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Superoxide Radical Derived Metal-Free Spiro-OMeTAD for Highly Stable Perovskite Solar Cells

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

In this manuscript, Ye et al. explore a new doping strategy for Spiro-OMeTAD by using an additive of Eu(TFSI)2 salt which is thought to generate ·O2- to oxidize Spiro-OMeTAD. Compared with the traditional strategy using tBP and LiTFSI, the new doping strategy can oxidize the Spiro-OMeTAD very quickly, which is an interesting phenomenon. The new doping strategy also provides higher efficiency and better stability for both small devices and modules. The method is novel and the results are good, but the significance of the doping strategy is doubtful, the proposed reaction mechanisms are unreasonable, and the performance improvement is also not so convincing. I think the overall quality of the current manuscript cannot meet the high standards of Nature Communication. The detailed comments are as follows.

1) Both tBP and LiTFSI are involved in the doping process mentioned in the method section. Even though the oxidation time is shortened in the developed doping strategy, the need of tBP and LiTFSI would be a drawback that weakens the advantages and importance of this doping strategy. Meanwhile, the use of tBP and LiTFSI is not mentioned in the proposed reaction mechanism. The role of tBP and LiTFSI should be analyzed.

2) The ratio of Eu(TFSI)2 to LiTFSI is given as 0.4:1. The significance of this value should be explained. How the pre-oxidized spiro-OMeTAD is used is not clear in the methods section. Is it the prepared oxidized solution or the collected powder of pre-oxidized spiro-OMeTAD?

3) In the proposed reaction mechanism, O2 was reduced to ·O2- by Eu2+, and further reduced to O2- by Spiro-OMeTAD. Considering that Eu2+ should have a stronger reducing power than Spiro-OMeTAD, it is incomprehensible why O2 was not directly reduced to O2- by Eu2+. It is also difficult to understand that Spiro-OMeTAD was oxidized by ·O2-, not by O2, since O2 should have a stronger oxidation property than ·O2-. Furthermore, there seems to be no evidence to prove the formation of ·O2- in the paper.

4) The authors use ·O2--derived spiro-OMeTAD to describe the radical formed. This leads to confusion with the radical formed. Based on the reaction, the final radical is Spiro-OMeTAD+-TFSI-, the same as the radical formed by using tBP and LiTFSI.

5) It is difficult to understand the explanation of the diminished peaks in the HNMR of spiro-OMeTAD and radical solution by the effective electron exchange. Reference or evidence is needed.

6) The efficiency of the devices reaches up to 25.06%, much higher than the 22.40% of traditional devices. The improvement is very high and explained by the lower conductivity and unsuitable energy levels of Spiro-OMeTAD in the traditional doping strategy. If so, is it possible to further increase the conductivity of the traditional recipe by forming more radicals through the addition of more LiTFSI or longer oxidation? The authors should make sure that the traditional doped Spiro-OMeTAD has been optimized, as the reported devices based on traditionally doped Spiro-OMeTAD can also reach over 25%.

7) Some sentences are incomprehensible. For example: 'These peaks diminish significantly following •O2-- doping, demonstrating that the effective electron exchange takes place between spiro-OMeTAD and spiro-OMeTAD+TFSI - in the presence of residual TFSI-.' Where does the residual TFSI- come from? 'This indicates substantially reduced trap-assisted recombination within PSCs, which results from the decreased charge extraction barrier at the interface between perovskite and •O2--derived spiro-OMeTAD.' How the reduced charge extraction barrier reduces trap-assisted recombination should be explained.

8) The authors mention that 'The Eu(TFSI)2 precursor solution is very stable for more than several months and can be used directly without re-filtration'. The storage conditions (in the glove box or in air) should be specified.

Reviewer #2 (Remarks to the Author):

This article demonstrates a synthesis method of spiro-OMeTAD hole transport materials for the solar cell application, where HTL developed do not require post-oxidation treatment. Despite the promising PCE and stability of fabricated solar cells, the author has to consider the practical significance of the proposed strategies since the synthesis process of O2--derived spiro-OMeTAD HTL requires pumping oxygen into the solution, and it increases the fabrication cost. Moreover, the author should specify the advantage of the proposed strategy when compared to the pioneering work (Ref.1 and Ref. 4). More technical comments are attached below. Therefore, I recommend that the critical issues are addressed and the necessary amendments are made before the manuscript can be considered further.

In the control group, the spiro-OMeTAD solution was not treated by O2 bubbling. To consolidate the novelty of the proposed strategies, the O2 bubbling for the control spiro-OMeTAD must be performed and other related instrumental analyses should be made. Ref. 4 has confirmed the O2 bubbling of traditional spiro-OMeTAD can kinetically promote the oxidation of spiro-OMeTAD and improve the solar cell performance.

The author verifies the effectiveness of Eu(TFSI)2 on the generation of O2 radicals by performing electron paramagnetic resonance (line 114-119). It is suggested to proceed with EPR measurement for the control spiro-OMeTAD (with O2 bubbling) as well. Besides, please provide references for the statement in line 117-118, “The EPR recorded at room temperature in dark shows 6 peaks for the O2-bubbled spiro-118 OMeTAD:Eu(TFSI)2 solution, demonstrating the generation of •O2-”

The author declares doping saturation is reached when the Eu(TFSI)2 concentration increases to 40 mol% (line 182). The statement of doping saturation desires a more detailed interpretation. The NMR (Fig. 3c) only confirms there is a chemical interaction between Eu(TFSI)2 and spiro-OMeTAD. Besides, please specify how the mobility is calculated from SCLC, and the fitting line should be presented over the spectra.

The author declares the quenching of PL (Fig. 3d-e) is due to the optimised band structure at the contact. However, the generation of defects at the contact could also quench the PL. Related comments should be given.

The charge transfer resistance of the solar cell is more than 5000 ohms for both the control and optimised devices (Fig. 4h). This Rct is huge compared to other reports (Nature Communications volume 10, Article number: 1574 (2019); Nature Communications volume 9, Article number: 3239 (2018)). Please justify these results and specify the active area of the device in the EIS measurement.

Reviewer #3 (Remarks to the Author):

In this work, the authors developed a rapid and Li-free doping strategy for spiro-OMeTAD that avoids post-oxidation by constructing •O2- in the spiro-OMeTAD solution. The •O2- can be facilely formed in the spiro-OMeTAD solution in air with the addition of variant-valence Eu(TFSI)2 salts obtained from the chemical reactions between Eu metal and HTFSI. During this process, O2 obtains an electron from the Eu2+-Eu3+ redox shuttle and rapidly produces the •O2-, resulting in the subsequent oxidation of spiro-OMeTAD and its p-type doping. In stark contrast to conventional LiTFSI doping with air exposure, •O2--derived spiro-OMeTAD HTLs can instantly obtain high conductivity and ideal work function without requiring post-treatments, delivering their PSCs with PCEs over 25%. Furthermore, the long-term stability of the PSCs based on the •O2--derived spiro-OMeTAD HTLs is significantly enhanced due to the increased resistance toward moisture and ion migration, in addition to the lack of Li+ and air exposure. However, I have a few questions to ask as follows：

1. Recent work has reported that the pre-synthesized spiro-OMeTAD2•+(TFSI–)2 radical accompanied by the doping modulation of ionic salts has been found to be directly involved in the spiro-OMeTAD HTL of PSCs without the oxidation process. This has resulted in delivering PCEs of > 25% and much-improved device stability under harsh conditions. Compared with previous work, what's the innovation or technological breakthrough in this work? Please comment on it.

2. It is not clear why the •O2- show improved reaction rate compared with O2 when it involved in an in situ oxidation of spiro-MeOTAD in solution.

3. The HTL solution needs to react with oxygen in the air to oxidize spiro-OMeTAD. During this process, will the environment (such as temperature, humidity, etc.) affect the degree of oxidation of spiro-OMeTAD and thus affect the repeatability of the device?

4. Figure 5c shows that the perovskite/•O2--derived spiro-OMeTAD sample undergoes severe degradation after humidity aging, while the perovskite/LiTFSI-doping spiro-OMeTAD sample shows good stability. Is this correct?

5. There are some typos in the manuscript, such as, in line 195, is reduced from 67.1 ns to .8 ns for the perovskite/•O2--derived HTLs. I guess the .8 ns shoule be 0.8 ns.

6. The optimized energy level of the HTL enables lower the interfacial charge transfer barrier. The sentence could be further revised, and please further check the entire manuscript.

7. The O2--derived HTLs show much improved glass transition temperature up to 130 □C, which is a good sign for the perovskite solar cell community. Can the authors further demonstrate the thermal stability of this HTL, to confirm whether this HTL can withstand the stringent conditions in the practical applications.

Replies to Reviewer 1

Q1: In this manuscript, Ye et al. explore a new doping strategy for Spiro-OMeTAD by using an additive of $Eu(TFSI)_2$ salt which is thought to generate $\bullet O_2^-$ to oxidize Spiro-OMeTAD. Compared with the traditional strategy using tBP and LiTFSI, the new doping strategy can oxidize the Spiro-OMeTAD very quickly, which is an interesting phenomenon. The new doping strategy also provides higher efficiency and better stability for both small devices and modules. The method is novel and the results are good, but the significance of the doping strategy is doubtful, the proposed reaction mechanisms are unreasonable, and the performance improvement is also not so convincing. I think the overall quality of the current manuscript cannot meet the high standards of Nature Communication. The detailed comments are as follows.

Reply: Thank you very much for your positive comments to our work, and we much appreciate for the raised comments below, which are all valuable and helpful for improving our manuscript. We have tried our best to revise our manuscript accordingly, and those revisions have been marked in red color in the revised manuscript. Below are the points to point replies.

Q2: Both tBP and LiTFSI are involved in the doping process mentioned in the method section. Even though the oxidation time is shortened in the developed doping strategy, the need of tBP and LiTFSI would be a drawback that weakens the advantages and importance of this doping strategy. Meanwhile, the use of tBP and LiTFSI is not mentioned in the proposed reaction mechanism. The role of tBP and LiTFSI should be analyzed.

Reply: Thank you very much for the comments and concerns. We are sorry to create confusion among the reviewers regarding the involvement of LiTFSI and tBP in $\bullet O_2^-$ doping, owing to the mistakes in corresponding descriptions in Methods section. We have checked and corrected them in the revised manuscript, and read as: "For the $\bullet O_2^-$-derived spiro-OMeTAD, $Eu(TFSI)_2$ with different mole ratios to spiro-OMeTAD including 0.05:1,0.10:1, 0.20:1, 0.30:1, 0.40:1, and 0.50:1, along with 15 μL *t*BP that was employed to improve the dispersibility of $Eu(TFSI)_2$,[38] were added into the spiro-OMeTAD:CB solution, respectively. The mixtures were then bubbled with O_2 for different

durations. The optimal mole ratio of $Eu(TFSI)_2$ to spiro-OMeTAD was determined to be 0.40:1. After filtration (0.22 μm, PTFE), the oxidized spiro-OMeTAD solution was consequently obtained, ...".

We would like to stress that the general LiTFSI was not involved in the doping of spiro-OMeTAD in our present strategy of $\bullet O_2^-$. It should be noted that the $\bullet O_2^-$ was formed by adding an as-synthesized $Eu(TFSI)_2$ into the spiro-OMeTAD:chlorobenzene solution. The spiro-OMeTAD can be fully oxidized by $\bullet O_2^-$ in its solution within 30 s, and then directly used to deposit as the hole transport layer without post-oxidization in air, contributing thus to high efficient and stable PSCs.

Regarding the involved tBP in present strategy of $\bullet O_2^-$, it should be noted that only a small amount of tBP (15 μL) was introduced into the spiro-OMeTAD:chlorobenzene solution just to improve the uniformity and dispersibility of $Eu(TFSI)_2$, in which the $\bullet O_2^-$ can thus be generated uniformly and realize rapid oxidation of spiro-OMeTAD in its solution. It is worth noting that the tBP was never be involved in the doping process of spiro-OMeTAD, and was used just for better dispersion of $Eu(TFSI)_2$ in solution, which has been discussed in the previous work (*J. Am. Chem. Soc.* 2018, 140, 16720-16730).

Q3: The ratio of $Eu(TFSI)_2$ to LiTFSI is given as 0.4:1. The significance of this value should be explained. How the pre-oxidized spiro-OMeTAD is used is not clear in the methods section. Is it the prepared oxidized solution or the collected powder of pre-oxidized spiro-OMeTAD?

Reply: We appreciate the reviewer for bringing these points to our attention. We sincerely apologize for the mistakes made in the description of "The optimal mole ratio of $Eu(TFSI)_2$/LiTFSI was 0.40:1" in the Methods section. It is important to clarify that the correct ratio of 0.4:1 refers actually to the mole ratio of $Eu(TFSI)_2$ to spiro-OMeTAD, not LiTFSI. We have double checked and corrected corresponding descriptions in the revised manuscript, and read as: "For the $\bullet O_2^-$-derived spiro-OMeTAD, $Eu(TFSI)_2$ with different mole ratios to spiro-OMeTAD including 0.05:1,0.10:1, 0.20:1, 0.30:1, 0.40:1, and 0.50:1, along with 15 μL *t*BP that was employed to improve the dispersibility of $Eu(TFSI)_2$,[38] were added into the spiro-OMeTAD:CB solution, respectively. The mixtures were then bubbled with O_2 for different durations. The optimal mole

ratio of $Eu(TFSI)_2$ to spiro-OMeTAD was determined to be 0.40:1. After filtration (0.22 μm, PTFE), the oxidized spiro-OMeTAD solution was consequently obtained, ...". Meanwhile, we have double-checked the whole manuscript to ensure that there are no similar incorrect descriptions.

Regarding the determination of the 0.40:1 rate, we have actually conducted a series of characterizations in the present work, including UV-Vis spectra, conductivity/mobility tests, and PCE optimization (Fig. 2f, Fig. 3b, Fig. 4 a-c and Supplementary Fig. 3, Fig. 5, Table 3). These results demonstrated that the doping of spiro-OMeTAD in solution reached saturation at the concentration up to 40 mol% of $Eu(TFSI)_2$ to spiro-OMeTAD. Moreover, it has been demonstrated that higher concentrations of $Eu(TFSI)_2$ exceeding 40 mol% are not beneficial to the photovoltaic performance of PSCs.

Regarding the use of the pre-oxidized spiro-OMeTAD solution, we have actually presented two recipes in our work, including the direct spin-coating as HTL and the extraction of spiro-OMeTAD powder from its oxidized solution. In this manuscript, we focused on the investigation and discussion of pre-oxidizing spiro-OMeTAD in solution. The resulting solution can be directly deposited as the HTL of Li-free spiro-OMeTAD for highly stable perovskite photovoltaics, without the need for a time-consuming and detrimental post-oxidation process. After elaborately observations, we found the pre-oxidized spiro-OMeTAD solution can be extracted as powders through facile drying (see the inset in Fig. 2e). Such spiro-OMeTAD powder can then be redissolved and deposited as HTLs without any additional treatments, delivering nearly identical PCE regardless of the storage time compared to that of its fresh solution counterpart. This is particularly crucial for the commercialization and scaling-up of spiro-OMeTAD based *n-i-p* PSCs, further highlighting the advantages of our $\bullet O_2^-$ strategy over conventional LiTFSI-doping. It should be noted that the core point both of these two recipes is focused on the oxidization of spiro-OMeTAD in its solution, with the latter being a further supplement and application of the former.

We have also supplemented corresponding descriptions in Methods section in the revised manuscript regarding the use of the pre-oxidized spiro-OMeTAD solution, and read as: "After filtration (0.22 μm, PTFE), the oxidized spiro-OMeTAD solution was consequently obtained, and can be directly deposited as the HTL of Li-free spiro-OMeTAD for PSCs, without the need for a post-oxidation process. Also, the pre-oxidized spiro-OMeTAD solution can be extracted as powders

through facile drying. These spiro-OMeTAD powders can then be redissolved and deposited as HTLs of PSCs without any additional treatments.".

Q4: In the proposed reaction mechanism, O_2 was reduced to $\bullet O_2^-$ by Eu^{2+}, and further reduced to O_2^- by Spiro-OMeTAD. Considering that Eu^{2+} should have a stronger reducing power than Spiro-OMeTAD, it is incomprehensible why O_2 was not directly reduced to O^{2-} by Eu^{2+}. It is also difficult to understand that Spiro-OMeTAD was oxidized by $\bullet O_2^-$, not by O_2, since O_2 should have a stronger oxidation property than $\bullet O_2^-$. Furthermore, there seems to be no evidence to prove the formation of $\bullet O_2^-$ in the paper.

Reply: Thank you very much for the comments and concerns. Regarding the oxidation property comparison between $\bullet O_2^-$ and O_2, it should be noted that the superoxide radical ($\bullet O_2^-$) actually exhibits higher reactivity compared to molecular oxygen (O_2), primarily attributed to differences in their electronic structures. The $\bullet O_2^-$ is formed when one electron is individually stripped from an oxygen molecule, resulting in an unpaired electron. This unpaired electron gives the superoxide radical higher reactivity as it is more prone to engage in chemical reactions, such as electron transfer or redox reactions, with other substances including the spiro-OMeTAD. In contrast, molecular oxygen consists of two oxygen atoms sharing a pair of electrons, which contributes to its relative stability. To initiate a reaction with molecular oxygen, one must overcome its stability and the sharing of electron pairs, resulting in slower reaction rates. Therefore, the superoxide radical, with its unpaired electron characteristic, exhibits higher reactivity compared to molecular oxygen, which is consist with previous reports in other fields (*Adv. Mater.* 2022, 34, 2200612; *Chem. Rev.* 2016, 116, 5, 3029-3085).

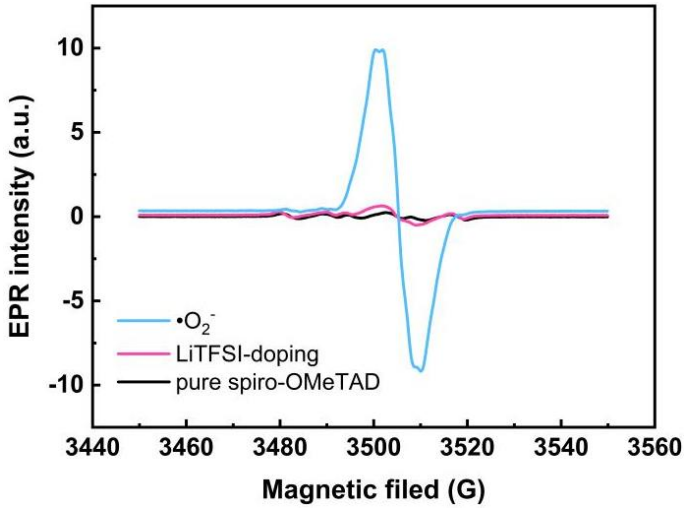
Experimentally, we have conducted a series of characterizations to confirm the higher reaction rate of the $\bullet O_2^-$. For example, by adding the $Eu(TFSI)_2$ with an concentration of 40 mol% into the as-prepared spiro-OMeTAD solution, it can be seen that the color of the spiro-OMeTAD:$Eu(TFSI)_2$ solution rapidly changes from light yellow to dark red after 30 seconds of bubbling with O_2. However, in the conventional spiro-OMeTAD:LiTFSI solution there is not much change in color when bubbled with O_2 for even 2 minutes (Fig. 2b). The spiro-OMeTAD:$Eu(TFSI)_2$ solution bubbled with O_2 exhibits a gradually increased polaron absorption peak centered at about 521 nm

with the increasing bubbling time or concentration of $Eu(TFSI)_2$. In contrast, there are no peaks emerging in the UV-Vis spectra for the conventional spiro-OMeTAD:LiTFSI solution with or without O_2 bubbling (Fig. 2f and Supplementary Fig. 3). In addition, we have supplemented the Electron Paramagnetic Resonance (EPR) spectra to compared the oxidation rate of $\bullet O_2^-$ and molecular oxygen in spiro-OMeTAD solutions (see Supplementary Fig. 2b and **Reply Fig. 1**). It is found that the $\bullet O_2^-$ strategy exhibits a higher oxidation peak than that of the conventional LiTFSI-dpoing. These results significantly demonstrate that $\bullet O_2^-$ shows an improved reaction rate compared with O_2 when involved in the *in situ* oxidation of spiro-OMeTAD in solution.

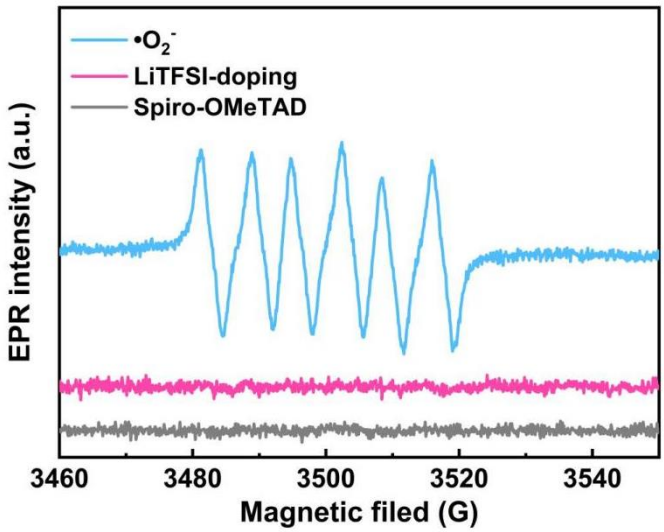
Regarding the determination of $\bullet O_2^-$, previous studies (Dvoranova, D. et al. Radical intermediates in photoinduced reactions on TiO_2 (An EPR spin trapping study). *Molecules*, 2014, 19, 17279-17304.) have proven the generation of superoxide radicals in solution via the EPR measurement. We have added references about the EPR of superoxide radicals in the revised manuscript, which is listed Ref 27. To make a comparison and see if there are existing $\bullet O_2^-$, we have also supplemented the EPR measurements for the pure spiro-OMeTAD and LiTFSI-doped spiro-OMeTAD solutions with O_2 bubbling (see Fig. 2d in the revised manuscript and **Reply Fig. 2**). It is observed that there is no EPR signals in both the pure and LiTFSI-doped spiro-OMeTAD solutions, indicating the absence of $\bullet O_2^-$ generation in these solutions.

On the basis of above observations and analyses, we proposed the oxidation mechanism of $\bullet O_2^-$ for spiro-OMeTAD solutions, which can be described as follow: The lost electron from the Eu^{2+}-Eu^{3+} redox shuttle would first be recovered by O_2, contributing rapidly to the generation of the $\bullet O_2^-$. The resultant $\bullet O_2^-$ then oxidize the spiro-OMeTAD to a TFSI-stabilized spiro-OMeTAD$^+$ radical cation along with the Eu^{3+} reaction products. We would like to stress that it is difficult to form O^{2-} from O_2 by Eu^{2+} in solution during the process of spiro-OMeTAD oxidation, owing to the imbalance in the involved amount between O_2 and Eu^{2+} (O_2 is excessive compared to Eu^{2+}). The conversion from O_2 molecule to O^{2-} requires four electrons. In other words, for such conversion to occur, one oxygen molecule needs to interact with four Eu^{2+} ions simultaneously. However, due to the electrostatic repulsion, the distance between Eu^{2+} ions in solution is relatively large, limiting the interaction of O_2 with only one Eu^{2+} ion, resulting thus in the formation of superoxide radicals. When the concentration of Eu^{2+} is excessively high, the generated $\bullet O_2^-$ will react with Eu^{2+},

resulting in a decrease in the concentration of $\bullet O_2^-$ in solution and subsequently reducing the oxidation of spiro-OMeTAD.



Reply Fig. 1 EPR spectra of different spiro-OMeTAD solutions bubbled with O_2 for 10 s and tested after 5 min.



Reply Fig. 2. EPR spectra of different solutions (pure, LiTFSI-doping and $\bullet O_2^-$-derived spiro-OMeTAD) bubbled with O_2 for 10 s and tested immediately.

Q5: The authors use $\bullet O_2^-$-derived spiro-OMeTAD to describe the radical formed. This leads to confusion with the radical formed. Based on the reaction, the final radical is Spiro-OMeTAD$^+$-TFSI$^-$, the same as the radical formed by using tBP and LiTFSI.

Reply: Thank you very much for the comment and concern. Indeed, the actually doping process of spiro-OMeTAD is to form a TFSI-stabilized radical cation (spiro-OMeTAD$^{\bullet+}$ TFSI^{-}), contributing consequently to the generation of free hole polarons and the increase in the conductivity. For the conventional LiTFSI-doping, O_2, as the actual dopant, oxidizes the spiro-OMeTAD film while LiTFSI mediates the reaction between O_2 and spiro-OMeTAD along with detrimental unreacted reactants and by-products that causes instability of PSCs (e.g., Li_xO_y). This process relies on very slow O_2 ingress into and diffusion through spiro-OMeTAD:LiTFSI, which usually takes 12-24 h of oxidation time, and is dependent on the ambient conditions. In the present work, we employed the variant-valence $Eu(TFSI)_2$ salts that could generate $\bullet O_2^-$ in air for facile and adequate pre-oxidation of spiro-OMeTAD in solution within 30 s, obtaining instantly high conductivity and ideal work function without requiring post-treatments, which differs from the time-consuming post-oxidation process for LiTFSI-doping counterparts.

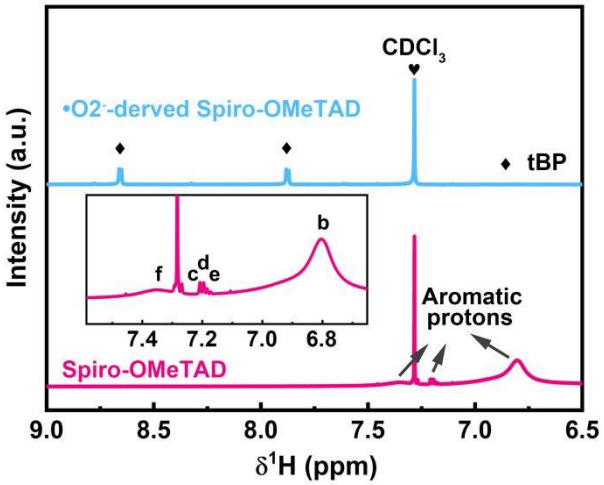
Regarding the description of $\bullet O_2^-$, superoxide radicals are a specific type of radicals (refer to chemical entities that possess one or more unpaired electrons), characterized by their particular oxidizing ability and reactivity in chemical reactions (*Chem. Rev.* 2016, 116, 3029-3085). In comparison with the conventional dopant of O_2, the superoxide radical ($\bullet O_2^-$) is more reactive than molecular oxygen (O_2) primarily due to differences in their electronic structures. The $\bullet O_2^-$ is formed when one electron is individually stripped from an oxygen molecule, resulting in an unpaired electron. This unpaired electron gives the superoxide radical higher reactivity as it is more prone to engage in chemical reactions, such as electron transfer or redox reactions, with other substances including the spiro-OMeTAD.

Q6: It is difficult to understand the explanation of the diminished peaks in the HNMR of spiro-OMeTAD and radical solution by the effective electron exchange. Reference or evidence is needed.

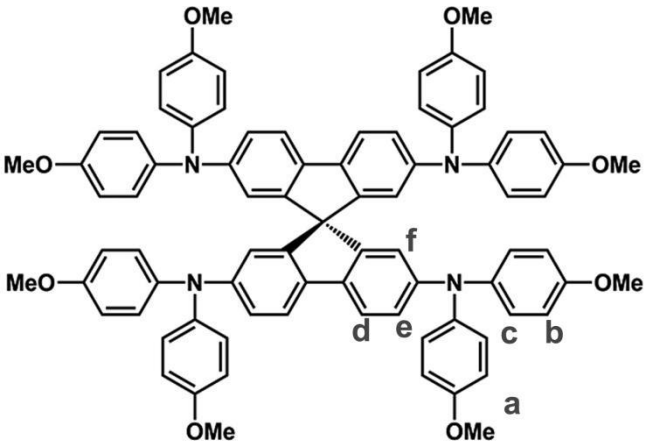
Reply: Thank you very much for the comment and suggestion. From the HNMR (Fig. 3c and **Reply Fig. 3**), we observed that the aromatic proton peaks (b-f, Supplementary Fig. 6 and **Reply Fig. 4**) near N in spiro-OMeTAD were significantly broadened and diminished after $\bullet O_2^-$-doping. These diminished signals suggested that spiro-OMeTAD$\bullet^+$TFSI$^-$ and neutral spiro-OMeTAD were near

each other and mutually exchanging electrons, which could be attributed to p-p stacking between fluorene moieties of spiro-OMeTAD and spiroOMeTAD•$^{+}$TFSI^{-} according to the previous reports (*Angew. Chem. Int. Ed*. 2024, 63, e202316183; *Science* 2022, 377, 495-501).

We thus updated corresponding descriptions in the analysis of HNMR in the revised manuscript, which now reads as follow: "These peaks diminish significantly following •O_2^--doping, demonstrating that the effective electron exchange takes place between spiro-OMeTAD and spiro-OMeTAD^{+}TFSI^{-} in the presence of the TFSI^{-} stabilizer originating from Eu(TFSI)$_2$, which is consistent with previous reports.[1,2]", and added the Ref 1 and 2.



Reply Fig. 3 1H NMR characterization of the spiro-OMeTAD solution with or without •O_2^- doping.



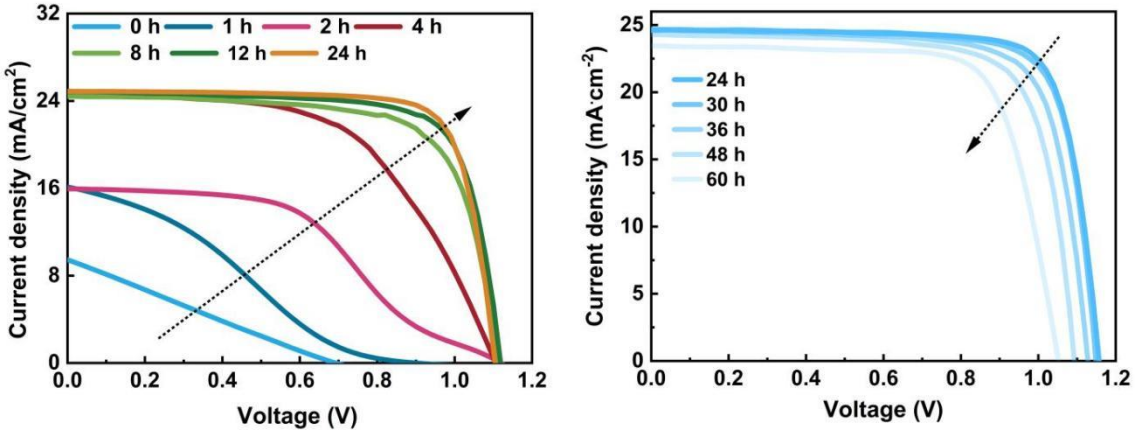
Reply Fig. 4 The molecular structure of spiro-OMeTAD.

Q7: The efficiency of the devices reaches up to 25.06%, much higher than the 22.40% of traditional devices. The improvement is very high and explained by the lower conductivity and unsuitable energy levels of Spiro-OMeTAD in the traditional doping strategy. If so, is it possible to further increase the conductivity of the traditional recipe by forming more radicals through the addition of more LiTFSI or longer oxidation? The authors should make sure that the traditional doped Spiro-OMeTAD has been optimized, as the reported devices based on traditionally doped Spiro-OMeTAD can also reach over 25%.

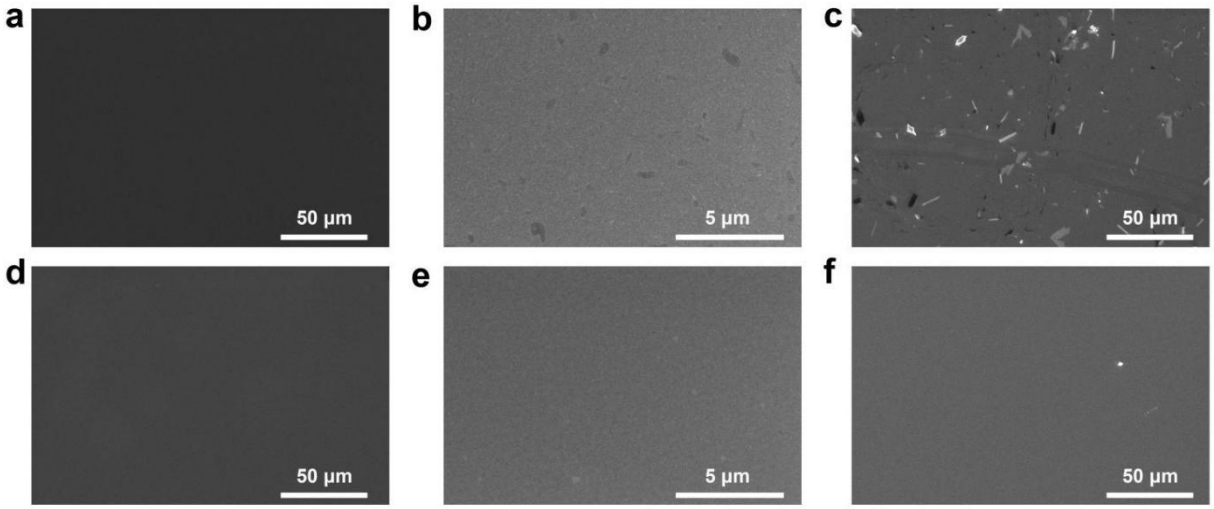
Reply: Thank you very much for the comments and concerns. We strongly agree that maximizing the conductivity and work function of spiro-OMeTAD HTLs through a well-modulated doping strategy could inspire further optimization in perovskite photovoltaics and other optoelectronic devices. However, previous studies (*ACS Energy Lett*. 2019, 4, 2547-2551; *J. Phys. Chem. C* 2012, 116, 26300-26305) have shown that the dopants like LiTFSI do not have a doping efficiency of >100%. Instead, the doping efficiency is closer to less than 20%. This highlights that only a fraction of spiro-OMeTAD (~8 mol %) is oxidized by the addition of LiTFSI up to a concentration of 50 mol%. This can be attributed to the doping saturation, which is consistent with previous reports in other organic semiconductor systems and arises due to the increase in energetic disorder induced by long-range Coulomb interactions when increasing the number of dopants (*Science* 2022, 377, 495-501; *Adv. Funct. Mater*. 2015, 25, 2701-2707). Therefore, it becomes challenging to further enhance the conductivity of spiro-OMeTAD HTLs solely by increasing the amount of LiTFSI dopant.

Regarding the longer oxidation time, we have actually tracked the evolution of PCE for PSCs with LiTFSI-doped spiro-OMeTAD HTLs. As shown in **Reply Fig. 5**, upon increasing the aging time form 0 to 60 h, the PCE first augments and subsequently decreases with a peak at 24 h. However, with further increase in the aging time, all photovoltaic parameters exhibited a decrease. This trend suggests that the optimal oxidation time for achieving the highest efficiency is 24 hours. As we have summarized in the introduction of the manuscript and discussed in the stability analyses, it is important to consider the negative impacts of LiTFSI and its by-products (e.g., Li_xO_y) on device stability (**Reply Fig. 6 and Reply Fig. 7**). These species are not only diffusible but also sensitive to humidity and heat, leading to a degradation in device performance over time. Therefore,

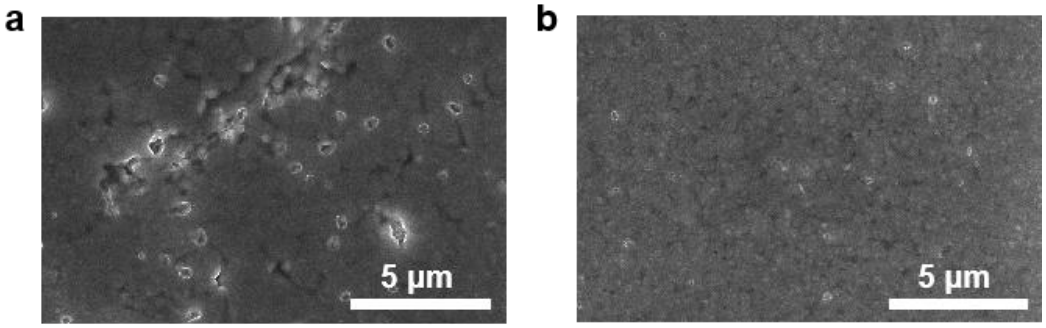
it is not feasible to increase the conductivity of spiro-OMeTAD by adding more LiTFSI or prolonging the oxidation time. There exists a trade-off between achieving high efficiency and maintaining stability in *n-i-p* PSCs.



Reply Fig. 5 *J-V* curves of the LiTFSI-doped PSCs device under different oxidation time.



Reply Fig. 6 SEM images of different spiro-OMeTAD films. LiTFSI-doped spiro-OMeTAD before oxidation (a) and after oxidation of 12 h (b) and 30 days (c) in air, respectively. (d) $\bullet O_2^-$-derived spiro-OMeTAD before and after exposure of 12 h and 30 days in air, respectively.



Reply Fig. 7 SEM images of different spiro-OMeTAD deposited on perovskite films after aging in double 85 condition (85% RH and 85°C) for 40 min. (a) LiTFSI-doped spiro-OMeTAD. (b) $\bullet O_2^-$-derived spiro-OMeTAD.

Q8: Some sentences are incomprehensible. For example: 'These peaks diminish significantly following $\bullet O^{2-}$-doping, demonstrating that the effective electron exchange takes place between spiro-OMeTAD and spiro-OMeTAD$^+$TFSI$^-$ in the presence of residual TFSI$^-$.' Where does the residual TFSI- come from? 'This indicates substantially reduced trap-assisted recombination within PSCs, which results from the decreased charge extraction barrier at the interface between perovskite and •O2--derived spiro-OMeTAD.' How the reduced charge extraction barrier reduces trap-assisted recombination should be explained.

Reply: Thank you very much for the comments and suggestions. Regarding the statement of "residual TFSI$^-$", it is indeed difficult to comprehend. What we have stated concerning the "residual TFSI$^-$" in the original manuscript is based on the step-by-step reaction of the oxidation of spiro-OMeTAD by the $\bullet O^{2-}$ strategy in solution:

$$Eu^{2+} + O_2 \rightarrow Eu^{3+} + \bullet O_2^- \quad (1)$$

$$\text{spiro-OMeTAD} + \bullet O_2^- \rightarrow \text{spiro-OMeTAD}^+ + O^{2-} \quad (2)$$

$$\text{spiro} - \text{OMeTAD}^+ + \text{TFSI}^- \rightarrow \text{spiro-OMeTAD}^+\text{-TFSI}^- \quad (3)$$

The overall reaction can be follows:

$$\text{spiro-OMTeAD} + O_2 + Eu(TFSI)_2 \rightarrow \text{spiro-OMeTAD}^+\text{-TFSI}^- + EuO_xTFSI_{(3-2x)} \quad (4)$$

In this process, the divalent Eu^{2+} ($Eu(TFSI)_2$) transformed into trivalent $EuO_xTFSI_{(3-2x)}$ precipitate, while the spiro-OMeTAD was oxidized by $\bullet O^{2-}$ to form spiro-OMeTAD$^+$, which was then stabilized by TFSI$^-$. What we would like to emphasize is that a portion of TFSI$^-$ from $Eu(TFSI)_2$ was used to

form the Eu^{3+} precipitate, while another portion was used to stabilize spiro-$OMeTAD^{+}$ radical cation.

We have thus revised and corrected corresponding descriptions in the revised manuscript, which read as: "These peaks diminish significantly following $•O_2^-$-doping, demonstrating that the effective electron exchange takes place between spiro-OMeTAD and spiro-$OMeTAD^{+}TFSI^{-}$ in the presence of the $TFSI^-$ stabilizer originating from $Eu(TFSI)_2$, which is consistent with previous reports.[1,2].".

Regarding the statement of "the reduced charge extraction barrier reduces trap-assisted recombination", we truly appreciate the reviewer pointing out this inappropriate description. Reducing the interfacial charge transfer barrier does not necessarily imply reducing trap-induced recombination. As we have discussed in Fig. 3d-f and Fig. 4g-i, charge transfers at the interfaces, interface band alignment, and energy barriers have a strong impact on electrical device characteristics. For PSCs with LiTFSI-doped spiro-OMeTAD HTLs, there is a large interface barrier due to the energy level mismatch between the perovskite layer and the spiro-OMeTAD layer. This barrier makes it difficult for the photo-generated charge carriers to transfer to the electrode, increasing the probability of recombination. In contrast, the optimized energy level of the $•O_2^-$-derived HTLs lowers the interfacial charge transfer barrier, facilitating hole extraction and thereby minimizing carrier recombination. We thus revised and corrected the corresponding description, and read as: "This indicates substantially reduced carrier recombination within PSCs, which results from the decreased charge extraction barrier at the interface between perovskite and $•O_2^-$-derived spiro-OMeTAD.".

Q9: The authors mention that 'The $Eu(TFSI)_2$ precursor solution is very stable for more than several months and can be used directly without re-filtration'. The storage conditions (in the glove box or in air) should be specified.

Reply: We thank the reviewer for pointing this out. We have updated corresponding descriptions regarding the storage conditions of the $Eu(TFSI)_2$ precursor solution in the Methods section of the revised manuscript, which has been marked in red and reads as follows: "After reaction, the formed $Eu(TFSI)_2$ solution was filtered using an organic filter (0.22 μm, PTFE), and then stored in brown

bottles in a nitrogen-filled glovebox. The $Eu(TFSI)_2$ precursor solution is very stable in the inert atmosphere for more than several months and can be used directly without re-filtration.".

Replies to Reviewer 2

Q1: This article demonstrates a synthesis method of spiro-OMeTAD hole transport materials for the solar cell application, where HTL developed do not require post-oxidation treatment. Despite the promising PCE and stability of fabricated solar cells, the author has to consider the practical significance of the proposed strategies since the synthesis process of O_2^--derived spiro-OMeTAD HTL requires pumping oxygen into the solution, and it increases the fabrication cost. Moreover, the author should specify the advantage of the proposed strategy when compared to the pioneering work (Ref.1 and Ref. 4). More technical comments are attached below. Therefore, I recommend that the critical issues are addressed and the necessary amendments are made before the manuscript can be considered further.

Reply: Thank you very much for the comments and concerns. Regarding the practical significance of the synthesis process of $\bullet O_2^-$-derived spiro-OMeTAD, we have actually presented two synthetic routes in our work, including pumping O_2 into the spiro-OMeTAD solution and exposing the spiro-OMeTAD solution to air. (see Supplementary Movie 1, Movie 2, and Movie 3). Given that the amount of oxygen involved and the time spent of less than 30 s in the entire synthesis process, we believe that the corresponding preparation cost is negligible, especially for the second route. In this manuscript, we focused on the investigation and discussion of pre-oxidizing spiro-OMeTAD in solution by the route of pumping O_2. We aimed to provide a comprehensive understanding the formation of the $\bullet O_2^-$ and its effects on oxidation of spiro-OMeTAD.

Regarding the novelty of present work, it is true that many papers concerning doping modulation of spiro-OMeTAD HTLs have been published, which reflects the importance of developing Li-free spiro-OMeTAD for high efficient and stable PSCs. As we have summarized in the introduction of the manuscript, LiTFSI-doped spiro-OMeTAD is widely used as a HTL for high-efficiency *n-i-p* PSCs, but unfortunately facing awkward instability for commercialization arising from the intrinsic Li^+ migration and hygroscopicity. Meanwhile, the LiTFSI-doped spiro-OMeTAD typically requires a time-consuming air-oxidization process, which is uncontrollabe and not conducive to the scaling-up of PSCs. In this aspect, developing a rapid and Li-free (even metal-free) doping strategy for spiro-OMeTAD that avoids post-oxidation is of particularly

significance for pursuing low-cost and high-performance PSCs. This is why we carry out the present work of **Superoxide Radical Derived Metal-Free Spiro-OMeTAD**.

Regarding the advantages of the $\bullet O_2^-$ strategy, we believe that our work clearly distinguishes from the reported works on doping process and preparation cost of spiro-OMeTAD HTLs, and shows obvious advantages in the following three aspects: **(1)** Different from the Ref 4 that involves bubbling a spiro-OMeTAD:LiTFSI solution with CO_2/O_2 under ultraviolet light illumination, we employ in present work a variant-valence $Eu(TFSI)_2$ salt that could generate $\bullet O_2^-$ in air for facile and adequate oxidation of spiro-OMeTAD in solution within 30 s, without necessitating the adding of LiTFSI and UV light irradiation. As highlighted in the introduction of the manuscript, the $\bullet O_2^-$-derived Li-free (even metal-free) spiro-OMeTAD HTLs possess notable advantages, especially in terms of environmental stability, compared to those described in Ref 4. **(2)** Fast synthetic route and low-cost preparation. The Ref 1 developed a doping strategy of spiro-OMeTAD using the spiro-$OMeTAD^{2\bullet+}(TFSI^-)_2$ radical as the dopant and the ionic salt of $TBMP^+TFSI^-$ as the doping modulator. It should be noted that both the organic radical and ionic salt process need be subjected to a complicated and tedious wet-chemical synthetic procedure, including solvent exchange, filtration, drying, recrystallization, purification, working under reduced pressure/low temperature/inert atmosphere, and more. Completing the entire route for doping spiro-OMeTAD HTLs using these methods typically takes several days, thereby significantly increasing the associated costs. In contrast, the $\bullet O_2^-$ in present work can be facilely formed in the spiro-OMeTAD solution in air with the addition of variant-valence Eu $(TFSI)_2$ salts obtained from the chemical reactions between Eu metal and HTFSI, and realizes a rapid and Li-free doping for spiro-OMeTAD within 30 s. (3) New efficiency benchmark for regular planar PSCs employing Li-free spiro-OMeTAD as HTLs. The $\bullet O_2^-$-derived HTLs increase the PSCs efficiency up to 25.45% and 20.76% for 0.05 active area and 6 × 6 cm^2 module, respectively, which is as far as we know the highest value among the reports on PSCs employing post-oxidation-free and Li-free spiro-OMeTAD HTLs. More importantly, by virtue of the above features of the $\bullet O_2^-$-derived spiro-OMeTAD, the unencapsulated PSCs retain 80% of their initial efficiency after 5,000 hours of air storage at a relative humidity of 70%, and impressively deliver robust environmental stability under various harsh conditions, i.e., maintain over 90% of their initial efficiency after 1000 h of

operation at the maximum power point and after 80 light-thermal cycles under simulated low earth orbit conditions, respectively.

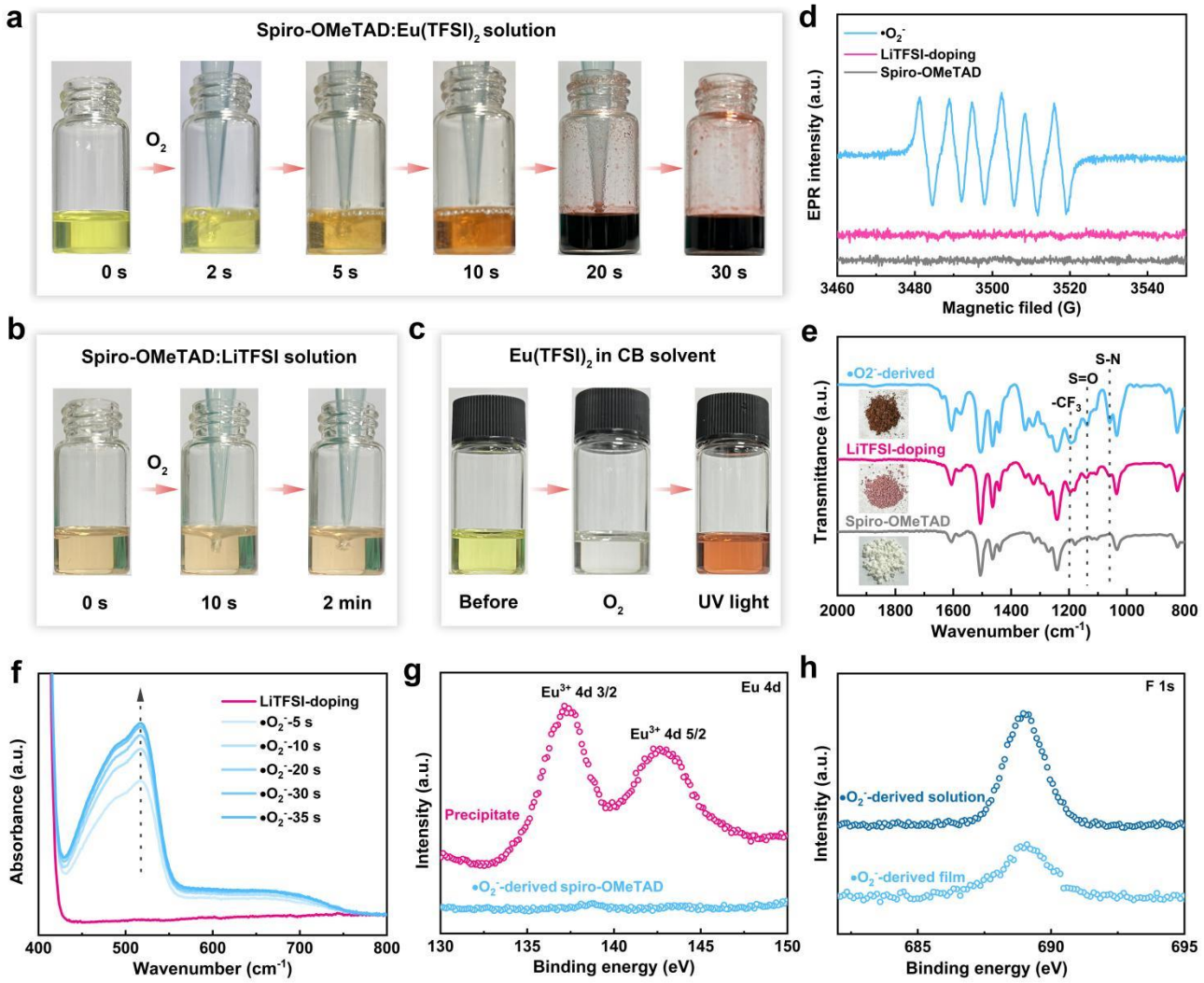
Given these striking merits, we believe such $\bullet O_2^-$-deriving strategy for metal-free HTLs will be inspiring for researchers working on low-cost and shortened processing of *n-i-p* PSCs employing spiro-OMeTAD as HTLs, and should thus be of great interest to the perovskite community. We highlighted the novelty of present work in comparison with other literature, and summarized the unique advantages of the $\bullet O_2^-$ strategy on obtaining metal-free spiro-OMeTAD HTLs with low-cost manufacturing as well as its pronounced capability for boosting stability of PSCs in Discussion section in the revised manuscript, and added details in Supplementary Note 6 in the revised manuscript.

Q2: In the control group, the spiro-OMeTAD solution was not treated by O_2 bubbling. To consolidate the novelty of the proposed strategies, the O_2 bubbling for the control spiro-OMeTAD must be performed and other related instrumental analyses should be made. Ref. 4 has confirmed the O_2 bubbling of traditional spiro-OMeTAD can kinetically promote the oxidation of spiro-OMeTAD and improve the solar cell performance.

Reply： Thank you very much for the comment and suggestion. We would like to stress that we have actually conducted the experiment of bubbling O_2 in the conventional LiTFSI-doped spiro-OMeTAD solution (see Fig. 2b and **Reply Fig. 8b**). The result showed that in the conventional spiro-OMeTAD:LiTFSI solution there is not much change in color when bubbled with O_2 for even 2 minutes, indicating no oxidation of the spiro-OMeTAD solution. We are sorry to create confusion among the reviewers regarding the comparison experiment, owing to the mistakes in caption of Fig. 2b and 2c.

Regarding the Ref 4, it is indeed reported that O_2 bubbling of traditional spiro-OMeTAD:LiTFSI solution can kinetically promote the oxidation of spiro-OMeTAD. However, it should be noted that their recipe necessitates the UV light irradiation. Even under these conditions, they only achieved an efficiency of 17.3%, suggesting a less-than-ideal route. Different from the Ref 4 that involves bubbling a spiro-OMeTAD:LiTFSI solution with CO_2/O_2 under ultraviolet light illumination, we employ in present work a variant-valence $Eu(TFSI)_2$ salt that could generate $\bullet O_2^-$

in air for facile and adequate oxidation of spiro-OMeTAD in solution within 30 s, without necessitating the adding of LiTFSI and UV light irradiation. The $\bullet O_2^-$-derived HTL of Li-free spiro-OMeTAD is then employed for highly efficient and stable perovskite photovoltaics with a new benchmark PCE of 25.45% in regular planar PSCs.

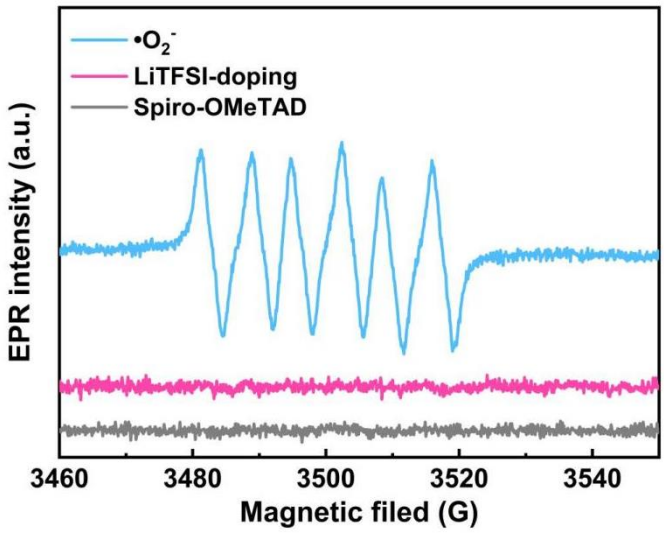


Reply Fig. 8 $\bullet O_2^-$ doping mechanism. The colour evolution of different solutions bubbled with O_2 under different time: **a** spiro-OMeTAD:$Eu(TFSI)_2$, **b** spiro-OMeTAD:LiTFSI, and **c** $EuTFSI_2$:CB. **d** EPR spectra of different solutions (pure, LiTFSI-doping and $\bullet O_2^-$-derived spiro-OMeTAD) bubbled with O_2 for 10 s and tested immediately. **e** FTIR spectra of the raw, LiTFSI-doped and $\bullet O_2^-$-derived spiro-OMeTAD powder. The insets show the optical images of three powers. **f** UV-Vis spectra of the $\bullet O_2^-$-derived spiro-OMeTAD solution under different time. **g** High-resolution XPS spectra of Eu 4d for the $\bullet O_2^-$-derived spiro-OMeTAD film and the residual precipitate. **h** High-resolution XPS spectra of F 1s for the $\bullet O_2^-$-derived spiro-OMeTAD solution and film.

Q3: The author verifies the effectiveness of $Eu(TFSI)_2$ on the generation of O2 radicals by performing electron paramagnetic resonance (line 114-119). It is suggested to proceed with EPR measurement for the control spiro-OMeTAD (with O2 bubbling) as well. Besides, please provide references for the statement in line 117-118, "The EPR recorded at room temperature in dark shows 6 peaks for the O2-bubbled spiro-118 OMeTAD:$Eu(TFSI)_2$ solution, demonstrating the generation of $\bullet O_2^-$"

Reply: Thank you very much for the comments and suggestions. We have added references about the EPR of superoxide radicals in the revised manuscript, which is listed Ref 27 (Dvoranova, D., Barbieriková, Z. & Brezová, V. Radical intermediates in photoinduced reactions on TiO_2 (An EPR spin trapping study). *Molecules*, **19**, 17279-17304 (2014)). This work reported that the photoexcitation of TiO_2 in non-aqueous solvents (dimethylsulfoxide, acetonitrile, methanol and ethanol) in the presence of 5,5-dimethyl-1-pyrroline N-oxide spin trap displayed a stabilization of the superoxide radical anions generated via electron transfer reaction to molecular oxygen, and various oxygen- and carbon-centered radicals from the solvents were generated.

We have also supplemented the EPR measurement for the pure spiro-OMeTAD and LiTFSI-doped spiro-OMeTAD solutions with O_2 bubbling (see Fig. 2d in the revised manuscript and **Reply Fig. 9)**. It is observed that there is no EPR signals in both the pure and LiTFSI-doped spiro-OMeTAD solutions, indicating the absence of $\bullet O_2^-$ generation in these solutions.



Reply Fig. 9 EPR spectra of different solutions (pure, LiTFSI-doping and $\bullet O_2^-$-derived spiro-OMeTAD) bubbled with O_2 for 10 s and tested immediately.

Q4: The author declares doping saturation is reached when the Eu(TFSI)2 concentration increases to 40 mol% (line 182). The statement of doping saturation desires a more detailed interpretation. The NMR (Fig. 3c) only confirms there is a chemical interaction between $Eu(TFSI)_2$ and spiro-OMeTAD. Besides, please specify how the mobility is calculated from SCLC, and the fitting line should be presented over the spectra.

Reply: Thank you very much for the comment and suggestion. Regarding the determination of doping saturation in the 40 mol%, we have actually conducted a series of characterizations in the present work, including UV-Vis spectra, conductivity/mobility tests, and PCE optimization (Fig. 2f, Fig. 3b, Fig. 4 a-c and Supplementary Fig. 3, Fig. 5, Table 3). In brief, both the polaron absorption peak centered at about 521 nm and the conductivity/hole mobility of the $\bullet O_2^-$-derived spiro-OMeTAD with the doping concentration up to 40 mol% reached peak values. Upon further increasing the concentration of $\bullet O_2^-$ (e.g., 50 mol%), all corresponding parameters showed either no change or a decrease (**Reply Fig. 10**). These results demonstrated that the doping of spiro-OMeTAD in solution reached saturation at the concentration up to 40 mol% of $Eu(TFSI)_2$ to spiro-OMeTAD. Moreover, it has been demonstrated that higher concentrations of $Eu(TFSI)_2$ exceeding 40 mol% are not beneficial to the photovoltaic performance of PSCs (Supplementary Table 3).

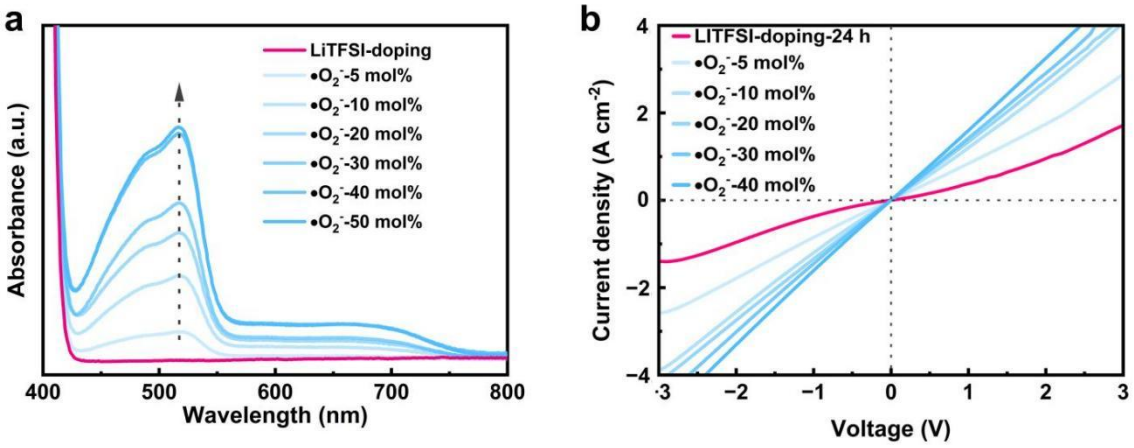
In addition, previous studies (*ACS Energy Lett*. 2019, 4, 2547-2551; *J. Phys. Chem. C* 2012, 116, 26300-26305) have shown that the dopants do not have a doping efficiency of >100%. Instead, the doping efficiency is closer to less than 20%. This highlights that only a fraction of spiro-OMeTAD (~8 mol %) is oxidized by the addition of dopants (e.g., LiTFSI) up to a concentration of 50 mol%. This can be attributed to doping saturation, which is consistent with previous reports in other organic semiconductor systems and arises due to the increase in energetic disorder induced by long-range Coulomb interactions when increasing the number of dopants (*Science* 2022, 377, 495-501; *Adv. Funct. Mater*. 2015, 25, 2701-2707).

Regarding the measurement of the hole mobilities, we estimate the hole mobilities of the spiro-OMeTAD films as reported in the literature (*Angew. Chem. Int. Ed*. 2024, 63, e202316183; *Adv. Mater.* 2016, 6, 1601156) using the hole-only devices with a structure of FTO/PEDOT:PSS/spiro-OMeTAD/Au. The hole mobility (μ) of different HTLs was calculated

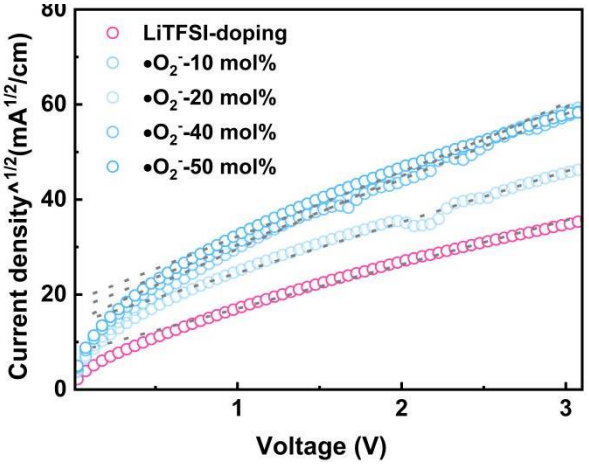
using SCLC model:

$$\mu = \frac{8JL^3}{9\varepsilon\varepsilon_0(V - V_r - V_{bi})^2}$$

where J is the current density; L is the thickness of HTLs; ε_0 and ε are the vacuum permittivity and the dielectric permittivity, respectively. V is the applied voltage, V_r is the voltage loss resulting from radiative recombination, and V_{bi} is the built-in potential. The hole mobilities were accordingly calculated to be 3.63×10^{-4}, 5.69×10^{-4}, 9.79×10^{-4}, 1.01×10^{-3} and 7.43×10^{-4} cm^2 V^{-1} s^{-1} for the LITFSI-doped HTL, 10 mol%, 20 mol%, 40 mol%, and 50 mol% $\bullet O_2^-$-derived HTLs (**Reply Fig. 11**), respectively. We have supplemented this calculation section in Supporting Information of the revised manuscript (see Supplementary Note 3).



Reply Fig. 10 (a) UV-Vis spectra of the $\bullet O_2^-$-derived spiro-OMeTAD solution under different concentrations of $Eu(TFSI)_2$. (b) *I-V* curves for the LiTFSI-doped spiro-OMeTAD (oxidation for 24 h) and the $\bullet O_2^-$-derived spiro-OMeTAD with different concentration of $Eu(TFSI)_2$, respectively.



Reply Fig. 11 Hole mobilities of different HTLs based on LiTFSI-doping and $\bullet O_2^-$-derived spiro-OMeTAD using the SCLC mode.

Q5: The author declares the quenching of PL (Fig. 3d-e) is due to the optimised band structure at the contact. However, the generation of defects at the contact could also quench the PL. Related comments should be given.

Reply: Thank you very much for the comment and concern. We strongly agree that interfacial defects could also lead to the PL quenching. However, the quenching in present work is primarily attributed to the charge extraction at the perovksite/spiro-OMeTAD interface, which has been reported in many previous works and observed in the LiTFSI-doped samples in our present work. It should be noted that depositing the $\bullet O_2^-$-derived spiro-OMeTAD HTLs onto perovskite films did not disturb the underlying surface morphology. Therefore, no new defects were generated at their interface, as confirmed by a series of characterizations in our present work, such as V_{OC} vs light intensity curves, *M-S* curves, dark *J-V* curves, and electrical impedance spectra (Fig. 4g-i and Supplementary Fig. 14). As it is well known, the deviation of the slope in V_{OC} vs light intensity curves suggests a trap-assisted recombination in solar cells, as discussed in a previous study (*Nat. Commun*. 2018, 9, 4609). In the case of the $\bullet O_2^-$-derived devices compared to the LiTFSI-doped devices, several key observations such as lower k_BT/q slope, decreased leakage current, and larger recombination resistance in the $\bullet O_2^-$-derived devices, demonstrate substantially reduced carrier recombination and accumulation at the interface between the perovskite and $\bullet O_2^-$-derived spiro-OMeTAD within the PSCs. These findings collectively indicate improved charge transport

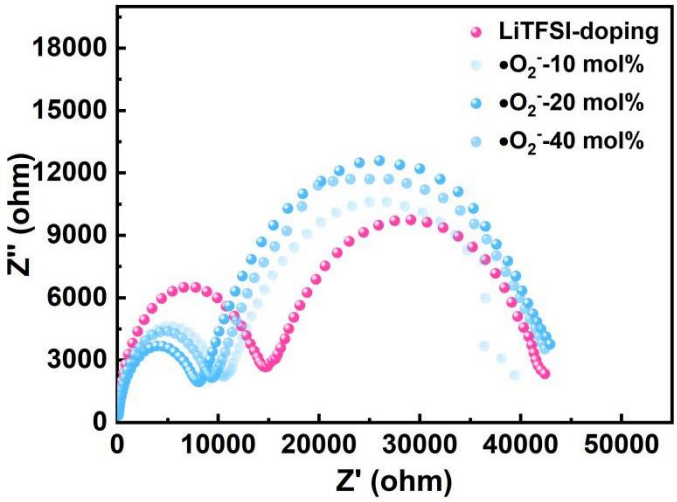
and reduced recombination, resulting in enhanced device performance.

Q6: The charge transfer resistance of the solar cell is more than 5000 ohms for both the control and optimised devices (Fig. 4h). This Rct is huge compared to other reports (Nature Communications volume 10, Article number: 1574 (2019); Nature Communications volume 9, Article number: 3239 (2018)). Please justify these results and specify the active area of the device in the EIS measurement.

Reply: We thank the reviewer for pointing this out. It is indeed that the R_{ct} in impedance spectra in present work is larger than that in some reports. The differences between them could be attributed to the measurement conditions including applied bias, light illumination/dark, frequency, and etc. (*Nat. Commun*. 2019, 10, 1574; *ACS Energy Lett.* 2018, 3, 1044-1048). Generally, under illumination, the impedance spectra show lower equivalent resistance and higher capacitance values. This is due to the increased charge carrier injection and enhanced charge transport rate within the solar cell, resulting in reduced resistance. Additionally, the presence of photogenerated carriers leads to increased capacitance as it requires charge accumulation for storage and movement. In contrast, under dark conditions, the impedance spectra typically exhibit higher equivalent resistance and lower capacitance values. In the absence or limited injection of photogenerated carriers, charge transport within the solar cell is primarily influenced by impurities, interface effects, and charge recombination, resulting in higher resistance. Moreover, the reduced capacitance values in the dark may be attributed to the absence of charge storage and movement associated with photogenerated carriers.

For the present work, on the basis of the measurement condition (applying a bias of 0.8 V in dark in a frequency range from 1 MHz to 0.1 H, and the active area of 0.05 cm^{-2}), the LiTFSI-doped devices show a charge transport resistance (R_{ct}) of 6039 Ω at high-frequency, as well as a charge recombination resistance (R_{rec}) of 1.09 $\times 10^5$ Ω at low-frequency. While the $\bullet O_2^-$-derived devices present lower R_{ct} of 5460 Ω and higher R_{rec} of 1.89 $\times 10^5$ Ω, indicating efficient charge collection and reduced recombination in PSCs. Furthermore, we have carefully checked and re-measured the EIS spectra of PSCs with different spiro-OMeTAD HTLS in dark (see **Reply Fig. 12**), and determined that the R_{ct} is more than 5000 ohms for both the control and optimized devices, which is consistent with many previous reports (*Adv. Mater.* 2023, 36, 2308969; *Angew. Chem. Int. Ed.* 2024, 63,

e202318754; *Adv. Funct. Mater.* 2024, 2308969, https://doi.org/10.1002/adfm.202404671).



Reply Fig. 12 Nyquist plots of PSCs with different HTLs measuring in a bias of 0.8 V in dark in a frequency range from 1 MHz to 0.1 H. The active area of devices is 0.05 cm^{-2}.

Replies to Reviewer 3

Q1: In this work, the authors developed a rapid and Li-free doping strategy for spiro-OMeTAD that avoids post-oxidation by constructing •O2- in the spiro-OMeTAD solution. The •O2- can be facilely formed in the spiro-OMeTAD solution in air with the addition of variant-valence Eu(TFSI)2 salts obtained from the chemical reactions between Eu metal and HTFSI. During this process, O2 obtains an electron from the Eu2+-Eu3+ redox shuttle and rapidly produces the •O2-, resulting in the subsequent oxidation of spiro-OMeTAD and its p-type doping. In stark contrast to conventional LiTFSI doping with air exposure, •O2--derived spiro-OMeTAD HTLs can instantly obtain high conductivity and ideal work function without requiring post-treatments, delivering their PSCs with PCEs over 25%. Furthermore, the long-term stability of the PSCs based on the •O2--derived spiro-OMeTAD HTLs is significantly enhanced due to the increased resistance toward moisture and ion migration, in addition to the lack of Li+ and air exposure.

Reply: Thank you very much for your positive comments to our work, and we much appreciate for the raised comments below, which are all valuable and helpful for improving our manuscript. We have tried our best to revise our manuscript accordingly, and those revisions have been marked in red color in the revised manuscript. Below are the points to point replies.

Q2: Recent work has reported that the pre-synthesized spiro-OMeTAD$^{2\bullet+}$(TFSI^{-})$_2$ radical accompanied by the doping modulation of ionic salts has been found to be directly involved in the spiro-OMeTAD HTL of PSCs without the oxidation process. This has resulted in delivering PCEs of > 25% and much-improved device stability under harsh conditions. Compared with previous work, what's the innovation or technological breakthrough in this work? Please comment on it.

Reply: Thank you very much for the comments and concerns. It is true that many papers concerning doping modulation of spiro-OMeTAD HTLs have been published, which reflects the importance of developing Li-free spiro-OMeTAD for high efficient and stable PSCs. As we have summarized in the introduction of the manuscript, LiTFSI-doped spiro-OMeTAD is widely used as a HTL for high-efficiency *n-i-p* PSCs, but unfortunately facing awkward instability for

commercialization arising from the intrinsic Li^+ migration and hygroscopicity. Meanwhile, the LiTFSI-doped spiro-OMeTAD typically requires a time-consuming air-oxidization process, which is uncontrollabe and not conducive to the scaling-up of PSCs. In this aspect, developing a rapid and Li-free (even metal-free) doping strategy for spiro-OMeTAD that avoids post-oxidation is of particularly significance for pursuing low-cost and high-performance PSCs. This is why we carry out the present work of **Superoxide Radical Derived Metal-Free Spiro-OMeTAD**.

Regarding the advantages of the $\bullet O_2^-$ strategy compared to Ref 4, we believe that our work clearly distinguishes from the reported work on doping process and preparation cost of spiro-OMeTAD HTLs, and shows obvious advantages in the following three aspects: **(1)** Fast synthetic route and low-cost preparation. The Reference (Zhang et al., *Science* 2022, 377, 495-501) developed a doping strategy of spiro-OMeTAD using the spiro-$OMeTAD^{2\bullet+}(TFSI^-)_2$ radical as the dopant and the ionic salt of $TBMP^+TFSI^-$ as the doping modulator. It should be noted that both the organic radical and ionic salt process need be subjected to a complicated and tedious wet-chemical synthetic procedure, including solvent exchange, filtration, drying, recrystallization, purification, working under reduced pressure/low temperature/inert atmosphere, and more. Completing the entire route for doping spiro-OMeTAD HTLs using these methods typically takes several days, thereby significantly increasing the associated costs. In contrast, the $\bullet O_2^-$ in present work can be facilely formed in the spiro-OMeTAD solution in air with the addition of variant-valence Eu $(TFSI)_2$ salts obtained from the chemical reactions between Eu metal and HTFSI, and realizes a rapid and Li-free doping for spiro-OMeTAD within 30 s. In addition, we have actually presented two synthetic routes in our work, including pumping O_2 into the spiro-OMeTAD solution and exposing the spiro-OMeTAD solution to air. (see Supplementary Movie 1, Movie 2, and Movie 3). Given that the amount of oxygen involved and the time spent of less than 30 s in the entire synthesis process, we believe that the corresponding preparation cost is negligible, especially for the second route. **(2)** Different from the approach in Ref 1 that involves additional ionic salts to modulate the work function of spiro-OMeTAD HTLs, we employ in present work only a variant-valence $Eu(TFSI)_2$ salt that could generate $\bullet O_2^-$ in air for facile and adequate oxidation of spiro-OMeTAD in solution within 30 s, obtaining instantly high conductivity and ideal work function as well as high PCEs of >25%, without necessitating the adding of additional additives. It is also noteworthy that the

reported PCE of >25% in Ref 1 is actually based on the co-regulation of the spiro-OMeTAD$^{2\bullet+}$(TFSI$^-$)$_2$ radical and the TBMP$^+$TFSI$^-$ salt. Without the addition of the ioinc salts, they obtained a PCE of only 18.7%. **(3)** New efficiency benchmark for regular planar PSCs employing Li-free spiro-OMeTAD as HTLs. The •O_2^--derived H ng post-oxidation-free and Li-free spiro-OMeTAD HTLs. More importantly, by virtue of the above features of the •O_2^--derived spiro-OMeTAD, the unencapsulated PSCs retain 80% of their initial efficiency after 5,000 hours of air storage at a relative humidity of 70%, and impressively deliver robust environmental stability under various harsh conditions, i.e., maintain over 90% of their initial efficiency after 1000 h of operation at the maximum power point and after 80 light-thermal cycles under simulated low earth orbit conditions, respectively.

Given these striking merits, we believe such •O_2^--deriving strategy for metal-free HTLs will be inspiring for researchers working on low-cost and shortened processing of *n-i-p* PSCs employing spiro-OMeTAD as HTLs, and should thus be of great interest to the perovskite community.

We highlighted the novelty of present work in comparison with other literature, and summarized the unique advantages of the •O_2^- strategy on obtaining metal-free spiro-OMeTAD HTLs with low-cost manufacturing as well as its pronounced capability for boosting stability of PSCs in Discussion section in the revised manuscript, and added details in Supplementary Note 6 in the revised manuscript.

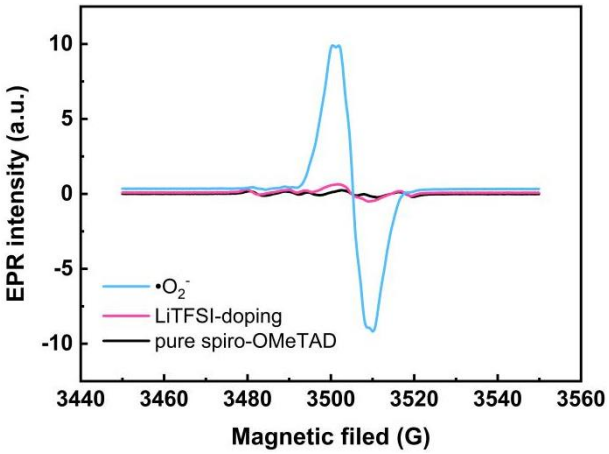
Q3: It is not clear why the •O_2^- show improved reaction rate compared with O_2 when it involved in an in situ oxidation of spiro-MeOTAD in solution.

Reply: Thank you very much for the comment and concern. The superoxide radical (•O_2^-) is more reactive than molecular oxygen (O_2) primarily due to differences in their electronic structures. The •O_2^- is formed when one electron is individually stripped from an oxygen molecule, resulting in an unpaired electron. This unpaired electron gives the superoxide radical higher reactivity as it is more prone to engage in chemical reactions, such as electron transfer or redox reactions, with other substances including the spiro-OMeTAD. In contrast, molecular oxygen consists of two oxygen atoms sharing a pair of electrons, which contributes to its relative stability. To initiate a reaction with molecular oxygen, one must overcome its stability and the sharing of electron pairs, resulting

in slower reaction rates. Therefore, the superoxide radical, with its unpaired electron characteristic, exhibits higher reactivity compared to molecular oxygen, which is consist with previous reports in other fields (*Adv. Mater.* 2022, 34, 2200612; *Chem. Rev.* 2016, 116, 5, 3029-3085).

Experimentally, we have conducted a series of characterizations to confirm the higher reaction rate of the $\bullet O_2^-$. For example, by adding the $Eu(TFSI)_2$ with an concentration of 40 mol% into the as-prepared spiro-OMeTAD solution, it can be seen that the color of the spiro-OMeTAD:$Eu(TFSI)_2$ solution rapidly changes from light yellow to dark red after 30 seconds of bubbling with O_2. However, in the conventional spiro-OMeTAD:LiTFSI solution there is not much change in color when bubbled with O_2 for even 2 minutes (Fig. 2b). The spiro-OMeTAD:$Eu(TFSI)_2$ solution bubbled with O_2 exhibits a gradually increased polaron absorption peak centered at about 521 nm with the increasing bubbling time or concentration of $Eu(TFSI)_2$. In contrast, there are no peaks emerging in the UV-Vis spectra for the conventional spiro-OMeTAD:LiTFSI solution with or without O_2 bubbling (Fig. 2f and Supplementary Fig. 3). In addition, we have supplemented the Electron Paramagnetic Resonance (EPR) spectra to compared the oxidation rate of $\bullet O_2^-$ and molecular oxygen in spiro-OMeTAD solutions (see **Reply Fig. 13**). It is found that the $\bullet O_2^-$ strategy exhibits a higher oxidation peak than that of the conventional LiTFSI-dpoing. These results significantly demonstrate that $\bullet O_2^-$ shows an improved reaction rate compared with O_2 when involved in the *in situ* oxidation of spiro-MeOTAD in solution.

We have also supplemented the details in comparison of oxidation property between $\bullet O_2^-$ and O_2 in Supplementary Note 1 in the revised manuscript.



Reply Fig. 13 EPR spectra of different spiro-OMeTAD solutions bubbled with O_2 for 10 s and tested after 5 min.

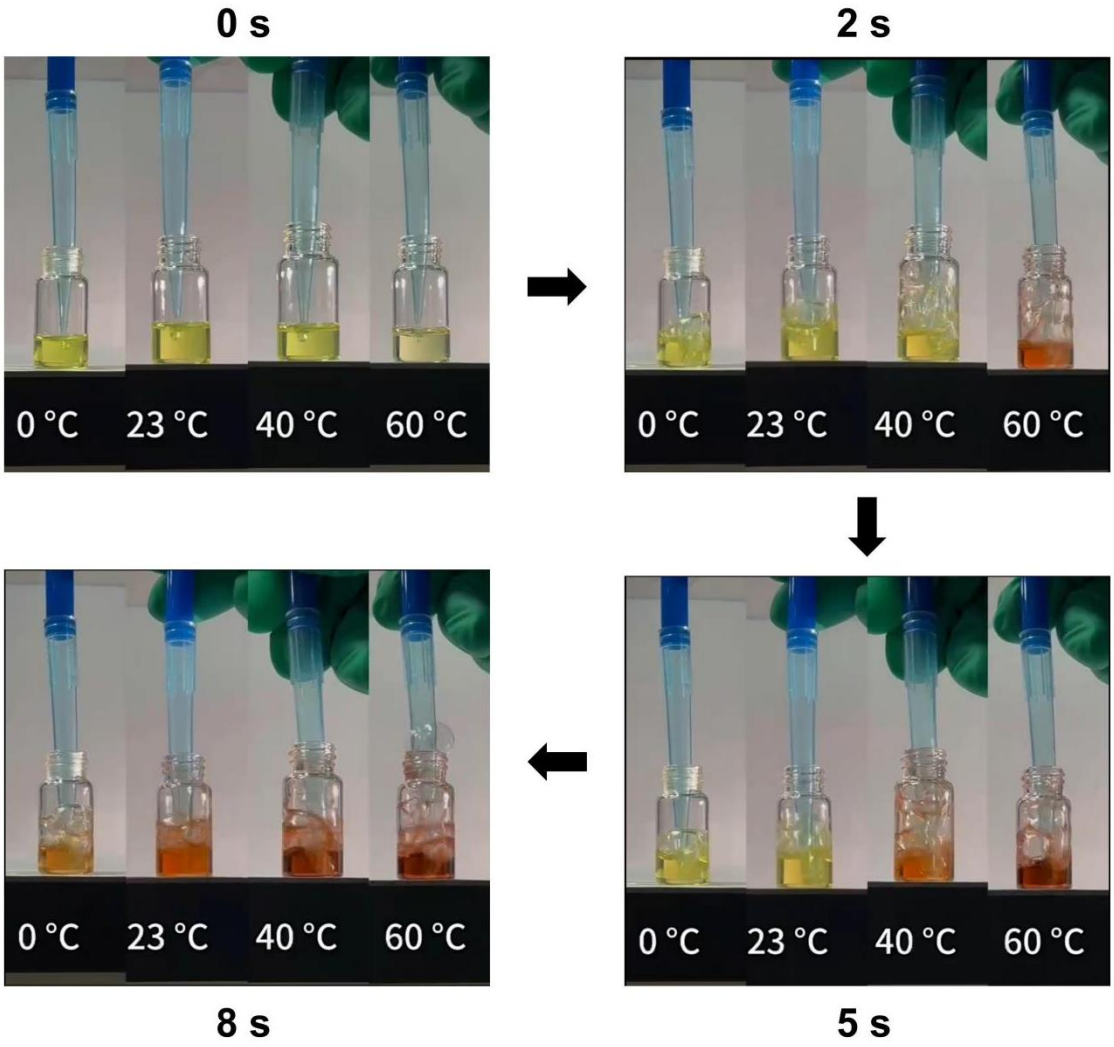
Q4: The HTL solution needs to react with oxygen in the air to oxidize spiro-OMeTAD. During this process, will the environment (such as temperature, humidity, etc.) affect the degree of oxidation of spiro-OMeTAD and thus affect the repeatability of the device?

Reply: Thank you very much for your comments and concerns. For the conventional post-oxidation of LITFSI-doped spiro-OMeTAD HTLs, the environmental factors such as temperature and humidity indeed affect the degree of oxidation of spiro-OMeTAD and the repeatability of devices. However, for the oxidation of spiro-OMeTAD solutions, we would like to stress that we have actually presented two recipes in our work, including pumping O_2 into the spiro-OMeTAD solution in air and exposing the spiro-OMeTAD solution to air (see Supplementary Movie 1, Movie 2, and Movie 3). These routes actually involved the oxidation of spiro-OMeTAD in solution under different humidity conditions. The route I of pumping O_2 was conducted in ambient atmosphere with a relative humidity (RH) of 40-70%, Movie 1). While the route II of exposing the spiro-OMeTAD solution was was carried out either in the ambient atmosphere or in an air glovebox (RH of ~10%, Movie 2 and 3). It appears that the humidity condition did not affect the device performance (see Supplementary Fig. 16, the device was prepared by re-dissolving the spiro-OMeTAD powder from route II) when compared to route I (Fig. 5a-c). We did not highlight the variate in humidity in the present work owing to the remarkable repeatability of the obtained devices regardless of the environmental humidity. More importantly, the absence of hygroscopic LiTFSI in spiro-OMeTAD solution, along with the ultrafast oxidation process in air (30 s), could contribute to minimizing the impact of the external environment.

(1) Regarding the effect of temperature on the degree of oxidation of spiro-OMeTAD in solution, it is well known that properties such as viscosity, O_2 diffusion coefficient, solubility, and individual ion diffusion coefficients can change with different temperatures, and play a primary role in the generation of $\bullet O_2^-$ and its stability (*Chem. Rev.* 2016, 116, 5, 3029-3085). An increase in temperature can also influence the reactivity of $\bullet O_2^-$ and spiro-OMeTAD, thereby affecting the rate of oxidation of spiro-OMeTAD. Experimentally, we further conducted the experiments by pumping O_2 in spiro-OMeTAD:$Eu(TFSI)_2$ solutions at different temperatures (0°C, 23°C, 40°C, and 60°C). It was observed that the oxidation rate of the spiro-OMeTAD solution gradually increased with higher temperatures. However, over a sufficient period of time, the degree of oxidation reached a relatively

consistent level (see the colour evolution in **Reply Fig. 14** and Supplementary Fig. 15 and Movie 4). We have also supplemented these data for investigating the effect of environmental factors on the $\bullet O_2^-$-doping rate in Supplementary Fig. 15 and Note 5 in the revised manuscript;

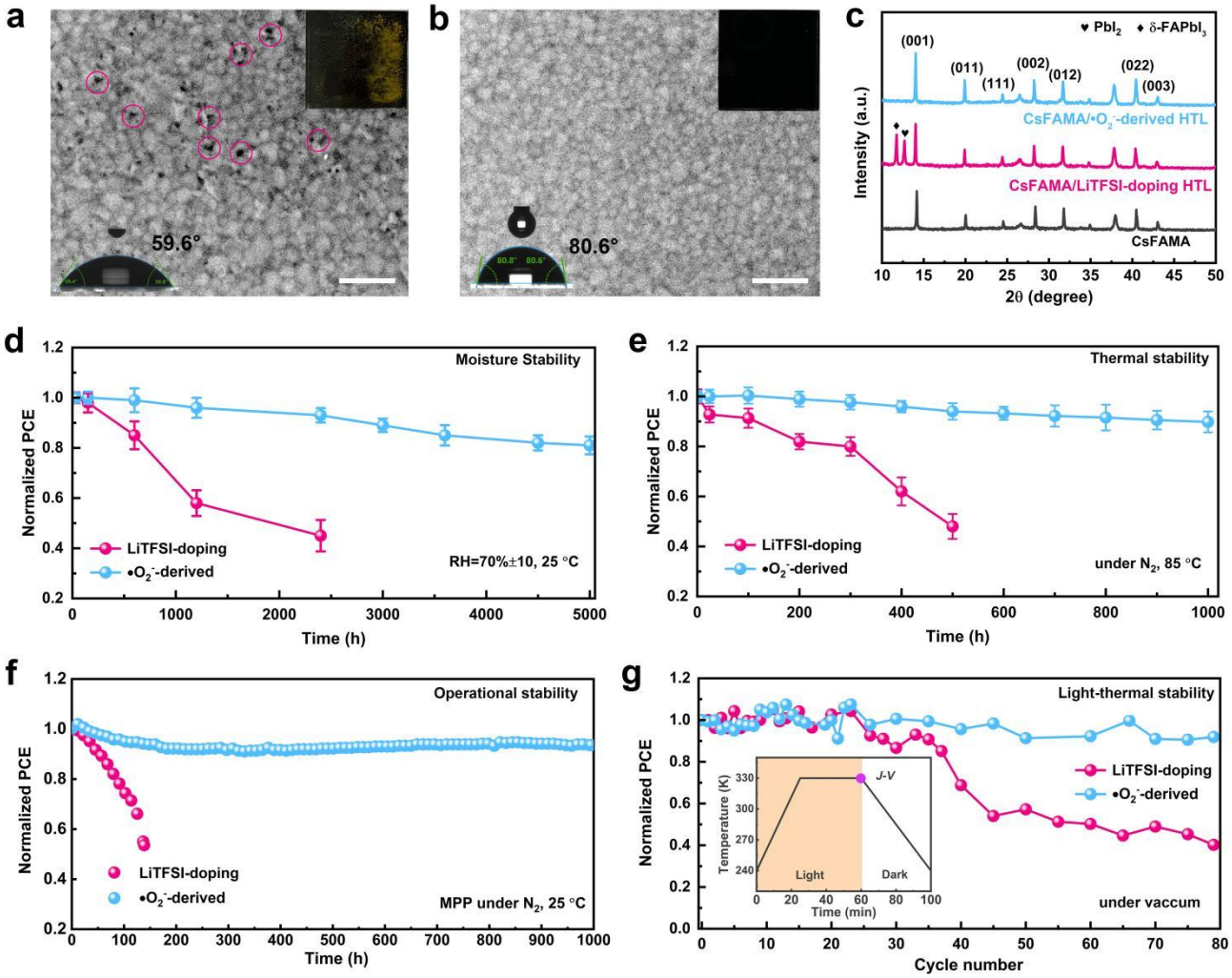
It should also be highlighted that $\bullet O_2^-$ has seldom been studied because of the difficulty of generating and maintaining $\bullet O_2^-$ in a stable state in room temperature. In our present work, we can facilely form $\bullet O_2^-$ in the spiro-OMeTAD solution with the addition of variant-valence Eu $(TFSI)_2$ salts, and can maintain its stability for over 5 min (Supplementary Fig. 2a). This is crucial to the oxidation of spiro-OMeTAD that typically conducted at room temperature, which is also a innovation point in the present work.



Reply Fig. 14 The colour evolution of spiro-OMeTAD:Eu$(TFSI)_2$ solutions bubbled with O_2 at different temperature.

Q5: Figure 5c shows that the perovskite/•O2--derived spiro-OMeTAD sample undergoes severe degradation after humidity aging, while the perovskite/LiTFSI-doping spiro-OMeTAD sample shows good stability. Is this correct?

Reply: We thank the reviewer for pointing this out, and we sincerely apologize for the mistakes made in the labels of Fig. 5c. It is important to clarify that the perovskite/LiTFSI-doping spiro-OMeTAD sample undergoes severe degradation after humidity aging, whiles the perovskite/•O^{2-}-derived spiro-OMeTAD sample shows good stability. We have double-checked and corrected the labels of Fig. 5c in the revised manuscript (see **Reply Fig. 15**) to accurately reflect these findings.



Reply Fig. 15 Stability of PSCs under various conditions. SEM images of different spiro-OMeTAD HTLs deposited on perovskite films after aging in air with 70% RH for 1000 h: **a** LiTFSI-doping, **b** •O_2^--derived. The scale bar is 2 μm and the insets (left) in (**a,b**) are corresponding

contact angle tests, and the insets (right) in (**a,b**) are corresponding optical images. **c** XRD patterns of different HTLs deposited on perovskite films before and after aging in air with 70% RH for 1000 h. CsFAMA pattern is included as reference for comparison. **d** Moisture stability of unencapsulated CsFAMA PSCs with different HTLs aged in air (70% of RH, 25 °C). **e** Thermal stability of CsFAMA PSCs with different HTLs under heating stress (85 °C) in an inert atmosphere. **f** Operational stability of CsFAMA PSCs with different HTLs under continuous illumination (100 mW cm^{-2}) under inert atmosphere. **g** Light-thermal cycling stability of CsFAMA PSCs with different HTLs under simulated LEO condition (see the inset in (**g**)).

Q6: There are some typos in the manuscript, such as, in line 195, is reduced from 67.1 ns to .8 ns for the perovskite/•O2--derived HTLs. I guess the .8 ns shoule be 0.8 ns.

Reply: We thank the reviewer for pointing this out. The correct statement of the ".8 ns" should be 21.8 ns in original manuscript. To further determine its valve, we have re-fitted the TRPL plots following bi-exponential rate law: $f(t) = A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2) + y_0$, and corresponding parameters were summarized in the updated Supplementary Table 2 in the revised manuscript. The τ_{ave} is calculated using $\tau_{ave} = \frac{\sum A_i \tau i^2}{\sum A_i \tau i}$ formula. The results show that The average carrier decay lifetime is reduced from 77.5 ns to 21.9 ns for the perovskite/•O_2^--derived HTLs .

Supplementary Table 2. Summaries of fitting parameters for TRPL spectra with a structure of FTO/CsFAMA/different spiro-OMeTAD.

Samples	A_1	τ_1 (ns)	A_2	τ_2 (ns)	τ_{ave} (ns)
CsFAMA/LiTFSI-doping-HTL	0.25	3.6	0.75	78.6	77.5
CsFAMA/•O_2^--derived -HTL	0.85	2	0.15	29.5	21.9

Q7: The optimized energy level of the HTL enables lower the interfacial charge transfer barrier. The sentence could be further revised, and please further check the entire manuscript.

Reply: We thank the reviewer for pointing this out. We have corrected corresponding description in

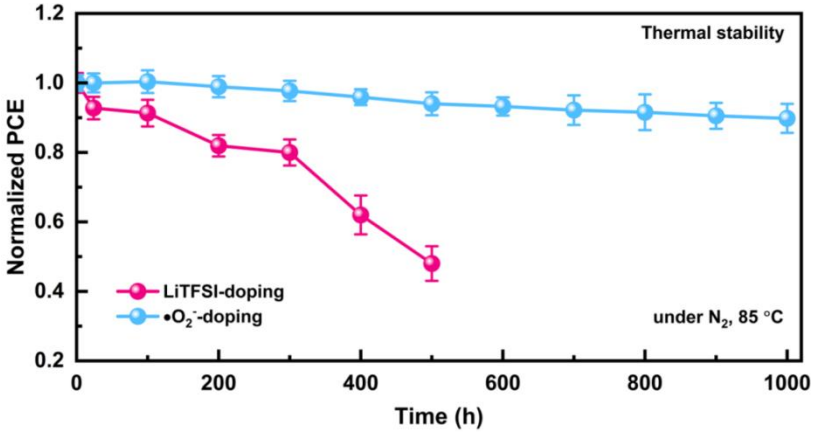
the revised manuscript**,** which reads as: "The interfacial band alignment using different HTLs could be depicted with the corresponding energy-level diagram (Fig. 3f). The optimized energy level of the $\bullet O_2^-$-derived HTLs lowers the interfacial charge transfer barrier, facilitating hole extraction and minimizing nonradiative recombination. This, in return, enhances photovoltaic performance of PSCs, especially with respect to achieving a high high open-circuit voltage (V_{OC}).". In addition, the grammar, spelling mistakes and confused statements have been thoroughly reviewed and corrected throughout the entire manuscript.

Q8: The $\bullet O_2^-$-derived HTLs show much improved glass transition temperature up to 130C, which is a good sign for the perovskite solar cell community. Can the authors further demonstrate the thermal stability of this HTL, to confirm whether this HTL can withstand the stringent conditions in the practical applications.

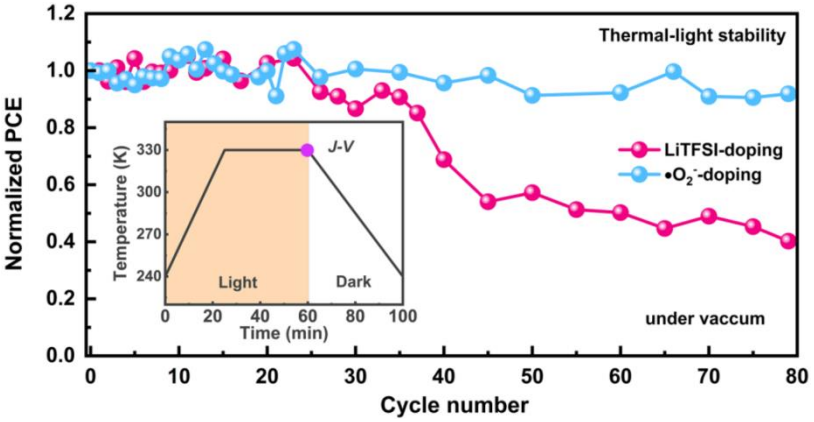
Reply: Thank you very much for the comments and suggestions. Regarding the thermal stability of $\bullet O_2^-$-derived spiro-OMeTAD HTLs, we have actually conducted the thermal stability of PSCs with such HTLs under heating stress of 85°C in an inert atmosphere (see Fig. 5e and **Reply Fig. 16**). It is found that the LiTFSI-doped devices retain only 48% of their initial PCE after 500 hours, while the $\bullet O_2^-$-derived devices retain 90% of their initial PCE for 1,000 hours, demonstrating remarkable thermal stability. As the electron transport layer and perovskite active layer used in the PSCs were the same for both cases, the significant improvement in thermal stability can primarily be attributed to the exceptional thermal stability of the $\bullet O_2^-$-derived spiro-OMeTAD HTL as well as the the avoidance of ionic diffusion-induced decomposition within the devices.

To confirm the pronounced capability of the $\bullet O_2^-$-derived HTLs for withstanding the harsh conditions in the practical applications (e.g., space and near-space), we investigated the effect of light-thermal cycle stability of the $\bullet O_2^-$-derived devices under the simulated low earth orbit (LEO) conditions (see Fig. 5g and **Reply Fig. 17**). It can be observed that the $\bullet O_2^-$-derived devices show higher stability, maintaining 90% of their initial PCE after 80 LEO cycles. On the contrary, the LiTFSI-doped devices retain only 40% of their initial PCE after an equivalent of 80 LEO cycles. This indicates that the $\bullet O_2^-$-derived HTLs endure the erosion caused by light-thermal cycles under LEO conditions, indicating their potential in near-space and polar region applications.

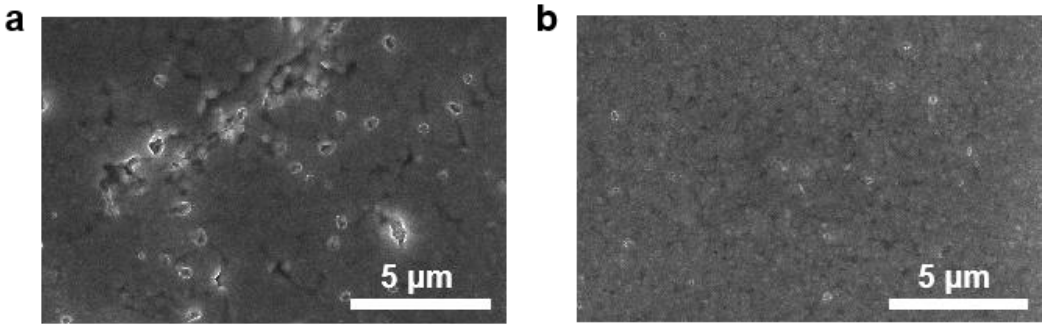
In addition, we have evaluated the damp-heat stability of different spiro-OMeTAD films under a harsh condition (85% RH and 85°C, see Supplementary Fig. 12 and and **Reply Fig. 18**). The conventional LiFTSI-doped samples show numerous large holes. These pinholes create pathways for moisture in the air to diffuse through the spiro-OMeTAD and degrade the perovskite underneath, whereas the $•O_2^-$-derived samples remain unchanged under such harsh conditions. This indicates that the damp-heat stability of the $•O_2^-$-derived samples has been improved, thereby inhibiting the thermal stress erosion and moisture infiltration.



Reply Fig. 16 Thermal stability of PSCs with different HTLs under 85°C in an inert atmosphere.



Reply Fig. 17 Light-thermal cycling stability of PSCs with different HTLs under simulated LEO condition



Reply Fig. 18 SEM images of different spiro-OMeTAD HTLs deposited on perovskite films after aging in double 85 condition (85% RH and 85°C) for 40 min. (a) LiTFSI-doped spiro-OMeTAD. (b) $\bullet O_2^-$-derived spiro-OMeTAD.

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

1) tBP (15 ul) is required for the mentioned strategy. Would tBP affect the thermal stability of the device at 85 oC, which is considered a disadvantage of tBP? If yes, then it is difficult to understand the reply Figures 17 and 18.

2) I still do not understand the authors' explanation about the difficulty of converting O2 ro O2-. Appropriate references are needed. The authors mention that 'When the concentration of Eu2+ is excessively high, the generated •O2 - will react with Eu2+ , resulting in a decrease in the concentration of •O2 - in solution and subsequently reducing the oxidation of spiro-OMeTAD.' What is the threshold for 'excessively high'? The EPR signal in Reply Figure 1 is attributed to •O2-. Why not spiro radicals?

Reviewer #1 (Additional Remarks):

Below are my comments on the authors' response to Reviewer #3.

About Q1: The authors mention the low cost of production as an advantage of their recipe compared to Ref. 4. This needs to be double-checked as the recipe contains Eu (TFSI)2, which should be very expensive. In the meantime, I do not understand why the authors compare the performance of the device with the recipe without the salts in Ref. 4.

About Q4: Besides the images of Reply Fig.14, the number of radicals formed at different temperatures should also be investigated to see if the temperature would affect the doping efficiency and stability.

In addition, the contents of several Figures do not match the corresponding descriptions and conclusions in the manuscript. Some explanations in SI still do not make sense.

1. In the revision, the authors mention that 'The lost electron from the Eu2+-Eu3+ redox shuttle would thus be recovered by O2, contributing rapidly to the generation of the •O2-, which is confirmed by the electron paramagnetic resonance (EPR, Fig. 2d)'. The description and the figure

mentioned do not match. This sentence describes the situation of adding O2 to a Eu(TFSI)2:CB solution, but the mentioned Figure 2d refers to the addition of O2 to a Eu(TFSI)2:CB:Spiro-OMeTAD solution. Further evidence is needed to confirm the formation of •O2-. For example, the authors can check the EPR of the solution of adding O2 in Eu(TFSI)2:CB without spori-OMeTAD to exclude the signal of spiro-OMeTAD radicals.

2. Also, the following description cannot be consistent with the mentioned Figure. 'The EPR recorded at room temperature in dark shows 6 peaks for the O2-bubbled spiro- OMeTAD:Eu(TFSI)2 solution, demonstrating the generation of •O2- in solution. Significantly, such •O2- can persist in solution for 5 minutes even in the presence of light (Supplementary Fig. 2a).' The sentence refers to an O2-bubbled spiro- OMeTAD:Eu(TFSI)2 solution, but Supplementary Fig. 2a refers to a Eu(TFSI)2:CB solution. Also, the author should explain more about how to get the conclusion of 5 minutes. How about after 5 min?

3. In the supplementary information, the authors mention that 'The conversion from O2 molecule to O2- requires four electrons. In other words, for such conversion to occur, one oxygen molecule needs to interact with four Eu2+ ions simultaneously. However, due to the electrostatic repulsion, the distance between Eu2+ ions in solution is relatively large, limiting the interaction of O2 with only one Eu2+ ion, resulting thus in the formation of superoxide radicals. When the concentration of Eu2+ is excessively high, the generated •O2- will react with Eu2+, resulting in a decrease in the concentration of •O2- in solution and subsequently reducing the oxidation of spiro-OMeTAD.' The explanations are difficult to understand. Corresponding evidence is required.

4. In the supplementary information, the equation and the figure (lines 77 and 78) should be on the same line.

5. In the supplementary information, the authors mention that 'higher concentrations of Eu(TFSI)2 exceeding 40 mol% are not beneficial to the photovoltaic performance of PSCs (Supplementary Table 3). This can be attributed that the excessive concentration of Eu(TFSI)2 causing the generated •O2- to react with Eu2+, resulting in a decrease in the concentration of •O2- in solution and subsequently reducing the oxidation of spiro-OMeTAD.' Related evidences are needed for the explanation.

6. The subtitle of Supplementary Fig 2 should be revised. I can't understand the meaning of '5min' in the sentence.

I would strongly suggest the authors carefully check the description and grammar of the entire manuscript again.

Reviewer #2 (Remarks to the Author):

The author has addressed most of my concerns raised previously and the manuscript has improved its quality. I suggest accepting this paper after minor revision.

1. It is true that due to the difference in experimental setup, the detected Rct would be different in solar cells. The author highlighted that some papers showed a similar Rct as obtained in this work. However, none of the references the author provided in the response letter detailed if their solar cells were biased during the EIS measurement. ((Adv. Mater. 2023, 36, 2308969; Angew. Chem. Int. Ed. 2024, 63,e202318754; Adv. Funct. Mater. 2024, 2308969, https://doi.org/10.1002/adfm.202404671).). The citation information is incorrect for “Adv. Funct. Mater. 2024, 2308969”.

2. Please specify the thickness of the thin film perovskite used in the PL/TRPL measurement and the excitation direction for perovskite.

3. A minor correction in line 709, where “dpoing” should be “doping”.

Reviewer #2 (Additional Remarks):

I have looked at the response letter to the reviewer 3, and believe that most of questions have been addressed appropriately. However, before the final decision is made, the new EPR data being presented necessitates clearer interpretation.

The author specified that Fig. S2b is used to “compare the oxidation rate of •O2- and molecular oxygen in spiro-OMeTAD solutions”. However, I noticed that 6 peaks in Fig. 2d were detected for spiro-OMeTAD:Eu(TFSI)2 while only 1 peak was detected in Fig. S2b. What is the mechanism behind such variation? Which radicals authors focus on in the respective measurement? As these are crucial for understanding the role of additives, careful analysis and scrutiny should be made.

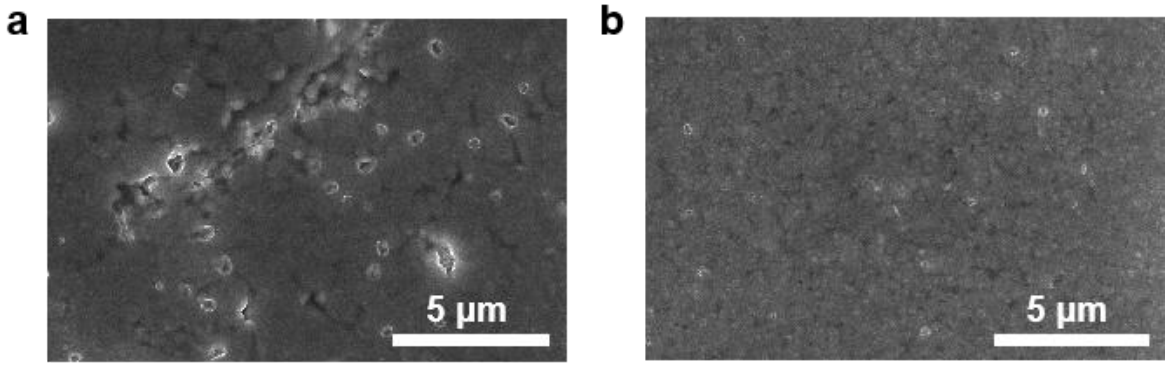
Replies to Reviewer 1

Q1: tBP (15 ul) is required for the mentioned strategy. Would tBP affect the thermal stability of the device at 85 °C, which is considered a disadvantage of tBP? If yes, then it is difficult to understand the reply Figures 17 and 18.

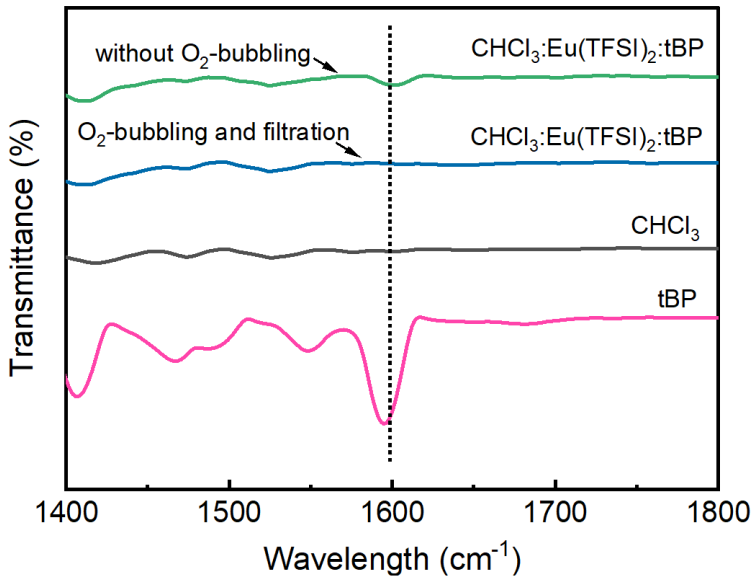
Reply: Thank you very much for the comments and concerns on using of tBP.

Regarding the effect of tBP on stability of PSCs, it has been reported that the volatile tBP has detrimental impact on thermal stability of PSCs (*ACS Energy Lett.* 2018, 3, 7, 1677-1682; *Chem* 2019, 5, 1806-1817; *J. Am. Chem. Soc.* 2018, 140, 48, 16720-16730; *ACS Appl. Mater. Interfaces* 2024, 16, 25, 32147-32159). The main reason was due to the voids formation in spiro-OMeTAD containing tBP upon the heat treatment, leading to the degradation of film quality. However, we would like to stress that in present work, even under double 85 condition (85% RH and 85°C), the $\bullet O_2^-$-derived spiro-OMeTAD HTLs still maintain a dense morphology (without formation of voids, **Reply Fig. 1**), thereby exhibiting long-term thermal and light-thermal stability of PSCs. This is mainly attributed to small amount of tBP adopted in this work (15 μL), which is half of the typical amount (~30 μL) required in the conventional LiTFSI-doped recipe. More importantly, as evidenced in FTIR analyses in **Reply Fig. 2**, the used tBP could be partially removed from the oxidized spiro-OMeTAD solution along with the Eu^{3+} precipitation during the filtration process, due to that tBP could coordinate with TFSI and Eu^{3+} as a precipitation, which was then removed from solution by filtration *(J. Am. Chem. Soc*. 2018, 140, 16720-16730). The reason why we use such small amount of tBP was just to effectively dissolve the $Eu(TFSI)_2$ salt for better dispersion of $Eu(TFSI)_2$ in spiro-OMeTAD solution.

Therefore, the preliminary conclusion can be drawn that the involved small amount of tBP, along with Li-free in the present $\bullet O_2^-$-doped work has little influence on the thermal stability of PSCs devices. However, it is still worth to investigate the role of tBP and explore potential solvent to replace tBP in the $\bullet O_2^-$-doping process, which we will carry out in our future work.



Reply Fig. 1. SEM images of different spiro-OMeTAD HTLs deposited on perovskite films after aging in double 85 condition (85% RH and 85°C) for 40 min. (a) LiTFSI-doped spiro-OMeTAD. (b) $\bullet O_2^-$-derived spiro-OMeTAD.



Reply Fig. 2. FTIR spectra of the tBP, $CHCl_3$, and $CHCl_3$:$Eu(TFSI)_2$:tBP solutions before and after bubbling with O_2. It is clearly seen that the involved tBP is removed from the oxidized spiro-OMeTAD solution by filtration, as evidenced by the diminished deformation vibration absorption peak of in-plane ring of the tBP at ~1600 cm^{-1}.

Q2: I still do not understand the authors' explanation about the difficulty of converting O_2 to O^{2-}. Appropriate references are needed. The authors mention that 'When the concentration of Eu^{2+} is excessively high, the generated $\bullet O_2^-$ will react with Eu^{2+}, resulting in a decrease in the concentration of $\bullet O_2^-$ in solution and subsequently reducing the oxidation of spiro-OMeTAD.' What is the threshold for 'excessively high'? The EPR signal in Reply Figure 1 is attributed to $\bullet O_2^-$. Why not spiro radicals?

Reply: Thank you very much for the comments and concerns. It has been reported that in previous literature (*Chem. Rev.* 2016, 116, 5, 3029-3085), the reduction of O_2 in various aqueous and nonaqueous solvents is extremely complicated. Therefore, disproportionation and protonation of intermediate species are unavoidable. Ordinary O_2 reacts poorly with most other molecules. However, it can be activated by adding naturally or artificially derived energy that converts an O_2 molecule into reactive O_2 species (i.e., $\bullet O_2^-$). Therefore, O_2 can form $\bullet O_2^-$ under specific conditions instead of directly forming oxides (O^{2-}). This is because in certain chemical reactions, oxygen can accept an electron, resulting in the formation of superoxide radicals with a single unpaired electron.

Regarding the conversion from O_2 to $\bullet O_2^-$ not O^{2-} in our present work, it has been experimentally demonstrated such conversion is difficult due to the poor reaction between O_2 and spiro-OMeTAD molecule in solution. This can be indirectly proved by the experiment involving bubbling O_2 into LiTFSI-doped spiro-OMeTAD solutions, where there is no change in color observed (**Fig. 2b**), indicating a lack of direct interaction between O_2 and spiro-OMeTAD. In contrast, by adding $Eu(TFSI)_2$ into the spiro-OMeTAD solution instead of LiTFSI, it can be seen that the color of the solution rapidly changes from light yellow to dark red after 30 seconds of bubbling with O_2 (**Fig. 2a**), indicating the formation of more reactive O_2 species that can oxidize spiro-OMeTAD, which we have determined to be $\bullet O_2^-$ (**Fig. 2d**). This result also suggests that the direct conversion of O_2 to oxides (O^{2-}) by the Eu^{2+}-Eu^{3+} redox shuttle is unlikely to occur. Otherwise, the spiro-OMeTAD solution would not have shown a change in color.

Regarding the conversion mechanism of 'why O_2 just accepts one electron to form $\bullet O_2^-$', it is indeed difficult to obtain direct evidence for reaction kinetics, it may require *in-situ* characterization techniques, which we can not carry out in current stage. However, on the basis of above observations and analyses, we proposed that the conversion from O_2 to $\bullet O_2^-$ not O^{2-} in our present

work is attributed to the imbalance in the involved amount between O_2 and Eu^{2+} (O_2 is excessive compared to Eu^{2+} when the concentration of $Eu(TFSI)_2$ is below 40 mol%), which could serve as a specific chemical condition. Such chemical condition can limit interaction of O_2 with only one Eu^{2+} ion, resulting thus in the formation of $\bullet O_2^-$. However, the conversion from O_2 molecule to O^{2-} requires four electrons. In other words, for such conversion to occur, one oxygen molecule needs to interact with four Eu^{2+} ions simultaneously, leading to the difficulty of converting O_2 to O^{2-}.

Regarding the threshold for 'excessively high', we have actually conducted a series of characterizations to determine the inflection point of the concentration of $\bullet O_2^-$ in the present work, including UV-Vis spectra, conductivity/mobility tests, and PCE optimization (**Fig. 2f, Fig. 3b, Fig. 4 a-c and Supplementary Fig. 3, Fig. 5, Table 3**). These results demonstrated that the doping of spiro-OMeTAD in solution reached saturation at the concentration up to 40 mol% of $Eu(TFSI)_2$ to spiro-OMeTAD. When the concentration of Eu^{2+} exceeds 40 mol% (e.g., >50 mol%), the absorption peak, conductivity, and device performance of the oxidized spiro-OMeTAD remained unchanged or decrease. This can be due to the decreased amount of $\bullet O_2^-$ in solution and subsequently reduced oxidation of spiro-OMeTAD, which can be evidenced by the color change of the spiro-OMeTAD solution in **Reply Fig. 3**. **Reply Fig. 3** shows the color evolution of spiro-OMeTAD solutions with different concentrations of Eu^{2+} bubbled with O_2 over different time. It is clearly seen that the spiro-OMeTAD solution with a concentration of 55 mol% of $Eu(TFSI)_2$ exhibits a slower color change and a lighter final color compared to the solution with a concentration of 40 mol%, indicating the decrease in the concentration of $\bullet O_2^-$ in solution. These results suggest that the threshold for 'excessively high' is the concentration of >40 mol%.

Regarding the EPR signal in 'Reply Figure 1' that is attributed to $\bullet O_2^-$ not spiro-OMeTAD radical, it is important to emphasize that the EPR signal with six specific peaks corresponds to the $\bullet O^{2-}$ while the EPR signal with one peak is attributed to the spiro-$OMeTAD^+$. The EPR signal in 'Reply Figure 1' exhibits clearly six peaks (see **Reply Fig. 5** in this version), which leads us to primarily attribute the radical mainly to $\bullet O^{2-}$ rather than spiro-$OMeTAD^+$.

We are sorry to create confusion among the reviewers regarding the EPR data and analyses, owing to the mistakes in corresponding descriptions in figure captions and main text. We have carefully checked all EPR data we provided in this manuscript, and determined that the EPR signal with six specific peaks corresponds to the $\bullet O^{2-}$ while the EPR signal with one peak is attributed to

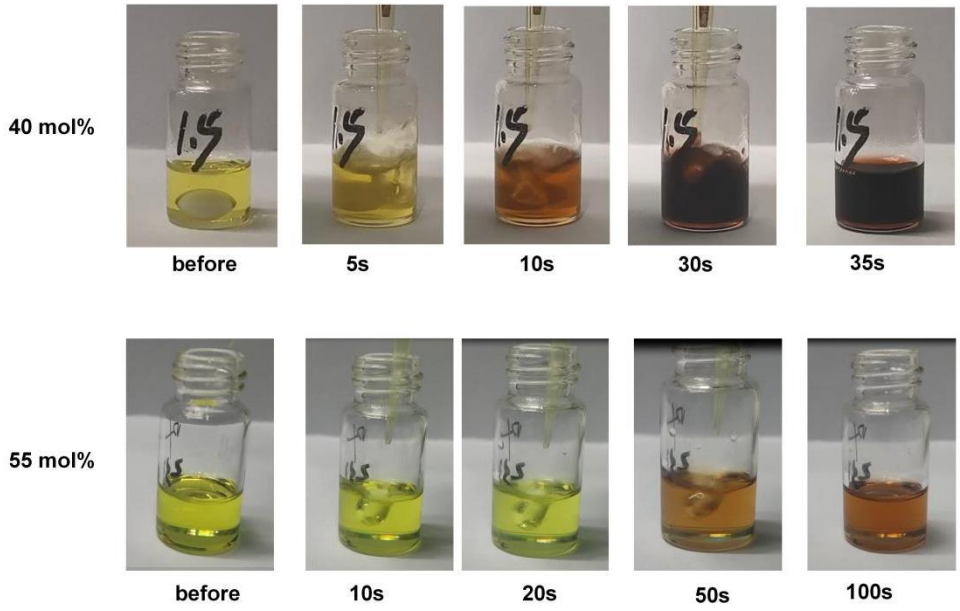
the spiro-OMeTAD^{+}. The signal difference between them is mainly attributed to the test conditions including solution type and test time. We would like to stress that we have actually conducted three EPR experiments for characterizing the $\bullet O^{2-}$ and spiro-OMeTAD^{+} signals in different solutions under different time: (1) EPR spectra of $Eu(TFSI)_2$:CB solution without spiro-OMeTAD bubbled with O_2 for 10 s and tested after 5min (**Reply Fig. 4**); (2) EPR spectra of spiro-OMeTAD:CB, spiro-OMeTAD:LiTFSI:CB, and spiro-OMeTAD:$Eu(TFSI)_2$:CB solutions bubbled with O_2 for 10 s and tested immediately (**Reply Fig. 5**); (3) EPR spectra of spiro-OMeTAD:CB, spiro-OMeTAD:LiTFSI:CB, and spiro-OMeTAD:$Eu(TFSI)_2$:CB bubbled with O_2 for 10 s and tested after 5 min (**Reply Fig. 6**).

Regarding the test (1), we performed the EPR spectra on the $Eu(TFSI)_2$:CB solution without spiro-OMeTAD to detect the signal of $\bullet O_2^-$. After bubbling with O_2 for 10 s, we confirmed the presence of $\bullet O_2^-$ in this solution based on the observation of its six peaks (**Reply Fig. 4**). It is important to note that we conducted the EPR spectra of this solution after 5 min to demonstrate that the formed $\bullet O_2^-$ can remain stable for an extended period of time (> 30 s), regardless of the conditions of darkness and light, indicating its capability to sufficiently oxidize spiro-OMeTAD in the solution.

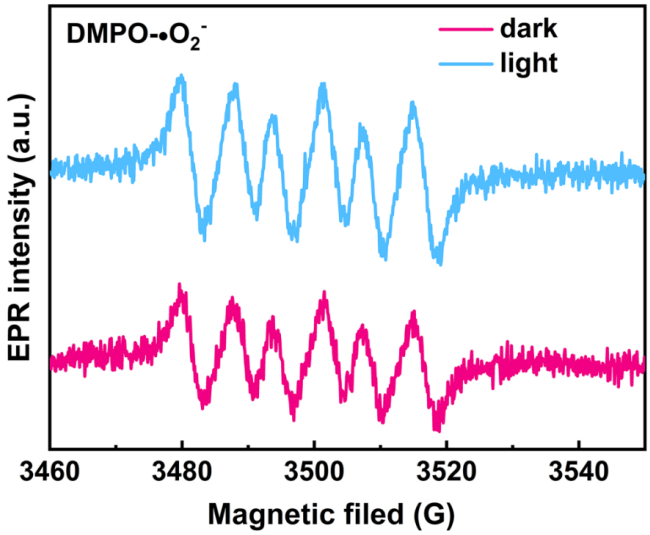
Regarding the test (2), we performed the EPR spectra on spiro-OMeTAD:CB, spiro-OMeTAD:LiTFSI:CB, and spiro-OMeTAD:$Eu(TFSI)_2$:CB solutions to specifically detect the signal of $\bullet O_2^-$ in solutions with spiro-OMeTAD. After bubbling with O_2 for 10 s, we immediately detected the signal of $\bullet O_2^-$ and found the presence of $\bullet O_2^-$ in the spiro-OMeTAD:$Eu(TFSI)_2$:CB solution based on the observation of its six peaks (**Reply Fig. 5**). We would like to stress that, although spiro-OMeTAD^{+} radicals are present at this stage, their amount is still relatively low compared to the $\bullet O_2^-$ (see the solution color in 10 s in Fig. 2a). Therefore, the EPR signals observed in this solution predominantly originate from the $\bullet O_2^-$.

Regarding the test (3), we performed the EPR spectra on spiro-OMeTAD:CB, spiro-OMeTAD:LiTFSI:CB, and spiro-OMeTAD:$Eu(TFSI)_2$:CB solutions to specifically detect the signal of spiro-OMeTAD^{+} radicals in solutions. After bubbling with O_2 for 10 s, we did not immediately conduct the EPR test as in test (2), but rather waited for 5 min before starting the test. The purpose of this delay was to allow sufficient oxidation of spiro-OMeTAD to generate

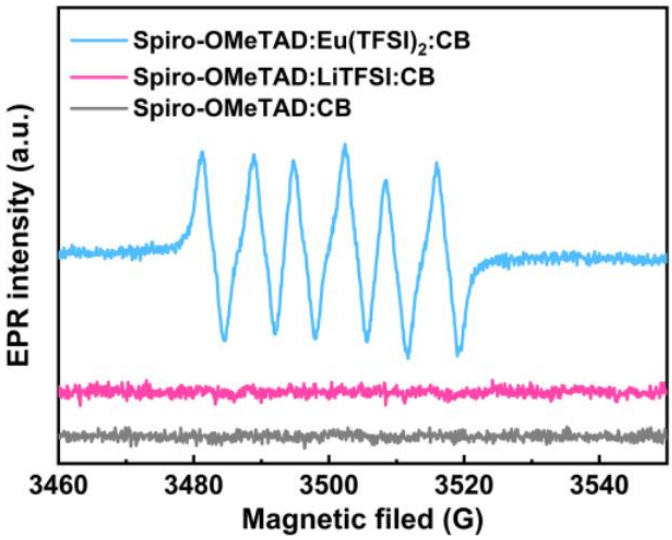
spiro-OMeTAD^{+} in solution. Therefore, the results in **Reply Fig. 6** clearly demonstrate the EPR signal of spiro-OMeTAD^{+} while no $\bullet O_2^-$ signal is observed. This indicates that, at this stage, the concentration of $\bullet O_2^-$ is significantly lower compared to spiro-OMeTAD^{+} in the solutions.



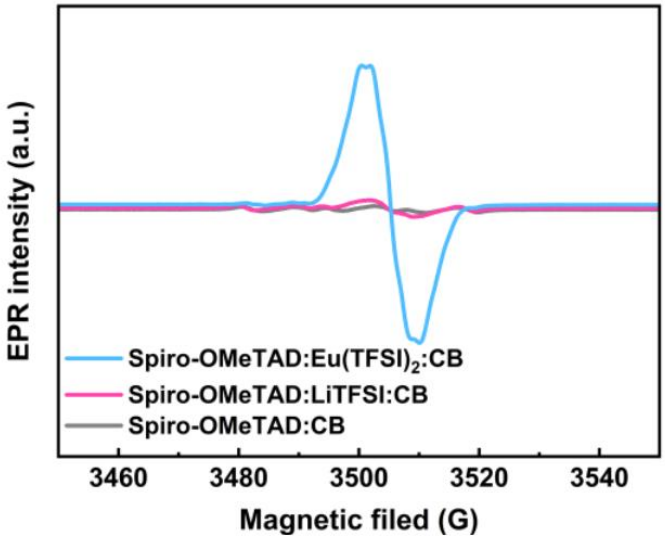
Reply Fig. 3. The color evolution of spiro-OMeTAD solutions with different concentrations of $Eu(TFSI)_2$ bubbled with O_2 over different time: 40 mol% (top) and 55 mol% (bottom).



Reply Fig. 4. EPR spectra of $Eu(TFSI)_2$:CB solution without spiro-OMeTAD bubbled with O_2 for 10 s and tested after 5min.



Reply Fig. 5. EPR spectra of different solutions (spiro-OMeTAD:CB, spiro-OMeTAD:LiTFSI:CB, and spiro-OMeTAD:Eu(TFSI)$_2$:CB) bubbled with O_2 for 10 s and tested immediately.



Reply Fig. 6. EPR spectra of different solutions (spiro-OMeTAD:CB, spiro-OMeTAD:LiTFSI:CB, and spiro-OMeTAD:Eu(TFSI)$_2$:CB) bubbled with O_2 for 10 s and tested after 5 min.

Additional comments on the authors' response to Reviewer #3

Q3: The authors mention the low cost of production as an advantage of their recipe compared to Ref. 4. This needs to be double-checked as the recipe contains Eu $(TFSI)_2$, which should be very expensive. In the meantime, I do not understand why the authors compare the performance of the device with the recipe without the salts in Ref. 4.

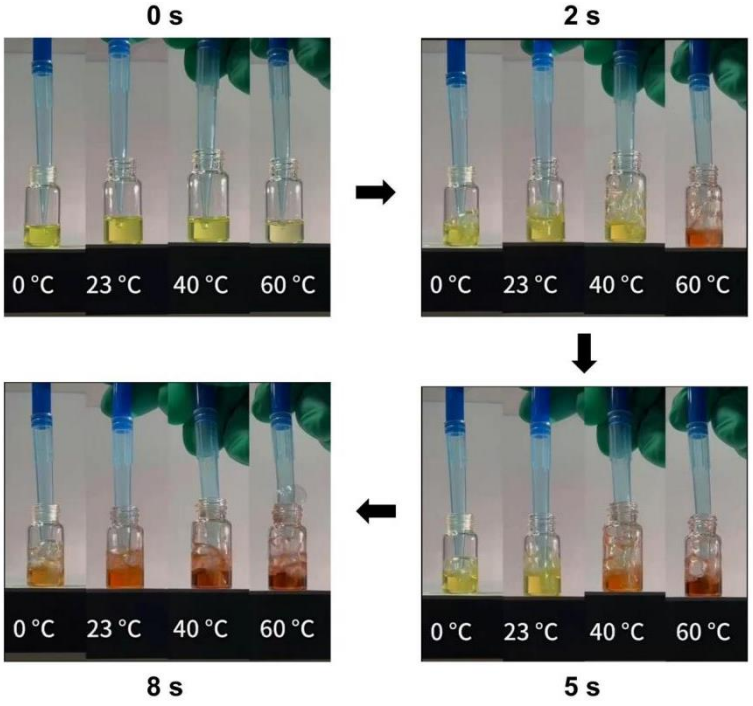
Reply: We thank the reviewer for pointing this out. As the Eu $(TFSI)_2$ salts is obtained from the chemical reactions between Eu metal and HTFSI, we checked the price of Eu metal, and found to be ~0.24 $/g (data from scrapmonster.com). Indeed, this price is higher than the commonly used Li metal (0.03 $/g, dailymetalprice.com). In addition, we made an inappropriate comparison of the PCE between our strategy and Ref.4. We acknowledge the lack of objectivity in making such a comparison and have therefore omitted the inappropriate descriptions concerning PCE.

Therefore, we have tuned down our statements regarding the advantages of our $\bullet O^{2-}$ strategy over previous reports (especially Ref.4), which is summarized below:

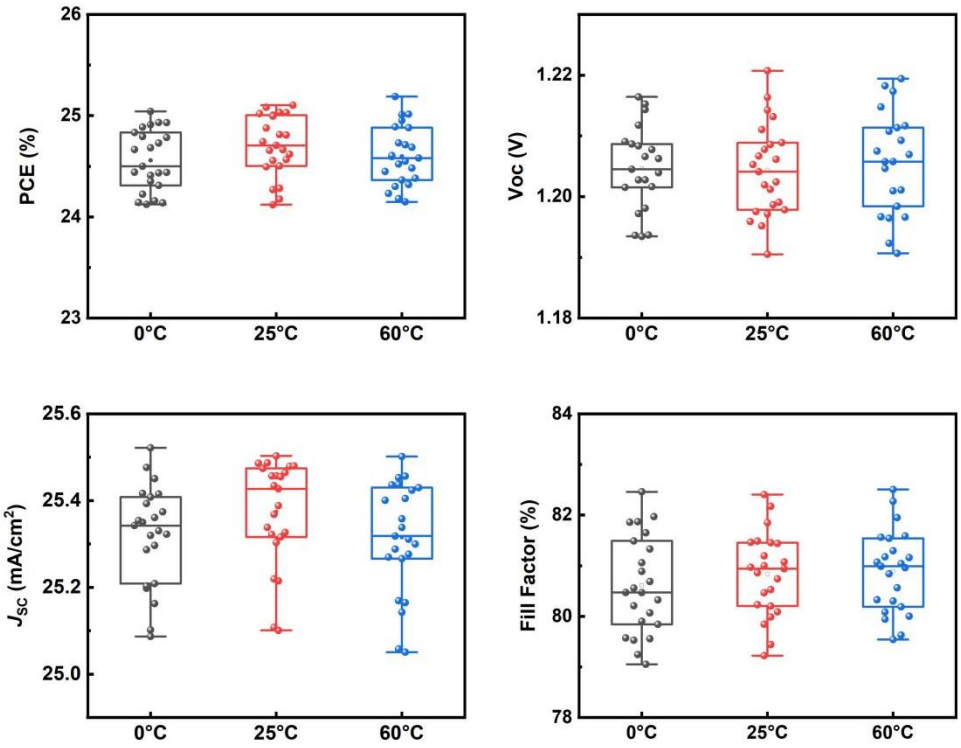
(1) Fast synthetic route. The Reference (Zhang et al., *Science* 2022, 377, 495-501) developed a doping strategy of spiro-OMeTAD using the spiro-$OMeTAD^{2\bullet+}(TFSI^-)_2$ radical as the dopant and the ionic salt of $TBMP^+TFSI^-$ as the doping modulator. It should be noted that both the organic radical and ionic salt process need be subjected to a complicated and tedious wet-chemical synthetic procedure, including solvent exchange, filtration, drying, recrystallization, purification, working under reduced pressure/low temperature/inert atmosphere, and more. Completing the entire route for doping spiro-OMeTAD HTLs using these methods typically takes several days. In contrast, the $\bullet O_2^-$ in present work can be facilely formed in the spiro-OMeTAD solution in air with the addition of variant-valence Eu $(TFSI)_2$ salts obtained from the chemical reactions between Eu metal and HTFSI, and realizes a rapid and Li-free doping for spiro-OMeTAD within 30 s. **(2)** Different from the approach in Ref 4 that involves additional ionic salts to modulate the work function of spiro-OMeTAD HTLs, we employed in present work only a variant-valence $Eu(TFSI)_2$ salt that could generate $\bullet O_2^-$ in air for facile and adequate oxidation of spiro-OMeTAD in solution within 30 s, obtaining instantly high conductivity and ideal work function without necessitating the adding of additional additives. Moreover, our approach yielded a high PCE of 25.45%, which rivals the efficiency of devices based on the co-regulated spiro-OMeTAD HTLs as reported in Ref.4.

Q4: Besides the images of Reply Fig.14, the number of radicals formed at different temperatures should also be investigated to see if the temperature would affect the doping efficiency and stability.

Reply: Thank you very much for the comment and suggestion. As discussed and analyzed in our previous version, we can determine that the oxidation rate of the spiro-OMeTAD solution through $\bullet O_2^-$ gradually increased with higher temperatures. However, over a sufficient period of time, the degree of oxidation reached consistent levels (see the final colour at 40°C and 60°C in Movie 4 and **Reply Fig. 7**, respectively), indicating the amount of formed $\bullet O_2^-$ at different temperatures is identical. These results suggest that the final amount of formed $\bullet O_2^-$ is predominantly influenced by the concentration of $Eu(TFSI)_2$ introduced and the duration of oxygen exposure. Therefore, it is expected that the doping of spiro-OMeTAD HTLs and the performance of their devices would not be affected by the applied temperatures. For confirming this point, we have also supplemented photovoltaic performance of PSCs based on the $\bullet O_2^-$-derived spiro-OMeTAD HTLs under different temperatures (see **Reply Fig. 8**). These results show that devices based on $\bullet O_2^-$-derived spiro-OMeTAD HTLs prepared at 0 °C, 25°C and 60°C deliver average PCEs of 24.56%, 24.70% and 24.60%, respectively, demonstrating almost consistent photovoltaic performance.



Reply Fig. 7. The colour evolution of spiro-OMeTAD:$Eu(TFSI)_2$ solutions bubbled with O_2 at different temperatures.



Reply Fig. 8. Statistical distribution of 25 individual PSC devices based on $\bullet O_2^-$-derived spiro-OMeTAD HTLs prepared at different temperatures. The employed concentration of $Eu(TFSI)_2$ for all devices is 40 mol%.

Q5: In the revision, the authors mention that 'The lost electron from the Eu^{2+}-Eu^{3+} redox shuttle would thus be recovered by O_2, contributing rapidly to the generation of the $\bullet O_2^-$, which is confirmed by the electron paramagnetic resonance (EPR, Fig. 2d)'. The description and the figure mentioned do not match. This sentence describes the situation of adding O_2 to a $Eu(TFSI)_2$:CB solution, but the mentioned Figure 2d refers to the addition of O_2 to a $Eu(TFSI)_2$:CB:Spiro-OMeTAD solution. Further evidence is needed to confirm the formation of $\bullet O_2^-$. For example, the authors can check the EPR of the solution of adding O_2 in $Eu(TFSI)_2$:CB without spiro-OMeTAD to exclude the signal of spiro-OMeTAD radicals.

Reply: We thank the reviewer for pointing this out. We are sorry to create confusion among the reviewers regarding the EPR data and analyses, owing to the mistakes in corresponding descriptions in figure captions and main text. As we replied in **Q2,** we have actually conducted three EPR experiments for characterizing the $\bullet O_2^-$ and spiro-OMeTAD$^+$ signals in different solutions under

different time: (1) EPR spectra of $Eu(TFSI)_2$:CB solution without spiro-OMeTAD bubbled with O_2 for 10 s and tested after 5min (**Reply Fig. 4**); (2) EPR spectra of spiro-OMeTAD:CB, spiro-OMeTAD:LiTFSI:CB, and spiro-OMeTAD:$Eu(TFSI)_2$:CB solutions bubbled with O_2 for 10 s and tested immediately (**Reply Fig. 5**); (3) EPR spectra of spiro-OMeTAD:CB, spiro-OMeTAD:LiTFSI:CB, and spiro-OMeTAD:$Eu(TFSI)_2$:CB bubbled with O_2 for 10 s and tested after 5 min (**Reply Fig. 6**). These results confirm the formation of $\bullet O^{2-}$ in the $Eu(TFSI)_2$:CB solution without spiro-OMeTAD.

We thus updated corresponding figures and their descriptions in the revised manuscript, and read as: "The lost electron from the Eu^{2+}-Eu^{3+} redox shuttle would thus be recovered by O_2, contributing rapidly to the generation of the $\bullet O_2^-$, which is confirmed by the electron paramagnetic resonance (EPR, Fig. 2d). The EPR recorded at room temperature in both dark and light conditions shows 6 peaks for the O_2-bubbled $Eu(TFSI)_2$:CB solution, demonstrating the generation of $\bullet O_2^-$ in solution.[27] Furthermore, we conducted the EPR spectra on the O_2-bubbled spiro-OMeTAD:$Eu(TFSI)_2$:CB solution to specifically detect the signal of $\bullet O_2^-$ in solutions with spiro-OMeTAD. After bubbling with O_2 for 10 s, we immediately detected the signal of $\bullet O_2^-$ and found the presence of $\bullet O_2^-$ in this solution based on the observation of its six peaks (Supplementary Fig. 2a). The resultant $\bullet O_2^-$ will instantly oxidize the spiro-OMeTAD to a TFSI-stabilized spiro-$OMeTAD^+$ radical cation along with the Eu^{3+} reaction products, as evidenced by the color evolution of their solutions (Fig. 2a) and EPR spectra after sufficient oxidation (Supplementary Fig. 2b). These results significantly demonstrate that $\bullet O_2^-$ shows an improved reaction rate compared with O_2 when involved in the *in situ* oxidation of spiro-OMeTAD in solution (Supplementary Note1).".

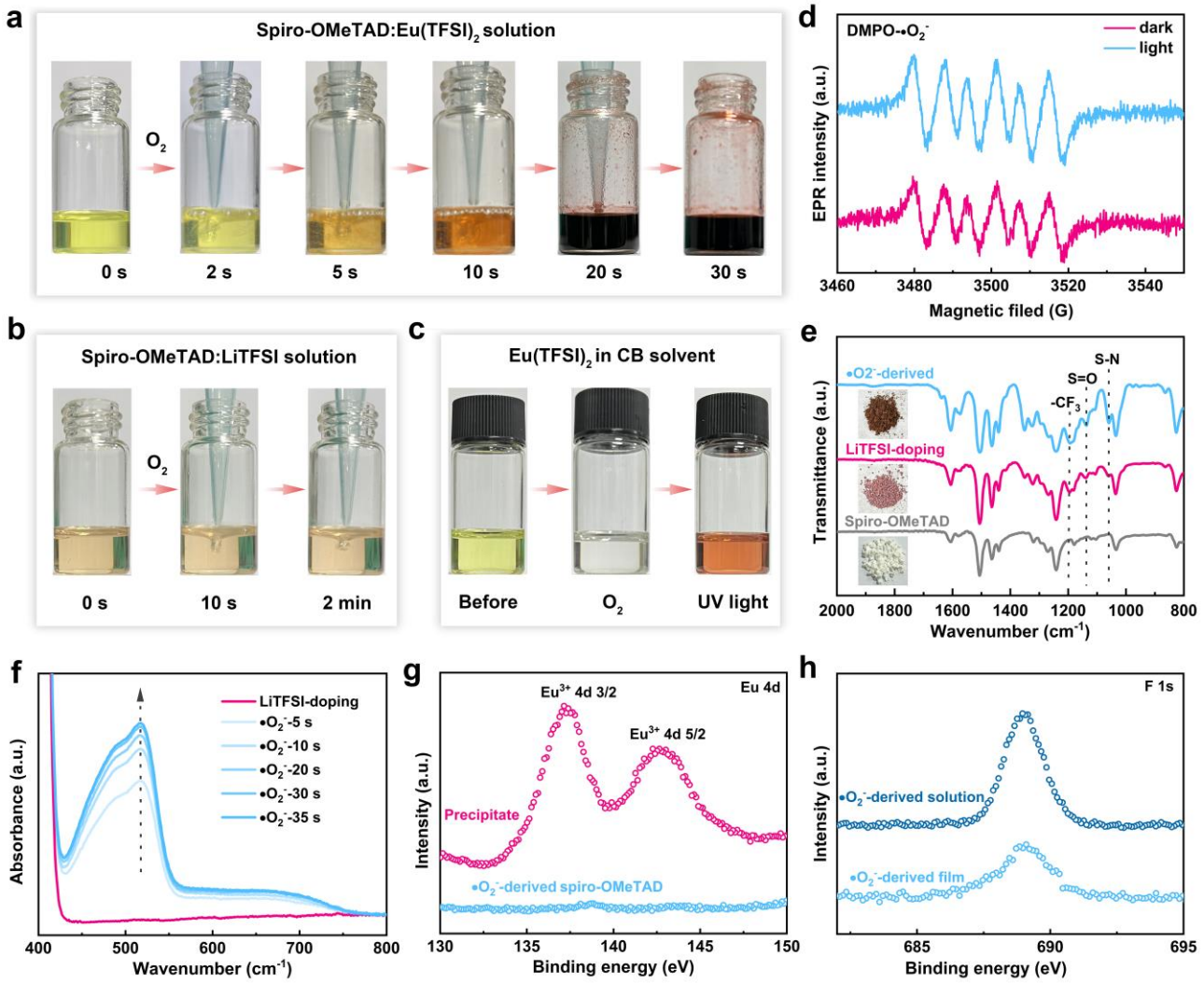
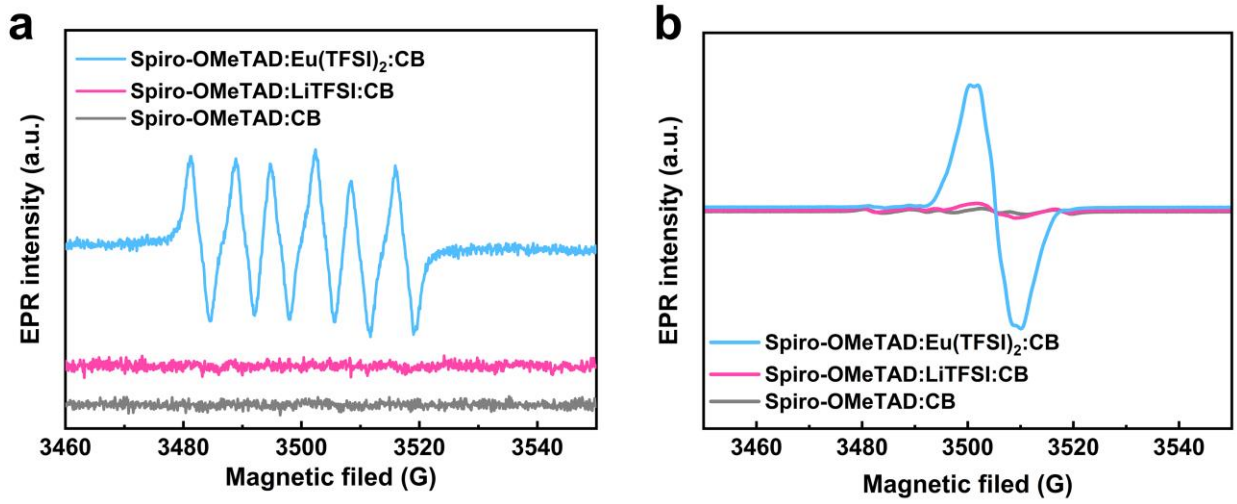


Fig. 2 •O_2^- doping mechanism. The colour evolution of different solutions bubbled with O_2 under different time: **a** spiro-OMeTAD:Eu(TFSI)$_2$, **b** spiro-OMeTAD:LiTFSI, and **c** EuTFSI$_2$:CB. **d** EPR spectra of the EuTFSI$_2$:CB solution bubbled with O_2 for 10 s and tested after 5 min. **e** FTIR spectra of the raw, LiTFSI-doped and •O_2^--derived spiro-OMeTAD powder. The insets show the optical images of three powers. **f** UV-Vis spectra of the •O_2^--derived spiro-OMeTAD solution under different time. **g** High-resolution XPS spectra of Eu 4d for the •O_2^--derived spiro-OMeTAD film and the residual precipitate. **h** High-resolution XPS spectra of F 1s for the •O_2^--derived spiro-OMeTAD solution and film.



Supplementary Fig. 2. EPR spectra of different solutions (spiro-OMeTAD:CB, spiro-OMeTAD:LiTFSI:CB, and spiro-OMeTAD:$Eu(TFSI)_2$:CB) bubbled with O_2 for 10 s and tested immediately (a) and after 5 min (b).

Q6: Also, the following description cannot be consistent with the mentioned Figure. 'The EPR recorded at room temperature in dark shows 6 peaks for the O_2-bubbled spiro-OMeTAD:$Eu(TFSI)_2$ solution, demonstrating the generation of $\bullet O_2^-$ in solution. Significantly, such $\bullet O_2^-$ can persist in solution for 5 minutes even in the presence of light (Supplementary Fig. 2a).' The sentence refers to an O_2-bubbled spiro-OMeTAD:$Eu(TFSI)_2$ solution, but Supplementary Fig. 2a refers to a $Eu(TFSI)_2$:CB solution. Also, the author should explain more about how to get the conclusion of 5 minutes. How about after 5 min?

Reply: We thank the reviewer for pointing this out. We are sorry to create confusion among the reviewers regarding the EPR data and analyses, owing to the mistakes in corresponding descriptions in figure captions and main text. As we replied in **Q2** and **Q5**, we have corrected corresponding figures and their descriptions in the revised manuscript, which read as: "The lost electron from the Eu^{2+}-Eu^{3+} redox shuttle would thus be recovered by O_2, contributing rapidly to the generation of the $\bullet O_2^-$, which is confirmed by the electron paramagnetic resonance (EPR, Fig. 2d). The EPR recorded at room temperature in both dark and light conditions shows 6 peaks for the O_2-bubbled $Eu(TFSI)_2$:CB solution, demonstrating the generation of $\bullet O_2^-$ in solution.[27] Furthermore, we conducted the EPR spectra on the O_2-bubbled spiro-OMeTAD:$Eu(TFSI)_2$:CB solution to

specifically detect the signal of $\bullet O_2^-$ in solutions with spiro-OMeTAD. After bubbling with O_2 for 10 s, we immediately detected the signal of $\bullet O_2^-$ and found the presence of $\bullet O_2^-$ in this solution based on the observation of its six peaks (Supplementary Fig. 2a). The resultant $\bullet O_2^-$ will instantly oxidize the spiro-OMeTAD to a TFSI-stabilized spiro-OMeTAD$^+$ radical cation along with the Eu^{3+} reaction products, as evidenced by the color evolution of their solutions (Fig. 2a) and EPR spectra after sufficient oxidation (Supplementary Fig. 2b). These results significantly demonstrate that $\bullet O_2^-$ shows an improved reaction rate compared with O_2 when involved in the *in situ* oxidation of spiro-OMeTAD in solution (Supplementary Note1).".

Regarding the statement of "5 min", we actually conducted the EPR spectra of the $Eu(TFSI)_2$:CB solution bubbled with O_2 for 10 s and tested after 5 min. The purpose of waiting 5 min is to demonstrate that the formed $\bullet O_2^-$ can remain stable for an extended period of time (> 30 s), thus confirming that the generated $\bullet O_2^-$ in solution is capable of fully oxidizing spiro-OMeTAD (The oxidation of spiro-OMeTAD in solution can be completed within 30 s through our $\bullet O_2^-$ strategy).

Q7: In the supplementary information, the authors mention that 'The conversion from O_2 molecule to O^{2-} requires four electrons. In other words, for such conversion to occur, one oxygen molecule needs to interact with four Eu^{2+} ions simultaneously. However, due to the electrostatic repulsion, the distance between Eu^{2+} ions in solution is relatively large, limiting the interaction of O_2 with only one Eu^{2+} ion, resulting thus in the formation of superoxide radicals. When the concentration of Eu^{2+} is excessively high, the generated $\bullet O_2^-$ will react with Eu^{2+}, resulting in a decrease in the concentration of $\bullet O_2^-$ in solution and subsequently reducing the oxidation of spiro-OMeTAD.' The explanations are difficult to understand. Corresponding evidence is required.

Reply: Thank you very much for the comments and concerns. <u>As we replied in **Q2**</u>, we have supplemented corresponding evidence and interpretation concerning the conversion from O_2 to $\bullet O_2^-$ not O^{2-}, which is further summarized below:

As reported in previous literature (*Chem. Rev.* 2016, 116, 5, 3029-3085), the reduction of O_2 in various aqueous and nonaqueous solvents is extremely complicated. Therefore, disproportionation

and protonation of intermediate species are unavoidable. Generally, ordinary O_2 reacts poorly with most other molecules. However, it can be activated by adding naturally or artificially derived energy that converts an O_2 molecule into reactive O_2 species (i.e., $\bullet O_2^-$). Therefore, O_2 can form $\bullet O_2^-$ under specific conditions instead of directly forming oxides (O^{2-}). This is because in certain chemical reactions, oxygen can accept an electron, resulting in the formation of superoxide radicals with a single unpaired electron.

Regarding the conversion from O_2 to $\bullet O_2^-$ not O^{2-} in our present work, it is indeed difficult to convert O_2 to O^{2-} due to the poor reaction between O_2 and spiro-OMeTAD molecule in solution. This can be indirectly proved by the experiment involving bubbling O_2 into LiTFSI-doped spiro-OMeTAD solutions, where there is no change in color observed (**Fig. 2b**), indicating a lack of direct interaction between O_2 and spiro-OMeTAD. By adding $Eu(TFSI)_2$ into the spiro-OMeTAD solution instead of LiTFSI, it can be seen that the color of the solution rapidly changes from light yellow to dark red after 30 seconds of bubbling with O_2 (**Fig. 2a**), indicating the formation of more reactive O_2 species that can oxidize spiro-OMeTAD, which we have determined to be $\bullet O^{2-}$ (**Fig. 2d**). Also, this result suggests that the direct conversion of O_2 to oxides (O^{2-}) by the Eu^{2+}-Eu^{3+} redox shuttle is unlikely to occur. Otherwise, the spiro-OMeTAD solution would not have shown a change in color.

Regarding the conversion mechanism of 'why O_2 just accepts one electron to form $\bullet O_2^-$', it is indeed difficult to obtain direct evidence for reaction kinetics, it may require *in-situ* characterization techniques, which we can not carry out in current stage. However, on the basis of above observations and analyses, we proposed that the conversion from O_2 to $\bullet O_2^-$ not O^{2-} in our present work is attributed to the imbalance in the involved amount between O_2 and Eu^{2+} (O_2 is excessive compared to Eu^{2+} when the concentration of $Eu(TFSI)_2$ is below 40 mol%), which could serve as a specific chemical condition. Such chemical condition can limit interaction of O_2 with only one Eu^{2+} ion, resulting thus in the formation of $\bullet O_2^-$. However, the conversion from O_2 molecule to O^{2-} requires four electrons. In other words, for such conversion to occur, one oxygen molecule needs to interact with four Eu^{2+} ions simultaneously, leading to the difficulty of converting O_2 to O^{2-}.

Our results have demonstrated that the doping of spiro-OMeTAD in solution reached saturation at the concentration up to 40 mol% of $Eu(TFSI)_2$ to spiro-OMeTAD. When the concentration of Eu^{2+} exceeds 40 mol% (e.g., >50 mol%), the spiro-OMeTAD solution exhibits a

slower color change and a lighter final color during the bubbling with O_2 compared to the solution with a concentration of 40 mol% (see **Reply Fig. 3**), indicating the decreased amount of $\bullet O_2^-$ in solution. Regarding the decrease in the amount of $\bullet O_2^-$ under high concentration of $Eu(TFSI)_2$, there may exist two types of reaction kinetics: (1) the generated $\bullet O_2^-$ reacts with Eu^{2+}, leading to a decrease in the amount of $\bullet O_2^-$; (2) Eu^{2+} directly reacts with oxygen to form O^{2-}, resulting in a decrease in the amount of $\bullet O_2^-$. Regardless of the specific kinetics, both processes are highly complicated and metastable, may require the in-situ characterization techniques. We would be much grateful if you could understand that we are difficult to perform such characterizations in current stage.

Q8: In the supplementary information, the equation and the figure (lines 77 and 78) should be on the same line.

Reply: We thank the reviewer for pointing this out. We have carefully checked and corrected all the formatting issues of the entire manuscript.

Q9: In the supplementary information, the authors mention that 'higher concentrations of $Eu(TFSI)_2$ exceeding 40 mol% are not beneficial to the photovoltaic performance of PSCs (Supplementary Table 3). This can be attributed that the excessive concentration of $Eu(TFSI)_2$ causing the generated $\bullet O_2^-$ to react with Eu^{2+}, resulting in a decrease in the concentration of $\bullet O_2^-$ in solution and subsequently reducing the oxidation of spiro-OMeTAD.' Related evidences are needed for the explanation.

Reply: Thank you very much for the comments and concerns. Regarding the threshold for 'excessively high', we have actually conducted a series of characterizations to determine the inflection point of the concentration of $\bullet O^{2-}$ in the present work, including UV-Vis spectra, conductivity/mobility tests, and PCE optimization (**Fig. 2f, Fig. 3b, Fig. 4 a-c and Supplementary Fig. 3, Fig. 5, Table 3**). These results demonstrated that the doping of spiro-OMeTAD in solution reached saturation at the concentration up to 40 mol% of $Eu(TFSI)_2$ to spiro-OMeTAD. When the concentration of Eu^{2+} exceeds 40 mol% (e.g., >50 mol%), the absorption peak, conductivity, and

device performance of the oxidized spiro-OMeTAD remained unchanged or decrease. This is because the generated $\bullet O^{2-}$ will react with Eu^{2+}, resulting in a decrease in the concentration of $\bullet O^{2-}$ in solution and subsequently reducing the oxidation of spiro-OMeTAD, which can be evidenced by the color change of the spiro-OMeTAD solution in **Reply Fig. 3**. **Reply Fig. 3** shows the color evolution of spiro-OMeTAD solutions with different concentrations of Eu^{2+} bubbled with O_2 over different time. It is clear seen that the spiro-OMeTAD solution with a concentration of 55 mol% of $Eu(TFSI)_2$ exhibits a slower color change and a lighter final color compared to the solution with a concentration of 40 mol%, indicating the decrease in the concentration of $\bullet O^{2-}$ in solution. These results suggest that the threshold for 'excessively high' is the concentration of >40 mol%.

Q10: The subtitle of Supplementary Fig 2 should be revised. I can't understand the meaning of '5min' in the sentence.

Reply: We thank the reviewer for pointing this out. As we replied in **Q5**, we have corrected the subtitle of Supplementary Fig. 2 in the revised manuscript. Regarding the statement of "5 min", we actually conducted the EPR spectra of the $Eu(TFSI)_2$:CB solution bubbled with O_2 for 10 s and tested after 5 min (Supplementary Fig. 2a). The purpose of waiting 5 min is to demonstrate that the formed $\bullet O_2^-$ can remain stable for an extended period of time (> 30 s), thus confirming that the generated $\bullet O_2^-$ in solution is capable of fully oxidizing spiro-OMeTAD (The oxidation of spiro-OMeTAD in solution can be completed within 30 s through our $\bullet O_2^-$ strategy). We further performed the EPR spectra on spiro-OMeTAD:CB, spiro-OMeTAD:LiTFSI:CB, and spiro-OMeTAD:$Eu(TFSI)_2$:CB solutions. After bubbling with O_2 for 10 s, we did not immediately conduct the EPR test, but rather waited for 5 min before starting the test (Supplementary Fig. 2b). The purpose of this delay was to allow sufficient oxidation of spiro-OMeTAD to generate spiro-$OMeTAD^+$ in solution. Therefore, the results in **Reply Fig. 6** clearly demonstrate the EPR signal of spiro-$OMeTAD^+$ while no $\bullet O_2^-$ signal is observed. This indicates that, at this stage, the concentration of $\bullet O_2^-$ is significantly lower compared to spiro-$OMeTAD^+$ in the solutions.

Q11: I would strongly suggest the authors carefully check the description and grammar of the entire manuscript again.

Reply: We thank the reviewer for pointing these out. We have double-checked the grammar, spelling, and formatting of the entire manuscript. In particular, the descriptions concerning $\bullet O_2^-$ in the main text and supplementary information have been carefully checked and updated accordingly.

Replies to Reviewer 2

Q1: The author has addressed most of my concerns raised previously and the manuscript has improved its quality. I suggest accepting this paper after minor revision.

Reply: Thank you very much for your positive comments to our work, and we much appreciate for the raised comments below, which are all valuable and helpful for improving our manuscript. We have tried our best to revise our manuscript accordingly, and those revisions have been marked in red color in the revised manuscript. Below are the points to point replies.

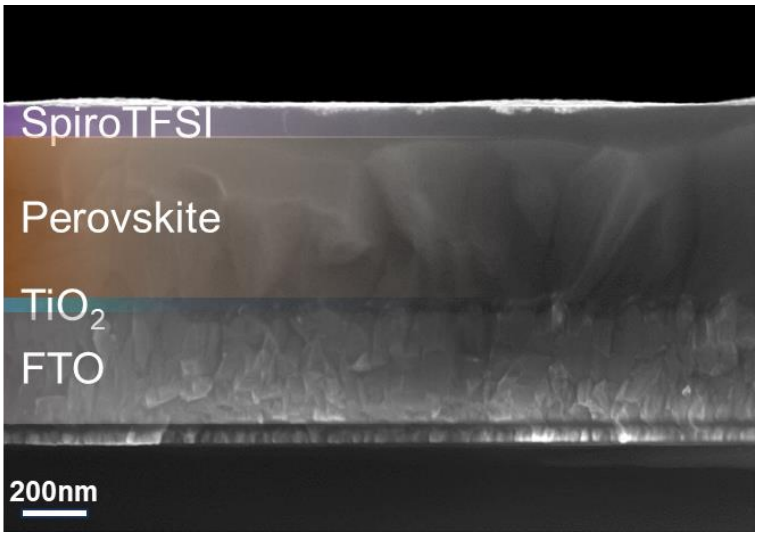
Q2: It is true that due to the difference in experimental setup, the detected Rct would be different in solar cells. The author highlighted that some papers showed a similar Rct as obtained in this work. However, none of the references the author provided in the response letter detailed if their solar cells were biased during the EIS measurement. ((Adv. Mater. 2023, 36, 2308969; Angew. Chem. Int. Ed. 2024, 63, e202318754; Adv. Funct. Mater. 2024, 2308969, https://doi.org/10.1002/adfm.202404671).). The citation information is incorrect for "Adv. Funct. Mater. 2024, 2308969".

Reply: We thank the reviewer for pointing these out. It is indeed a mistake in the citation information of *Adv. Funct. Mater*. 2024, https://doi.org/10.1002/adfm.202404671. We have carefully checked and corrected all citation information in the revised manuscript.

Regarding the references involving EIS we provided in previous version, we have carefully checked experimental details in referenced papers and found that they did not describe the corresponding information concerning bias during the EIS measurement. We thus re-searched some similar reports concerning EIS measurements (*Adv. Energy Mater*. 2023, 13, 2204370; *Chem. Rev.* 2021, 121, 14430-14484; *ACS Appl. Mater. Interfaces* 2019, 11, 14166-14174), in which these papers exhibit large R_{ct} when applying a bias in the dark. We thank the reviewer for the elaborate and helpful comment for improving our manuscript in terms of the EIS point.

Q3: Please specify the thickness of the thin film perovskite used in the PL/TRPL measurement and the excitation direction for perovskite.

Reply: Thank you very much for the comments and concerns. In this work, the thickness of the perovskite active layer is 550 nm, while the thickness of the spiro-OMeTAD HTL is 100 nm. These values were measured from the cross-sectional SEM image of PSCs (**Reply Fig. 9**). When performing the PL and TRPL measurements, the laser is incident from the perovskite/HTL side (top direction) in this work, which allows for the investigation of the hole extraction ability at the interface at the interface of perovskite/HTL.



Reply Fig. 9. Cross-sectional SEM image of PSCs based on the $\bullet O^{2-}$-derived spiro-OMeTAD HTLs.

Q4: A minor correction in line 709, where “dpoing” should be “doping”.

Reply: We thank the reviewer for pointing this out. We have double-checked the grammar, spelling, and formatting of the entire manuscript.

Q4: I have looked at the response letter to the reviewer 3, and believe that most of questions have been addressed appropriately. However, before the final decision is made, the new EPR data being presented necessitates clearer interpretation.

The author specified that Fig. S2b is used to "compare the oxidation rate of $\bullet O_2^-$ and molecular oxygen in spiro-OMeTAD solutions". However, I noticed that 6 peaks in Fig. 2d were detected for spiro-OMeTAD:Eu(TFSI)2 while only 1 peak was detected in Fig. S2b. What is the mechanism behind such variation? Which radicals authors focus on in the respective measurement? As these are crucial for understanding the role of additives, careful analysis and scrutiny should be made.

Reply: Thank you very much for the comments and concerns. We are sorry to create confusion among the reviewers regarding the EPR data and analyses, owing to the mistakes in corresponding descriptions in figure captions and main text. We have carefully checked all EPR data we provided in this manuscript, and determined that the EPR signal with six specific peaks corresponds to the $\bullet O^{2-}$ while the EPR signal with one peak is attributed to the spiro-OMeTAD$^+$. <u>The signal difference between them is mainly attributed to the test conditions including solution type and test time.</u> We would like to stress that we have actually conducted three EPR experiments for characterizing the $\bullet O^{2-}$ and spiro-OMeTAD$^+$ signals in different solutions under different time: (1) EPR spectra of $Eu(TFSI)_2$:CB solution without spiro-OMeTAD bubbled with O_2 for 10 s and tested after 5min (**Reply Fig. 10**); (2) EPR spectra of spiro-OMeTAD:CB, spiro-OMeTAD:LiTFSI:CB, and spiro-OMeTAD:$Eu(TFSI)_2$:CB solutions bubbled with O_2 for 10 s and tested immediately (**Reply Fig. 11**); (3) EPR spectra of spiro-OMeTAD:CB, spiro-OMeTAD:LiTFSI:CB, and spiro-OMeTAD:$Eu(TFSI)_2$:CB solutions bubbled with O_2 for 10 s and tested after 5 min (**Reply Fig. 12**).

Regarding the test (1), we performed the EPR spectra on the $Eu(TFSI)_2$:CB solution without spiro-OMeTAD to detect the signal of $\bullet O_2^-$. After bubbling with O_2 for 10 s, we confirmed the presence of $\bullet O_2^-$ in this solution based on the observation of its six peaks (**Reply Fig. 10**). It is important to note that we conducted the EPR spectra of this solution after 5 min to demonstrate that the formed $\bullet O_2^-$ can remain stable for an extended period of time (> 30 s), regardless of the conditions of darkness and light, indicating its capability to sufficiently oxidize spiro-OMeTAD in

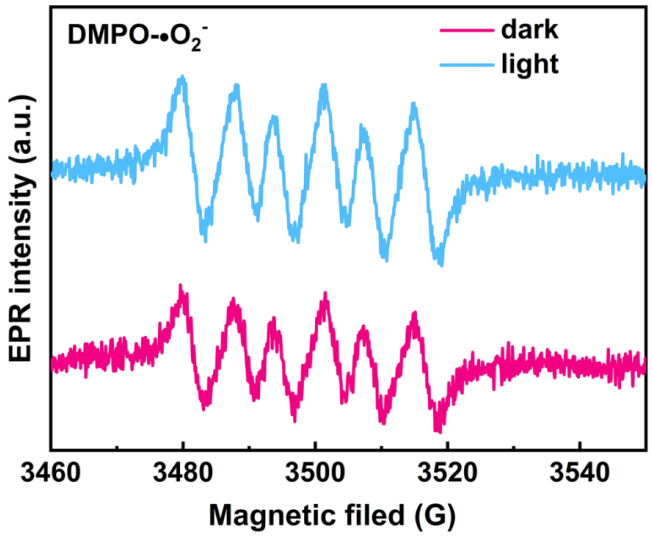
the solution.

Regarding the test (2), we performed the EPR spectra on spiro-OMeTAD:CB, spiro-OMeTAD:LiTFSI:CB, and spiro-OMeTAD:Eu(TFSI)$_2$:CB solutions to specifically detect the signal of $\bullet O_2^-$ in solutions with spiro-OMeTAD. After bubbling with O_2 for 10 s, we immediately detected the signal of $\bullet O_2^-$ and found the presence of $\bullet O_2^-$ in this solution based on the observation of its six peaks (**Reply Fig. 11**). We would like to stress that, although spiro-OMeTAD$^+$ radicals are present at this stage, their amount is still relatively low compared to the $\bullet O_2^-$ (see the solution color in 10 s in Fig. 2a). Therefore, the EPR signals observed in this solution predominantly originate from the $\bullet O_2^-$.

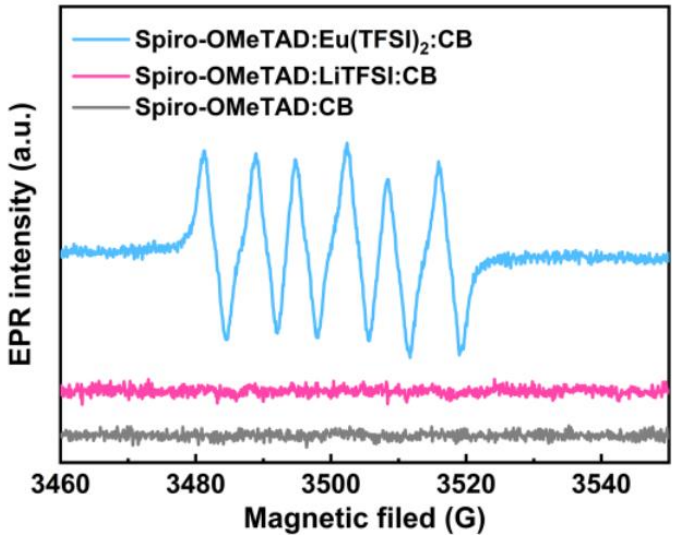
Regarding the test (3), we performed the EPR spectra on spiro-OMeTAD:CB, spiro-OMeTAD:LiTFSI:CB, and spiro-OMeTAD:Eu(TFSI)$_2$:CB solutions to specifically detect the signal of spiro-OMeTAD$^+$ radicals in solutions. After bubbling with O_2 for 10 s, we did not immediately conduct the EPR test as in test (2), but rather waited for 5 min before starting the test. The purpose of this delay was to allow sufficient oxidation of spiro-OMeTAD to generate spiro-OMeTAD$^+$ in solution. Therefore, the results in **Reply Fig. 12** clearly demonstrate the EPR signal of spiro-OMeTAD$^+$ with one peak while no $\bullet O_2^-$ signal is observed. This indicates that, at this stage, the concentration of $\bullet O_2^-$ is significantly lower compared to spiro-OMeTAD$^+$ in the solutions.

We thus updated corresponding figures and their descriptions in the revised manuscript, and read as: "The lost electron from the Eu^{2+}-Eu^{3+} redox shuttle would thus be recovered by O_2, contributing rapidly to the generation of the $\bullet O_2^-$, which is confirmed by the electron paramagnetic resonance (EPR, Fig. 2d). The EPR recorded at room temperature in both dark and light conditions shows 6 peaks for the O_2-bubbled Eu(TFSI)$_2$:CB solution, demonstrating the generation of $\bullet O_2^-$ in solution.[27] Furthermore, we conducted the EPR spectra on the O_2-bubbled spiro-OMeTAD:Eu(TFSI)$_2$:CB solution to specifically detect the signal of $\bullet O_2^-$ in solutions with spiro-OMeTAD. After bubbling with O_2 for 10 s, we immediately detected the signal of $\bullet O_2^-$ and found the presence of $\bullet O_2^-$ in this solution based on the observation of its six peaks (Supplementary Fig. 2a). The resultant $\bullet O_2^-$ will instantly oxidize the spiro-OMeTAD to a TFSI-stabilized spiro-OMeTAD$^+$ radical cation along with the Eu^{3+} reaction products, as evidenced by the color evolution of their solutions (Fig. 2a) and EPR spectra after sufficient oxidation (Supplementary Fig.

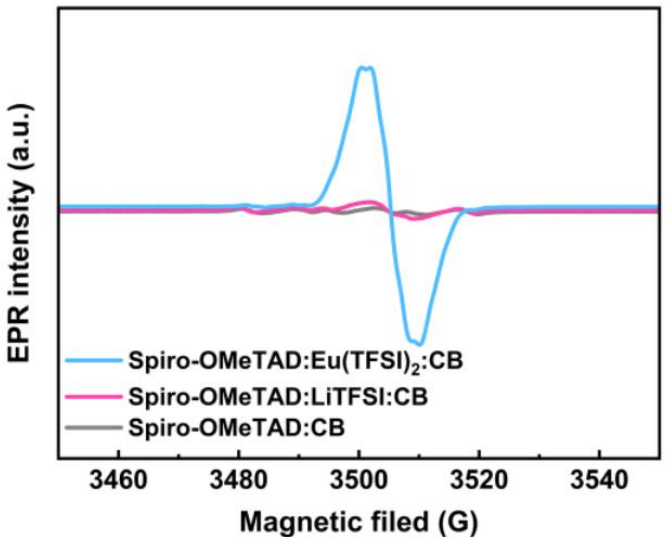
2b). These results significantly demonstrate that $\bullet O_2^-$ shows an improved reaction rate compared with O_2 when involved in the *in situ* oxidation of spiro-OMeTAD in solution (Supplementary Note1).".



Reply Fig. 10. EPR spectra of $Eu(TFSI)_2$:CB solution without spiro-OMeTAD bubbled with O_2 for 10 s and tested after 5min.



Reply Fig. 11. EPR spectra of different solutions (spiro-OMeTAD:CB, spiro-OMeTAD:LiTFSI:CB, and spiro-OMeTAD:$Eu(TFSI)_2$:CB) bubbled with O_2 for 10 s and tested immediately.



Reply Fig. 12. EPR spectra of different solutions (spiro-OMeTAD:CB, spiro-OMeTAD:LiTFSI:CB, and spiro-OMeTAD:Eu(TFSI)$_2$:CB) bubbled with O_2 for 10 s and tested after 5 min.

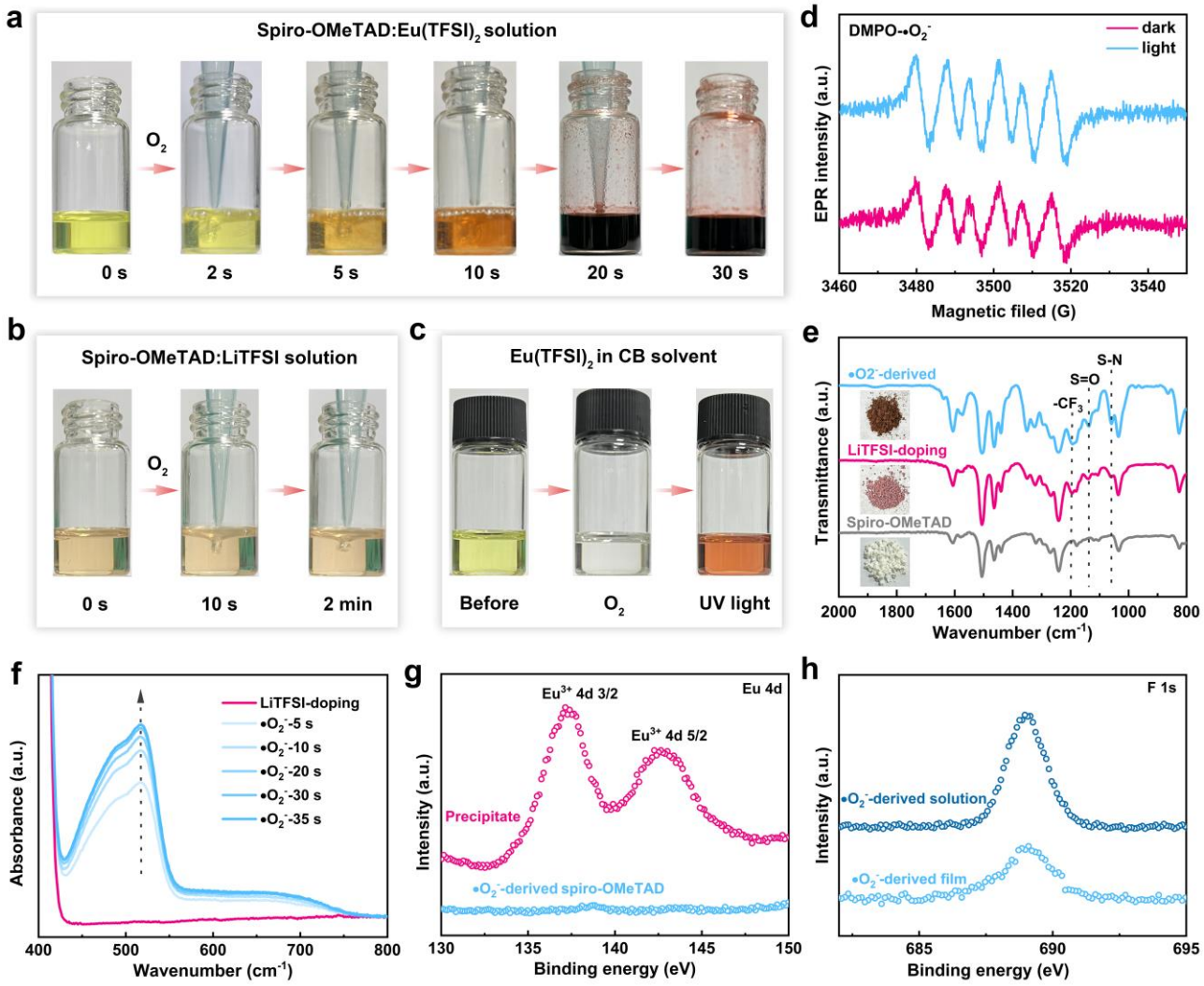
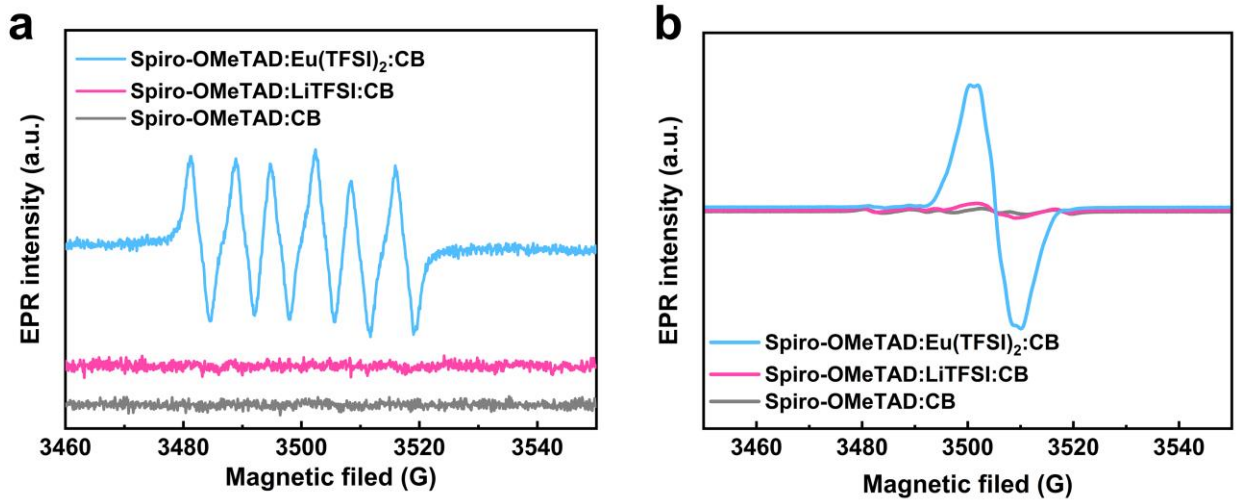


Fig. 2 •O_2^- doping mechanism. The colour evolution of different solutions bubbled with O_2 under different time: **a** spiro-OMeTAD:Eu(TFSI)$_2$, **b** spiro-OMeTAD:LiTFSI, and **c** EuTFSI$_2$:CB. **d** EPR spectra of the EuTFSI$_2$:CB solution bubbled with O_2 for 10 s and tested after 5 min. **e** FTIR spectra of the raw, LiTFSI-doped and •O_2^--derived spiro-OMeTAD powder. The insets show the optical images of three powers. **f** UV-Vis spectra of the •O_2^--derived spiro-OMeTAD solution under different time. **g** High-resolution XPS spectra of Eu 4d for the •O_2^--derived spiro-OMeTAD film and the residual precipitate. **h** High-resolution XPS spectra of F 1s for the •O_2^--derived spiro-OMeTAD solution and film.



Supplementary Fig. 2. EPR spectra of different solutions (spiro-OMeTAD:CB, spiro-OMeTAD:LiTFSI:CB, and spiro-OMeTAD:Eu(TFSI)$_2$:CB) bubbled with O_2 for 10 s and tested immediately (a) and after 5 min (b).

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

I am satisfied with most of the answers and the quality of the manuscript has greatly improved.

I still have a concern about the doping efficiency and stability at different temperatures related to the reply to Q4. The authors have compared the effects of temperature on doping at 0 oC, 23 oC, 40 oC, and 60 oC. I would suggest that the authors also compare the temperature of 85 oC, as the stability of the device is measured at this temperature.

Reviewer #2 (Remarks to the Author):

This paper has addressed all of my concerns, and I believe it is suitable for publication in Nature Communications. This work represents an interesting addition to the optimization of Spiro-OMeTAD, eliminating the need for a post-oxidation process.

Replies to Reviewer 1

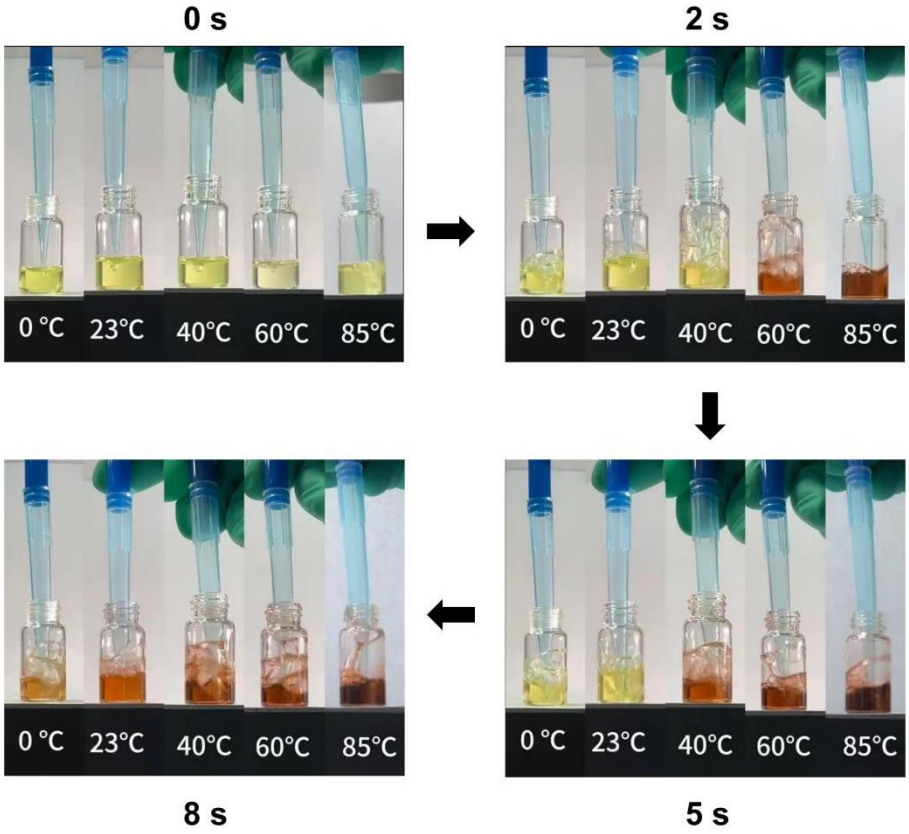
Q1: I am satisfied with most of the answers and the quality of the manuscript has greatly improved. I still have a concern about the doping efficiency and stability at different temperatures related to the reply to Q4. The authors have compared the effects of temperature on doping at 0 °C, 23 °C, 40 °C, and 60 °C. I would suggest that the authors also compare the temperature of 85 °C, as the stability of the device is measured at this temperature.

Reply: Thank you very much for your positive comments and suggestions to our work, which are all valuable and helpful for improving our manuscript.

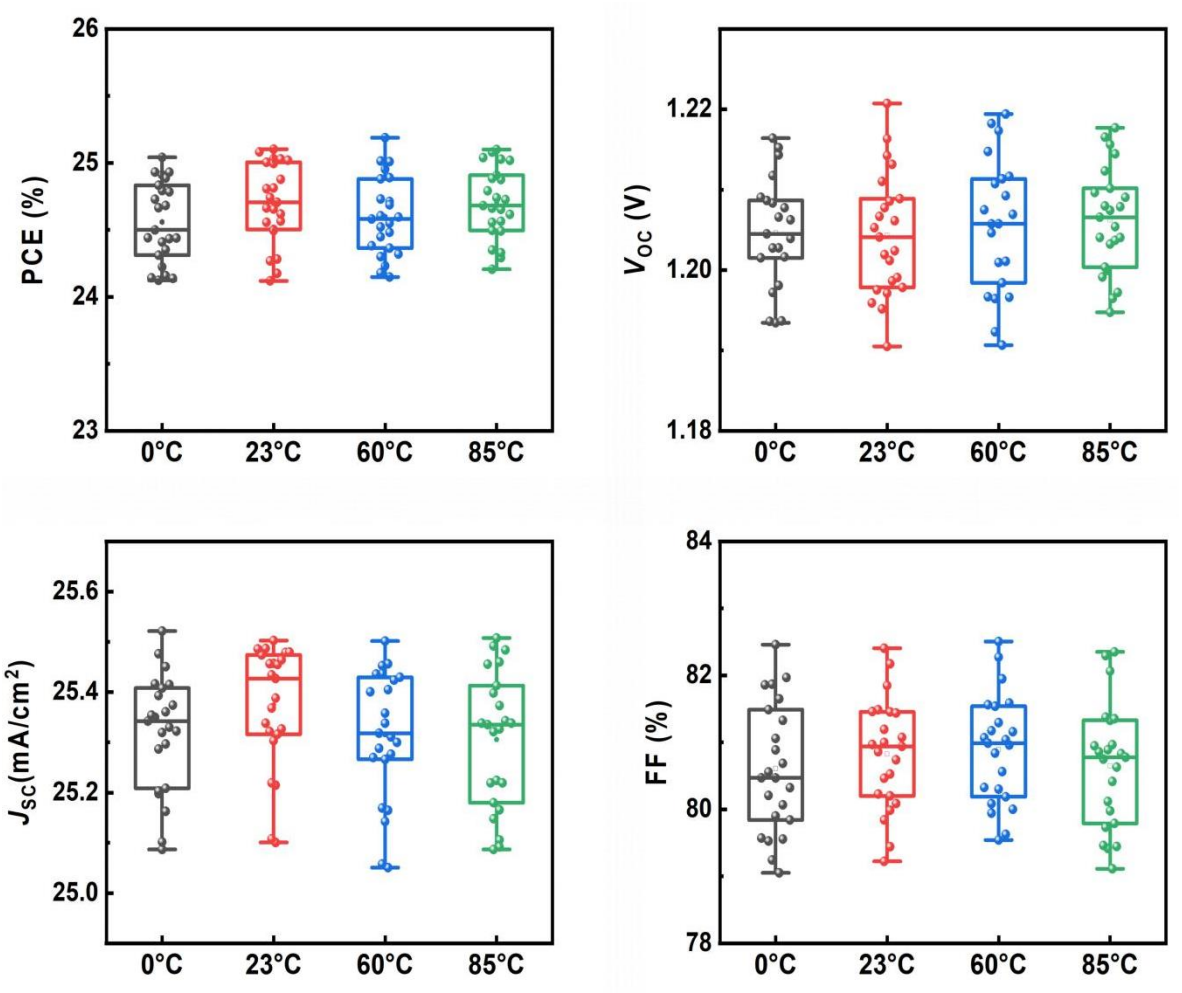
We have supplemented the effect of temperature on $\bullet O_2^-$-doping of spiro-OMeTAD solution at 85°C (**Reply Fig. 1**), and corresponding photovoltaic performance of PSCs based on the $\bullet O_2^-$-derived spiro-OMeTAD HTLs under different temperatures have been summarized in **Reply Fig. 2** and **Reply Table 1**. It was observed that the oxidation rate of the spiro-OMeTAD solution gradually increased with higher temperatures. However, over a sufficient period of time, the degree of oxidation reached consistent levels (see the final color at 40°C, 60°C and 85°C in Reply Fig. 1, respectively), indicating the amount of formed $\bullet O_2^-$ at different temperatures is identical. In addition, PSC devices based on $\bullet O_2^-$-derived spiro-OMeTAD HTLs prepared at 0°C, 23°C, 60°C and 85°C deliver average PCEs of 24.56%, 24.70%, 24.60%, and 24.70%, respectively, demonstrating almost consistent photovoltaic performance (**Reply Fig. 2**).

We have thus updated corresponding data and descriptions in supplementary Movie 4, Note 5, Fig.17 and Fig. 18 in the revised manuscript, which read as: "Experimentally, we further conducted the experiments by bubbling O_2 in spiro-OMeTAD:$Eu(TFSI)_2$ solutions at different temperatures (0°C, 23°C, 40°C, 60°C and 85°C). It was observed that the oxidation rate of the spiro-OMeTAD solution gradually increased with higher temperatures. However, over a sufficient period of time, the degree of oxidation reached consistent levels (see the final color at 40°C, 60°C and 85°C in Movie 4 and Supplementary Fig. 17, respectively), indicating the amount of formed $\bullet O_2^-$ at different temperatures is identical. These results suggest that the final amount of formed $\bullet O_2^-$ is predominantly influenced by the concentration of $Eu(TFSI)_2$ introduced and the duration of oxygen

exposure. Therefore, it is expected that the doping of spiro-OMeTAD HTLs and the performance of their devices would not be affected by the applied temperatures. For confirming this point, we have also supplemented photovoltaic performance of PSCs based on the $\bullet O_2^-$-derived spiro-OMeTAD HTLs under different temperatures (see Supplementary Fig. 18 and Table 4). These results show that devices based on $\bullet O_2^-$-derived spiro-OMeTAD HTLs prepared at 0°C, 23°C, 60°C and 85°C deliver average PCEs of 24.56%, 24.70%, 24.60%, and 24.70%, respectively, demonstrating almost consistent photovoltaic performance.”.



Reply Fig. 1. The colour evolution of spiro-OMeTAD:Eu(TFSI)$_2$ solutions bubbled with O_2 at different temperatures.



Reply Fig. 2. Statistical distribution of 25 individual PSC devices based on $\bullet O_2^-$-derived spiro-OMeTAD HTLs prepared at different temperatures. The employed concentration of $Eu(TFSI)_2$ for all devices is 40 mol%.

Reply Table 1. Statistical photovoltaic parameters of PSCs based on $\bullet O_2^-$-derived spiro-OMeTAD HTLs prepared at different temperatures.

Devices	Average V_{OC} (V)	Average J_{SC} (mA cm^{-2})	Average FF (%)	Average PCE (%)
0°C	1.205 ± 0.007	25.32 ± 0.11	80.61 ± 0.96	24.56 ± 0.30
23°C	1.204 ± 0.008	25.37 ± 0.12	80.83 ± 0.82	24.70 ± 0.30
60°C	1.206 ± 0.008	25.32 ± 0.13	80.89 ± 0.81	24.60 ± 0.29
85°C	1.206 ± 0.006	25.31 ± 0.13	80.65 ± 0.92	24.70 ± 0.27

Note: The employed concentration of $Eu(TFSI)_2$ for all devices is 40 mol%.