e) EQE spectrum of the control cell and the Perovskite-S-DTF cell.

Table 1

The illuminated output parameters of perovskite solar cells.

device		J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	PCE (%)
Control	R-S	22.7	1.09	75.7	18.8
	F-S	21.8	1.03	71.5	16.0
with-S-DTF	R-S	22.9	1.16	79.0	21.0
	F-S	22.9	1.16	78.0	20.7

obtained a short-circuit current density (J_{sc}) of 22.7 mA cm^{-2} , a V_{oc} of 1.09 V, and a 75.7 % factor filled (FF) to yield a modest PCE of 18.8 % (forward scan: $PCE = 16.0\%$; $V_{oc} = 1.03 \text{ V}$; $FF = 71.5\%$; $J_{sc} = 21.8 \text{ mA cm}^{-2}$). The V_{oc} , J_{sc} , FF and PCE of the S-DTF processed device significantly increased to 1.16 V, 22.9 mA cm^{-2} , 79.0 % and 21.0 % (forward scan: $PCE = 20.7\%$; $V_{oc} = 1.16 \text{ V}$; $FF = 78.0\%$; $J_{sc} = 22.9 \text{ mA cm}^{-2}$), respectively. We tested modified devices with 0 mL/mol, 0.1 mL/mol, 0.3 mL/mol, 0.5 mL/mol concentration S-DTF, and named the corresponding devices as control, perovskite-S-DTF-1, perovskite-S-DTF-2, perovskite-S-DTF-3, respectively (Fig. S4). Compared with the control device, the PCE of the S-DTF modified device is improved because the $-NH_2$ of the S-DTF can passivate the uncoordinated Pb^{2+} of the perovskite. Especially, the perovskite-S-DTF-2 obtained the best photovoltaic performance. The photovoltaic performance of perovskite-S-DTF-1 and perovskite-S-DTF-3 are lower than that of the perovskite-S-DTF-2. This is because that the insufficient S-DTF (perovskite-S-DTF-1) cannot comprehensively passivate the electronic defects inside the perovskite, and the excessive S-DTF (perovskite-S-DTF-3) may increase the resistance and interrupt the film crystallization, resulting in a decreased device performance. Electrochemical impedance spectroscopy (EIS) measurements are used to clarify the internal electrical properties of perovskite solar cells (Fig. S5). Compared with control devices, the charge transfer resistance (R_{ct}) of the perovskite-S-DTF devices is significantly reduced and the recombination resistance (R_{rec}) is increased, indicating that the S-DTF modified perovskite layer has lower resistance and recombination losses. The series resistance of control and perovskite-S-DTF devices are 12.1Ω and 6.5Ω , respectively, which yields a higher FF for the perovskite-S-DTF device compared to the control device. The PCE statistics of 42 devices shown in Fig. 2c demonstrate the reliability and reproducibility of the PCE enhancement. The efficiency measured at the maximum power point (0.96 V) are

presented in Fig. 2d, which confirms the device performance parameters extracted from the J - V curve and verifies the negligible of photocurrent hysteresis in our devices. Meanwhile, the calculated J_{sc} based on the external quantum efficiency (EQE) plots in Fig. 2e were close to the values obtained from current J - V measurements, confirming the reliability of the J - V results. Compared with the control cell, the EQE spectra shows enhancement over the whole absorption region of 400–800 nm for the perovskite-S-DTF device. Especially, a broad plateau over 90% is attained throughout the range of 450–700 nm for the Perovskite-S-DTF device.

In order to give a deep insight into the improved performance of Perovskite-S-DTF devices, we further conducted perovskite film crystallization and morphology measurements. The tetragonal phases for all perovskite films are displayed in X-ray diffraction (XRD) patterns (Fig. 3a), affirming that S-DTF is not doped in the perovskite crystal lattice thus can only exist at grain boundaries or surface of perovskite film. We conducted a high-resolution transmission electron microscope (HRTEM) test (Fig. 3b) to verify the specific location of the S-DTF. An amorphous region can be clearly distinguished between adjacent grains, which implies that the S-DTF molecules are successfully decorated into the perovskite grain boundaries. We further analyzed the crystallinity of the perovskite film by comparing the (110) reflection intensity and its full width at half maximum (FWHM) (Fig. S6a-b). Compared with the control samples, the Perovskite-S-DTF sample has stronger peak-intensities and smaller FWHM-values. In addition, the S-DTF treated film has preferred (110) crystal orientation than the control film (Fig. S6c). These suggest that the S-DTF network can improve the crystallinity of the perovskite films. In order to examine the changes in the morphology of the perovskite films treated with S-DTF, top-view scanning electron microscopy (SEM) and atomic force microscopy (AFM) were performed (Fig. 3c). Compared with the control film, the S-DTF treated film exhibits denser, smoother and larger grains. After S-DTF treatment, the perovskite films roughness was decreased from 12.3 nm to 6.9 nm. We speculate that the crystallization improvement of the Perovskite-S-DTF film may due to the interaction between S-DTF and the perovskite precursor solution. We tested the absorption spectra of MAI and S-DTF-MAI (Fig. S7). The absorption edge of the S-DTF-MAI has obvious red-shift and enhanced intensity compared to the pure MAI solution, which reveals that the S-DTF has an interaction with MAI. We also measured the liquid ^1H magnetic resonance (NMR) of the precursor solution with or without S-DTF (Fig. S8). Compared with the control, the

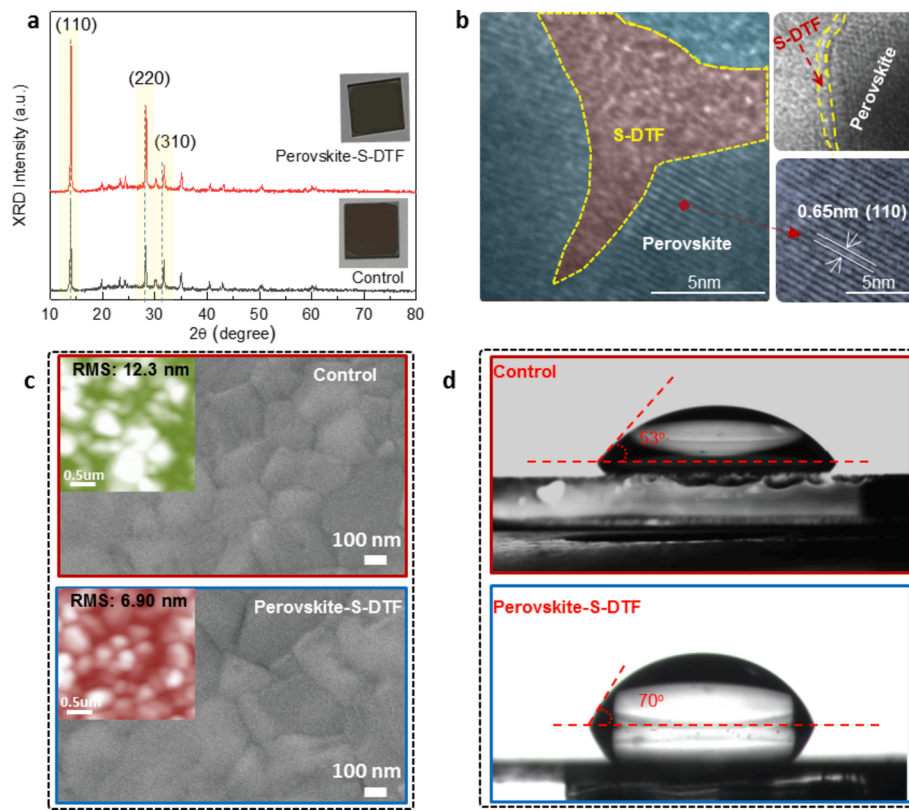


Fig. 3. Thin film crystallinity characterization. (a) The XRD patterns of perovskite films. (b) HRTEM images of the grain area of the perovskite-S-DTF sample. (c) SEM images of control and perovskite-S-DTF. Inset: the corresponding AFM images and RMS values. (d) Water contact angles of the control and the perovskite-S-DTF films. The contact angles were captured at ~ 5 s after applying the drop of water.

NH_3 protons of the Perovskite-S-DTF shifted to large deviation. This is attributed to the formation of hydrogen bonds between the perovskite and S-DTF, which help delay crystallization and promote the formation of large-sized grains. [35] In addition, in coordination with the Fig. 1e, we also found that the Perovskite-S-DTF film had a larger water contact angle than the control film (Fig. 2d), which will facilitate the moisture-resistance of perovskite film and be beneficial for improving the device stability.

Furthermore, in order to verify the intermolecular interactions between the perovskite and S-DTF, X-ray photoelectron spectroscopy (XPS) was performed. The Fig. 4a presents the states of Pb of the perovskite film, and two feature peaks of Pb 4f_{7/2} and Pb 4f_{5/2} can be observed. Compared with the control film, the Pb 4f signals of the Perovskite-S-DTF film shifts to the lower energy due to the increased electronic cloud density. [36] In addition, two small peaks located at 136.4 eV and 141.3 eV are attributed to metallic Pb⁰ on the surface of perovskite. The appearance of Pb⁰ is probably accompanied by the existence of iodine and cation vacancies, which are one of the major nonradiative centers. The intensity of the Pb⁰ is greatly suppressed in the S-DTF-passivated perovskite film, indicating that the uncoordinated Pb²⁺ have been effectively reduced by S-DTF (Fig. S10). In addition, the FTIR spectra of the S-DTF and S-DTF-PbI₂ also shows the N-H vibration red-shifted from 3392 cm⁻¹ in S-DTF to 3403 cm⁻¹ in S-DTF-PbI₂, respectively (Fig. S11), which may be caused by the interaction between uncoordinated Pb²⁺ and -NH₂. Actually, since the S-DTF is constructed by the electrostatic interaction between the -CF₃ and the diamine benzene of the DTF molecules, it has a large number of -NH₂ branches (electron donor), which can coordinate with the uncoordinated Pb²⁺ of the perovskite bridge adjacent grains without hindering charge transfer. [37] The space-charge-limited current (SCLC) was used to diagnosis the trap states density (N_t) of the perovskite films (Fig. S12). The N_t decreased from 1.5×10^{16} to 6.6×10^{15} cm⁻³ by adding the S-DTF. The

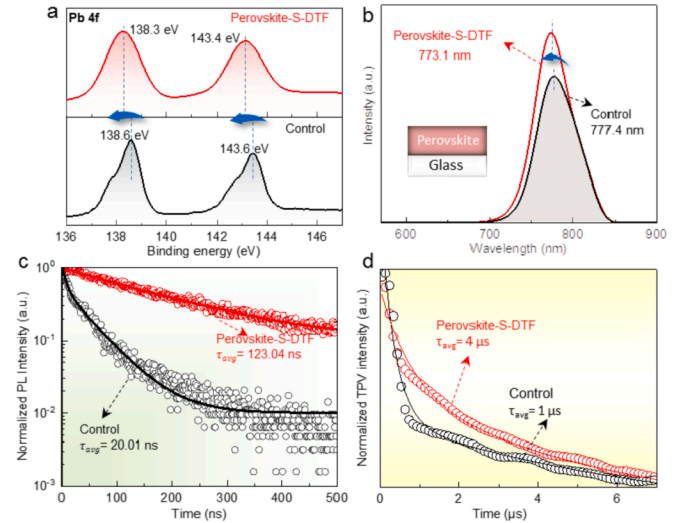


Fig. 4. Determine the coordination relationship between S-DTF and perovskite. (a) XPS spectra of the Pb 4f core level on the control and perovskite-S-DTF films. (b) Steady-state and (c) TRPL spectra of the control and perovskite-S-DTF films. (d) TPV decay of the control and the perovskite-S-DTF films.

recombination kinetics in the perovskite film was studied by steady-state photoluminescence (PL) and time resolved photoluminescence (TRPL) spectroscopy with a structure of Glass/perovskite (Fig. 4b-c). Compared with the control sample, Perovskite-S-DTF film has higher PL intensity and longer decay lifetime. Moreover, we also note that the PL peak of the perovskite-S-DTF is slightly blue-shifted, which may be caused by the

decreasing of the band tail density (Fig. S13). This was further verified by transient photovoltage (TPV) measurement. The Fig. 4d shows that the Perovskite-S-DTF film has a longer average charge lifetime ($\tau_{\text{avg}} = 4.0 \mu\text{s}$) than the control sample ($\tau_{\text{avg}} = 1.0 \mu\text{s}$). Therefore, it can be concluded that the unique network and $-\text{NH}_2$ branches of the S-DTF can not only improve the crystallization, but also passivate the defects and bind the grain boundaries, thus improving the quality of the perovskite films.

Besides the photovoltaic parameters, stability is another important metric for perovskite solar cells. we further assessed the long-time stability of unencapsulated device under the $\sim 70\%$ humidity at 25°C for 30 days. We regularly recorded the *PCE*, and the results are shown in Fig. 5a. All the treated perovskite devices (including DTF-device and S-DTF-device) significantly enhance the stability. Remarkably, the perovskite-S-DTF device maintained 93% of the initial *PCE*, whereas that of the control and perovskite-DTF device decreased to 60% and 85% after 30 days, respectively. In order to prove the reason for the device stability improvement, we individually tested the stability of perovskite films in 25°C and humidity $\sim 70\%$. As show Fig. 5b-d, the UV-vis absorption intensity of the control film dropped sharply at the wavelength range of $\sim 300\text{--}900 \text{ nm}$ over 30 days, while the DTF modified film presented a slight reduction. Under the same conditions, compared with regular additive engineering (DTF), the supramolecular bridged (S-DTF) device has not any noticeable change, indicating that the Perovskite-S-DTF is more stable than the perovskite-DTF (Insets in Fig. 5b-d shows the samples photographs). In order to further verify that the stability of Perovskite-S-DTF surpasses perovskite-DTF, the XRD test was performed. After aging, the PbI_2 peak is observed and the perovskite peak (14.1°) is lower than fresh film in the perovskite-DTF film, demonstrating the partially decomposed. As for the S-DTF modified film, there is almost no PbI_2 peak and the perovskite diffraction peak (14.1°) no significant changes, indicating the integrity of the film crystal structure. Fig. 5g shows the schematic diagram of the decomposition process of perovskite film in high-humidity condition. According to previous report, the moisture diffuses into the perovskite film through the grain boundary and induces to the perovskite decomposition. However, the S-DTF with a hydrophobic functional group can form a moisture-proof barrier. And more importantly, the S-DTF network can work as a binder between individual grains to consolidate the crystal structure, which hinders the moisture propagating inwards into the grain interiors from the boundaries. Therefore, the perovskite-S-DTF devices have much better long-term stability. Moreover, the photostability is also a key factor for the long-term operation of the device. As shown in Fig. S14, compared to the control device, all the modified devices

showed improved photostability. Especially, compared with DTF-modified devices, the S-DTF-modified devices are more stable, which may be attributed to the supramolecular network consolidates the structure and passivates the defects in the perovskite films.

Ultimately, in order to promote the commercialization of photovoltaic technology, except the photovoltaic performance and the stability, the environmental pollution introduced by Pb^{2+} leakage is also an important part of current attention. [38] Here, we studied the leakage of lead in the degraded perovskite solar cell and immersed the device in deionized water ($\text{PH} \sim 5.6$) to compare the concentration of the water-soluble lead component in the control and Perovskite-S-DTF (Fig. 6a-b). The Pb^{2+} concentration in the sewage was quickly checked with Pb^{2+} test paper, and it was found that the Pb^{2+} concentration of the control water extract was much higher than that of the Perovskite-S-DTF water extract. The EDS measurement is further used to quantify the Pb^{2+} concentration. We tested the Pb concentration on the ITO glass/perovskite/spiro-OMeTAD and ITO glass/perovskite-S-DTF/spiro-OMeTAD structure film for 15 days and 30 days, respectively (Fig. 6c-d). Compared with the Pb^{2+} on the control film, there is almost no Pb in the perovskite-S-DTF film. This may be due to the formation of S-DTF network at grain boundaries terminates the uncoordinated Pb^{2+} , thereby strengthening the films and inhibiting the leakage of lead ions (Fig. 6c). The above-mentioned lead leakage test shows that, compared with the control, the network S-DTF in the perovskite layer can form a built-in leakage barrier without increasing resistance to prevent toxic pollution and improve the environmental protection application potential of perovskite solar cells.

3. Conclusions

In summary, superior to emerging additive engineering, we here introduce a novel supramolecular bridging strategy to form a supramolecular-perovskite composite, which enables the perovskite solar cells with high performance and stability. We revealed the potential interaction mechanism between supramolecular network and the perovskite by a series of tests: the formation of adducts between S-DTF and perovskite precursor retards crystallization, resulting in high crystallinity and significantly enlarged grains. The Lewis base $-\text{NH}_2$ branch of the S-DTF network also effectively passivates the defect sites at the grain boundary without increasing the resistivity. The enlarged grains with the lower defect density improved the *PCE* to 21.0 % for target device. Benefiting from the self-sealing effect of the S-DTF, the perovskite solar cells with hydrophobic S-DTF exhibits a high long-term stability (maintaining 93% of their original efficiency for over 30 days

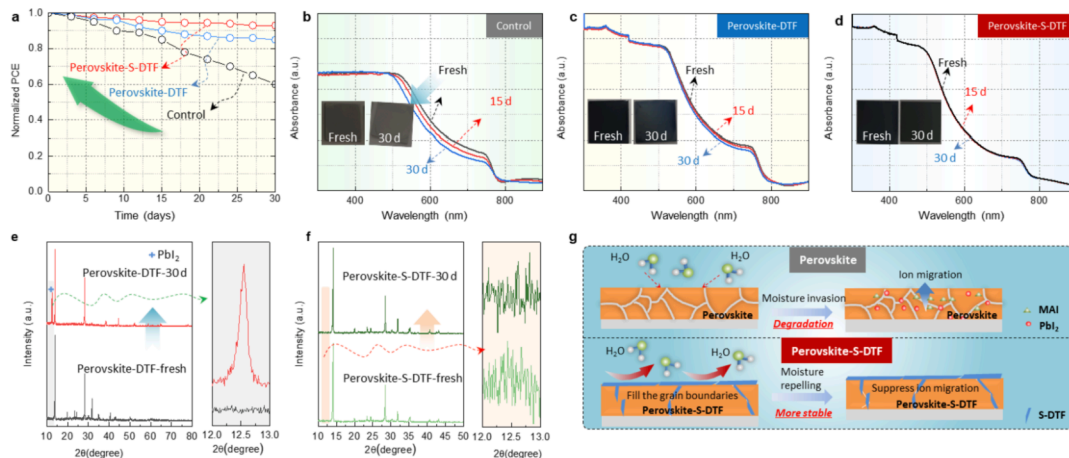


Fig. 5. Stability assessment of perovskite. (a) Evolution of *PCE* in relative humidity $\sim 70\%$. (b-d) The absorption spectra of the control, perovskite-DTF and perovskite-S-DTF films after aging for 15 days and 30 days, respectively. (e-f) XRD patterns of the control and the film perovskite-S-DTF after aging for 30 days. The films were kept in an ambient air environment. Side: Magnification of the XRD patterns at 12° . (g) the decomposition processes of different perovskite film.

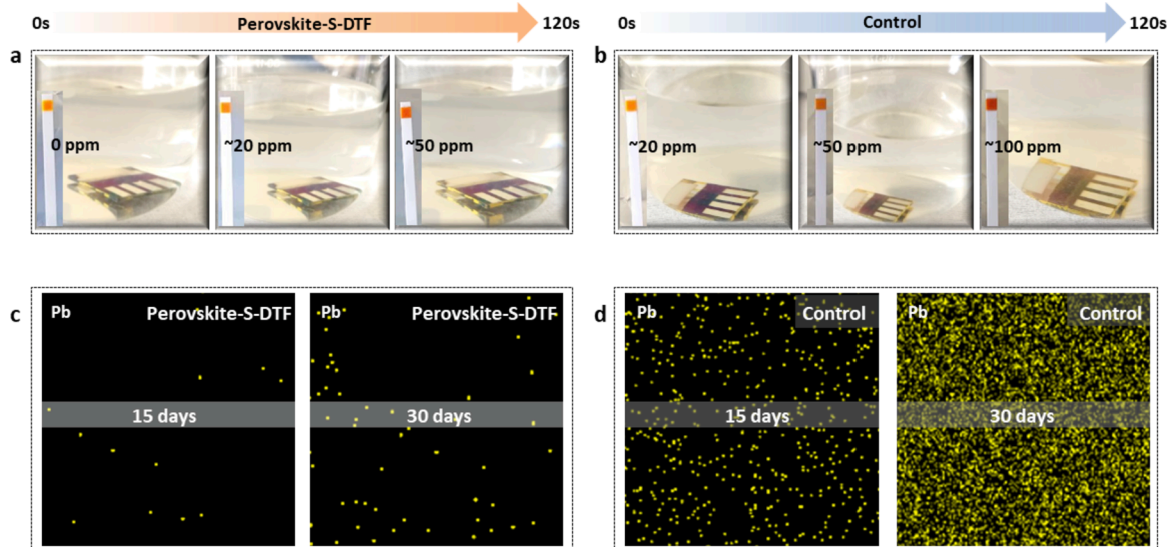


Fig. 6. Prevention of lead leakage. (a-b) Photographs of the control and Perovskite-S-DTF devices. All devices were placed in water with a pH of ~ 5.6 . The Pb ion test paper was used to quickly detect the Pb concentration in the effluent. (c-d) Detect the Pb concentration with ITO/perovskite/spiro-OMeTAD structure at $\sim 70\%$ humidity by EDS measurement.

($\sim 70\%$ humidity) in air without any encapsulation). Therefore, we believe that this work not only provides a new scheme for regulating perovskite materials, but also inspires us to pay more attention on the intermolecular design except simply exploring new type of additive for PSCs.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2022.137431>.

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