

# Doping organic hole-transport materials for high-performance perovskite solar cells

Dongmei He<sup>1</sup>, Shirong Lu<sup>2</sup>, Juan Hou<sup>3, †</sup>, Cong Chen<sup>4, †</sup>, Jiangzhao Chen<sup>1, †</sup>, and Liming Ding<sup>5, †</sup>

<sup>1</sup>Key Laboratory of Optoelectronic Technology & Systems (MoE), College of Optoelectronic Engineering, Chongqing University, Chongqing 400044, China

<sup>2</sup>Department of Material Science and Technology, Taizhou University, Taizhou 318000, China

<sup>3</sup>Department of Physics, Shihezi University, Shihezi 832003, China

<sup>4</sup>State Key Laboratory of Reliability and Intelligence of Electrical Equipment, School of Materials Science and Engineering, Hebei University of Technology, Tianjin 300401, China

<sup>5</sup>Center for Excellence in Nanoscience (CAS), Key Laboratory of Nanosystem and Hierarchical Fabrication (CAS), National Center for Nanoscience and Technology, Beijing 100190, China

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Single-junction and tandem perovskite solar cells (PSCs) have achieved impressive power conversion efficiencies (PCEs) of 25.7% and 31.3%, respectively, which makes it to be one of next-generation photovoltaic technologies<sup>[1–9]</sup>. Interface engineering<sup>[3, 5, 10–12]</sup>, composition engineering<sup>[13]</sup> and additive engineering<sup>[7, 14, 15]</sup> have made remarkable contributions to efficiency enhancement. Compared with efficiency, the long-term operational stability of PSCs jogs along, which is far from the requirements of commercialization. Currently, almost all regular n–i–p PSCs were accomplished with classical organic hole-transport materials (HTMs), i.e., PTAA<sup>[16]</sup> and spiro-OMeTAD<sup>[2, 4, 6]</sup>. However, the highly efficient PSCs with the above organic hole-transport layers (HTL) usually suffer from instability. To facilitate hole transport and extraction, LiTFSI and tBP are frequently employed to dope organic HTLs but this would sacrifice device stability. The use of these hygroscopic p-dopants endows the devices with poor moisture stability. It is worth noting that small-sized lithium ion (Li<sup>+</sup>) can easily diffuse into perovskite layer and metal electrode, which deteriorates device performance<sup>[17]</sup>. Consequently, a critical challenge limiting commercial applications of PSCs is the trade-off between high efficiency and high stability. The traditional doping strategy with LiTFSI and tBP requires a long time (usually several days) to reach optimal doping and device performance, which is not good for mass production. In addition, owing to the intrinsic soft nature of perovskites, iodide ions can easily migrate and diffuse into the HTL<sup>[18, 19]</sup>, and then interact with positive radicals in HTLs, diminishing hole transport<sup>[16]</sup>.

In order to mitigate hygroscopic problem of LiTFSI dopant, some p-type dopants with better hydrophobic property (e.g., metal organic complex<sup>[20–22]</sup>) were added into HTL solution. In addition, fluorine substitution in lithium salt was attempted to strengthen the moisture stability of HTLs and device<sup>[23]</sup>. However, the above methods can not solve thor-

oughly the instability issue induced by hygroscopic LiTFSI. Given this, a variety of alternative p-dopants to LiTFSI, such as protic ionic liquids<sup>[24, 25]</sup>, metal salts<sup>[26–28]</sup>, and ex situ synthesized spiro-OMeTAD<sup>2+</sup>(TFSI<sup>-</sup>)<sub>2</sub> radicals<sup>[2, 29, 30]</sup>, have been explored. Nevertheless, to guarantee doping effect, tBP is imperative during the doping process. It should be pointed out that whether tBP doping is conducive to ameliorating device stability is still debatable<sup>[31, 32]</sup>. By-products can be formed through the coordination between tBP and LiTFSI<sup>[31]</sup>, and the generated radicals can be consumed *via* its interaction with tBP<sup>[32]</sup>. The role of tBP in doping process needs further investigation to address the instability issue of classical doping recipe.

Some p-type dopants were used to fully supersede tBP and LiTFSI<sup>[33, 34]</sup>. Jia *et al.* doped PTAA HTL with a fluorine-containing hydrophobic Lewis acid and achieved a higher PCE of 19.01% than 17.77% for control devices doped by bi-dopants LiTFSI/tBP<sup>[33]</sup>. Moreover, smaller hysteresis and improved stability were demonstrated. Recently, Nazeeruddin *et al.* proposed a novel doping approach by employing DIC-PBA dopant with a diphenyl iodide cation and pentafluorophenyl boric acid anion<sup>[34]</sup>. The devices gave a small-area PCE of 22.86% and a module PCE of 19.13% (33.2 cm<sup>2</sup>) along with increased ambient stability. DIC-PBA can simultaneously p-dope PTAA and perovskite, which was attributed to ionic interaction-derived dipole arrangement. These results indicate that the total substitution strategy is promising but the PCE needs to be further enhanced. To further ameliorate doping, more doping molecules should be designed. The correlation between molecular structures and hole conductivity, energy levels, interfacial carrier dynamics as well as device performance should be established.

Gao *et al.* developed an ion-modulated (IM) radical doping strategy where pre-synthesized organic radicals spiro-OMeTAD<sup>2+</sup>(TFSI<sup>-</sup>)<sub>2</sub> and TBMP<sup>+</sup>TFSI<sup>-</sup> salt were used to dope spiro-OMeTAD HTL (Fig. 1(a))<sup>[2]</sup>. Spiro-OMeTAD can be immediately oxidized by spiro-OMeTAD<sup>2+</sup>(TFSI<sup>-</sup>)<sub>2</sub> into spiro-OMeTAD<sup>+</sup>TFSI<sup>-</sup> monoradical *via* comproportionation. The radicals can instantly augment the conductivity and workfunction (WF) through providing hole polarons. In the meantime, ionic salts can further tune WF *via* affecting the energetics of hole polarons. A very long oxidation time (~24 h) was re-

Correspondence to: J Hou, [hjuan05@shzu.edu.cn](mailto:hjuan05@shzu.edu.cn); C Chen, [chencong@hebut.edu.cn](mailto:chencong@hebut.edu.cn); J Z Chen, [jiangzhaochen@cqu.edu.cn](mailto:jiangzhaochen@cqu.edu.cn); L M Ding, [ding@nanocr.cn](mailto:ding@nanocr.cn)

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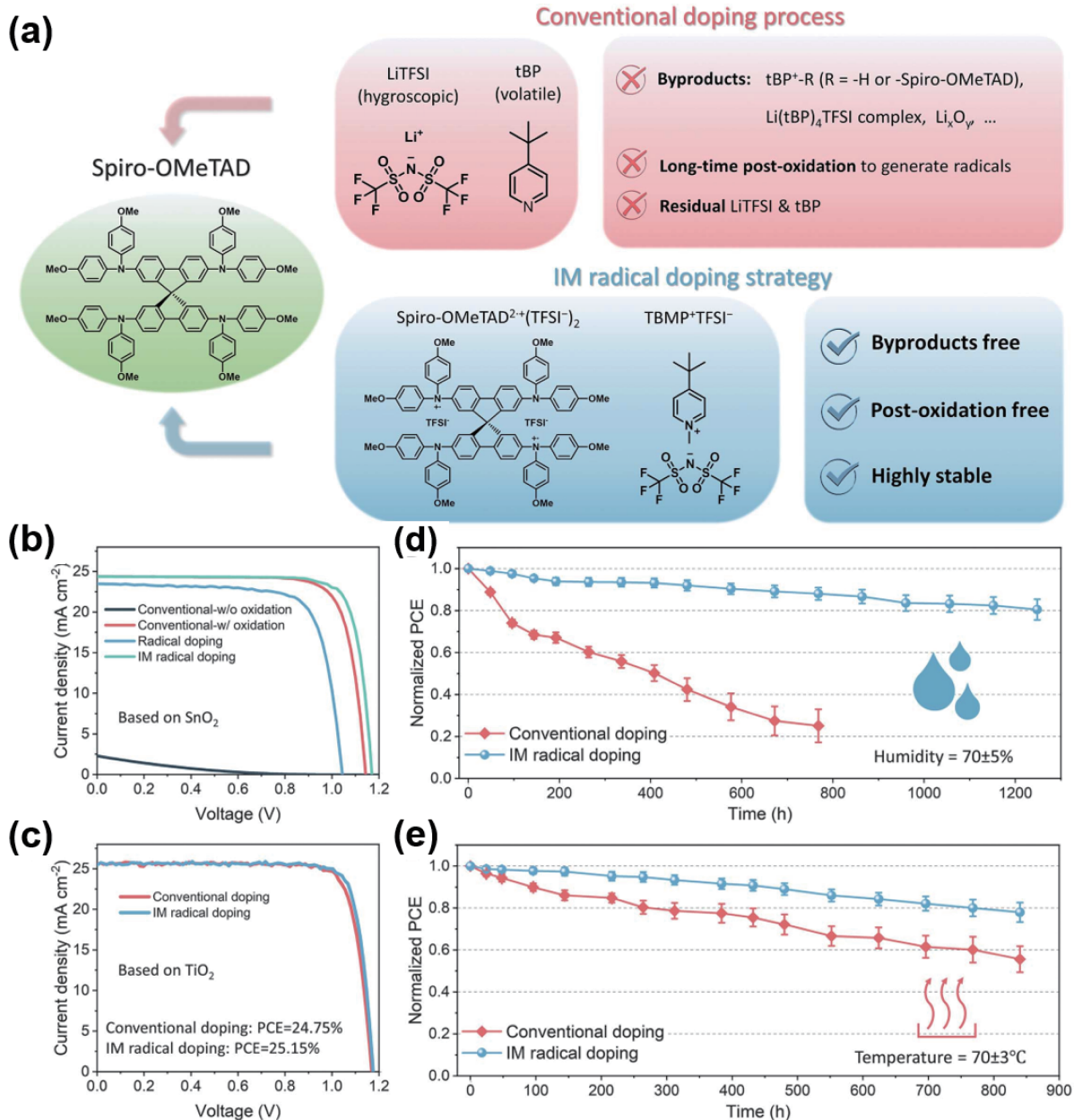
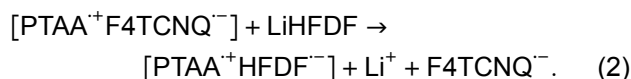


Fig. 1. (Color online) (a) Comparison between the conventional and ion-modulated (IM) radical doping strategies. (b) *J-V* characteristics for SnO<sub>2</sub>-based PSCs (under different doping). (c) *J-V* curves for TiO<sub>2</sub>-based PSCs (conventional doping vs IM radical doping). (d) Moisture stability for unencapsulated PSCs under 70 ± 5% humidity (conventional doping vs IM radical doping). (e) Thermal stability for the unsealed devices at 70 ± 3°C. Reproduced with permission<sup>[2]</sup>, Copyright 2022, American Association for the Advancement of Science.

quired to reach optimal PCE for the devices with conventional doping recipe (Fig. 1(b)). In comparison, the PCE for the device with IM radical doping instantly reaches maximum. Through IM radical doping, FAPbI<sub>3</sub> cells offered a PCE of 25.15% (Fig. 1(c)). Under high relative humidity of ~70 ± 5%, the device with IM radical doping showed a  $T_{80}$  of ~1240 h while  $T_{80}$  was only ~96 h for the device with conventional doping (Fig. 1(d)). The markedly improved thermal stability was also realized as confirmed by much larger  $T_{80}$  value for the target device with radical doping (~796 h) as compared to the control device (~264 h) (Fig. 1(e)). The generality for IM radical doping was revealed by comparing the photovoltaic performance of the devices based on different perovskite compositions and various organic salts with different cations and anions. Developing alternative dopant recipe could improve device performance.

I<sup>-</sup> can easily diffuse into HTL and react with positively charged radicals, which would deteriorate device performance. Besides, Li<sup>+</sup> ions can also diffuse into perovskite layer. To overcome these issues, Yang *et al.* reported a Li-free doping strategy by coupling positive polymer radicals with molecular anion 1,1,2,2,3,3-hexafluoropropane-1,3-disulfonimide (HFDF<sup>-</sup>) via an ion exchange process<sup>[16]</sup>. The molecular structures for PTAA, F4TCNQ and LiHFDF are exhibited in Fig. 2(a). The doping process can be completed in a few minutes. And the doping mechanism can be depicted as follows:



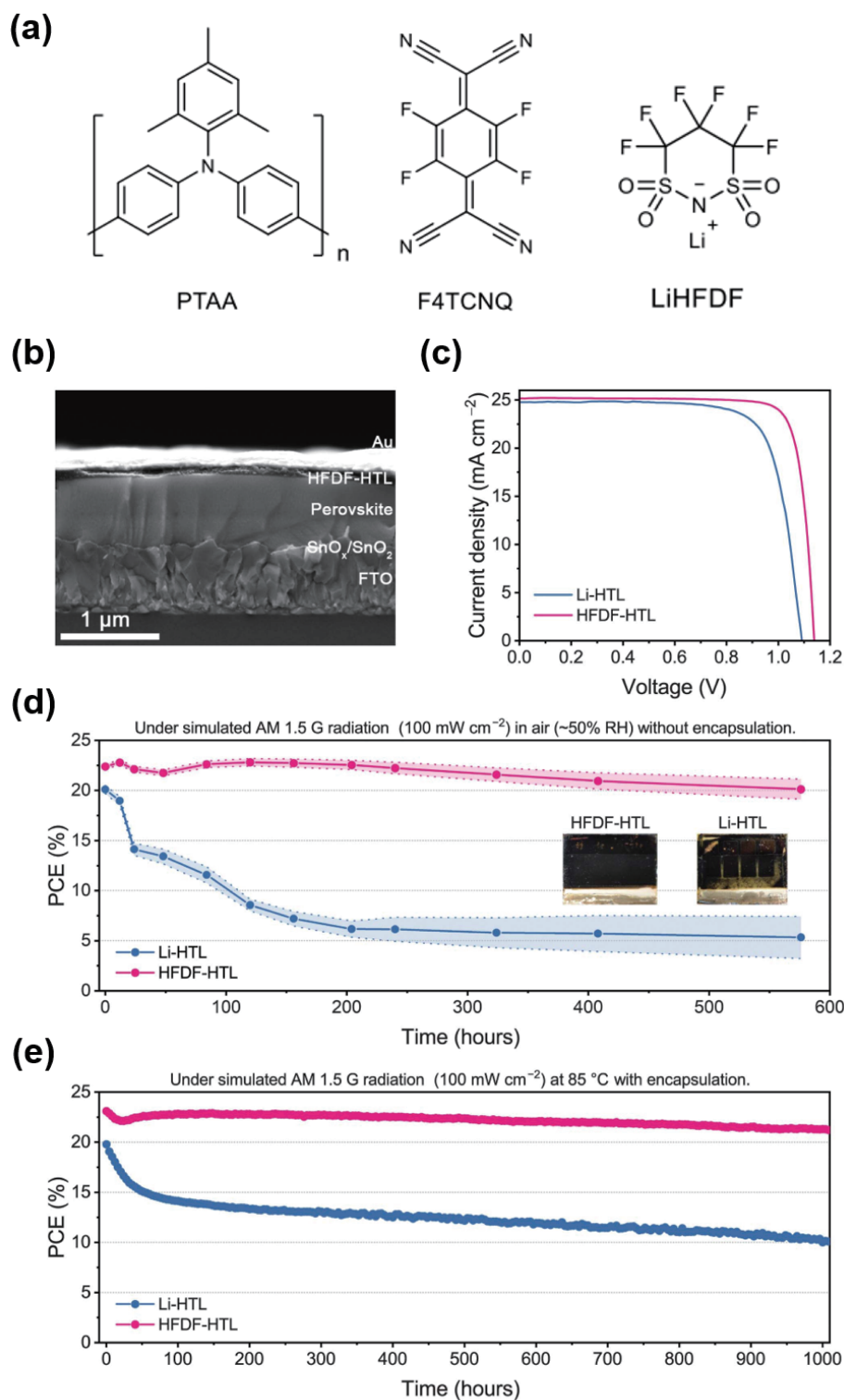


Fig. 2. (Color online) (a) Molecular structures for PTAA, F4TCNQ and LiHFDF. (b) Cross-sectional SEM image for PSCs with HFDF-HTL. (c) *J-V* curves for PSCs (Li-HTL vs HFDF-HTL). (d) Moisture stability for unsealed PSCs under AM1.5G radiation and ~50% RH (Li-HTL vs HFDF-HTL). (e) Thermal stability for the encapsulated devices with different HTLs under AM1.5G illumination at 85 °C. Reproduced with permission<sup>[16]</sup>, Copyright 2022, American Association for the Advancement of Science.

[PTAA<sup>+</sup>F4TCNQ<sup>-</sup>] was firstly generated by the reaction between PTAA and F4TCNQ. Subsequently, the ion exchange between F4TCNQ<sup>-</sup> in [PTAA<sup>+</sup>F4TCNQ<sup>-</sup>] and HFDF<sup>-</sup> led to the formation of a complex [PTAA<sup>+</sup>HFDF<sup>-</sup>] (named HFDF-HTL). The doping efficiency was prominently enhanced for the HFDF-HTL compared with traditional LiTFSI/tBP-doped HTL (Li-HTL) as evidenced by 80 times greater conductivity of the former. HFDF-HTL can maintain high hole conductivity and ex-

cellent energy band alignment upon extreme iodide invasion. The ion exchange doping strategy enabled the fabrication of PSCs with a PCE of 24.0% (certified 23.9%), much higher than 20.5% for the device with Li-HTL (Figs. 2(b) and 2(c)). The unsealed devices were evaluated under AM1.5G radiation and ambient humidity of ~50% (Fig. 2(d)). The device with HFDF-HTL degraded by about 10% after aging for 576 h while the device with Li-HTL degraded by 60% after only

100 h. As shown in Fig. 2(e), 92% of the original PCE was maintained for the device with HFDF-HTL after 1000 h aging while the device with Li-HTL exhibited a 49% drop in PCE. The HTL can operate stably under iodide intrusion through developing effective doping strategy.

Most efforts now focus on improving the hydrophobicity of HTL by developing hydrophobic dopants to replace LiTFSI. The moisture instability is easily resolved by encapsulation technology. The instability caused by migration and diffusion of Li<sup>+</sup> (from HTL to perovskite layer) and I<sup>-</sup> (from perovskite layer to HTL) is more challenging. More effective doping strategy should be developed.

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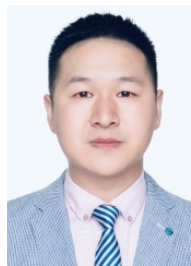
**Dongmei He** is now a research assistant at College of Optoelectronic Engineering in Chongqing University. She received her PhD from Central South University and is working as a postdoc at Chongqing University. Her current research interests focus on perovskite solar cells.



**Cong Chen** is an associate professor at Hebei University of Technology. He received his PhD from Jilin University in June 2019. His main interest is the design of solar cells with high efficiency and long-term stability. Recently, he has carried out a series of work on NIR photodetectors.



**Shirong Lu** is a professor in the Chongqing Institute of Green and Intelligent Technology and Taizhou University. He received his PhD on Organic Chemistry from Tohoku University in 2012 under the supervision of Professor Y. Yamamoto, and then continued his postdoctoral research in UCLA and The University of Melbourne. His research interest focuses on novel printable photovoltaic materials and devices.



**Jiangzhao Chen** is a professor at College of Optoelectronic Engineering in Chongqing University. He received his PhD from Huazhong University of Science and Technology and worked as a postdoc at Sungkyunkwan University and at the University of Hong Kong, respectively. His current research focuses on perovskite solar cells.



**Juan Hou** is a professor at College of Science in Shihezi University. She received her PhD from University of Chinese Academy of Sciences and worked as a postdoc at University of Electronic Science and Technology of China. Her current research interests focus on new energy materials and devices.



**Liming Ding** got his PhD from University of Science and Technology of China (was a joint student at Changchun Institute of Applied Chemistry, CAS). He started his research on OSCs and PLEDs in Olle Inganäs Lab in 1998. Later on, he worked at National Center for Polymer Research, Wright-Patterson Air Force Base and Argonne National Lab (USA). He joined Konarka as a Senior Scientist in 2008. In 2010, he joined National Center for Nanoscience and Technology as a full professor. His research focuses on innovative materials and devices. He is RSC Fellow, and the Associate Editor for *Journal of Semiconductors*