Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

# Versatile Roles of Functionalized Fullerenes in Perovskite Solar Cells

Yue Zhang<sup>‡</sup><sup>a</sup>, Shantao Zhang<sup>‡</sup><sup>a</sup>, Wenxin Dai<sup>a</sup>, Shangfeng Yang<sup>\*</sup>

Perovskite solar cells (PSCs) have emerged as a promising avenue for the development of next-generation solar cells due to their high efficiency and low production costs. Fullerene materials possess high electron affinity, high electron mobility, and minimal recombination energy. Through functionalization, they play versatile roles in PSCs, such as promoting electron transfer, defect passivation, crystallization improvement, and hysteresis inhibition, leading to effectively enhance the power conversion efficiency (PCE) and stability. This review focuses on the recent advancements in utilizing functionalized fullerenes in PSCs, particularly emphasizing their versatile roles as charge transport materials, interfacial modification layers, and additives in perovskite active layer. The relationship between the chemical structures of functionalized fullerenes and device performance has also been a focus of investigation, providing valuable insights into how molecules design impacts overall functionality. Lastly, an outlook of future trends for functionalized fullerenes is provided with the aim of offering valuable insights for innovating new multi-functionalized fullerenes towards efficiency enhancement of PSCs.

# 1. Introduction

With the advancement of science and technology, the demand for clean and inexpensive energy has spurred extensive research into novel low-cost and powerful photovoltaic technologies.<sup>1, 2</sup> As an emerging kind of solar cells, perovskite solar cells (PSCs) have drawn considerable attention due to high conversion efficiency, low manufacturing costs and broad application prospects.<sup>3</sup> Compared to traditional silicon-based solar cells, PSCs possess significant advantages in energy conversion efficiency, and their theoretical efficiency limit can reach 33.7% (single-junction cells) or even 44% (all-perovskite stacked cells), which is much higher than the theoretical efficiency limit of current crystalline silicon cells close to 29.4%.<sup>4-7</sup> Over the past decade, single-junction perovskite solar cell technology has developed rapidly, with certified power conversion efficiency (PCE) surpassing 26%,8,9 demonstrating competitiveness with commercial crystalline silicon cells and presenting a promising outlook for the effective utilization of sustainable energy.<sup>10</sup>

At present, the most prevalently utilized perovskite solar cells are mainly composed of metal electrodes, electron transport layer (ETL), perovskite light absorption layer, hole transport layer (HTL) and conductive glass.<sup>3</sup> The general formula of perovskite material as a light absorbing layer is ABX<sub>3</sub> (Fig. 1a), where A<sup>+</sup> is CH<sub>3</sub>NH<sub>3</sub><sup>+</sup> (MA<sup>+</sup>), NH<sub>2</sub>CH=NH<sub>2</sub><sup>+</sup> (FA<sup>+</sup>), Cs<sup>+</sup>, etc. B<sup>2+</sup> is mainly Pb<sup>2+</sup> or Sn<sup>2+</sup>, while the X site is composed of halogen ions, usually I<sup>-</sup>, B<sup>-</sup> or Cl<sup>-</sup>. It possesses the advantages of adjustable optical absorption band gap,<sup>11</sup> high

 $\ddagger$  These authors contributed equally.

absorption coefficient,<sup>12</sup> long carrier diffusion length,<sup>13</sup> small exciton binding energy<sup>14</sup> and high carrier mobility.<sup>15, 16</sup>

Depending on whether the mesoporous layer is combined with the perovskite layer, PSCs are mainly divided into two structures, namely mesoporous structure (Fig. 1b) and planar structure.<sup>17</sup> According to the order of HTL and ETL in PSCs, the planar PSCs structure can also be divided into the regular structure (Fig. 1c) and the inverted structure (Fig. 1d).<sup>18</sup> In the regular structure of PSCs, light first enters the ETL after incident on the transparent electrode, while in inverted PSCs, the light incident on the transparent electrode first enters the HTL. The regular PSCs, originating from dye-sensitized solar cells (DSSCs), undergo extensive examination in early stages and demonstrate high efficiency;<sup>8, 19</sup> however, the high temperature deposition process and poor stability limit their commercialization.<sup>20,</sup> <sup>21</sup> In contrast, with advancements in perovskite film preparation, the introduction of efficient charge transport materials, and the implementation of advanced optimization strategies, the efficiency of inverted PSCs has gradually closed the gap with regular PSCs, achieving a notable efficiency level.<sup>22</sup> Due to the special advantages in long-term stability and structural compatibility, inverted PSCs are widely used in the preparation of flexible, tandem, and large-scale devices, indicating a promising future for further development.<sup>23</sup>

At present, perovskite solar cells are still facing challenges such as enhancing their PCE to approach the theoretical limit, improving device stability and environmental sustainability.<sup>24</sup> In recent years, concerted efforts have been undertaken to address these challenges, including the development of novel transport and absorption layer materials,<sup>25, 26</sup> optimization of the interface<sup>27, 28</sup> and the utilization of additives.<sup>29, 30</sup> Among these, fullerene derivatives have gained prominence due to their exceptional electronic properties, including high electron affinity, tunable energy levels, and superior charge carrier mobility.<sup>31</sup> When integrated into PSCs as charge transport layer (CTL), interface modification layer or additive,<sup>32-34</sup>

<sup>&</sup>lt;sup>a</sup>Key Laboratory of Precision and Intelligent Chemistry, Collaborative Innovation Center of Chemistry for Energy Materials (iChEM), Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, China. E-mail: sfyang@ustc.edu.cn

functionalized fullerenes demonstrate multifunctional capabilities, including facilitating electron extraction and transport, passivating surface and grain boundary defects of perovskite, and suppressing non-radiative recombination.<sup>34-37</sup>

In this review, we systematically summarize the pivotal advances concerning perovskite solar cells utilizing functional fullerenes, with a specific focus on multiple functions of fullerenes as CTL, interface modification layer and perovskite additive. Building upon this functional framework, we examine recent progress in crosslinked fullerene derivatives, materials with varied substitution degrees, and isomeric configurations in fullerene derivatives, analyzing their respective impacts on device performance. Expanding beyond conventional leadbased systems, we further elucidate fullerene material applications in emerging tin-based and tin-lead perovskite solar cells, thereby demonstrating their universal adaptability across diverse PSCs platforms. Through a comprehensive analysis of these investigations, we delineate the multiple roles and mechanisms of functional fullerenes, and conclude with a forward-looking perspective on development trends for functionalized fullerenes in next-generation PSCs technologies.



Fig. 1 (a) Crystal structure of  $ABX_3$  halide perovskite materials. Common device structures of (b) mesoporous regular structure, (c) planar regular structure and (d) planar inverted structure.

# 2. The structure and properties of fullerene

Fullerene, the third allotrope of carbon, is exemplified by the C<sub>60</sub> molecule which adopts a truncated icosahedron structure comprising 60 vertices and 32 faces (12 pentagons and 20 hexagons).<sup>38</sup> The overlapping p orbitals of carbon atoms in C<sub>60</sub> form a closed-shell electron configuration with 60  $\pi$  electrons, establishing a super-conjugated system where both internal and external surfaces of the carbon cage are enveloped by electron clouds involving all constituent atoms. However, C<sub>60</sub> does not exhibit aromatic characteristics as it requires 72  $\pi$  electrons to achieve a

closed-shell aromatic configuration,<sup>39</sup> rendering it fundamentally electron-deficient. Electrochemical cyclic voltammetry combined with theoretical calculations reveal that  $C_{60}$  demonstrates sixelectron redox processes, with its lowest unoccupied molecular orbital (LUMO) existing as triply degenerate orbitals.<sup>40-42</sup> These findings confirm that fullerenes constitute an electron-deficient extended  $\pi$ -conjugated system with prominent electron-accepting properties. Moreover,  $C_{60}$  exhibit exceptional electron transport capabilities,<sup>43</sup> high electron affinity,<sup>44</sup> low electron reorganization energy,<sup>45</sup> and appropriate energy levels matching perovskite,<sup>18</sup> making them extensively applicable in optoelectronic devices such as organic solar cells and PSCs.<sup>32, 46</sup>

C<sub>60</sub> exhibits chemical properties analogous to an electron-deficient conjugated polyene.<sup>47</sup> In its structure, bonds shared between two hexagonal rings are termed [6,6] bonds, while those connecting pentagonal and hexagonal rings are called as [5,6] bonds. The [6,6] bonds demonstrate a shorter bond length of 1.38Å compared to 1.45Å for [5,6] bonds, endowing them with greater double-bond character and higher reactivity toward functionalization reactions.48 These reactions include nucleophilic addition,<sup>49</sup> reduction,<sup>50</sup> radical addition,<sup>51</sup> cycloaddition,<sup>52</sup> and electrochemical reactions.<sup>53</sup> Functionalization enables the preparation of modified fullerene materials with tailored properties. For instance, the introduction of long alkyl or ether chains significantly enhances solubility in organic solvents.<sup>16</sup> Additional substituents have been shown to change electron mobility,<sup>54</sup> while multiple functional groups typically increase the LUMO energy level of fullerenes.55 Therefore, appropriate functionalization strategies provide an effective approach to expand fullerene applications in optoelectronic devices through property optimization.<sup>16</sup>



**Fig. 2** (a) Structural schematic diagram of  $C_{60}$ . (b) Reduction of  $C_{60}$  in CH<sub>3</sub>CN/toluene at -10 °C using cyclic voltammetry at a 100 mV/s scan rate and differential pulse voltammetry (50-mV pulse, 50-ms pulse width, 300-ms period, 25 mV/s scan rate).<sup>41</sup> Copyright 1992, American Chemical Society.

# 3. Electron Transporting Layer

The electron transport layer plays a crucial role in perovskite solar cells by promoting charge-carriers transport and extraction.<sup>56</sup> Electron transport materials (ETMs) for ETL are broadly classified into two fundamental categories based on their composition - inorganic and organic materials.<sup>57, 58</sup> Inorganic ETMs, particularly metal oxides such as titanium dioxide (TiO<sub>2</sub>), zinc oxide (ZnO), and tin dioxide (SnO<sub>2</sub>), are predominantly employed in regular PSCs due to their excellent energy band alignment with perovskite, higher thermal and

long-term stability.<sup>59-61</sup> However, they typically require hightemperature processing and exhibit inherent instability under UV illumination, 62-64 which significantly limit device performance enhancement. In contrast, organic ETMs represented by fullerenes and their derivatives have demonstrated extensive applicability in inverted PSCs.<sup>65</sup> The widespread adoption of fullerene-based ETMs stems from four special advantages: (1) their superior electron affinity combined with high charge carrier mobility enables efficient interfacial electron selectivity and extraction;<sup>66</sup> (2) their excellent solubility in organic solvents permits solution-processable fabrication at low temperatures;<sup>67, 68</sup> (3) their molecularly tunable energy levels allow precise alignment with varied perovskite compositions, thereby suppressing non-radiative recombination while optimizing open-circuit voltage ( $V_{oc}$ ) characteristics.<sup>69</sup>(4) different functional groups of functionalized fullerenes exhibit selective passivation capabilities toward specific defect types in perovskite materials, including undercoordinated ions and interfacial trap states.<sup>16, 70</sup> Therefore, fullerene derivatives employed as ETMs play a critical role in both enhancing device stability and enabling reliable evaluation of photovoltaic performance parameters, thereby sustaining the potential for their continued development in photovoltaic applications.

### 3.1 Fullerene-based ETLs for Inverted PSCs

For the inverted perovskite solar cells, the ETL is positioned above the perovskite layer, which not only serves as a channel for electron transport, but also possesses a certain packaging effect, playing a crucial role in enhancing the PCE and stability of the device.18, 71 Currently, the most popular ETL for the inverted PSCs is fullerenes (mainly C<sub>60</sub>) and its derivatives.<sup>65, 72</sup> In 2013, Guo et al. first used C<sub>60</sub>, [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM) and indene-C<sub>60</sub> bisadduct (ICBA) in inverted CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> devices. Through the hybrid CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite/acceptor planar heterojunction (PHJ) configuration, the cell modified by PCBM delivered a 3.9% PCE.73 Alex et al. also used  $C_{60},\ PCBM$  and ICBA as ETLs to investigate the correlation between the charge-transporting properties of fullerenebased ETLs and photovoltaic performance.74 The energy diagram of each layer in devices was shown in Fig. 3a. The PCEs of the fullerenederived PSCs (8.06% for ICBA, 13.37% for PCBM, and 15.44% for  $C_{60}$ ) followed the trend of increased electron mobility in the fullerene layer ( $6.9 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for ICBA,  $6.1 \times 10^{-2}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for PCBM, and 1.6  $\mbox{cm}^2\,\mbox{V}^{\mbox{-1}}\,\mbox{s}^{\mbox{-1}}$  for  $C_{60}\mbox{)},$  which demonstrated that high-mobility fullerenes can effectively promote charge dissociation/transport in the devices. Despite the high electrical conductivity and electron mobility of C<sub>60</sub>, the strong  $\pi$ - $\pi$  interaction among the molecules results in poor solubility in common solvents.75 Thus, it is difficult to obtain a uniform film by solution treatment methods such as spin coating.<sup>76</sup> At present, C<sub>60</sub> is mostly deposited by vacuum thermal evaporation method which inevitably raises the equipment/material costs and complicates the advanced design of high-throughput production lines for commercialization.<sup>56</sup> Some research in pure C<sub>60</sub> ETLs were poised to address their solubility and processing challenges, potentially through the application of novel coating techniques that could simplify device fabrication while maintaining the high-performance characteristics of these materials.<sup>77, 78</sup> In 2023, Yang et al. obtained solution-processed C<sub>60</sub>-bowlene (CC) films through the ball-bowl interaction between  $C_{60}$  and bowlene.<sup>79</sup> The

# supramolecular assembly between these molecules significantly improved the morphology stability of the films, and effectively enhanced the electron transfer between CC film and perovskite. The final device achieved an excellent PCE of 21.69% and a $T_{90}$ (90% of initial PCE) lifetime of 1000 hours under continuous illumination. In addition to improving film formation by adding other molecules to

ARTICLE

final device achieved an excellent PCE of 21.69% and a  $T_{90}$  (90% of initial PCE) lifetime of 1000 hours under continuous illumination. In addition to improving film formation by adding other molecules to interact with pure fullerenes, the researchers also improved its solubility by functionalizing fullerene to feature specific functional groups.<sup>80</sup> This enabled processing with solution-based methods such as spin-coating, spray, or blade coating. PCBM is one of the most widely used fullerene derivatives with better solubility in common solvents than C<sub>60</sub>, making it suitable for spin coating and reducing costs.<sup>16, 81</sup> In 2014, Huang et al. demonstrated that the trap states on the surface and grain boundaries of the perovskite materials to be the origin of photocurrent hysteresis and that PCBM deposited on perovskites can effectively passivate these charge trap states and eliminate the notorious photocurrent hysteresis.<sup>82</sup> The device exhibited an enhancement of the PCE to 14.9%. Subsequent to the optimization of the process, there was a gradual increase in the efficiency of PCBM as a ETL in the inverted PSCs to 19.4% in 2016.83 Despite the fact that PCBM demonstrates excellent solubility, its inherently low conductivity imposes limitations on the performance of the device. Consequently, researchers have sought to address these issues by doping PCBM with other molecules.<sup>65, 84</sup> In 2024, Zang et al. induced tetramethylthiuram disulfide (TMDS) into the PCBM solution to induce the formation of reducing sulfur radicals through UV light irradiation, allowing for n doping of the PCBM material.<sup>85</sup> A schematic illustration of the mechanism is shown in Fig. 3b. The resulting modified PCBM layer exhibited enhanced conductivity and electron mobility, significantly suppressing charge recombination. As a result, the resulting devices incorporating TMDS achieved a champion efficiency of 26.10% (certified 25.39%) and 24.06% at a larger area (1.0 cm<sup>2</sup>) with negligible hysteresis. While improving the efficiency of the device, PCBM has the disadvantage of photothermal induced dimerization, resulting in uneven condition of the formed ETL layer under light, which is difficult to cover the perovskite layer below completely, resulting in reduced battery performance.<sup>86, 87</sup> Therefore, Wei et al. modified a phenyl group on the basis of PCBM to yield a new ETM, [6,6]- Phenyl -C<sub>61</sub>- butyric acid benzyl ester (PCBB).<sup>88</sup> Self-aggregation of the derivatives was effectively inhibited, and the corresponding device showed significantly improved stability, maintaining approximately 90% of its initial efficiency after 600 hours of solar irradiation at the maximum power point tracking.

In addition to PCBM, a variety of novel fullerene derivatives have been synthesized and used to prepare the ETL of inverted PSCs, to achieve better energy level matching and better defect passivation effect by using functionalized groups.<sup>89, 90</sup> Furthermore, they are thought to enhance electron extraction capabilities, thereby facilitating enhanced interfacial electron transport. In 2019, Yang et al. obtained a new fullerene derivative PDI-C<sub>60</sub> by functionalizing PDI and C<sub>60</sub>, which obtained a more matched energy level with perovskite, which was favorable for charge extraction and transfer, so that the PCE of the prepared device reached 18.6%.<sup>91</sup> In 2021, Hong et al. used two solution-processable azahomofullerene (AHF) derivatives (abbreviated as AHF-1 and AHF-2) as novel and effective ETLs in inverted PSCs.<sup>92</sup> AHF is prepared through the functionalization of fullerenes with organic azides, and the nitrogen

atom is positioned between five- and six-membered carbon rings within an open-cage framework.93-95 Compared to the PCBM-based devices, the AHF-based devices exhibited higher photovoltaic performance, which was attributed to enhanced charge transport performance and improved film morphology, with the AHF-2-based device achieving a maximum PCE of 20.21%. In addition, due to the better energy band alignment with the perovskite layer, reduced trap states, and suppressed charge recombination, devices based on AHF-2 exhibited significantly suppressed hysteresis and improved stability under both ambient and thermal conditions. In 2022, Zhan et al. designed a series of fullerene derivatives with a terpyridine chelating group via a flexible alkyl chain of varying lengths as spacer, FP-Cn (n = 4, 8, 12), to replace PCBM as ETL.<sup>96</sup> As shown in Fig. 3c, FP-C8 showed the most enhanced molecule ordering and adhesion with the perovskite surface due to the balanced decoupling between the chelation effect from terpyridine and the self-assembly of fullerene, leading to lower energy disorder and higher morphological stability relative to PCBM. In the inverted PSCs with FAPbI3 as the light absorber, the FP-C8-based device had a PCE of 23.08% and maintained 96% of the original efficiency after 1200 hours of operation. In 2023, Chen et al. developed fulleropyrrolidine (FMG)

with a polyether chain as an electron transport layer. Its multi-groups simultaneously passivated PSCs via Lewis acid-base and hydrogen bonding interactions.<sup>97</sup> As shown in Fig. 3d, the coating of FMG onto perovskite interestingly yielded a dense and interactive layer with the graded electron transport materials and perovskite heterojunction architecture, resulting in a 23.8% championship efficiency. In the same year, Chen et al. developed thermally stable fullerene-indanone derivatives (FIDOs) featuring tert-butyl groups, which induced amorphous film formation via steric hindrance (Fig. 3e), enabling the first evaporated fullerene-based ETM.98 Based on this ETL, the PCE of devices reached 22.11%. Recently, Li et al. combined non-fullerene receptor (NFA) fragments with C<sub>60</sub>, effectively improving the solubility of derivatives, which was conducive to obtaining uniform ETL by solvent treatment.<sup>99</sup> In addition, through the accumulation of NFA and C<sub>60</sub> shown in Fig. 3f, the self-polymerization of C<sub>60</sub> was reduced, thus improving the electron extraction ability and passivating the defects on perovskite. The optimal PCE reached 25.3%, and after 1500 hours of aging at 85°C in N2, the PCE retained nearly 90% of the initial value, significantly improving device stability.



**Fig. 3** (a) Device configuration of the PHJ PSCs, the chemical structures of the n-type fullerene derivatives and the energy diagram of each layer in devices.<sup>74</sup> Copyright 2015, Wiley-VCH. (b) Formation of sulfur radicals and n-doping mechanism of PCBM.<sup>85</sup> (c) Schematic illustration of the interfacial interactions between the perovskite and PCBM (left) or FP-C8 (right).<sup>96</sup> Copyright 2022, American Chemical Society. (d) Schematic illustration of passivation groups of PCBM and FMG to perovskite.<sup>97</sup> Copyright 2023, Science China Press. (e) Schematic of intermolecular interactions between fullerenes C<sub>60</sub> and tBu-FIDO.<sup>98</sup> Copyright 2023, American Chemical Society. (f) Schematic diagram of C<sub>60</sub> and BTPC<sub>60</sub> film preparation.<sup>99</sup> Copyright 2024, Wiley-VCH.

In addition to passivating defects, matching energy levels, and enhancing interfacial transport, fullerene derivatives are demonstrating to enhance the stability of the PSCs markedly by introducing cross-linked groups. These cross-linked fullerene derivatives with strong electron extraction capability and superior solvent-resistance can achieve uniform coverage over the perovskite layer to simultaneously reduce the penetration of water and oxygen, thereby enhancing the long-term operational stability of the inverted PSCs. <sup>26, 100, 101</sup> Huang et al. reported a specific crosslinked ETL by bonding cross-linkable silane coupling agent, which have hydrophobic functional groups onto C<sub>60</sub>-substituted benzoic acid self-assembled monolayer (C<sub>60</sub>-SAM) to make the fullerene layer have high waterproof performance, as shown in Fig. 4a.<sup>102</sup> The PCE of the device reached 19.5%, and the FF was as high as 80.6%. Moreover, the water and humidity stability of the unencapsulated device was effectively improved with the original efficiency of nearly 90% maintaining after 30 days of exposure in the environment. Chen et al. developed a new type of ETM, PFBS-C12, by polymerizing C<sub>60</sub> with an aromantic linker unit.<sup>103</sup> It not only maintained the good photoelectric performance of fullerene, but also solved the selfaggregation problem. The PCE of the device was as high as 23.2%, and the initial efficiency of 96% can be maintained after 1300 hours of light immersion. As demonstrated in Fig. 4b, Wei et al. designed a novel cross-linkable fullerene molecule, bis((3-methyloxetan-3yl)methyl) malonate-C<sub>60</sub> monoadduct (BCM) as an ETL in PSCs.<sup>104</sup> BCM underwent in-situ cross-linking to form a robust crosslinked

BCM (CBCM) film, which demonstrated excellent electron mobility and a suitable band structure for efficient PSCs. The intramolecular covalent interactions within CBCM films effectively prevented aggregation and enhanced film compactness, creating an internal encapsulation layer that mitigated the decomposition and ion migration of perovskite components. Consequently, CBCM-based PSCs were more stable than PCBM-based PSCs, maintaining 97.8% of their initial efficiency after 1000 hours of maximum power point tracking.

The alteration of the functional groups of functionalized fullerenes has been demonstrated to engender divergent passivation effects, modify electron mobility, and influence the arrangement of energy levels to impact the performance of PSCs.<sup>16, 69, 105, 106</sup> Moreover, the isomerism of fullerene-based ETM also has a significant impact on the performance of PSCs.<sup>107-109</sup> Yang et al. synthesized three novel pyridine-functionalized fullerene derivatives (C<sub>60</sub>-n-Py) whose electron transport properties were found to sensitively depend on the nitrogen site within the pyridine moiety as shown in Fig. 4c.<sup>110</sup> The stronger coordination interaction between the pyridine moiety and the  $Pb^{2+}$  ion for the C<sub>60</sub>-3-Py-based device led to reinforced passivation of the trap state within the perovskite film, affording improved device performance and ambient stability of the C<sub>60</sub>-3-Py device. Hence, The C<sub>60</sub>-3-Py-based device showed the highest PCE of 17.57%, surpassing those of C<sub>60</sub>-2-Py- and C<sub>60</sub>-4-Py-based devices (12.79% and 16.51%, respectively). Since most fullerene derivatives exist in the form of isomer mixtures when applied, the effect on the



Fig. 4 (a) Device structure of the perovskite planar heterojunction solar cells and schematic illustration for the crosslinking of C<sub>60</sub>-SAM with silane-coupling agent.<sup>102</sup> (b) Schematic diagram of PCBM and CBCM films on the perovskite layer.<sup>104</sup> Copyright 2024 Wiley-VCH. (c) The crystal structure and corresponding molecular packing of  $C_{60}$ -2-Py,  $C_{60}$ -3-Py, and  $C_{60}$ -4-Py.<sup>110</sup>

PSCs of fullerene-based ETL is unclear. Based on this, Kong et al prepared inverted PSCs by using bis [60] phenyl-C61-butyric acid methyl ester derivative (anti)16, 17-bis [60] PCBM and compared the performance of enantiomerically pure material to the corresponding racemate.<sup>111</sup> The enantiomerically pure ETL demonstrated a higher electron extraction rate and improved electron mobility while more effectively suppressing ion migration, enabling the resultant PSCs to achieve a promising PCE of 23.2% and superior operational stability compared with the racemate-based devices. In addition, Wei et al. synthesized and isolated four well-defined regional isomers (trans-2, trans-3, trans-4, and e) of diethylmalonate-C<sub>60</sub> bisadduct (DCBA) for

ETL of tin-based inverted PSCs.<sup>112</sup> They found that the chemical structures of the regioisomers not only affect their energy levels, but also lead to significant differences in their molecular packings and interfacial contacts. The trans-3-based device achieved the best certified efficiency at 14.30%. Subsequently, the same group synthesized single-isomer  $C_{60}\text{-}$  and  $C_{70}\text{-}based$  diethylmalonate functionalized bisadducts (C<sub>60</sub>BB and C<sub>70</sub>BB) by utilizing the sterichindrance-assisted strategy to save time and cost of separation.<sup>113</sup> Through solvent engineering, C<sub>60</sub>BB- and C<sub>70</sub>BB-based tin-based PSCs showed impressive efficiencies up to 14.51 and 14.28%, respectively.

Compound	LUMO/HOM Oª (eV)	Electron mobility (cm <sup>2</sup> V <sup>-1</sup> s <sup>-</sup> <sup>1</sup> )	Device structure	V <sub>oc</sub> (V)	FF (%)	J <sub>sc</sub> (mA cm <sup>-2</sup> )	PCE (%)	Ref
C <sub>60</sub>	-4.5/-6.2	-	ITO/PEDOT:PSS/MAPbl <sub>3</sub> /C <sub>60</sub> /BCP/Al	0.55	61	9.02	3.0	73
PCBM	-3.9/-5.9	-	ITO/PEDOT:PSS/MAPbl <sub>3</sub> /PCBM/BCP/Al	0.60	63	10.32	3.9	73
ICBA	-3.7/-5.6	-	ITO/PEDOT:PSS/MAPbI <sub>3</sub> /ICBA/BCP/AI	0.58	58	10.03	3.4	73
C <sub>60</sub>	-3.9/-5.6	1.6	ITO/PEDOT:PSS/MAPbI <sub>3</sub> /C <sub>60</sub> /Bis-C60/Ag	0.92	80	21.07	15.44	74
PCBM	-3.8/-5.9	6.1×10 <sup>-2</sup>	ITO/PEDOT:PSS/MAPbI <sub>3</sub> /PCBM/Bis-C60/Ag	0.89	80	18.85	13.37	74
ICBA	-3.6/-5.6	6.9×10 <sup>-3</sup>	ITO/PEDOT:PSS/MAPbI <sub>3</sub> /ICBA/Bis-C60/Ag	0.95	75	11.27	8.06	74
C <sub>60</sub> - corannulen e (CC)	-4.62/-6.40	(5.87±0.27 ) ×10 <sup>-4</sup>	(ITO)/NiO <sub>x</sub> /PTAA/Cs <sub>0.05</sub> (FA <sub>0.95</sub> MA <sub>0.05</sub> ) <sub>0.95</sub> Pb(I <sub>0.9</sub> <sub>5</sub> Br <sub>0.05</sub> ) <sub>3</sub> /ETL/BCP/Ag	1.09	81	24.43	21.69	79
PCBM	-	10 <sup>-3</sup>	ITO/PTAA/MAPbI <sub>3</sub> /PCBM/C <sub>60</sub> /BCP/AI	1.13	75	22.6	19.4	82
PCBM+TMD S	-4.06/-6.22	2.4 × 10 <sup>-3</sup>	ITO/NiO <sub>x</sub> /PTAA/Al <sub>2</sub> O <sub>3</sub> /FA <sub>0.95</sub> Cs <sub>0.05</sub> Pbl <sub>3</sub> /ETL/BC P/Ag	1.182	84.7	26.07	26.10	85
РСВВ	-3.90/-5.62	$3.09 \times 10^{-4}$	FTO/NiO <sub>x</sub> /Cs <sub>0.05</sub> FA <sub>0.79</sub> MA <sub>0.16</sub> Pb(I <sub>0.85</sub> Br <sub>0.15</sub> ) <sub>3</sub> /ETL /BCP/Ag	1.08	80.3 9	22.85	19.84	88
PDI-C <sub>60</sub>	-3.96/-5.40	8.76 × 10 <sup>-4</sup>	ITO/P3CT-Na/MAPbl <sub>3</sub> /ETLs/BCP/Ag	1.061	79.2	22.1	18.6	91
AHF-1	-4.01/-5,89	1.7	FTO/PTAA/Cs <sub>0.5</sub> (MA <sub>0.17</sub> FA <sub>0.83</sub> ) <sub>0.95</sub> Pb(I <sub>0.83</sub> Br <sub>0.17</sub> ) <sub>3</sub> /ETL/ BCP/Au	1.097	22.9 5	75.43	19.50	92
AHF-2	-4.13/-6.0	2.5	FTO/PTAA/Cs <sub>0.5</sub> (MA <sub>0.17</sub> FA <sub>0.83</sub> ) <sub>0.95</sub> Pb(I <sub>0.83</sub> Br <sub>0.17</sub> ) <sub>3</sub> /ETL/ BCP/Au	1.115	23.0 3	76.31	20.21	92
FP-C4	-4.08/-	$3.4 \times 10^{-4}$	Br/Cs <sub>0.05</sub> FA <sub>0.90</sub> MA <sub>0.05</sub> Pbl <sub>2.85</sub> Br <sub>0.15</sub> /ETL/C <sub>60</sub> /BCP/ Ag	1.07	68.7 0	22.92	16.90	96
FP-C8	-4.15/-	4.9 × 10 <sup>-3</sup>	ITO/PTAA/PFN- Br/Cs <sub>0.05</sub> FA <sub>0.90</sub> MA <sub>0.05</sub> PbI <sub>2.85</sub> Br <sub>0.15</sub> /ETL/C <sub>60</sub> /BCP/ Ag	1.10	82.7 6	23.83	21.69	96
FP-C12	-4.17/-	2.6 × 10 <sup>-3</sup>	ITO/PTAA/PFN- Br/Cs <sub>0.05</sub> FA <sub>0.90</sub> MA <sub>0.05</sub> PbI <sub>2.85</sub> Br <sub>0.15</sub> /ETL/C <sub>60</sub> /BCP/ Ag	1.09	81.3 5	23.36	20.71	96
FMG	-	-	ITO/NiO <sub>x</sub> /(Cs <sub>0.05</sub> FA <sub>0.95</sub> Pbl <sub>3</sub> ) <sub>0.97</sub> (MAPbBr <sub>3</sub> ) <sub>0.03</sub> /E TM/BCP/ Ag ITO/NiO./Me-4PCA7/	1.16	83.2	24.7	23.8	97
tBu-FIDO	-3.95/-5.85	-	Cs <sub>0.04</sub> (FA <sub>0.95</sub> MA <sub>0.05</sub> ) <sub>0.96</sub> Pb(I <sub>0.95</sub> Br <sub>0.05</sub> ) <sub>3</sub> )/ETL/BCP /Ag	1.16	77	24.84	22.11	98
BTPC <sub>60</sub>	-3.80/-5.60	1.02×10 <sup>-3</sup>	н 0/ме0-2РАС2+4РАДВС/ Cs <sub>0.05</sub> (FA <sub>0.98</sub> MA <sub>0.02</sub> ) <sub>0.95</sub> Pb(I <sub>0.98</sub> Br <sub>0.02</sub> ) <sub>3</sub> /ETMs/BC P/Ag	1.18	84.0	25.5	25.3	99

6 | J. Name., 2012, 00, 1-3

This journal is © The Royal Society of Chemistry 20xx

**Journal Name** 

doped crosslinked				4.07	00.0	22.6	10 5	102
C <sub>60</sub> -SAM (CLCS)	-	-	IIU/PIAA/MAPDI3/EIM/BCP/CU	1.07	8U.b	22.6	19.2	102
PFBS-C12	-3.95/-5.96	3.5× 10 <sup>-4</sup>	ITO/PTAA/MA <sub>0.7</sub> FA <sub>0.3</sub> PbI <sub>3</sub> /ETL/BCP/Cu	1.16	82.9	24.1	23.2	103
CBCM	-3.97/-5.72	3.89×10 <sup>-4</sup>	ITO/NiO <sub>x</sub> /Me- 4PACz/Cs <sub>0.05</sub> (FA <sub>0.98</sub> MA <sub>0.02</sub> ) <sub>0.95</sub> PbI <sub>3</sub> /CBCM/BCP/ Ag	1.183	84.4 5	25.93	25.89	104
C <sub>60</sub> -2-Py	-3.78/-5.51	1.02×10 <sup>-3</sup>	FTO/NiO <sub>x</sub> /MAPbI <sub>3</sub> /ETL/BCP/Ag	0.95	64.6 7	20.45	12.68	110
C <sub>60</sub> -3-Py	-3.80/-5.51	2.95×10 <sup>-3</sup>	FTO/NiO <sub>x</sub> /MAPbI <sub>3</sub> /ETL/BCP/Ag	1.02	76.4 2	22.46	17.57	110
C <sub>60</sub> -4-Py	-3.81/-5.52	2.64×10 <sup>-3</sup>	FTO/NiO <sub>x</sub> /MAPbI <sub>3</sub> /ETL/BCP/Ag	1.00	74.2 0	22.85	16.83	110
Pure (anti)16,17- bis[60]PCB M	-3.970/-5.67 3	3.1×10⁻³	ITO/PTAA/FAPbI <sub>3</sub> /ETM/BCP/Cu	1.15	80	25.2	23.2	111
Racemate (anti)16,17- bis[60]PCB M	-3.970/-5.67 3	1.2×10 <sup>-3</sup>	ITO/PTAA/FAPbI <sub>3</sub> /ETM/BCP/Cu	1.11	75	24.2	20.1	111
DCBA (trans-2)	-3.88/-5.53	6.81×10 <sup>-5</sup>	ITO/PEDOT:PSS/PEA <sub>0.15</sub> FA <sub>0.85</sub> SnI <sub>3</sub> /ETL/BCP/Ag	0.73	75.5 1	21.17	11.69	112
DCBA (trans-3)	-3.71/-5.41	1.03×10 <sup>-4</sup>	ITO/PEDOT:PSS/PEA <sub>0.15</sub> FA <sub>0.85</sub> SnI <sub>3</sub> /ETL/BCP/Ag	0.90	75.7 0	21.39	14.58	112
DCBA (trans-4)	-3.74/-5.48	3.54×10 <sup>-5</sup>	ITO/PEDOT:PSS/PEA <sub>0.15</sub> FA <sub>0.85</sub> SnI <sub>3</sub> /ETL/BCP/Ag	0.84	71.9 1	20.89	12.59	112
DCBA (e)	-3.70/-5.41	2.47×10 <sup>-5</sup>	ITO/PEDOT:PSS/PEA <sub>0.15</sub> FA <sub>0.85</sub> SnI <sub>3</sub> /ETL/BCP/Ag	0.75	70.2 9	20.07	10.55	112
C <sub>60</sub> BB	-3.70/-5.41	1.031×10 <sup>-4</sup>	ITO/PEDOT:PSS/PEA <sub>0.15</sub> FA <sub>0.85</sub> Snl <sub>3</sub> /C <sub>60</sub> BB/BCP/ Ag	0.81	71.8 4	25.08	14.51	113
C <sub>70</sub> BB	-3.74/-5.37	0.937×10 <sup>-4</sup>	ITO/PEDOT:PSS/PEA <sub>0.15</sub> FA <sub>0.85</sub> SnI <sub>3</sub> /C <sub>60</sub> BB/BCP/ Ag	0.80	71.5 0	24.92	14.28	113

<sup>a</sup> Highest Occupied Molecular Orbital (HOMO), Lowest Unoccupied Molecular Orbital (LUMO)

# 3.2 Fullerene-based ETLs for Regular PSCs

The electron transport layer in regular PSCs, primarily composed of inorganic oxides such as ZnO, TiO<sub>2</sub>, and SnO<sub>2</sub>, faces challenges including complex fabrication processes, prevalent oxygen vacancy defects, and significant hysteresis.59, 114 The incorporation of fullerene derivatives as ETL has been shown to effectively mitigate hysteresis and enhance defect passivation, thereby facilitating the fabrication of efficient and stable PSCs.<sup>115, 116</sup> In comparison with inorganic oxide ETL, fullerene derivatives possess certain flexibility and tensile properties, which renders them a suitable candidate for utilization in regular PSCs. In 2016, Choi et al. prepared C<sub>60</sub> layer on ITO/ glass substrate through thermal evaporation in a vacuum environment as ETL, controlling the thickness of the C<sub>60</sub> layer to 35 nm, which not only passivated the grain boundary and surface of perovskite layer, but also enhanced the charge transport performance, thus eliminating the photocurrent lag and improving the efficiency of the battery.<sup>117</sup> In 2017, Fang et al. used carboxylfunctionalized carbon buckyballs,  $C_{60}$  pyrrolidine tris-acid (CPTA), to anchor onto the surface of ITO(Fig. 5a), significantly suppressing hysteresis and enhancing the flexural strength in the CPTA-modified PSCs.<sup>118</sup> The best device yielded a PCE of 18.39% on ITO/ glass

substrate and 17.04% on flexible substrates. They also showed longterm stability of more than 100 days and exhibited excellent durability against mechanical bending over 1000 times. In 2019, Zheng et al. synthesized a novel pyridine functionalized fullerene derivative [6,6]- (4-pyridyl) -C<sub>61</sub>-ethyl acetate (PyCEE), which exhibited high electron mobility and suitable energy levels that matched those of perovskite. A PCE of 18.27% was obtained through the interaction of pyridine with uncoordinated lead ions and passivation defects as shown in Fig. 5b.<sup>119</sup> In 2024, Egelhaaf et al used fullerene self-assembled monolayer (SAM), FAPA, with phosphoric acid anchor group as an interface dipole for electron selective contact and hole selective contact in fully printed PSCs.120 This contact layer provided good charge selectivity and minimized the interface recombination of the bottom electrode. Therefore, the PCE losses from rigid substrate to flexible substrate and from flexible battery (0.1 cm<sup>2</sup>) to flexible module (20.25 cm<sup>2</sup>) were significantly reduced.

In regular devices, ETL is located on the light-incidence side, meaning it is required to have a certain photothermal stability.<sup>58</sup> However, common fullerene-based ETM (e.g. PCBM) tend to aggregate under photothermal conditions,<sup>121</sup> which can adversely affect the quality and stability of the perovskite films. Furthermore, fullerene derivatives exhibit a certain degree of solubility in the solvents

**ARTICIF** 

# Journal Name

employed for the perovskite precursor solution, which can result in the degradation of the fullerene-based ETL during the subsequent deposition process, thereby degrading device performance.<sup>122</sup> Crosslinked fullerene derivatives not only inhibit the tendency of selfaggregation,<sup>123</sup> but also enhance the solvent resistance,<sup>124</sup> thereby stabilizing fullerene-based ETL and enhancing the efficiency and stability of the devices, representing a promising prospect for development in regular PSCs. In 2016, Snaith et al. used two crosslinked fullerene derivatives Solgel- $C_{60}$  and PCBCB to prepare ETL respectively (Fig. 5c), and demonstrated that the cross-linked derivative films could effectively resist N,N-dimethylformamide (DMF) and chlorobenzene cleaning, thereby obtaining uniform ETL films with controllable thickness, improving the electron extraction ability, and the highest PCE was close to 18%.<sup>125</sup> In 2017, Petrozza et

al. obtained a robust self-assembled monomolecular fullerene ETL by covalently combining a self-assembled siloxane-functionalized fullerene molecule (Sil-C60) with FTO, which was shown in Fig. 5d.<sup>126</sup> This method not only eliminated the need for high-temperature processing and increased the stability of the device against UV irradiation but also greatly simplified large-scale deposition. The final device reached 15% of stabilized PCE and showed unaffected performance after 67 h of UV light exposure. In 2018, Gervaldo et al. used the electropolymerization method to form the C<sub>60</sub>-EDOT film on the FTO electrode and realized electron extraction from perovskite to C<sub>60</sub>.<sup>127</sup>Although the PCE of the device was only 11%, it demonstrated a new approach in the fabrication of efficient energy conversion systems.



Fig. 5 (a) Schematic device structure of planar PSCs with CPTA as the ETL.<sup>118</sup> Copyright 2017, Wiley-VCH. (b) Schematic illustration of the interfacial interactions between the perovskite and PyCEE.<sup>119</sup> Copyright 2019, American Chemical Society. (c) Schematic illustration of the connection of Solgel-C<sub>60</sub> and PCBCB on FTO.<sup>125</sup> Copyright 2016, American Chemical Society. (d) Illustration of the fullerene self-assembled monolayer (Sil-C60) fabrication process, involving the covalent anchoring of Sil-C60 on an oxygen plasma-activated FTO substrate.<sup>126</sup>

Table 2 D	evice perfo	rmance of PSCs wi	th fullerene-based ETL in the regular PSCs					
Compo und	LUMO/ HOMO (eV)	Electron mobility (cm² V <sup>-1</sup> s <sup>-1</sup> )	Device structure	V <sub>oc</sub> (V)	FF (%)	J <sub>sc</sub> (mA cm <sup>-2</sup> )	PCE (%)	Ref
0	4 5 /6 2	1.6	ITO/C <sub>60</sub> /MAPbI <sub>3</sub> /spiro-OMeTAD/Au	1.1	74.0	23.7	19.1	117
C <sub>60</sub>	4.5/0.2	1.0	PEN/ITO/C₀₀/MAPbl₃/spiro-OMeTAD/Au	1.02	67.33	23.21	16.00	
CPTA	3.9/5.7	5.4 × 10 <sup>-3</sup>	ITO/CPTA/MAPbl₃/spiro-OMeTAD/Au	1.10	75.61	22.06	18.39	118

This journal is C The Royal Society of Chemistry 20xx

			ITO/PET/CPTA/MAPbI₃/spiro-OMeTAD/Au	1.091	73.13	21.35	17.04	
	-3.94/-		FTO/ETL/MAPbI <sub>3</sub> /spiro-OMeTAD/Ag	1.05	75.83	22.95	18.27	119
PyCEE	5.67	-	PEN/ITO/ETL/Cs <sub>0.1</sub> (FA <sub>0.83</sub> MA <sub>0.17</sub> ) <sub>0.9</sub> Pb(I <sub>0.83</sub> Br <sub>0.17</sub> ) <sub>3</sub> /sp iro-OMeTAD/Au	1.09	69.55	20.11	15.25	
	-3.68/-		$ITO/FAPA/Cs_{0.7}FA_{0.63}MA_{0.3}PbI_{2.79}I_{0.21}/FAPA/Carbon$	1.11	73.1	22.9	18.6	120
FAPA	5.78	-	PET-IMI/FAPA/Cs <sub>0.05</sub> FA <sub>0.75</sub> MA <sub>0.2</sub> PbBr <sub>0.3</sub> I <sub>2.7</sub> /FAPA/Carbon	1.10	68.0	21.5	16.3	-
Sol-gel C <sub>60</sub>	-3.85/-	3.8 × 10 <sup>-4</sup> ± 0.5 × 10 <sup>-4</sup> a	FTO/ETL/CH <sub>3</sub> NH <sub>3</sub> Pbl <sub>3x</sub> Cl <sub>x</sub> /spiro-OMeTAD/Au	1.07	73	23.0	17.9	125
PCBCB	-	5.9 × 10 <sup>-3</sup> ± 1.8 × 10 <sup>-3 a</sup>	FTO/ETL/CH <sub>3</sub> NH <sub>3</sub> Pbl <sub>3x</sub> Cl <sub>x</sub> /spiro-OMeTAD/Au	1.11	73	22.4	17.9	125
Sil-C60	-3.51/- 6.04	-	FTO/ETL/Cs <sub>0.05</sub> FA <sub>0.75</sub> MA <sub>0.2</sub> PbBr <sub>0.3</sub> I <sub>2.7</sub> /spiro- OMeTAD/Au	1.04	74	19.4	15.2	126
EDOT- C <sub>60</sub>	-4.09/-	-	FTO/ETL/CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> /spiro-OMeTAD/Au	0.969	65	17	11.0	127
EDOT- C <sub>60</sub>	6.04 -4.09/-	-	OMeTAD/Au FTO/ETL/CH <sub>3</sub> NH <sub>3</sub> Pbl <sub>3</sub> /spiro-OMeTAD/Au	0.969	65	17	11.0	12

a The Electron mobility of the fullerene after cross-linking





# 4. Fullerene-based HTMs for PSCs

Functional fullerenes are generally considered to be excellent electron transporters and excellent hole blockers.<sup>65</sup> However, the charge transport properties of fullerenes have been shown to be intrinsically ambipolar<sup>128</sup>, and chemical modification can be used to reduce the intrinsically high ionization values of C<sub>60</sub> and C<sub>70</sub> to achieve a better match with the work function of the common electrode, and to promote the hole injection.<sup>129, 130</sup> Compared to conventional hole transport materials (HTMs) such as Spiro-OMeTAD, fullerene-based HTMs exhibit distinct advantages, including: (1)inherent hydrophobicity that enhances the long-term stability of devices under humid conditions;<sup>131</sup> (2)dopant-free operation to eliminate the need for hygroscopic dopants (e.g., Li-TFSI) that cause degradation;<sup>132</sup> (3)functionalized moieties that effectively passivate surface defects in perovskite layers.<sup>133, 134</sup> These merits position fullerene-based HTMs as promising candidates for further development in PSCs.

In 2018, Delgado et al. synthesized a new hole-transporting fullerene material, FU7, and for the first time used fullerene materials as HTL in PSCs.132 FU7 is a hexa-additive derivative obtained by functionalizing 12 "super triarylamine" fragments outside the fullerene cell. The HOMO and LUMO values of FU7 are 5.04 eV and 3.50 eV respectively, and the electron affinity of FU7 is significantly reduced, showing p-type semiconductor properties. Consequently, FU7 is deemed suitable for utilization as HTM. The presence of  $C_{60}$ played a structural role in the FU7, facilitating charge separation, ensuring efficient transport, and maintaining structural order, resulting in higher device performance compared with the chemical precursor of FU7 which did not contain fullerene. When FU7 was used as the HTL without any other additives, PCE had been shown to achieve 0.77 times the average PCE of reference cells prepared with doped spiro-OMeTAD (0.81 times for champion devices), while demonstrating higher stability. In addition, efficient "fullerene sandwich" PSCs were prepared with both selective contacts being fullerene-based materials, resulting in a PCE close to 9%. Six years later, the same group introduced optical cross-linking technology to fullerene-based HTM to produce a new material FT12 with 12  $\pi$ -

extended triarylamine units and two additional functional groups, comprising tetraethylene glycol and allyl moieties.135 The introduction of an allyl group has been shown to facilitate the crosslinking process with the introduced mercaptan pentaerythritol tetris (3-mercaptopropionic acid) (PETMP) under light conditions, thereby yielding the photo-cross-linked polycaprolactone (PCL FT12). This process demonstrated to be advantageous in achieving a more uniform and smoother surface. In addition, UV irradiation caused partial oxidation of the triphenylamine group, which improved the hole transport performance. The final device PCE reached 15.5% and the device stability is significantly improved compared to devices with doped spiro-OMeTAD, due to the hydrophobicity of FT12 and PCL FT12. Similarly, Wei et al. synthesized a new fullerene-based hole transport molecule (FHTM) and applied it as a modified layer to the NiO<sub>x</sub>/ perovskite interface of inverted PSCs.<sup>136</sup> The in situ self-doping effect caused by electron transfer between carbazole and  $C_{60}$  and the extended  $\pi$ -conjugated part of the carbazole groups significantly enhanced the hole mobility of FHTM. In addition, the strong

interaction of FHTM with perovskite and NiO<sub>x</sub> was beneficial for passivating defects and promoting uniform nucleation of perovskite, thus producing high-quality perovskite films. With an efficiency of 25.58 %, the device demonstrated significantly enhanced operational stability, maintaining 93% of its initial efficiency after undergoing 1,000 hours of maximum power point tracking under continuous solar illumination exposure.

As demonstrated in the previous literature, fullerene-based HTMs exhibit notable advantages including well-ordered molecular architectures, tunable energy levels and intrinsic stability requiring no stabilizing additives. Nevertheless, the currently reported derivatives mainly involve complex synthesis processes that compromise scalability and practical implementation. Consequently, it is worthwhile to simplify the synthesis scheme to improve repeatability, develop low-cost production strategies without sacrificing performance and explore structural diversity through rational molecular design to produce efficient fullerene-based HTMs in future studies.

Table 3      Device performance of PSCs with fullerene-based HTM in PSCs										
Compound	LUMO/HOMO (eV)	Hole mobility (cm² V <sup>-1</sup> s <sup>-1</sup> )	Device structure	V <sub>oc</sub> (V)	FF (%)	J <sub>sc</sub> (mA cm <sup>-2</sup> )	PCE (%)	Ref		
FU7	-3.50/-5.04	-	FTO/compact-TiO2/mesoporous TiO2/CH3NH3Pbl3/FU7/Au	0.985	67	20.8	13.7	132		
	-3.50/-5.04		$FTO/C_{60}/CH_3NH_3PbI_3$ : C <sub>60</sub> /FU7/Au	0.92	62.5	15.8	9	101		
FT12	-3.36/-5.13	$1.19 \times 10^{-4}$	ITO/C <sub>60</sub> /MAPbI <sub>3</sub> /FT12/Au	1.01	70	19.4	13.7	135		
PCL FT12	-	1.87 × 10 <sup>-4</sup>	ITO/C <sub>60</sub> /MAPbI <sub>3</sub> /PCL FT12/Au	1.00	75	20.8	15.5	135		
FHTM	-1.85/-5.46	5.875 × 10 <sup>-4</sup>	ITO/NiO <sub>x</sub> /FHTM/Cs <sub>0.05</sub> MA <sub>0.05</sub> FA <sub>0.90</sub> PbI <sub>3</sub> /C <sub>60</sub> / BCP/Ag	1.18	83.72	25.82	25.58	136		



FU7

FT12

FHTM

**Fig. 7** Summary of the structures with fullerene-based HTMs of inverted PSCs and regular PSCs.<sup>132, 135, 136</sup> Copyright 2018, Wiley-VCH. Copyright 2024, Wiley-VCH.

# 5. Fullerene-based additives in perovskite active layer

In order to obtain efficient and stable perovskite solar cells, it is essential to ensure optimal film quality and charge transport characteristics of the perovskite layer.137 However, the solutionprocessing nature and rapid crystallization kinetics of perovskite thin films inevitably generate various defects within the bulk phase and grain boundaries. which substantially degrade device performance.<sup>138, 139</sup> Among established defect mitigation strategies, additive engineering emerges as an effective approach to enhance perovskite film quality,<sup>140, 141</sup> modulate energy level alignment,<sup>142</sup> and suppress non-radiative recombination.<sup>143, 144</sup> Notably, fullerene materials, as conventional additives, primarily distribute on perovskite film surfaces and grain boundaries rather than incorporating into the crystal lattice owing to their considerable molecular size.145 This characteristic spatial arrangement allows efficient passivation of surface and grain boundary defects.<sup>32</sup> The intrinsic high conductivity of fullerene additives enhances charge carrier transport through grain boundaries, while their surface localization creates effective interfacial contact with ETL, thereby promoting carrier transfer between the ETL and perovskite phase.<sup>146</sup> Furthermore, fullerene additives provide steric hindrance that physically restricts mobile ion migration along grain boundaries, ultimately improving device operational stability.<sup>147</sup>

In 2014, Sargent et al. firstly introduced PCBM into the perovskite solution as an additive to obtain hybrid solid material containing perovskite-PCBM.145 The distribution of PCBM in the grain boundaries of perovskite was demonstrated through the use of secondary ion mass spectrometry and X-ray diffraction. Furthermore, PCBM effectively passivated the iodine-rich defects on the grain surface and inhibited ion migration, thus significantly reducing hysteresis and recombination loss, and improving device performance. In 2016, Wu et al. prepared a Pbl<sub>2</sub>-PCBM hybrid film by a two-step spin coating method, so as to prepare Bulk heterojunction (BHJ) CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>-PCBM inverted PSCs.<sup>148</sup> By controlling the amount of PCBM in  $PbI_2$  precursor solution and the volume and concentration of MAI/IPA solution, BHJ perovskite-PCBM thin films with larger grains and fewer grain boundaries were prepared, thus obtaining higher conductivity, more balanced electron and hole mobility, and longer charge diffusion length. Ultimately, the FF of inverted heterogeneous perovskite-PCBM solar cells reached 0.82, while the PCE reached 16.0% without obvious photocurrent hysteresis. In the same year, Alex et al. designed  $DF-C_{60}$ , a polyfluoroalkyl functionalized fullerene derivative, and added it into perovskite precursor solution.149 This resulted in the effective passivation of defects in perovskite films, the facilitation of charge extraction in PSCs, and a notable reduction of the hysteresis phenomenon of the device. The champion PCE reached 18.11%. Even in the absence of PCBM as ETL, the DF-C $_{60}$  based PSCs obtained 15.14% PCE with minimal hysteresis. Furthermore, the functionalized polyfluoroalkyl group exhibited strong hydrophobicity, thus significantly improving the environmental stability of the device. Following a storage period of one month in an environment with a relative humidity of 60 ± 5%, the PCE of the device still retained 83% of the original value. In 2019, Hu et al. introduced fullerene-

terminated polyethylene glycol (C60-PEG) as an additive by using the antisolvent method.<sup>150</sup> This resulted in the formation of a thin and uniform C60-PEG film on the surface of the perovskite film, which deactivated the internal and surface defects of perovskite and was beneficial to the formation of larger perovskite grains. The inhibition of non-radiation recombination resulted in a final PCE of 17.71%. Furthermore, the amphiphilicity of C60-PEG enabled the hydrophobic portion to be exposed to air, thereby enhancing the moisture resistance of the device, as shown by the fact that the unpackaged device maintained 93% and 86% of the original PCE value after 40 days under N<sub>2</sub> and ambient conditions (25°C, 60% humidity), respectively. In 2021, Yang et al. synthesized a new fullerene derivative  $C_{60}$ -PyF15 with the functionalization of pyridine and fluorine.<sup>151</sup> As shown in Fig. 8a, the coordination between pyridine and Pb<sup>2+</sup>, and the hydrogen bond between fluorine and MA<sup>+</sup>, resulted in the double passivation of perovskite which led to a reduction in non-radiative recombination. Furthermore, as a heterogeneous nuclear site, the perovskite film was induced to grow along the (110) crystal plane in order to improve the crystallinity of the perovskite film, and the device ultimately achieved a PCE of 20.10%. In the same year, Wei et al. also synthesized a new fullerene derivative (FPD) with three pentafluorophenyl groups.<sup>152</sup> The strong interaction between FPD and the perovskite lattices was shown in Fig. 8b, thereby enhancing the defect passivation effect and preventing the decomposition of perovskite under irradiation. Consequently, the device incorporating FPD exhibited an enhanced efficiency of 23%. Furthermore, it was demonstrated that FPD could in fact realize the in-situ sedimentation of lead ions through the formation of a stable and water-insoluble FPD-Pb complex, thereby providing a novel approach to address the possible environmental problems caused by lead leakage. In 2022, Jeon et al. synthesized fullerene derivatives PC<sub>61</sub>B-TEG and PC<sub>61</sub>B-BiTEG linked to triethylene glycol monomethyl ether chains, which exhibited good solubility in polar solvents.<sup>153</sup> Through a 'spinning and waiting' method, the fullerene derivatives gradually penetrated into the fullerene-doped perovskite active film, resulting in a vertical concentration gradient (Fig.8c), which effectively passivated the perovskite defect site and enhanced charge transfer. The device efficiency finally reached 23.34%. Peng et al. used a high electron mobility self-healing polymer (C<sub>60</sub>-PU) as a perovskite additive.<sup>154</sup> C<sub>60</sub>-PU effectively regulated the nucleation and crystallization of perovskite crystals, decreased the trap states and carrier recombination, and accelerated the charge transfer, resulting in an improved PCE of 21.36%. Moreover, the dynamic disulfide bonds in C<sub>60</sub>-PU repaired the perovskite film defects formed during operation. Consequently, the performance was repaired by a heat treatment which resulted in the 78% recovery of the initial efficiency of the degraded PSCs, increasing operational lifespan of the device. In 2023, Li et al. introduced a fullerene derivative, CPPA, into the perovskite layer to interact with the perovskite through hydrogen bonding, coordinative bonding and fullerene-halide radical interactions.<sup>155</sup> As shown in Fig. 8d. it beneficially passivated bulk phase defects, accelerated electron carrier transport between grain boundaries, and effectively inhibited phase segregation to enhance the stability of perovskite film to light, high temperature and humidity. The devices were able to maintain an initial efficiency of 95.5% after 3265 hours of maximum power point tracking at a continuous solar irradiation of 70±5°C. Yang et al. synthesized a

functionalized fullerene (C<sub>60</sub>-Rhd-CN) containing two cyano groups to construct inverted BHJ-PSCs with an antisolvent method.<sup>156</sup> The involvement of two electron-withdrawing cyano groups within C<sub>60</sub>-Rhd-CN obviously increased the dielectric constant ( $\epsilon_r$ ), hence lowering the dielectric mismatch between perovskite and fullerene ETL, and facilitating exciton dissociation and interfacial charge transport. As a result, C<sub>60</sub>-Rhd-CN-incorporated inverted devices showed a PCE enhancement from 18.43% to 20.81%.

Tin-based perovskite solar cells (TPSCs) have received increasing attention due to their low toxicity, preferable bandgaps and high theoretical efficiency.<sup>157, 158</sup> Additive engineering is a widely employed approach to enhance the performance of TPSCs to regulate crystallization,159 passivate defects,160 and inhibit tin ion oxidation,<sup>161</sup> thereby enhancing cell performance.<sup>162, 163</sup> Fullerene derivatives demonstrate distinct advantages including structural tunability and exceptional electrical conductivity.<sup>16</sup> These materials enable precise incorporation of diverse functional moieties to synergistically passivate both surface and bulk defects, 107 enhance electron mobility and optimize energy level alignment.<sup>164</sup> This multifunctional nature establishes fullerene derivatives as effective additives for improving the optoelectronic performance of tin-based perovskite devices. Wu et al. designed a series of new ionic fullerene derivatives, C<sub>60</sub>-NH<sub>3</sub>-X (X=Cl, Br, I), as light absorption layer additives for tin-based perovskite solar cells.<sup>165</sup> These additives not only

improved the quality of tin perovskite films, but also adjusted the valence band energy to better match PEDOT:PSS. In addition, oxygen on the carbonyl and ether groups interacted with uncoordinated Sn<sup>2+</sup> in perovskite, while halogen ions filled I-vacancy and deactivate defects in tin perovskite films. Finally, the highest efficiency of the device achieved 11.74% and the fill factor was up to 73%. Cho et al. also used a fulleropyrrolidine with a triethylene glycol monoethyl ether side chain (PTEG-1) as a multifunctional molecular additive to passivate the defect in surfaces and grain boundaries.<sup>166</sup> The ether group and fullerene group in PTEG-1 interacted with Sn<sup>2+</sup> and I<sup>-</sup>, respectively, thereby inhibiting the formation of Sn<sup>4+</sup> and I<sub>3</sub><sup>-</sup>. This multifunctional passivation effectively suppressed nonradiative recombination and improved the stability of Sn-PSCs. As illustrated in Fig. 8e, Wei et al. used a chlorofullerene, C<sub>60</sub>Cl<sub>6</sub>, to modulate the crystallization process and passivate grain boundary defects of the perovskite film.<sup>167</sup> The chemical interactions between C<sub>60</sub>Cl<sub>6</sub> and perovskite components retarded the transforming process of precursors to perovskite crystals and obtained a high-quality tinbased perovskite film. Additionally, the C60Cl6 existing at the grain boundaries has been shown to stitch the grain boundaries, increasing the resistance of the perovskite film to water and oxygen erosion. As a result, the C60Cl6-based device yielded a remarkably improved device efficiency from 10.03% to 13.30% with enhanced stability. In



**Fig. 8** (a) Schematic illustration of the interactions between  $C_{60}$ -PyF15 and MAPbl<sub>3</sub>.<sup>151</sup> Copyright 2021, Elsevier. (b) Schematic view of the FPD-assisted lead leakage prevention and performance improvement strategy for PSCs.<sup>152</sup> Copyright 2021, Wiley-VCH. (c) Illustration of synthesis and mixing of PC<sub>61</sub>B-TEG and PC<sub>61</sub>B-BiTEG and typical device structure of fullerene-doped regular PSCs.<sup>153</sup> Copyright 2022, Wiley-VCH. (d) The scheme of interaction modes between CPPA and perovskites. And the evolution of PL spectra of MAPb( $I_{0.5}Br_{0.5}$ )<sub>3</sub> and MAPb( $I_{0.5}Br_{0.5}$ )<sub>3</sub>-CPPA films under continuous blue-light irradiation.<sup>155</sup> Copyright 2023, The American Association for the Advancement of Science. (e) Schematic diagram of the  $C_{60}CI_{6}$ -assisted strategy for device performance enhancement.<sup>167</sup> (f) Molecular structure of FTAI and diagram of cross-linked FTAI interact with perovskite.<sup>169</sup> Copyright 2024, Wiley-VCH.

# ARTICLE

2024, the same group synthesized a fullerene pyrrolidine (PPF) with two pyridinyl substituents: cis-CPPF and trans-TPPF configuration to investigate the effect of additive configuration on device performance.<sup>168</sup> The spatial configuration of CPPF and TPPF had a significant impact on their electron density distribution and interaction with perovskite components. Compared with CPPF, TPPF had spatially separated pyridine groups that trap more perovskite colloids through coordination bonds, thus slowing down the perovskite crystallization process. A more crystalline and dense perovskite film was produced, enhancing the interfacial energy level configuration and inhibiting Sn<sup>2+</sup> oxidation. The device exhibited a highest PCE of 15.38% and demonstrated excellent stability. Besides, they also designed a thioctic acid functionalized fullerene derivative (FTAI) that can be crosslinked at 70°C.<sup>169</sup> It acted as a grain boundary connector, improving conductivity and elasticity, thus providing excellent bending resistance. As shown in Fig 8f, FTAI had multiple interactions with perovskite components, forming larger grains and aligning the energy level with the electron transport material, which

effectively improved the carrier extraction efficiency. Finally, the FTAI-based rigid device attained the highest efficiency of 14.91 % and enhanced stability. The resulting wearable device exhibited an efficiency of 12.35 % and demonstrated robust bending durability, retaining approximately 90% of its initial efficiency after 10,000 bends. Recently, the same group designed three cis-configured pyridyl-substituted fulleropyrrolidines (PPF), specifically 2-pyridyl (PPF2), 3-pyridyl (PPF3), and 4-pyridyl (PPF4), and utilized them as precursor additives to regulate the crystallization kinetics during film formation.<sup>170</sup> As the spatial distance between the pyridine groups in PPF2, PPF3, and PPF4 increased, the two pyridine groups within the same molecule tended to interact with different perovskite colloids, resulting in high-quality PPF4-based perovskite films with reduced defect density and lower exciton binding energy. Additionally, with a fullerene bis-adduct, C60BB, as an interlayer between the perovskite and PCBM layers to optimize energy level alignment, the champion device achieved an efficiency of 16.05% (certified: 15.86%).

-								
Compound	LUMO/HOM O (eV)	Electron mobility (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	Device structure	V <sub>oc</sub> (V)	FF (%)	J <sub>sc</sub> (mA cm⁻ ²)	PCE (%)	Ref
PCBM	-	-	FTO/TiO2/MAPbI3+PCBM/Spiro- OMeTAD/Au	1.086	75	18.0	14.4	145
PCBM	-	3.81 x 10 <sup>-5 b</sup>	ITO/PEDOT:PSS/MAPbI <sub>3</sub> +PCBM/Ca /PCBM/AI	0.97	82	20.2	16	148
DF-C <sub>60</sub>	-3.9/-5.4 ª	1.8 x 10 <sup>-3</sup>	ITO/Cu-doped NiO <sub>x</sub> /MAPbI <sub>3</sub> +DF- C <sub>60</sub> /PCBM/bis-C <sub>60</sub> /Ag	1.09	78.7	21.08	18.11	149
C60-PEG	-	0.95 <sup>b</sup>	ITO/NiO <sub>x</sub> /Cs <sub>0.1</sub> FA <sub>0.7</sub> MA <sub>0.2</sub> PbI <sub>3-x</sub> Br <sub>x</sub> + C60-PEG/PCBM/BCP/Ag	1.05	81.81	20.62	17.71	150
C <sub>60</sub> -PyF15	-3.92/-5.66	8.32×10 <sup>-4 b</sup>	FTO/NiO <sub>x</sub> /MAPbI <sub>3</sub> +C <sub>60</sub> - PyF15/PCBM/BCP/Ag	1.073	80.96	23.14	20.10	151
C <sub>60</sub> -PyH15	-3.87/-5.61	5.58×10 <sup>-4 b</sup>	FTO/NiO <sub>x</sub> /MAPbI <sub>3</sub> +C <sub>60</sub> - PyH15/PCBM/BCP/Ag	1.046	79.89	23.00	19.22	151
FPD	-	-	ITO/SnO <sub>2</sub> /Cs <sub>0.07</sub> FA <sub>0.67</sub> MA <sub>0.26</sub> PbI <sub>0.99</sub> B r <sub>0.01</sub> +FPD/spiro-OMeTAD/Ag	1.13	81	25.19	23	152
PC <sub>61</sub> B-TEG	-3.78/-5.91	9.71×10 <sup>-4</sup>	FTO/c-TiO <sub>2</sub> /m- TiO <sub>2</sub> /FA <sub>0.65</sub> MA <sub>0.35</sub> PbI <sub>3-6</sub> Cl <sub>6</sub> + PC <sub>61</sub> B-	1.143	81.16	25.16	23.34	153
PC <sub>61</sub> B-BiTEG	-3.86/-5.82	-	ITEG/Spiro-OMETAD/AU ITO/SnO2/MAPbl3+PC61B- BiTEG/Spiro-OMeTAD/Au	1.08	73	22.1	17.4	153
C <sub>60</sub> -PU	-	2.1 x 10 <sup>-2 b</sup>	FTO/SnO <sub>2</sub> /FAPbI <sub>3</sub> +C <sub>60</sub> -PU/Spiro- OMeTAD/Ag	1.15	82.66	22.44	21.36	154
СРРА	-	-	ITO/SnO <sub>2</sub> /Cs <sub>0.05</sub> FA <sub>0.85</sub> MA <sub>0.10</sub> Pb(I <sub>0.97</sub> Br <sub>0.03</sub> ) <sub>3</sub> +CPPA/spiro-OMeTAD/Ag	1.15	80.0	24.8	22.8 <sup>c</sup>	155
C <sub>60</sub> -Rhd-CN	-3.90/-5.63	1.69×10 <sup>-3</sup>	or Au FTO/NiO <sub>x</sub> /MAPbI <sub>3</sub> +C <sub>60</sub> -Rhd- CN/PC <sub>61</sub> BM/ BCP/Ag	1.07	82.96	23.38	20.81	156
C <sub>60</sub> -Rhd-S	-3.89/-5.62	1.11×10 <sup>-3</sup>	FTO/NiO <sub>x</sub> /MAPbI <sub>3</sub> +C <sub>60</sub> -Rhd- S/PC <sub>61</sub> BM/ BCP/Ag	1.05	80.36	23.07	19.45	156
C <sub>60</sub> -RNH <sub>3</sub> -Cl	-		ITO/PEDOT:PSS/FA <sub>0.98</sub> EDA <sub>0.01</sub> SnI <sub>3</sub> + C <sub>60</sub> -RNH <sub>3</sub> -CI/C <sub>60</sub> /BCP/Ag	0.60	61	21.99	8.08	165
C <sub>60</sub> -RNH <sub>3</sub> -Br	-3.66/-5.46	3.48×10 <sup>-4 b</sup>	ITO/PEDOT:PSS/FA <sub>0.98</sub> EDA <sub>0.01</sub> SnI <sub>3</sub> + C <sub>60</sub> -RNH <sub>3</sub> -Br/C <sub>60</sub> /BCP/Ag	0.66	73	24.26	11.74	165
C <sub>60</sub> -RNH <sub>3</sub> -I	-	-	ITO/PEDOT:PSS/FA <sub>0.98</sub> EDA <sub>0.01</sub> SnI <sub>3</sub> + C <sub>60</sub> -RNH <sub>3</sub> -I/C <sub>60</sub> /BCP/Ag	0.58	62	21.42	7.65	165

# Table 4 Device performance of PSCs with fullerene-based Additives in PSCs

**Journal Name** 

PTEG-1	-3.8/-6.93	3.42 x 10 <sup>-3 b</sup>	ITO/PEDOT:PSS/FASnI <sub>3</sub> +PTEG- 1/C <sub>60</sub> /BCP/AI	0.625	67.8	20.70	8.78	166
C <sub>60</sub> Cl <sub>6</sub>	-3.74/-5.8	-	ITO/PEDOT: PSS/PEA <sub>0.15</sub> FA <sub>0.85</sub> Snl <sub>3</sub> + C <sub>60</sub> Cl <sub>6</sub> /PCBM/BCP/Ag	0.86	76	20.31	13.30	167
TPPF	-3.80/-5.16 ª	-	ITO/PEDOT:PSS/FA <sub>0.98</sub> EDA <sub>0.01</sub> SnI <sub>3</sub> + TPPF/PCBM/BCP/Ag	0.856	72.37	24.81	15.38	168
CPPF	-3.73/-5.09 ª	-	ITO/PEDOT:PSS/PEA <sub>0.15</sub> FA <sub>0.85</sub> SnI <sub>3</sub> + CPPF/PCBM/BCP/Ag	0.825	71.73	24.13	14.29	168
FTAI	-3.78/-5.17 ª	-	ITO/PEDOT: PSS/PEA <sub>0.15</sub> FA <sub>0.85</sub> SnI <sub>3</sub> +FTAI/PCBM/ BCP/Ag	0.866	69.98	24.62	14.91	169
	·		PET/ITO/PEDOT:PSS/PEA <sub>0.15</sub> FA <sub>0.85</sub> S nI <sub>3</sub> +FTAI /PCBM/BCP/Ag	0.760	73.26	22.17	12.35	
PPF2	-3.69/-5.04ª	-	ITO/PEDOT:PSS/PEA <sub>0.15</sub> FA <sub>0.85</sub> Snl <sub>3</sub> (P PF2)/PCBM/BCP/Ag	0.843	69.93	24.73	14.58	170
PPF3	-3.73/-5.08ª	-	ITO/PEDOT:PSS/PEA <sub>0.15</sub> FA <sub>0.85</sub> SnI <sub>3</sub> (P PF3)/PCBM/BCP/Ag	0.845	70.31	25.29	15.04	170
DDE/	-3 76/-5 11 ª	_	ITO/PEDOT:PSS/PEA <sub>0.15</sub> FA <sub>0.85</sub> SnI <sub>3</sub> (P PF4)/PCBM/BCP/Ag	0.850	71.02	25.76	15.58	170
F F I 4	-3.70/-3.11	-	ITO/PEDOT:PSS/PEA <sub>0.15</sub> FA <sub>0.85</sub> SnI <sub>3</sub> (P PF4)/C <sub>60</sub> BB/PCBM/BCP/Ag	0.86	71.35	26.17	16.05	170

<sup>a</sup> The HOMO/LUMO of fullerene-based perovskite films

<sup>b</sup> The Electron mobility of fullerene-based perovskite films

<sup>c</sup> The PCE of the device only adding CPPA



**Fig. 9** Summary of the structures with fullerene-based materials for the additives of PSCs.

# 6. Interface modification layer

Perovskite solar cells comprise a number of interfaces, including the electrode/ETL interface, the ETL/ perovskite interface, the perovskite/HTL interface, and the HTL/electrode interface.<sup>18, 171</sup> These heterojunction interfaces, where charge carriers travel through, not only determine the coverage, uniformity, and crystallinity of the post-deposited materials but also strongly affect the charge extraction, injection, transport, and recombination by modulating defect density and electric field in the devices.<sup>172-174</sup> Therefore, gaining a full understanding of the properties of the interface and its engineering principles is crucial for developing high-performance and stable PSCs.<sup>25, 175</sup>

#### 6.1. Fullerene-based interface modification layer for Inverted PSCs

In the inverted PSCs, fullerene derivatives are employed primarily to modify the perovskite/electron transport layer interface with the objective of enhancing electron extraction,176 passivating surface defects,<sup>177</sup> and improving device stability.<sup>33</sup> In 2019, Li et al designed a fullerene electrolyte (PCBB-3N-3I) dipole layer, as shown in Fig. 10a.<sup>178</sup> Through electrostatic interaction, PCBB-3N-3I simultaneously passivated positive charge defects on the perovskite surface and formed a dipole interlayer to reconfigure interfacial energy band structure, leading to enhanced built-in potential and charge collection. As a result, the devices exhibited the promising PCE of 21.1% and robust ambient stability. In 2020, Yao et al. compared the effects of four interfacial modified molecules, mPy, mPyl, bPy and bPyI, on the performance of MA-free PSCs.<sup>179</sup> Compared with uniodized molecules, zwitterionic molecules simultaneously passivated positive and negative charged defects and induced band bending at the interface, enhancing the internal power of electron transfer, which was benefit for electron extraction and prevents

charge accumulation. Due to these advantages, the bPyI-modified device exhibited a best PCE of 21.1%. In the same year, Xie et al. designed a fullerene derivative that can be crosslinked in situ: 1-(pbenzoate-(p-methylvinylbenzene)-indomenol [2,3][60] fullerene (FPPS), which was used for interface modification on perovskite to significantly improve electron mobility and passivate defects, thus facilitating electron transport at the interface.<sup>180</sup> The device showed enhanced stability with a  $t_{80}$  (the time required to reach 80% of the initial PCE) of 300 hours in ambient air due to the hydrophobicity and density of the crosslinked FPPS films. In 2022, Yang et al. synthesized a novel amino-functionalized fullerene derivative (C<sub>60</sub>-BPAM).<sup>181</sup> As shown in Fig. 10b, upon dissolution in antisolvent chlorobenzene and addition to the precursor layer of perovskite, the interaction of the [PbI<sub>6</sub>]<sup>4-</sup> octahedron with the amino (-NH<sub>3</sub><sup>+</sup>) groups in C<sub>60</sub>-BPAM<sup>2+</sup> resulted in the formation of a 2D perovskite layer in situ, which is mixed with 3D perovskite to form a 2D/3D hybrid perovskite structure. The addition of C<sub>60</sub>-BPAM with high conductivity induces additional built-in electric fields, facilitating electron transport in 2D/3D PSCs. Therefore, the PCE of devices was increased from 19.36% to 20.21%. In addition, C<sub>60</sub>-BPAM exhibited moisture resistance, enabling the 2D/3D hybrid perovskite device to retain its original PCE of approximately 70% after storage at 40% humidity for 2300 hours. In 2024, the same group designed a fullerene derivative containing triple methyl acrylate groups (C<sub>60</sub>-TMA) as a multifunctional interfacial modification layer (Fig. 10c).<sup>182</sup> The modification of C<sub>60</sub>-TMA not only passivated perovskite surface defects through the coordination interaction between C=O groups and Pb<sup>2+</sup> cations, but also promoted electron extraction at the interface as an electron bridge between C<sub>60</sub> and perovskite. In addition, the strong bonding effect effectively induced secondary grain growth in the perovskite film, thus effectively improving the quality of the perovskite film. Accordingly, the PCE of the C<sub>60</sub>-TMA treated device reached 24.89%, and the device exhibited a notable enhancement in performance, with an initial efficiency of over 90% sustained after aging at 85°C for 1200 h.

The interface between the ETL and the top electrode is of equal importance in the inverted PSCs. The top metal electrode typically utilizes metals with high work function (W<sub>F</sub>), such as gold and silver, as electrodes.<sup>183, 184</sup> In contrast, the ETL in inverted PSCs is commonly composed of fullerenes and their derivatives, which  $W_F$  do not match with that of the metal electrode.<sup>185, 186</sup> Thus, a Schottky barrier is formed on the contact surface, hindering the electron transfer and thus reducing the device performance.<sup>187</sup> Moreover, the interface between ETL/metal has a significant impact on factors affecting cell stability, such as water permeation and chemical interactions.<sup>188, 189</sup> Consequently, several interface materials, such as fullerene derivatives, are introduced to modulate the interfacial energy barriers to facilitate carrier transport and improve the cell stability.<sup>34,</sup> <sup>171</sup> Azimi et al. reported an amine functionalized fullerene derivative, DMAPA-C $_{60}$ , as a chemisorbed dipolar interface layer.<sup>190</sup> The formation of a dipole layer directly impacted the  $W_F$  of Ag contact and suppressed the energy barrier at the interface between PCBM and Ag, and ultimately the PCE of device reached 13.4%. Russell et al. demonstrated the fulleropyrrolidine (C<sub>60</sub>-N) interlayer between the silver electrode and ETL enhanced recombination resistance, increased electron extraction rate and prolonged free carrier lifetime, resulting in an enhancement of PCE from 7.5% to 15.5%.<sup>191</sup>Alex et al.

# ARTICLE

utilized two fullerene derivatives (F-C<sub>60</sub> and bis-C<sub>60</sub>) to form a robust and efficient cathode interlayer for addressing the stability issues.<sup>192</sup> Benefitting from the hydrophobicity introduced by F-C<sub>60</sub>, the device showed a much better ambient stability, retaining 80% of its initial PCE even after being exposed in ambient condition with 20% relative humidity for 14 days. Yang et al. applied a hydrophobic PCBDAN interlayer to improve the efficiency and air stability for the unsealed devices.<sup>193</sup> The PCBDAN layer not only reduced the interface barrier through facilitating an efficient electron transport, but also protected the device from the damage of moisture in air. The maximum efficiency of PSCs with PCBDAN reached 17.2% and the devices with PCBDAN kept their high performance with no obvious PCE loss in 10% humidity and >90% of the initial PCE in 45% humidity after 20 days. In recent years, fullerene derivatives have also been attempted as interfacial modification layers in mixed tin-lead PSCs and tin-based PSCs to enhance electron extraction and interfacial passivation, thereby improving device performance.<sup>131, 194</sup> In 2018, Hayase et al. introduced PCBM to the interface between the perovskite layer and the C<sub>60</sub> layer in mixed tin-lead PSCs.<sup>195</sup> This interlayer produced conduction band offset of ~0.15 eV and provided a sharp peak between the absorber layer and the ETL (C<sub>60</sub>) layer to reduce interfacial traps and carrier recombination, resulting in an increase of V<sub>oc</sub> to 0.75 V with best solar cell performance of 17.6%. In 2021, Nejand et al. investigated the role of fullerene interlayers (IPB and IPH) in Sn-Pb mixed narrow-bandgap (NBG) PSCs.<sup>196</sup> The incorporation of IPH reduced the trap density at the interface and induced a conduction band shift of approximately 0.2 eV to prevent recombination of backward carrier transfers. Consequently, the devices with IPH-interlayer showed the highest performance with a remarkable  $J_{sc}$  of 30.7 mA cm<sup>-2</sup> and a low deficit in  $V_{oc}$  of 0.43 V. Using a NBG device with an IPH interlayer, a respectable PCE of 24.8% was demonstrated in a fourterminal all-perovskite tandem solar cell. In 2022, Zhu et al. introduced fullerene-n-butyl pyridine (C<sub>60</sub>-BPy) into the perovskite/ETL interface of tin-based PSCs.<sup>197</sup> It showed strong anchoring on the perovskite surface through the coordination interaction of pyridine and Sn<sup>2+</sup>, effectively passivating the trap state on the surface as shown in Fig. 10d. Additionally, C<sub>60</sub>-BPy effectively modified the band arrangement at the interface, facilitating electron extraction. The resulting device exhibited a PCE of up to 14.14%, with significantly enhanced stability. In 2024, Wei et al. synthesized four kinds of polyfullerene molecules, FM3, FM4, FM5 and FM6, with 3, 4, 5 and 6 diethylmalonic acid groups respectively, and employed them as the interface layer of TPSCs.<sup>198</sup> By increasing the number of added functional groups, the LUMO energy level of the molecules gradually became shallow and the interaction with perovskite gradually increased. The energy level and interaction of FM5 were optimized, resulting in a PCE of up to 15.05%. Moreover, the compact packing of the carbon cage on the perovskite surface inhibited the erosion of water and oxygen, significantly improving the stability of the device. In the same year, Spanopoulos et al. employed an aminefunctionalized C<sub>60</sub> mono-adduct derivative, bis(2-aminoethyl) malonate-C<sub>60</sub> (C<sub>60</sub>-2NH<sub>3</sub>), to synthesis the first crystalline fullerenebased 2D metal halide semiconductor, namely (C<sub>60</sub>-2NH<sub>3</sub>) Pb<sub>2</sub>I<sub>6</sub>.<sup>199</sup> The use of C<sub>60</sub>-2NH<sub>3</sub> as the interface modification layer allowed for the energy level matching of the interface, reduced non-radiative recombination and facilitated interface carrier transport. The device efficiency reached 21.64%, and 90% of the initial efficiency retained

after 2400 hours of storage under N<sub>2</sub> condition. Additionally, Li et al. used C-PCBSD, a cross-linked fullerene molecule, as the interface modification layer in mixed tin-lead (Sn-Pb) PSCs.<sup>200</sup> Through the coordination of C=O with Sn<sup>2+</sup> and Pb<sup>2+</sup>, C-PCBSD delayed the crystallization rate, inhibited the oxidation of Sn<sup>2+</sup>, increased the crystallinity of perovskite, reduced the surface trap density, and

effectively improved the charge extraction at the interface. A champion PCE of 23.4% was achieved, and the stability of the device was improved due to the formation of a C-PCBSD polymerization network by thermal crosslinking, which effectively inhibited the intrusion of water and oxygen (Fig. 10e)



**Fig. 10** (a) Schematic illustration of molecular orientation of PCBB-3N-3I and PCBB-3N on MAPbl<sub>3</sub>.<sup>178</sup> (b) Schematic illustration of the structure of Dion–Jacobson phase 2D/3D ( $C_{60}$ -BPAM)(MA)<sub>n-1</sub>Pb<sub>n</sub>I<sub>3n+1</sub> perovskite.<sup>181</sup> Copyright 2022 Wiley-VCH. (c) Schematic diagram of the C<sub>60</sub>-TMA-assisted strategy for device performance enhancement.<sup>182</sup> Copyright 2024 Wiley-VCH. (d) schematic illustration of the interfacial interactions between the perovskite and C<sub>60</sub> (or C<sub>60</sub>-BPy).<sup>197</sup> Copyright 2022, Wiley-VCH. (e) Schematic diagram of device structure of Sn-Pb PSCs treated with C-PCBSD and perovskite lattice protected from water and oxygen.<sup>200</sup>

Table 5 Device performance of PSCs with fullerene-based interface modification layer in the inverted PSCs

Compound	LUMO/HOMO (eV)	Electron mobility (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	Device structure	V <sub>oc</sub> (V)	FF (%)	J <sub>sc</sub> (mA cm <sup>-</sup> <sup>2</sup> )	PCE (%)	Ref
PCBB-3N-3I	3.66/5.88	9.24×10 <sup>-4</sup>	ITO/PTAA/MAPbI₃/PCBB-3N- 3I/PCBM/AI	1.105	81.36	23.46	21.10	178
PCBB-3N	3.62/5.84	2.90×10 <sup>-4</sup>	ITO/PTAA/MAPbI₃/PCBB- 3N/PCBM/AI ITO/PTAA/PFN-	1.046	71.65	21.05	15.77	178
bFPI	3.97/6.25 ª	-	Br/Cs <sub>0.17</sub> FA <sub>0.83</sub> Pb(I <sub>0.8</sub> Br <sub>0.2</sub> ) <sub>3</sub> /bFPI/C <sub>60</sub> / BCP/Ag ITO/PTAA/PFN-	1.15	81	22.58	21.11	179
bFP	3.91/6.19 ª	-	Br/Cs <sub>0.17</sub> FA <sub>0.83</sub> Pb(I <sub>0.8</sub> Br <sub>0.2</sub> ) <sub>3</sub> /bFP/C <sub>60</sub> /B CP/Ag	1.12	80.8	22.14	20.04	179
FPPS	-3.96/-5.62	2.21×10 <sup>-4</sup>	ITO/PTAA/(FA <sub>0.83</sub> MA <sub>0.17</sub> ) <sub>0.95</sub> Cs <sub>0.05</sub> Pb(I <sub>0.9</sub> Br <sub>0.1</sub> ) <sub>3</sub> /FPPS/PCBM/BCP/Ag	1.07	71.15	23.46	17.82	180
(C <sub>60</sub> - BPAM)I <sub>2</sub>	-3.87/-5.47 ª	1.31×10 <sup>-3</sup>	FTO/NiO <sub>x</sub> /MAPbI <sub>3</sub> /(C <sub>60</sub> - BPAM)I <sub>2</sub> /PCBM/BCP/Ag	1.090	78.53	23.61	20.21	181

This journal is © The Royal Society of Chemistry 20xx

			ITO/NiO <sub>x</sub> /MeO-					
C <sub>60</sub> -TMA	-4.15/-5.89	-	2PACz/Cs <sub>0.05</sub> MA <sub>0.10</sub> FA <sub>0.85</sub> PbI <sub>3</sub> /C <sub>60</sub> - TMA/C <sub>60</sub> /BCP/Ag	1.172	83.56	25.42	24.89	182
DMAPA-C <sub>60</sub>	-	-	ITO/PEDOT:PSS/MAPbl <sub>3</sub> . <sub>x</sub> Cl <sub>x</sub> /PCBM/DMAPA-C <sub>60</sub> /Ag	0.97	77	17.9	13.4	190
C <sub>60</sub> -N	-3.9/-5.7	-	ITO/PEDOT:PSS/FA <sub>0.43</sub> MA <sub>0.57</sub> PbI <sub>3</sub> /PC BM/C <sub>60</sub> -N/Ag	-	-	20.50	15.5	191
bis-C <sub>60</sub> &F- C <sub>60</sub>	-	1.07 × 10 <sup>-3</sup>	ITO/PEDOT:PSS/MAPbCl <sub>3</sub> . <sub>x</sub> l <sub>x</sub> /PCBM/bis-C <sub>60</sub> &F-C <sub>60</sub> /Ag	0.97	75.4	21.2	15.5	192
PCBDAN	-	-	FTO/NiO <sub>x</sub> /MAPbI <sub>3</sub> /PCBM/PCBDAN/ Ag	1.08	77	20.71	17.2	193
PCBM	-4.0/-6.0	-	ITO/PEDOT:PSS/MAFAPbI <sub>3</sub> /PCBM/C <sub>6</sub> <sub>0</sub> /BCP/Ag	0.75	76	30.56	17.59	195
IPB	-3.8/-5.9	-	ITO/PTAA/Cs <sub>0.025</sub> (FA <sub>0.8</sub> MA <sub>0.2</sub> ) <sub>0.975</sub> Sn <sub>0.</sub> <sub>5</sub> Pb <sub>0.5</sub> I <sub>3</sub> /IPB/C <sub>60</sub> /BCP/Ag	0.83	71	30.2	17.8	196
IPH	-3.8/-5.9	-	ITO/PTAA/Cs <sub>0.025</sub> (FA <sub>0.8</sub> MA <sub>0.2</sub> ) <sub>0.975</sub> Sn <sub>0.</sub> <sub>5</sub> Pb <sub>0.5</sub> I <sub>3</sub> /IPH/C <sub>60</sub> /BCP/Ag	0.83	73	30.7	18.6	196
C <sub>60</sub> -BPy	-3.81/-5.52	-	ITO/PEDOT:PSS/FASnI <sub>3</sub> /C <sub>60</sub> - BPy/C <sub>60</sub> /BCP/Ag	0.820	73.1	23.45	14.14	197
FM3	-3.64/-5.77	1.11×10 <sup>-6</sup>	ITO/PEDOT:PSS/PEA <sub>0.15</sub> FA <sub>0.85</sub> SnI <sub>3</sub> /F M3/PCBM/BCP/Ag	0.77	71.74	24.51	13.54	198
FM4	-3.47/-5.36	0.46×10 <sup>-6</sup>	ITO/PEDOT:PSS/PEA <sub>0.15</sub> FA <sub>0.85</sub> SnI <sub>3</sub> /F M4/PCBM/BCP/Ag	0.84	70.60	24.18	14.34	198
FM5	-3.42/-5.59	0.26×10 <sup>-6</sup>	ITO/PEDOT:PS/PEA <sub>0.15</sub> FA <sub>0.85</sub> SnI <sub>3</sub> /FM 5/PCBM/BCP/Ag	0.86	71.06	24.54	15.05	198
FM6	-3.34/-5.37	0.94×10 <sup>-7</sup>	ITO/PEDOT:PSS/PEA <sub>0.15</sub> FA <sub>0.85</sub> SnI <sub>3</sub> /F M6/PCBM/BCP/Ag	0.85	70.70	22.89	13.75	198
C <sub>60</sub> -2NH <sub>3</sub>	-4.05/-5.40 ª	4.43 × 10 <sup>-3 b</sup>	ITO/PEDOT:PSS/FA <sub>0.6</sub> MA <sub>0.4</sub> Pb <sub>0.7</sub> Sn <sub>0.3</sub> I <sub>3</sub> /C <sub>60</sub> -2NH <sub>3</sub> /C <sub>60</sub> /BCP/Cu	0.86	81.84	30.79	21.64	199
C-PCBSD	-4.18/-5.44 ª	-	$\label{eq:FTO/PEDOT:PSS/Cs} \begin{split} &FTO/PEDOT:PSS/Cs_{0.1}FA_{0.6}MA_{0.3}Sn_{0.5} \\ &Pb_{0.5}I_3/CPCBSD/C_{60}/BCP/Ag \end{split}$	0.88	80.0	33.1	23.4	200

<sup>a</sup> The HOMO/LUMO of fullerene-based perovskite films

<sup>b</sup> The Electron mobility of fullerene-based perovskite films

#### 6.2 Fullerene-based Interface modification layer for regular PSCs

In the regular PSCs, ETLs are primarily inorganic oxides, including TiO<sub>2</sub>, ZnO and SnO<sub>2</sub> with TiO<sub>2</sub> and SnO<sub>2</sub> being the most extensively employed.<sup>56</sup> But these two ETM possess a considerable number of uncoordinated defects at the ETL/perovskite interface, leading to the emergence of a large electron extraction barrier, and hinders the attainment of efficient PSCs.<sup>58, 59</sup> Consequently, fullerene materials with robust electron absorption ability are frequently employed to modify the TiO<sub>2</sub> (or SnO<sub>2</sub>) /perovskite interface, thereby facilitating enhanced electron extraction,<sup>177</sup> passivating the buried interface defects<sup>201</sup> and improving the quality of the perovskite film and, in turn, enhancing battery performance. <sup>202, 203</sup>

In 2014, Snaith et al used  $C_{60}$ -SAM to modify TiO<sub>2</sub> and demonstrated that  $C_{60}$ -SAM could change the N-type contact and facilitate electron transfer at the interface.<sup>204</sup> The device changed from "i-p" perovskite hole transport heterojunction drove to n-i and i-p heterojunction drive(n refers to an n-type semiconductor, i represents a perovskite, and p denotes a p-type semiconductor). The average PCE of the devices was increased from 11.5% to 14.8%, with a maximum stable power output is 15.7%. In 2015, Yang et al. synthesized a triblock fullerene derivative (PCBB-2CN-2C8) for interface engineering to passivate the TiO<sub>2</sub> surface and reduce charge recombination loss caused by the deep trap states of TiO<sub>2</sub> as shown in Fig. 11a.<sup>205</sup> The PCE of the best devices resulted in 20.7%, as well as reduction of the hysteresis. Moreover, the shelf stability of unencapsulated devices

under normal ambient conditions was significantly improved compared with the control devices. In 2016, Chen et al. employed a hydroxylated fullerene, fullerenol, between perovskite and TiO2.206 The insertion of a single layer of fullerenol dramatically facilitated charge transport and reduced interfacial resistance, thus improving device performance and achieving a higher PCE of 14.69%. In 2017, Diau et al. employed two cross-linked fullerene derivatives C-PCBSD and C-PCBOD with suitable energy level to modify TiO<sub>2</sub> prepared at low temperature(Fig. 11b).<sup>207</sup> The two fullerene materials effectually improved the crystal quality of the perovskite, inhibited charge recombination at the interface and enhanced electron extraction. As a result, J<sub>sc</sub> of the device was significantly improved, and PCE reached 15.3% and 15.9% respectively. Moreover, the device modifying mesoporous TiO<sub>2</sub> with C-PCBOD gave a PCE of 18.3%. In 2018, Wang et al. designed three novel fullerene derivatives, N-ethyl-2-arylvinyl-5-methyl fulleropyrrolidine (NAMF) with H, Cl and Br substitutions on the pyrrolidine side-chain (namely NAMF-H, NAMF-Cl and NAMF-Br) as an interface layer to modify TiO<sub>2</sub>.<sup>208</sup> The PCE of NAMF-Cl-modified devices reached 19.2% due to the more matched energy levels and the better passivation of interfacial defects. In 2020, Wang et al. synthesized two fullerene derivatives, NMPPF and NMTTF, as interlayers between the MAPbI<sub>3</sub> and TiO<sub>2</sub> layer.<sup>209</sup> The thiophene terminals of NMTTF have been found to effectively passivate the uncoordinated Pb<sup>2+</sup> of perovskite, reduce trap density and charge recombination of PSCs as well as facilitate charge transport at the perovskite and TiO<sub>2</sub> interface. As a result, the performance and

stability of NMTTF-based devices were improved. The same group also synthesized novel fulleropyrrolidine (NMBF-X, X=H or Cl) monomers and dimers to incorporated between metal oxides and perovskite.<sup>210</sup> They demonstrated that the NMBF-Cl dimer featuring chlorine terminals could interact with both perovskite and metal oxides (TiO<sub>2</sub> and SnO<sub>2</sub>) at the interface and was most effective at healing defects of perovskite crystals. The non-encapsulated planar device delivered a maximum PCE of 22.3% without any hysteresis, while maintaining over 98% of initial efficiency after ambient storage for 1000 h. In 2022, Meng et al. applied fullerene derivatives [6,6] phenyl-C<sub>61</sub>-butyric acid (PCBA) and 3-carboxypropyl triphenyl phosphorus bromide (CPTPB) as functionalized C-PCBA SAM to comodify the TiO<sub>2</sub>/ perovskite interface.<sup>211</sup> As shown in Fig. 11c, CPTPB was distributed uniformly on the surface of TiO<sub>2</sub> via  $\pi$ - $\pi$  interaction, which strengthened the chemical bond interaction with the TiO<sub>2</sub> substrate and provided an ordered distribution space for fullerene cages in PCBA. And the strong Fullerene cage-iodide interaction between PCBA and perovskite effectually facilitated the passivation of interface defects and enhanced electron transport. This synergistic effect resulted in a PCE of 24.8% for C-PCBA-modified PSCs, with minimal hysteresis and significantly enhanced stability.

In addition to modifying the TiO<sub>2</sub>/perovskite interface, functionalized fullerenes are also employed for modification of the SnO<sub>2</sub>/perovskite interface. In 2016, Yan et al. reported the synergistic effect of SnO<sub>2</sub> and PCBM to improve battery performance PCBM to improve the performance of PSCs.<sup>212</sup> They found that PCBM was redissolved by the perovskite precursor, which allowed only ultra-thin fullerenes to be retained at the interface and some dissolved fullerenes infiltrate into perovskite grain boundaries. Therefore, PCBM effectively passivated both the ETL/perovskite interface and perovskite grain boundaries, and the best-performing device achieved a PCE of 19.12%. In 2018, Zhan et al. used a long-chain fullerene derivative 9-(1-(6-(3,5-bis (hydroxymethyl) phenoxy)-1-hexyl)-1H-1,2,3-triazole-4-yl)-1-nonyl [60]fullerenoacetate (C9) with two hydroxyl anchoring groups on the side chain to modify the SnO<sub>2</sub> surface in PSCs.<sup>213</sup> The LUMO energy level and high electron affinity of C9 enabled effective extraction of photogenerated electrons from perovskite films and transferred them to the SnO<sub>2</sub> ETL. The hydroxyl functional group was



**Fig. 11** (a) Schematic diagram of the PCBB-2CN-2C8-assisted strategy for device performance enhancement.<sup>205</sup> Copyright 2015, American Chemical Society. (b) Schematic diagram of an n-i-p planar heterojunction PSCs with potential-energy levels of each layer. Either C-PCBOD or C-PCBSD cross-linked fullerene served as an interfacial layer between TiO<sub>2</sub> and perovskite.<sup>207</sup> Copyright 2017, American Chemical Society. (c) Schematic illustration of pure PCBA modification, basic CPTPB SAM modification, and functionalized C-PCBA SAM modification in PSCs.<sup>211</sup> Copyright 2022, Wiley-VCH. (d) Device structure with the different fullerene passivation thin film between the SnO<sub>2</sub> and perovskite layers.<sup>216</sup> Copyright 2022, Wiley-VCH. (e) Charge density difference distribution of  $F_{60}$ PD and  $F_{70}$ PD adsorbed on SnO<sub>2</sub> surface and PbI<sub>2</sub>-termination of perovskite surface.<sup>218</sup> Copyright 2023, Wiley-VCH.

capable of forming the Lewis adduction with the undercoordinated  $Sn^{4+}$  in  $SnO_2,$  which effectively passivated the oxygen-vacancy related defects on the surface of the SnO<sub>2</sub>, thus inhibiting the non-radiative recombination. Furthermore, the long alkyl chain of C9 made it hydrophobic to inhibit heterogeneous nucleation, which was beneficial for enhancing perovskite quality. Due to these functions, C9-modified SnO<sub>2</sub> enhanced the photovoltaic performance of PSCs, reaching 21.3% efficiency with negligible hysteresis, and improved the stability of devices. In 2019, Li et al. synthesized a fullerene derivative pyrrolidinofullerene C<sub>60</sub>-substituted phenol (NPC<sub>60</sub>-OH) to modify the SnO<sub>2</sub>.<sup>214</sup> After the introduction of an NPC<sub>60</sub>-OH, the perovskite films in the corresponding device showed enlarged grain size and lower trap-state density. The devices presented enhanced electron transport and decreased charge recombination velocity with a champion PCE of 21.39%. In 2020, Chen et al. introduced CPTA and PCBM as modifying layer and resolved the interfacial carrier dynamics in PSCs consisting of fullerene-modified ETLs using ultrafast spectroscopy.<sup>215</sup> They confirmed that the interfacial chemical bond was tailored between the SnO<sub>2</sub> surface and carboxylic acids of CPTA, thus establishing interface dipoles which was beneficial for improving electron injection and reducing recombination rates. Therefore, the PSCs based on the SnO<sub>2</sub>/CPTA ETL yielded a PCE of more than 19%, which was superior to that of the reference PSCs using PCBM as a passivator (<18%). In 2022, Ma et al. designed and

synthesized a crosslinked fullerene derivative [6,6] -phenyl-C<sub>61</sub>methyl butyrate (CL-PC $_{61}$ BM), which was thermally annealed to form a thin fullerene-modified layer on the surface of SnO<sub>2</sub> and remained stable during the deposition of perovskite, as shown in Fig. 11d.<sup>216</sup> Experiments demonstrated that CL-PC61BM can immobilize Li\* in PSCs, and inhibit the migration of Li<sup>+</sup>, thus eliminating the prevalent "aging" degradation in PSCs, significantly improving the stability and PCE of the device. In 2023, Prochowicz et al. designed and synthesized a new azahomoene (AHF) as the  $SnO_2$ /perovskite interface layer.<sup>217</sup> Compared with PCBM, AHF exhibited enhanced charge transfer capabilities, improved the quality of the perovskite film, and reduced the charge recombination in PSCs. The maximum efficiency of the device was 21.43%. Similarly, Wei et al. synthesized C<sub>60</sub>- and C<sub>70</sub>-porphyrin derivatives F<sub>60</sub>PD and F<sub>70</sub>PD containing polyfluoride to modify the heterogeneous interface of SnO<sub>2</sub>/ perovskite.<sup>218</sup> As shown in Fig.11e, the strong interaction between the two components and SnO<sub>2</sub> facilitated the production of highquality perovskite films and passivated interface defects. The optimized energy level arrangement was also conducive to the extraction of interfacial charge, so the performance of the modified device was significantly improved. The stability of the device was also improved by increasing the activation energy of perovskite ion migration

Compound	LUMO/HOM O (eV)	Electron mobility (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	Device structure	V <sub>oc</sub> (V)	FF (%)	J <sub>sc</sub> (mA cm <sup>-2</sup> )	PCE (%)	Ref
C <sub>60</sub> -SAM	-	-	FTO/TiO2/C60-SAM/MAPbI2Cl/spiro- OMeTAD/Au	1.04	75	22.1	17.3	204
PCBB-2CN- 2C8	4.01/-	4.8×10 <sup>-3</sup>	ITO/TiO <sub>2</sub> /PCBB-2CN-2C8/MAPbI <sub>3</sub> /spiro- OMeTAD/Au	1.06	79.1	20.68	17.35	205
Fullerenol	-	-	ITO/TiO <sub>2</sub> /fullerenol /MAPbI <sub>3</sub> /P3HT/MoO <sub>3</sub> /Ag	0.95	71.5	20.91	14.69	206
C-PCBSD	-3.8/-6.1	4.54 ×10 <sup>-4</sup>	ITO/TiO <sub>2</sub> (Au)/C-PCBSD/MAPbI <sub>3</sub> /spiro- OMeTAD/Au	1.01	68.22	22.23	15.3	207
			ITO/TiO <sub>2</sub> (Au)/C-PCBOD/MAPbI <sub>3</sub> /spiro- OMeTAD/Au	0.98	70.85	22.95	15.9	207
С-РСВОД	-3.8/-6.1	-	FTO/mp-TiO <sub>2</sub> /C-PCBOD/MAPbl <sub>3</sub> /spiro- OMeTAD/Ag	1.041	73.25	23.99	18.3	
NAMF-H	-4.05/-5.95	3.73 ×10 <sup>-4</sup>	ITO/TiO <sub>2</sub> /NAMF-H/MAPbI <sub>3</sub> /spiro- OMeTAD/Ag	1.08	78.4	22.4	19.0	208
NAMF-CI	-4.08/-5.91	1.44 ×10 <sup>-3</sup>	ITO/TiO <sub>2</sub> /NAMF-Cl/MAPbl <sub>3</sub> /spiro- OMeTAD/Ag	1.08	78.6	22.7	19.3	208
NAMF-Br	-4.13/-5.97	3.61 ×10 <sup>-4</sup>	ITO/TiO <sub>2</sub> /NAMF-Br/MAPbI <sub>3</sub> /spiro- OMeTAD/Ag	1.10	79.7	21.8	19.1	208
NMTTF	-4.10/-5.89	6.1 ×10 <sup>-4</sup>	ITO/TiO <sub>2</sub> /NMTTF/MAPbl <sub>3</sub> /spiro- OMeTAD/Ag	1.09	77.8	23.0	19.5	209
NMPPF	-3.80/-5.61	1.9 ×10 <sup>-4</sup>	ITO/TiO <sub>2</sub> /NMPPF/MAPbI <sub>3</sub> /spiro- OMeTAD/Ag	1.07	73.5	22.9	18.0	209
NIMBE-CI			ITO/TiO <sub>2</sub> /NMBF-Cl Dimer /MAPbI <sub>3</sub> /Spiro- OMeTAD/Ag	1.11	77	23.7	19.9	210
Dimer	-3.94/-5.65	5.0 ×10 <sup>-3</sup>	ITO/SnO <sub>2</sub> /NMBF-Cl Dimer/(FAPbI <sub>3</sub> ) <sub>x</sub> (MAPbBr <sub>3</sub> ) <sub>1-x</sub> /Spiro-	1.12	77	26.0	22.3	210
NMBF-H Dimer	-3.90/-5.61	4.2 ×10 <sup>-3</sup>	OMeTAD/Ag ITO/TiO <sub>2</sub> / NMBF-H Dimer / MAPbI <sub>3</sub> /Spiro- OMeTAD/Ag	1.11	75	22.8	19.0	210

# ARTICLE

**Journal Name** 

			ITO/SnO <sub>2</sub> /NMBF-H					
			Dimer/(FAPbI <sub>3</sub> ) <sub>x</sub> (MAPbBr <sub>3</sub> ) <sub>1-x</sub> /Spiro- OMeTAD/Ag	1.10	75	25.0	21.3	
			ITO/TiO <sub>2</sub> /NMBF-Cl/MAPbI <sub>3</sub> /Spiro- OMeTAD/Ag	1.10	71	23.0	17.6	210
NMBF-CI	-3.93/-5.64	2.8×10 <sup>-3</sup>	ITO/SnO <sub>2</sub> /NMBF-					210
			Cl/(FAPbI <sub>3</sub> ) <sub>x</sub> (MAPbBr <sub>3</sub> ) <sub>1-x</sub> /Spiro-	1.08	73	24.9	20.7	
			OMETAD/Ag					
			ΟΜεταρ/Δσ	1.03	71	22.2	16.9	
NMBF-H	-3.86/-5.64	3.4 ×10 <sup>-3</sup>	ITO/SnO <sub>2</sub> /NMBF-					210
			H/(FAPbl <sub>3</sub> ) <sub>x</sub> (MAPbBr <sub>3</sub> ) <sub>1-x</sub> /Spiro-	1.05	67	24.7	18.9	
			OMeTAD/Ag					
C-PCBA	-	5 76 ×10 <sup>-3</sup>	FTO/compact TiO <sub>2</sub> /C-PCBA/ CsMAFA-Pb-	1 1 4 8	82.8	26.1	24 81	211
01007		5170 120	perovskite /spiro-OMeTAD/Au	1.1.10	02.0	20.1	21.01	
PCBM	-	-	FTO/SnO <sub>2</sub> /PCBM/MAPbI <sub>3</sub> /spiro-	1.12	75.83	22.61	19.12	212
			UNIETAD/AU					
C9	4.03/6.05	-	/sniro-OMeTAD/Au	1.12	78.9	24.1	21.3	213
			ITO/SnO <sub>2</sub> /NPC <sub>60</sub> -					
NPC <sub>60</sub> -OH	-	-	OH/(FAPbl <sub>3</sub> ) <sub>x</sub> (MAPbBr <sub>3</sub> ) <sub>1-x</sub> /Spiro-	1.13	80.73	23.37	21.39	214
			OMeTAD/Ag					
CPTΔ	_	_	ITO/SnO <sub>2</sub> /CPTA/MAPbI <sub>3</sub> /spiro-	1.06	79 5	22.67	19.2	215
CITA			OMeTAD/Au	1.00	75.5	22.07	13.2	215
			ITO/SnO <sub>2</sub> /CL-PCBM/Cs <sub>0.05</sub> (FA <sub>0.85</sub> MA	= 0				
			$_{0.15}$ ) $_{0.95}$ Pb( $I_{0.85}$ Br $_{0.15}$ ) $_{3}$ /spiro-	1.1/8	/9.6/	23.63	22.16	216
CL-PCBIVI	-	-	$UMETAD/WOO_3/Ag$					
			OMeTAD/MoO <sub>2</sub> /Ag	1.125	83.30	25.66	24.19	
			ITO/SnO <sub>2</sub> /AHF-4/CsMAFA-Pb-					
AHF-4	-4.18/-6.21	5.95 × 10⁻⁵	perovskite/Spiro-OMeTAD/Au	1.16	76.52	24.04	21.43	217
	2 92/E 0E		ITO/SnO <sub>2</sub> /AHF-3/CsMAFA-Pb-	1 1 6	76.25	22 CE	20 OF	217
АПГ-Э	-3.82/-3.95	-	perovskite/Spiro-OMeTAD/Au	1.10	70.25	25.05	20.95	217
FeoPD	-3.85/-5.40 ª	9.75 ×10 <sup>-4 b</sup>	ITO/SnO <sub>2</sub> /F <sub>60</sub> PD/CsMAFA-Pb-perovskite	1.16	80.00	25.43	23.65	218
00	,		/Spiro-OMeTAD/Ag					
F <sub>70</sub> PD	-3.71/-5.26ª	2.33 ×10 <sup>-3 b</sup>	IIO/SnO <sub>2</sub> /F <sub>70</sub> PD/CsMAFA-Pb-perovskite /Spiro-OMeTAD/Ag	1.17	81.20	25.33	24.09	218
			/ Shi n-Ower AD/ Ag					

<sup>a</sup> The HOMO/LUMO of fullerene-based perovskite films

<sup>b</sup> The Electron mobility of SnO<sub>2</sub>/fullerene

# 7. Summary and outlook

Fullerene materials (e.g., C<sub>60</sub>, C<sub>70</sub>) demonstrate significant potential in PSCs due to their superior electron affinity and charge transport capabilities, coupled with minimized recombination energy and versatile functionalization potential. Targeted chemical modifications through specific functional group introductions enable precise tailoring of their material properties to meet distinct functional requirements in various device components, including charge transport layers, perovskite additives, and interface modification layers. When employed as charge transport layers, optimized fullerene derivatives typically exhibit five properties: (1) high electron mobility for enhanced charge transport efficiency, (2) superior solution processability, (3) energy level alignment with perovskite materials, (4) excellent photo and thermal stability, (5) chemically interactions between functional groups and perovskite components. As perovskite additives, fullerene material design prioritizes solubility optimization, charge transport enhancement,

and interfacial interactions with perovskite to regulate crystallization processes and improve material stability. When utilized as interface modification layers, the functionalization strategy of fullerene emphasizes energy level matching optimization, construction of efficient charge transport pathways, and design of defect-passivating functional groups. Thus, functionalized fullerene materials can effectively improve the efficiency and stability of PSCs.

Despite the extensive utilization of fullerene materials in PSCs, several challenges still remain:

(1) The incorporation of targeted functional groups can effectively enhance the solubility of fullerene-based materials, enabling lowtemperature solution processing while simultaneously passivating defects, reducing non-radiative recombination, and thus, improving the PCE of PSCs. Nevertheless, such structural modifications inevitably compromise the integral conjugated framework of fullerene molecules, thereby diminishing intrinsic charge transport capabilities. The resultant deterioration in electrical conductivity adversely impacts carrier mobility and extraction efficiency at electrode interfaces which is significant to the performance of PSCs. Consequently, achieving an optimal balance between defect-



PSCs.

passivation efficacy and charge-transport characteristics remains a critical challenge in the rational design of next-generation fullerene derivatives for photovoltaic applications.

(2) The photothermal stability of fullerene materials greatly influences the overall device performance. The rigid skeleton and complete  $\pi$ -conjugated structure of carbon cages confer excellent moisture and oxygen resistance to fullerenes. Nevertheless, research has demonstrated that fullerenes exhibit inadequate photostability and thermal stability, with the potential to undergo chemical or physical transformations when subjected to ultraviolet radiation or extended thermal stress. This significantly constrains their deployment as the bottom ETL or interface modification layer in PSCs. It is therefore essential to enhance the photostability of fullerene materials through functionalization or interaction with other organic compounds to develop a stable fullerene ETL or interface layer and thereby improve the operational and storage stability of PSCs.

(3) Despite progressive research efforts, the fundamental operational mechanisms governing fullerene-based materials in PSCs remain inadequately elucidated. This includes the accumulation mode of fullerene spheres, the strength of interaction with fullerene and adjacent layers including perovskite or inorganic oxide ETL layers, and the structure-property relationships underlying defect passivation efficacy and charge transport pathways. The theoretical explanation and experimental proof of these mechanisms have yet

to be established fundamentally constrains the strategic deployment and performance optimization of fullerene derivatives in PSCs. It is therefore evident that, in the future development of fullerenes, researchers should not only propose new ideas in molecular design, but also combine more theoretical calculations and simulations in order to establish a new regulatory mechanism for the properties of fullerenes in PSCs. It is hoped that these issues will stimulate further development and provide new impetus for the fullerene functionalization of PSCs, as well as encouraging joint efforts to prepare efficient and stable PSCs.

# Author contributions

Y. Z., S. Z. and W. D. wrote the original manuscript draft. S. Y. revised the manuscript. All authors read, corrected and approved the manuscript.

# **Conflicts of interest**

There are no conflicts to declare.

# Data availability

No primary research results, software or codes were included and no new data were generated or analyzed as part of this review.

# Acknowledgements

S. Y. acknowledges the National Natural Science Foundation of China (51925206, 52461160328), the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB0450301) and the Fundamental Research Funds for the Central Universities (20720220009, WK2490000002).

# Notes and references

- 1. G. Dastgeer, S. Nisar, M. W. Zulfiqar, J. Eom, M. Imran and K. Akbar, *Nano Energy*, 2024, **132**, 110401.
- L. Zhang, L. Mei, K. Wang, Y. Lv, S. Zhang, Y. Lian, X. Liu, Z. Ma, G. Xiao, Q. Liu, S. Zhai, S. Zhang, G. Liu, L. Yuan, B. Guo, Z. Chen, K. Wei, A. Liu, S. Yue, G. Niu, X. Pan, J. Sun, Y. Hua, W. Q. Wu, D. Di, B. Zhao, J. Tian, Z. Wang, Y. Yang, L. Chu, M. Yuan, H. Zeng, H. L. Yip, K. Yan, W. Xu, L. Zhu, W. Zhang, G. Xing, F. Gao and L. Ding, *Nano-micro Lett.*, 2023, **15**, 177.
- J. Y. Kim, J. W. Lee, H. S. Jung, H. Shin and N. G. Park, Chem. Rev., 2020, 120, 7867-7918.
- 4. E. Aydin, T. G. Allen, M. De Bastiani, A. Razzaq, L. Xu, E. Ugur, J. Liu and S. De Wolf, *Science*, 2024, **383**, 162.
- 5. T. Leijtens, K. A. Bush, R. Prasanna and M. D. McGehee, *Nat. Energy*, 2018, **3**, 828-838.
- W. Shockley and H. J. Queisser, J. Appl. Phys., 1961, 32, 510-519.
- 7. A. Polman, M. Knight, E. C. Garnett, B. Ehrler and W. C. Sinke, *Science*, 2016, **352**, aad4424.
- J. Zhou, L. Tan, Y. Liu, H. Li, X. Liu, M. Li, S. Wang, Y. Zhang, C. Jiang, R. Hua, W. Tress, S. Meloni and C. Yi, *Joule*, 2024, 8, 1691-1706.
- G. Qu, L. Zhang, Y. Qiao, S. Gong, Y. Ding, Y. Tao, S. Cai, X. Chang, Q. Chen, P. Xie, J. Feng, C. Gao, G. Li, H. Xiao, F. Wang, H. Hu, J. Yang, S. Chen, A. K. Y. Jen, X. Chen and Z.-X. Xu, *Nat. Commun.*, 2025, **16**, 86.
- M. A. Green, E. D. Dunlop, M. Yoshita, N. Kopidakis, K. Bothe, G. Siefer, X. J. Hao and J. Y. Jiang, *Prog Photovoltaics*, 2025, **33**, 3-15.
- 11. C. C. Stoumpos and M. G. Kanatzidis, Acc. Chem. Res., 2015, 48, 2791-2802.
- 12. J. H. Noh, S. H. Im, J. H. Heo, T. N. Mandal and S. I. Seok, *Nano Lett.*, 2013, **13**, 1764-1769.
- 13. G. Xing, N. Mathews, S. Sun, S. S. Lim, Y. M. Lam, M. Grätzel, S. Mhaisalkar and T. C. Sum, *Science*, 2013, **342**, 344-347.
- A. Miyata, A. Mitioglu, P. Plochocka, O. Portugall, J. T.-W. Wang, S. D. Stranks, H. J. Snaith and R. J. Nicholas, *Nat. Phys.*, 2015, 11, 582-587.
- 15. J. Gebhardt and A. M. Rappe, Adv. Mater., 2019, **31**, 1802697.
- L. B. Jia, M. Q. Chen and S. F. Yang, *Mater. Chem. Front.*, 2020, 4, 2256-2282.
- 17. X. Zhang, S. F. Wu, H. Zhang, A. K. Y. Jen, Y. Q. Zhan and J. H. Chu, *Nat Photonics*, 2024, **18**, 1243-1253.
- W. Zhang, X. Guo, Z. Cui, H. Yuan, Y. Li, W. Li, X. Li and J. Fang, Adv. Mater., 2024, 36, 2311025.
- L. Shen, P. Song, K. Jiang, L. Zheng, J. Qiu, F. Li, Y. Huang, J. Yang, C. Tian, A. K. Y. Jen, L. Xie and Z. Wei, *Nat. Commun.*, 2024, **15**, 10908.

- Z. Li, C. Xiao, Y. Yang, S. P. Harvey, D. H. Kim, J. A. Christians, M. Yang, P. Schulz, S. U. Nanayakkara, C.-S. Jiang, J. M. Luther, J. J. Berry, M. C. Beard, M. M. Al-Jassim and K. Zhu, *Energy Environ. Sci.*, 2017, **10**, 1234-1242.
- Y. Zhao, T. Heumueller, J. Zhang, J. Luo, O. Kasian, S. Langner, C. Kupfer, B. Liu, Y. Zhong, J. Elia, A. Osvet, J. Wu, C. Liu, Z. Wan, C. Jia, N. Li, J. Hauch and C. J. Brabec, *Nat. Energy*, 2021, 7, 144-152.
- K. Zhao, Q. Liu, L. Yao, C. Deger, J. Shen, X. Zhang, P. Shi, Y. Tian, Y. Luo, J. Xu, J. Zhou, D. Jin, S. Wang, W. Fan, S. Zhang, S. Chu, X. Wang, L. Tian, R. Liu, L. Zhang, I. Yavuz, H. F. Wang, D. Yang, R. Wang and J. Xue, *Nature*, 2024, 632, 301-306.
- O. Malinkiewicz, A. Yella, Y. H. Lee, G. M. Espallargas, M. Graetzel, M. K. Nazeeruddin and H. J. Bolink, *Nat. Photonics*, 2013, 8, 128-132.
- 24. T. P. Li, F. F. He, J. Liang and Y. B. Qi, *Joule*, 2023, 7, 1966-1991.
- M. Li, M. Liu, F. Qi, F. R. Lin and A. K. Jen, *Chem. Rev.*, 2024, **124**, 2138-2204.
- X. Yin, Z. Wang, Y. Zhao, S. Zhang, Y. Zhang and Y. Song, *Energy Environ. Sci.*, 2023, **16**, 4251-4279.
- F. H. Isikgor, S. Zhumagali, L. V. T. Merino, M. De Bastiani, I. McCulloch and S. De Wolf, *Nat. Rev. Mater.*, 2023, 8, 89-108.
- C. Zhao, Z. Zhou, M. Almalki, M. A. Hope, J. Zhao, T. Gallet, A. Krishna, A. Mishra, F. T. Eickemeyer, J. Xu, Y. Yang, S. M. Zakeeruddin, A. Redinger, T. J. Savenije, L. Emsley, J. Yao, H. Zhang and M. Grätzel, *Nat. Commun.*, 2024, **15**, 7139.
- 29. M. Vasilopoulou, A. Fakharuddin, A. G. Coutsolelos, P. Falaras, P. Argitis, A. Yusoff and M. K. Nazeeruddin, *Chem. Soc. Rev.*, 2020, **49**, 4496-4526.
- X. Wang, S. Liu, H. Wang and J. Luo, *Adv. Funct. Mater.*, 2024, 34, 2403104.
- H. Wang, Z. Y. Zhang, C. Y. Zhang, Y. G. Yao and K. Wang, J. Mater. Chem. A, 2024, 12, 22442-22457.
- M. Ai, M. Q. Chen and S. F. Yang, Chin. J. Chem., 2023, 41, 2337-2353.
- 33. Z. Xing, S. H. Li and S. H. Yang, *Small Struct.*, 2022, **3**, 2200012.
- C. H. Cui, Y. W. Li and Y. F. Li, *Adv. Energy Mater.*, 2016, 7, 1601251.
- 35. K. Liu, C. Tian, Y. Liang, Y. Luo, L. Xie and Z. Wei, *Nano Res.*, 2022, **15**, 7139-7153.
- 36. Z. Xing, F. Liu, S. H. Li, Z. C. Chen, M. W. An, S. Zheng, A. K. Y. Jen and S. Yang, *Adv. Funct. Mater.*, 2021, **31**, 2107695.
- T. Ahmad, B. Wilk, E. Radicchi, R. Fuentes Pineda, P. Spinelli, J. Herterich, L. A. Castriotta, S. Dasgupta, E. Mosconi, F. De Angelis, M. Kohlstädt, U. Würfel, A. Di Carlo and K. Wojciechowski, *Adv. Funct. Mater.*, 2020, **30**, 2004357.
- H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl and R. E. Smalley, *Nature*, 1985, **318**, 162-163.
- A. Hirsch, Z. Chen and H. Jiao, Angew. Chem. Int. Ed., 2000, 39, 3915-3917.
- 40. A. Rosén and B. Wästberg, J. Chem. Phys., 1989, 90, 2525-2526.
- 41. L. Echegoyen and L. E. Echegoyen, *Acc. Chem. Res.*, 1998, **31**, 593-601.
- 42. Q. Xie, E. Perez-Cordero and L. Echegoyen, J. Am. Chem. Soc., 2002, **114**, 3978-3980.
- C.-Z. Li, C.-C. Chueh, H.-L. Yip, J. Zou, W.-C. Chen and A. K. Y. Jen, J. Mater. Chem., 2012, 22, 14976.
- 44. C. A. Reed and R. D. Bolskar, Chem. Rev., 2000, 100, 1075-1120.
- 45. H. Imahori and Y. Sakata, Adv. Mater., 2004, 9, 537-546.
- 46. Q. Huang and H. Li, Chin. Sci. Bull., 2013, 58, 2677-2685.
- 47. P. J. Fagan, J. C. Calabrese and B. Malone, *Science*, 1991, **252**, 1160-1161.
- 48. J. M. Hawkins, A. Meyer, T. A. Lewis, S. Loren and F. J. Hollander, *Science*, 1991, **252**, 312-313.
- 49. P. J. Fagan, P. J. Krusic, D. H. Evans, S. A. Lerke and E. Johnston, *J. Am. Chem. Soc.*, 2002, **114**, 9697-9699.
- P. D. W. Boyd, P. Bhyrappa, P. Paul, J. Stinchcombe, R. Bolskar, Y. Sun and C. A. Reed, J. Am. Chem. Soc., 2002, **117**, 2907-2914.

- 51. W. T. Ford, T. Nishioka, F. Qiu, F. D'Souza and J. Choi, *J. Org. Chem.*, 2000, **65**, 5780-5784.
- M. Maggini, G. Scorrano and M. Prato, J. Am. Chem. Soc., 2002, 115, 9798-9799.
- C. Caron, R. Subramanian, F. D'Souza, J. Kim, W. Kutner, M. T. Jones and K. M. Kadish, *J. Am. Chem. Soc.*, 2002, **115**, 8505-8506.
- 54. N. R. Tummala, S. A. Elroby, S. G. Aziz, C. Risko, V. Coropceanu and J.-L. Brédas, *J. Phys. Chem. C*, 2016, **120**, 17242-17250.
- M. Lenes, G. J. A. H. Wetzelaer, F. B. Kooistra, S. C. Veenstra, J. C. Hummelen and P. W. M. Blom, *Adv. Mater.*, 2008, **20**, 2116-2119.
- 56. L. Zang, C. Zhao, X. Hu, J. Tao, S. Chen and J. Chu, *Small*, 2024, **20**, e2400807.
- 57. J. R. Lian, B. Lu, F. F. Niu, P. J. Zeng and X. W. Zhan, *Small Methods*, 2018, **2**, 1800082.
- 58. S. Z. Zheng, G. P. Wang, T. F. Liu, L. Y. Lou, S. Xiao and S. H. Yang, *Sci. China Chem.*, 2019, **62**, 800-809.
- L. Y. Lin, T. W. Jones, T. C. J. Yang, N. W. Duffy, J. H. Li, L. Zhao,
  B. Chi, X. B. Wang and G. J. Wilson, *Adv. Funct. Mater.*, 2021, **31**, 2008300.
- M. J. Paik, Y. Lee, H. S. Yun, S. U. Lee, S. T. Hong and S. I. Seok, Adv. Energy Mater., 2020, 10, 2001799.
- 61. Q. Jiang, X. Zhang and J. You, Small, 2018, 14, 1801154.
- 62. T. Leijtens, G. E. Eperon, S. Pathak, A. Abate, M. M. Lee and H. J. Snaith, *Nat. Commun.*, 2013, **4**, 2885.
- X. Li, Z. Shi, F. Behrouznejad, M. Hatamvand, X. Zhang, Y. Wang, F. Liu, H. Wang, K. Liu, H. Dong, F. Mudasar, J. Wang, A. Yu and Y. Zhan, *J. Energy Chem.*, 2022, 67, 1-7.
- Z. Suo, Z. Xiao, S. Li, J. Liu, Y. Xin, L. Meng, H. Liang, B. Kan, Z. Yao, C. Li, X. Wan and Y. Chen, *Nano Energy*, 2023, **118**, 109032.
- 65. A. A. Said, J. Xie and Q. Zhang, *Small*, 2019, **15**, e1900854.66. K. Zhang, H. Yu, X. Liu, Q. Dong, Z. Wang, Y. Wang, N. Chen, Y.
- Zhou and B. Song, *Sci. China Chem.*, 2016, **60**, 144-150. 67. J. You, Z. Hong, Y. Yang, Q. Chen, M. Cai, T.-B. Song, C.-C. Chen,
- S. Lu, Y. Liu, H. Zhou and Y. Yang, *ACS Nano*, 2014, **8**, 1674-1680. 68. H. Sun, K. Xiao, H. Gao, C. Duan, S. Zhao, J. Wen, Y. Wang, R. Lin,
- X. Zheng, H. Luo, C. Liu, P. Wu, W. Kong, Z. Liu, L. Li and H. Tan, *Adv. Mater.*, 2024, **36**, 2308706.
- 69. H. Ueno, K. Uchiyama, Y. Ma, K. Watanabe, K. Yoza, Y. Matsuo and H. Moriyama, *J. Org. Chem.*, 2018, **83**, 10655-10659.
- T. Zheng, L. Fan, B. Jin and R. Peng, J. Colloid Interface Sci., 2023, 642, 497-504.
- 71. Z. Xing, S. H. Li, F. F. Xie, P. Y. Xu, L. L. Deng, X. Zhong and S. Y. Xie, *ACS Appl. Mater. Interfaces*, 2020, **12**, 35081-35087.
- 72. R. Zahran and Z. Hawash, *Adv. Mater. Interfaces*, 2022, **9**, 2201438.
- 73. J. Y. Jeng, Y. F. Chiang, M. H. Lee, S. R. Peng, T. F. Guo, P. Chen and T. C. Wen, *Adv. Mater.*, 2013, **25**, 3727–3732.
- 74. P. W. Liang, C. C. Chueh, S. T. Williams and A. K. Y. Jen, *Adv. Energy Mater.*, 2015, **5**, 1402321.
- 75. N. O. McHedlov-Petrossyan, Chem. Rev., 2013, 113, 5149-5193.
- A. A. Said, E. Aydin, E. Ugur, Z. Xu, C. Deger, B. Vishal, A. Vlk, P. Dally, B. K. Yildirim, R. Azmi, J. Liu, E. A. Jackson, H. M. Johnson, M. Gui, H. Richter, A. R. Pininti, H. Bristow, M. Babics, A. Razzaq, S. Mandal, T. G. Allen, T. D. Anthopoulos, M. Ledinský, I. Yavuz, B. P. Rand and S. De Wolf, *Nat. Commun.*, 2024, **15**, 708.
- 77. T. Tian, J. X. Zhong, M. Yang, W. Feng, C. Zhang, W. Zhang, Y. Abdi, L. Wang, B. X. Lei and W. Q. Wu, *Angew. Chem. Int. Ed.*, 2021, **60**, 23735-23742.
- 78. Z. Jia, H. Zhong, J. Shen, Z. Yu, J. Tao, S. Yin, X. Liu, S. Chen, S. Yang and W. Kong, *Chem. Eng. J.*, 2022, **446**, 136897.
- 79. Z. Xing, F. Liu, S. H. Li, X. Huang, A. Fan, Q. Huang and S. Yang, Angew. Chem. Int. Ed., 2023, 62, e202305357.
- Z.-c. Cheng, Y.-y. Fang, A.-f. Wang, T.-t. Ma, F. Liu, S. Gao, S.-h. Yan, Y. Di and T.-s. Qin, *J. Cen. South Univ.*, 2022, 28, 3714-3727.
- J. C. Hummelen, B. W. Knight, F. Lepeq, F. Wudl, J. Yao and C. L. Wilkins, *J. Org. Chem.*, 1995, **60**, 532-538.

- 82. Y. Shao, Z. Xiao, C. Bi, Y. Yuan and J. Huang, *Nat. Commun.*, 2014, **5**, 5784.
- 83. Y. C. Shao, Y. B. Yuan and J. S. Huang, *Nat. Energy*, 2016, 1, 15001.
- C. Z. Li, C. C. Chueh, F. Ding, H. L. Yip, P. W. Liang, X. Li and A. K. Jen, *Adv. Mater.*, 2013, 25, 4425–4430.
- C. Gong, H. Li, Z. Xu, Y. Li, H. Wang, Q. Zhuang, A. Wang, Z. Li, Z. Guo, C. Zhang, B. Wang, X. Li and Z. Zang, *Nat. Commun.*, 2024, 15, 9154.
- A. Distler, T. Sauermann, H. J. Egelhaaf, S. Rodman, D. Waller, K. S. Cheon, M. Lee and D. M. Guldi, *Adv. Energy Mater.*, 2013, 4, 1300693.
- S. Pont, F. Foglia, A. M. Higgins, J. R. Durrant and J. T. Cabral, Adv. Funct. Mater., 2018, 28, 1802520.
- C. Tian, G. Betancourt-Solis, Z. Nan, K. Liu, K. Lin, J. Lu, L. Xie, L. Echegoyen and Z. Wei, *Sci. Bull.*, 2021, 66, 339-346.
- Y.-C. Zhai, K. Yamanaka, C.-Y. Yu, J.-Z. Wang, X.-L. Zheng, M. Huda, N. Imai, T. Igarashi, S. Aoyagi and Y. Matsuo, *Chem. Commun.*, 2024, **60**, 9420-9423.
- 90. Q. Yuan, D. Han, S. Yi, D. Zhou and L. Feng, *Organic Electronics*, 2020, **77**, 105492.
- Z. Luo, F. Wu, T. Zhang, X. Zeng, Y. Xiao, T. Liu, C. Zhong, X. Lu, L. Zhu, S. Yang and C. Yang, *Angew.Chem.Int. Ed.*, 2019, **58**, 8520-8525.
- R. D. Chavan, D. Prochowicz, B. Bończak, M. Fiałkowski, M. M. Tavakoli, P. Yadav, M. J. Patel, S. K. Gupta, P. N. Gajjar and C. K. Hong, ACS Appl. Mater. Interfaces 2021, 13, 20296-20304.
- C. Yang, S. Cho, A. J. Heeger and F. Wudl, Angew. Chem. Int. Ed., 2009, 48, 1592-1595.
- C. Chen, Y.-Z. Zhu, H.-Y. Zhao and J.-Y. Zheng, *Tetrahedron Letters*, 2013, 54, 1607-1611.
- 95. B. Bończak, W. Lisowski, A. Kamińska, M. Hołdyński and M. Fiałkowski, J. Phys. Chem. C, 2019, **123**, 6229-6240.
- Y. Jiang, J. Wang, H. Zai, D. Ni, J. Wang, P. Xue, N. Li, B. Jia, H. Lu, Y. Zhang, F. Wang, Z. Guo, Z. Bi, H. Xie, Q. Wang, W. Ma, Y. Tu, H. Zhou and X. Zhan, *J. Am. Chem. Soc.*, 2022, **144**, 5400-5410.
- 97. K. R. Yan, Z. Q. Shen, B. F. Niu, Y. C. Huang, D. Wang, E. Gu, B. Y. Yan, J. Z. Yao, H. Z. Chen and C. Z. Li, *Sci. China Chem.*, 2023, **66**, 1795-1803.
- 98. Q. J. Shui, S. Q. Shan, Y. C. Zhai, S. Aoyagi, S. Izawa, M. Huda, C. Y. Yu, L. J. Zuo, H. Z. Chen, H. S. Lin and Y. Matsuo, *J. Am. Chem. Soc.*, 2023, **145**, 27307-27315.
- 99. X. Sun, C. Zhang, D. Gao, X. Yu, B. Li, X. Wu, S. Zhang, Y. He, Z. Yu, L. Qian, J. Gong, S. Li, N. Li, Z. Zhu and Z. Li, *Angew. Chem. Int. Ed.*, 2025, **64**, e202412819.
- 100.G. Zhou, X. Luo, Z. Wang, C. Ding, Y. Guo, C. Ma and B. Xu, ChemSusChem, 2025, 18, e202401629.
- 101.T. Zheng, H. Zhou, B. Fan, Y. Zhao, B. Jin, L. Fan and R. Peng, *Chem. Eng. J.*, 2021, **415**, 128816.
- 102.Y. Bai, Q. Dong, Y. Shao, Y. Deng, Q. Wang, L. Shen, D. Wang, W. Wei and J. Huang, *Nat. Commun.*, 2016, **7**, 12806.
- 103.J. Yin, X. Shi, L. Wang, H. Yan and S. Chen, Angew. Chem. Int. Ed., 2022, 61, e202210610.
- 104.E. Hou, S. Cheng, Y. Qiu, X. Chen, J. Chen, C. Sun, H. Zhang, J. Yang, X. Zhao, L. Xie, Z. Chen, C. Tian and Z. Wei, *Angew. Chem. Int. Ed.*, 2024, **64**, e202416703.
- 105.A. Pal, L. K. Wen, C. Y. Jun, I. Jeon, Y. Matsuo and S. Manzhos, *Phys. Chem. Chem. Phys.*, 2017, **19**, 28330-28343.
- 106.B. Li, J. Zhen, Y. Wan, X. Lei, Q. Liu, Y. Liu, L. Jia, X. Wu, H. Zeng, W. Zhang, G.-W. Wang, M. Chen and S. Yang, ACS Appl. Mater. Interfaces, 2018, **10**, 32471-32482.
- 107.F. Zhang, W. Shi, J. Luo, N. Pellet, C. Yi, X. Li, X. Zhao, T. J. S. Dennis, X. Li, S. Wang, Y. Xiao, S. M. Zakeeruddin, D. Bi and M. Grätzel, *Adv. Mater.*, 2017, **29**, 1606806.
- 108.S.-M. Dai, X. Zhang, W.-Y. Chen, X. Li, Z. a. Tan, C. Li, L.-L. Deng, X.-X. Zhan, M.-S. Lin, Z. Xing, T. Wen, R.-M. Ho, S.-Y. Xie, R.-B. Huang and L.-S. Zheng, *J. Mater. Chem. A*, 2016, **4**, 18776-18782.

- 109.E. Castro, O. Fernandez-Delgado, A. Artigas, G. Zavala, F. Liu, A. Moreno-Vicente, A. Rodríguez-Fortea, J. D. Velasquez, J. M. Poblet and L. Echegoyen, *J. Mater. Chem. C*, 2020, **8**, 6813-6819.
- 110.B. R. Li, J. M. Zhen, Y. Y. Wan, X. Y. Lei, L. B. Jia, X. J. Wu, H. L. Zeng, M. Q. Chen, G. W. Wang and S. F. Yang, *J. Mater. Chem. A*, 2020, **8**, 3872-3881.
- 111.W. D. Shi, Q. Zhuang, R. Zhou, X. Y. Hou, X. M. Zhao, J. Kong and M. J. Fuchter, *Adv. Energy Mater.*, 2023, **13**, 2300054.
- 112.C. Sun, P. Yang, Z. Nan, C. Tian, Y. Cai, J. Chen, F. Qi, H. Tian, L. Xie, L. Meng and Z. Wei, *Adv. Mater.*, 2023, **35**, 2205603.
- 113.P. Yang, C. Sun, X. Fu, S. Cheng, J. Chen, H. Zhang, Z. A. Nan, J. Yang, X. J. Zhao, L. Q. Xie, L. Meng, C. Tian and Z. Wei, *J. Am. Chem. Soc.*, 2024, **146**, 2494-2502.
- 114.S. S. Shin, S. J. Lee and S. I. Seok, *Adv. Funct. Mater.*, 2019, **29**, 1900455.
- 115.X. Y. Meng, Y. Bai, S. Xiao, T. Zhang, C. Hu, Y. L. Yang, X. L. Zheng and S. H. Yang, *Nano Energy*, 2016, **30**, 341-346.
- 116.T. Zheng, B. Fan, Y. Zhao, B. Jin, L. S. Fan and R. F. Peng, *Chem. Eng. J.*, 2021, **420**, 129730.
- 117.H. Yoon, S. M. Kang, J. K. Lee and M. Choi, *Energy Environ. Sci.*, 2016, **9**, 2262-2266.
- 118.Y. C. Wang, X. D. Li, L. P. Zhu, X. H. Liu, W. J. Zhang and J. F. Fang, *Adv. Energy Mater.*, 2017, **7**, 1701144.
- 119.H. R. Liu, S. H. Li, L. L. Deng, Z. Y. Wang, Z. Xing, X. Rong, H. R. Tian, X. Li, S. Y. Xie, R. B. Huang and L. S. Zheng, ACS Appl. Mater. Interfaces, 2019, **11**, 23982-23989.
- 120.L. R. Dong, S. D. Qiu, S. Feroze, M. Wagner, O. Kasian, H. Peisert, F. U. Kosasih, C. Ducati, J. G. Cerrillo, J. J. Tian, C. H. Li, D. Jang, V. M. Le Corre, N. Li, F. Yang, T. Du, C. J. Brabec and H. J. Egelhaaf, *Energy Environ. Sci.*, 2024, **17**, 7147-7154.
- 121.S. Pont, J. R. Durrant and J. T. Cabral, *Adv. Energy Mater.*, 2019, 9, 1803948.
- 122.K. Wojciechowski, T. Leijtens, S. Siprova, C. Schlueter, M. T. Hörantner, J. T.-W. Wang, C.-Z. Li, A. K. Y. Jen, T.-L. Lee and H. J. Snaith, J. Phys. Chem. Lett., 2015, **6**, 2399-2405.
- 123.S. A. Dowland, M. Salvador, J. D. Perea, N. Gasparini, S. Langner, S. Rajoelson, H. H. Ramanitra, B. D. Lindner, A. Osvet, C. J. Brabec, R. C. Hiorns and H.-J. Egelhaaf, ACS Appl. Mater. Interfaces, 2017, 9, 10971-10982.
- 124.B. L. Watson, N. Rolston, K. A. Bush, T. Leijtens, M. D. McGehee and R. H. Dauskardt, ACS Appl. Mater. Interfaces, 2016, 8, 25896-25904.
- 125.K. Wojciechowski, I. Ramirez, T. Gorisse, O. Dautel, R. Dasari, N. Sakai, J. M. Hardigree, S. Song, S. Marder, M. Riede, G. Wantz and H. J. Snaith, *ACS Energy Lett.*, 2016, **1**, 648-653.
- 126.P. Topolovsek, F. Lamberti, T. Gatti, A. Cito, J. M. Ball, E. Menna, C. Gadermaier and A. Petrozza, J. Mater. Chem. A, 2017, 5, 11882-11893.
- 127.M. B. Suárez, C. Aranda, L. Macor, J. Durantini, D. A. Heredia, E. N. Durantini, L. Otero, A. Guerrero and M. Gervaldo, *Electrochim. Acta*, 2018, **292**, 697-706.
- 128.N. B. Kotadiya, P. W. M. Blom and G. A. H. Wetzelaer, *Phys. Rev. Applied*, 2019, **11**, 024069.
- 129.G. J. A. H. Wetzelaer and P. W. M. Blom, *J. Mater. Chem. C*, 2021, **9**, 16068-16077.
- 130.E. Cho, V. Coropceanu and J. L. Brédas, *Organic Electronics*, 2023, **118**, 106798.
- 131.A. Rajagopal, P. W. Liang, C. C. Chueh, Z. B. Yang and A. K. Y. Jen, *ACS Energy Lett.*, 2017, **2**, 2531-2539.
- 132.S. F. Volker, M. Valles-Pelarda, J. Pascual, S. Collavini, F. Ruiperez, E. Zuccatti, L. E. Hueso, R. Tena-Zaera, I. Mora-Sero and J. L. Delgado, *Chem. Eur.J.*, 2018, **24**, 8524-8529.
- 133.C. Tian, K. Lin, J. Lu, W. Feng, P. Song, L. Xie and Z. Wei, *Small Methods*, 2019, **4**.
- 134.Y. Xing, C. Sun, H. L. Yip, G. C. Bazan, F. Huang and Y. Cao, *Nano Energy*, 2016, **26**, 7-15.

- 135.A. Cabrera-Espinoza, S. Collavini, J. G. Sanchez, I. Kosta, E. Palomares and J. L. Delgado, *ACS Appl. Mater. Interfaces* 2024, **16**, 20852-20864.
- 136.J. Luo, H. Zhang, C. Sun, E. Hou, X. Wang, S. Guo, J. Chen, S. Cheng, S. Chen, X. Zhao, L. Xie, L. Meng, C. Tian and Z. Wei, *Angew. Chem. Int. Ed.*, 2024, **63**, e202411659.
- 137.S. Liu, Y. J. Guan, Y. S. Sheng, Y. Hu, Y. G. Rong, A. Y. Mei and H. W. Han, *Adv. Energy Mater.*, 2020, **10**, 1902492.
- 138.J. R. Wang, L. Y. Bi, Q. Fu and A. K. Y. Jen, *Adv. Energy Mater.*, 2024, **14**, 2401414.
- 139.E. Aydin, M. De Bastiani and S. De Wolf, *Adv. Mater.*, 2019, **31**, 1900428.
- 140.Q. Y. Ma, Y. S. Wang, L. M. Liu, P. Yang, W. J. He, X. Zhang, J. Z. Zheng, M. G. Ma, M. X. Wan, Y. Z. Yang, C. L. Zhang, T. Mahmoudi, S. H. Wu, C. Liu, Y.-B. Hahn and Y. H. Mai, *Energy Environ. Sci.*, 2024, **17**, 1637-1644.
- 141.B. Ding, Y. Ding, J. Peng, J. Romano-deGea, L. E. K. Frederiksen, H. Kanda, O. A. Syzgantseva, M. A. Syzgantseva, J. N. Audinot, J. Bour, S. Zhang, T. Wirtz, Z. Fei, P. Dorflinger, N. Shibayama, Y. Niu, S. Hu, S. Zhang, F. F. Tirani, Y. Liu, G. J. Yang, K. Brooks, L. Hu, S. Kinge, V. Dyakonov, X. Zhang, S. Dai, P. J. Dyson and M. K. Nazeeruddin, *Nature*, 2024, **628**, 299-305.
- 142.C. Chen, Z. Song, C. Xiao, D. Zhao, N. Shrestha, C. Li, G. Yang, F. Yao, X. Zheng, R. J. Ellingson, C.-S. Jiang, M. Al-Jassim, K. Zhu, G. Fang and Y. Yan, *Nano Energy*, 2019, **61**, 141-147.
- 143.D. K. Lee and N. G. Park, Appl. Phys. Rev., 2023, 10, 011308.
- 144.F. Zhang and K. Zhu, Adv. Energy Mater., 2019, 10, 1902579.
- 145.J. Xu, A. Buin, A. H. Ip, W. Li, O. Voznyy, R. Comin, M. Yuan, S. Jeon, Z. Ning, J. J. McDowell, P. Kanjanaboos, J. P. Sun, X. Lan, L. N. Quan, D. H. Kim, I. G. Hill, P. Maksymovych and E. H. Sargent, *Nat. Commun.*, 2015, **6**, 7081.
- 146.Y.-N. Zhang, B. Li, L. Fu and L.-W. Yin, *J. Power Sources*, 2019, **419**, 27-34.
- 147.C. Kan, Z. Tang, Y. Yao, P. Hang, B. Li, Y. Wang, X. Sun, M. Lei, D. Yang and X. Yu, *ACS Energy Lett.*, 2021, **6**, 3864-3872.
- 148.C. H. Chiang and C. G. Wu, Nat Photonics, 2016, 10, 196-200.
- 149.X. Liu, F. Lin, C. C. Chueh, Q. Chen, T. Zhao, P. W. Liang, Z. L. Zhu, Y. Sun and A. K. Y. Jen, *Nano Energy*, 2016, **30**, 417-425.
- 150.Q. Fu, S. Xiao, X. Tang, Y. Chen and T. Hu, *ACS Appl. Mater. Interfaces* 2019, **11**, 24782-24788.
- 151.L. B. Jia, F. Y. Huang, H. H. Ding, C. Niu, Y. B. Shang, W. P. Hu, X. C. Li, X. Yu, X. F. Jiang, R. G. Cao, J. F. Zhu, G. W. Wang, M. Q. Chen and S. F. Yang, *Nano Today*, 2021, **39**, 101164.
- 152.Y. M. Liang, P. Q. Song, H. R. Tian, C. B. Tian, W. J. Tian, Z. A. Nan, Y. T. Cai, P. P. Yang, C. Sun, J. F. Chen, L. Q. Xie, Q. Y. Zhang and Z. H. Wei, *Adv. Funct. Mater.*, 2021, **32**, 2110139.
- 153.K. Kim, Z. A. Wu, J. Y. Han, Y. Ma, S. S. Lee, S.-K. Jung, J.-W. Lee, H. Y. Woo and I. Jeon, *Adv. Energy Mater.*, 2022, **12**, 2200877.
- 154.T. Zheng, Q. Zhou, T. Yang, Y. Zhao, B. Fan, J. Bo, L. S. Fan and R. F. Peng, *Carbon*, 2022, **196**, 213-219.
- 155.S. You, H. Zeng, Y. Liu, B. Han, M. Li, L. Li, X. Zheng, R. Guo, L. Luo, Z. Li, C. Zhang, R. Liu, Y. Zhao, S. Zhang, Q. Peng, T. Wang, Q. Chen, F. T. Eickemeyer, B. Carlsen, S. M. Zakeeruddin, L. Mai, Y. Rong, M. Gratzel and X. Li, *Science*, 2023, **379**, 288-294.
- B. Jia, X. B. Ma, W. H. Xiang, X. F. Jiang, H. H. Ding, X. C. Li, Y.
  B. Shang, J. F. Zhu, Z. Y. Li, Y. F. Qiu, M. Q. Chen, J. Z. Chen and S.
  F. Yang, *Sci. China Mater.*, 2023, **66**, 2146-2158.
- 157.X. Zhang, S. Wang, W. Zhu, Z. Cao, A. Wang and F. Hao, *Adv. Funct. Mater.*, 2021, **32**, 2108832.
- 158.S. Hu, J. A. Smith, H. J. Snaith and A. Wakamiya, *Precis. Chem.*, 2023, **1**, 69-82.
- 159.X. Meng, Y. Wang, J. Lin, X. Liu, X. He, J. Barbaud, T. Wu, T. Noda, X. Yang and L. Han, *Joule*, 2020, **4**, 902-912.
- 160.C. Zheng, P. Qiu, S. Zhong, X. Luo, S. Wu, Q. Wang, J. Gao, X. Lu, X. Gao, L. Shui, S. Wu and J. M. Liu, *Adv. Funct. Mater.*, 2023, **33**, 2212106.

- 161.C. Wang, F. Gu, Z. Zhao, H. Rao, Y. Qiu, Z. Cai, G. Zhan, X. Li, B. Sun, X. Yu, B. Zhao, Z. Liu, Z. Bian and C. Huang, *Adv. Mater.*, 2020, **32**, 1907623.
- 162.R. Li, M. Guli, W. He, C. Lan, Y. Zhou and Y. Zhang, *Nano Energy*, 2024, **126**, 109664.
- 163.W. Ke, C. C. Stoumpos and M. G. Kanatzidis, *Adv. Mater.*, 2019, 31, 1803230.
- 164.Y. Wu, X. Yang, W. Chen, Y. Yue, M. Cai, F. Xie, E. Bi, A. Islam and L. Han, *Nat. Energy*, 2016, **1**, 16148.
- 165.Y. F. Chen, Z. M. Luo, C. H. Chiang and C. G. Wu, ACS Appl. Mater. Interfaces, 2022, 14, 46603-46614.
- 166.J. Choi, S. J. Yang, S. G. Han, W. Sung, D. Yoo and K. L. Cho, *Chem. Mater.*, 2023, **35**, 1148-1158.
- 167.J. F. Chen, C. B. Tian, C. Sun, P. P. Yang, W. J. Feng, L. F. Zheng, L. Yang, E. L. Hou, J. F. Luo, L. Q. Xie and Z. H. Wei, *Energy Environ. Mater.*, 2022, **7**, e12529.
- 168.J. Chen, J. Luo, E. Hou, P. Song, Y. Li, C. Sun, W. Feng, S. Cheng, H. Zhang, L. Xie, C. Tian and Z. Wei, *Nat. Photonics*, 2024, **18**, 464-470.
- 169.E. Hou, J. Chen, J. Luo, Y. Fan, C. Sun, Y. Ding, P. Xu, H. Zhang, S. Cheng, X. Zhao, L. Xie, J. Yan, C. Tian and Z. Wei, *Angew. Chem. Int. Ed.*, 2024, **63**, e202402775.
- 170.J. Chen, J. Luo, Y. Li, X. Chen, Z. Song, E. Hou, C. Sun, H. Zhang, S. Cheng, Y. Xing, S. Chen, X. Zhao, L. Xie, C. Tian and Z. Wei, *Angew. Chem. Int. Ed.*, 2025, **64**, e202420150.
- 171.Y. Li, Y. Wang, Z. Xu, B. Peng and X. Li, ACS Nano, 2024, 18, 10688-10725.
- 172.J. Xia, M. Sohail and M. K. Nazeeruddin, *Adv. Mater.*, 2023, **35**, 2211324.
- 173.S. Y. Kim, S. J. Cho, S. E. Byeon, X. He and H. J. Yoon, *Adv. Energy Mater.*, 2020, **10**, 2002606.
- 174.Y. X. Shen, C. W. Li, C. Liu, S. A. Reitz, B. Chen and E. H. Sargent, *Appl. Phys. Rev.*, 2024, **11**, 041306.
- 175.J. Z. Chen and N. G. Park, ACS Energy Lett., 2020, 5, 2742-2786.

176.Z. Xing, S.-H. Li, Y. Hui, B.-S. Wu, Z.-C. Chen, D.-Q. Yun, L.-L. Deng, M.-L. Zhang, B.-W. Mao, S.-Y. Xie, R.-B. Huang and L.-S. Zheng, *Nano Energy*, 2020, **74**, 104859.

- 177.C. Wang, X. Yu, L. Fan, W. Ge, B. Fan, Q. Huang, R. Peng and B. Jin, *Carbon*, 2023, **215**, 118398.
- 178.M. Zhang, Q. Chen, R. Xue, Y. Zhan, C. Wang, J. Lai, J. Yang, H. Lin, J. Yao, Y. Li, L. Chen and Y. Li, *Nat. Commun.*, 2019, **10**, 4593.
- 179.S. B. Li, K. Fan, Y. Y. Cui, S. F. Leng, Y. R. Ying, W. J. Zou, Z. L. Liu, C. Z. Li, K. Yao and H. T. Huang, ACS Energy Lett., 2020, 5, 2015-2022.
- 180.M. W. An, Z. Xing, B. S. Wu, F. F. Xie, S. Y. Zheng, L. L. Deng, X. Wang, B. W. Chen, D. Q. Yun, S. Y. Xie, R. B. Huang and L. S. Zheng, *Rare Met.*, 2021, **40**, 1691-1697.
- 181.W. R. Zhou, L. B. Jia, M. Q. Chen, X. C. Li, Z. H. Su, Y. B. Shang, X. F. Jiang, X. Y. Gao, T. Chen, M. T. Wang, Z. L. Zhu, Y. L. Lu and S. F. Yang, *Adv. Funct. Mater.*, 2022, **32**, 2201374.
- 182.X. Jiang, L. Jia, S. Zhang, Y. Gao, N. Yan, T. Hou, S. Gao, X. Wang, X. Li, W. Chen, Z. Xiao, X. Wu, Z. Fang, S. F. Liu and S. Yang, *Angew. Chem. Int. Ed.*, 2024, **63**, e202412409.
- 183.H. Zhang, H. Azimi, Y. Hou, T. Ameri, T. Przybilla, E. Spiecker, M. Kraft, U. Scherf and C. J. Brabec, *Chem. Mater.*, 2014, **26**, 5190-5193.
- 184.J. Min, Z.-G. Zhang, Y. Hou, C. O. Ramirez Quiroz, T. Przybilla, C. Bronnbauer, F. Guo, K. Forberich, H. Azimi, T. Ameri, E. Spiecker, Y. Li and C. J. Brabec, *Chem. Mater.*, 2014, **27**, 227-234.
- 185.C. Y. Chang, W. K. Huang and Y. C. Chang, *Chem. Mater.*, 2016, **28**, 6305-6312.
- 186.S. B. Xiong, M. Yuan, J. M. Yang, J. N. Song, X. W. Guo, X. Li, B. Li, X. J. Liu, C. G. Duan, F. Liu, M. Fahlman and Q. Y. Bao, *Adv. Optical Mater.*, 2019, **7**, 1900542.
- 187.J. Wang, J. Li, Y. Zhou, C. Yu, Y. Hua, Y. Yu, R. Li, X. Lin, R. Chen, H. Wu, H. Xia and H. L. Wang, *J. Am. Chem. Soc.*, 2021, **143**, 7759-7768.

- 188.D. Z. Wang, C. Kang, T. L. Ye, D. Q. He, S. Jin, X. R. Zhang, X. C. Sun and Y. Zhang, *J. Energy Chem.*, 2023, **82**, 334-342.
- 189.C.-Y. Chang, W.-K. Huang, Y.-C. Chang, K.-T. Lee and C.-T. Chen, J. Mater. Chem. A, 2016, 4, 640-648.
- 190.H. Azimi, T. Ameri, H. Zhang, Y. Hou, C. O. R. Quiroz, J. Min, M. Y. Hu, Z. G. Zhang, T. Przybilla, G. J. Matt, E. Spiecker, Y. F. Li and C. J. Brabec, Adv. Energy Mater., 2015, 5, 1401692.
- 191.Y. Liu, M. Bag, L. A. Renna, Z. A. Page, P. Kim, T. Emrick, D. Venkataraman and T. P. Russell, *Adv. Energy Mater.*, 2015, 6, 1501606.
- 192.Z. Zhu, C. C. Chueh, F. Lin and A. K. Jen, *Adv. Sci.*, 2016, **3**, 1600027.
- 193.J. S. Xie, X. G. Yu, X. Sun, J. B. Huang, Y. H. Zhang, M. Lei, K. Huang, D. K. Xu, Z. G. Tang, C. Cui and D. R. Yang, *Nano Energy*, 2016, **28**, 330-337.
- 194.A. Rajagopal, Z. Yang, S. B. Jo, I. L. Braly, P. W. Liang, H. W. Hillhouse and A. K. Jen, *Adv. Mater.*, 2017, **29**, 1702140.
- 195.G. Kapil, T. S. Ripolles, K. Hamada, Y. Ogomi, T. Bessho, T. Kinoshita, J. Chantana, K. Yoshino, Q. Shen, T. Toyoda, T. Minemoto, T. N. Murakami, H. Segawa and S. Hayase, *Nano Lett.*, 2018, **18**, 3600-3607.
- 196.H. Hu, S. Moghadamzadeh, R. Azmi, Y. Li, M. L. Kaiser, J. C. Fischer, Q. H. Jin, J. L. Maibach, I. M. Hossain, U. W. Paetzold and B. Abdollahi Nejand, *Adv. Funct. Mater.*, 2021, **32**, 2107650.
- 197.B. Li, X. Wu, H. Zhang, S. F. Zhang, Z. Li, D. P. Gao, C. L. Zhang, M. Q. Chen, S. Xiao, A. K. Y. Jen, S. F. Yang and Z. L. Zhu, *Adv. Funct. Mater.*, 2022, **32**, 2205870.
- 198.C. Sun, H. Zhang, S. Cheng, J. Chen, Y. Xing, Z. Nan, P. Yang, Y. Wang, X. Zhao, L. Xie, C. Tian and Z. Wei, *Adv. Mater.*, 2024, **36**, 2410248.
- 199.W. C. Shen, A. Azmy, G. Li, A. Mishra, Z. Syrgiannis, W. W. Zheng, G. Volonakis, M. Kepenekian, J. Even, L. Wojtas, C. Wang, L. S. Huang, W. Q. Chen, S. Zhou, J. Zhou, G. J. Zeng, D. X. Pu, H. L. Guan, G. J. Fang, W. J. Ke and I. Spanopoulos, *Adv. Energy Mater.*, 2024, **14**, 2400582.
- 200.J. Zhao, Z. Su, J. Pascual, H. Wu, H. Wang, M. H. Aldamasy, Z. Zhou, C. Wang, G. Li, Z. Li, X. Gao, C. S. Hsu and M. Li, *Adv. Mater.*, 2024, **36**, 2406246.
- 201.S. Zhang, M. Li, H. Zeng, X. Zheng, L. Luo, S. You, Y. Zhao, R. Liu, C. Tian and X. Li, ACS Energy Lett., 2022, 7, 3958-3966.
- 202.P. J. Zhao, B. J. Kim and H. S. Jung, *Mater. Today Energy*, 2018, **7**, 267-286.
- 203.S. Wang, H. Chen, J. Zhang, G. Xu, W. Chen, R. Xue, M. Zhang, Y. Li and Y. Li, Adv. Mater., 2019, **31**, 1903691.
- 204.K. Wojciechowski, S. D. Stranks, A. Abate, G. Sadoughi, A. Sadhanala, N. Kopidakis, G. Rumbles, C. Z. Li, R. H. Friend, A. K. Jen and H. J. Snaith, ACS Nano, 2014, 8, 12701-12709.
- 205.Y. Li, Y. Zhao, Q. Chen, Y. M. Yang, Y. Liu, Z. Hong, Z. Liu, Y. T. Hsieh, L. Meng, Y. Li and Y. Yang, J Am. Chem. Soc., 2015, 137, 15540-15547.
- 206.T. Cao, Z. Wang, Y. Xia, B. Song, Y. Zhou, N. Chen and Y. Li, ACS Appl. Mater. Interfaces, 2016, **8**, 18284-18291.
- 207.T. Kang, C. M. Tsai, Y. H. Jiang, G. Gollavelli, N. Mohanta, E. W. Diau and C. S. Hsu, ACS Appl. Mater. Interfaces, 2017, 9, 38530-38536.
- 208.H. Wang, F. L. Cai, M. Zhang, P. Wang, J. X. Yao, R. S. Gurney, F. B. Li, D. Liu and T. Wang, *J. Mater. Chem. A*, 2018, **6**, 21368-21378.
- 209.H. Wang, M. T. Chen, F. B. Li, R. Sun, P. Wang, F. H. Ye, H. J. Zhang, W. Q. Miao, D. Liu and T. Wang, *Acs Appl. Energy Mater.*, 2020, **3**, 9824-9832.
- 210.H. Wang, F. B. Li, P. Wang, R. Sun, W. Ma, M. T. Chen, W. Q. Miao, D. Liu and T. Wang, *Adv. Energy Mater.*, 2020, **10**, 2000615.
- 211.Z. J. Chen, Y. M. Li, Z. H. Liu, J. J. Shi, B. C. Yu, S. Tan, Y. Q. Cui, C. Y. Tan, F. B. Tian, H. J. Wu, Y. H. Luo, D. M. Li and Q. B. Meng, *Adv. Energy Mater.*, 2022, **13**, 2202799.

- 212.W. J. Ke, D. W. Zhao, C. X. Xiao, C. L. Wang, A. J. Cimaroli, C. R. Grice, M. J. Yang, Z. Li, C. S. Jiang, M. Al-Jassim, K. Zhu, M. G. Kanatzidis, G. J. Fang and Y. F. Yan, *J. Mater. Chem. A*, 2016, 4, 14276-14283.
- 213.K. Liu, S. Chen, J. H. Wu, H. Y. Zhang, M. C. Qin, X. H. Lu, Y. F. Tu, Q. B. Meng and X. W. Zhan, *Energy Environ. Sci.*, 2018, **11**, 3463-3471.
- 214.T. Cao, K. Chen, Q. Chen, Y. Zhou, N. Chen and Y. Li, *ACS Appl. Mater. Interfaces*, 2019, **11**, 33825-33834.
- 215.S. K. Huang, Y. C. Wang, W. C. Ke, Y. T. Kao, N. Z. She, J. X. Li, C. W. Luo, A. Yabushita, D. Y. Wang, Y. J. Chang, K. Tsukagoshi and C. W. Chen, *J. Mater. Chem. A*, 2020, **8**, 23607-23616.
- 216.C. Z. Ding, L. Yin, J. L. Wang, V. Larini, L. P. Zhang, R. Huang, M. Nyman, L. Y. Zhao, C. Zhao, W. S. Li, Q. Luo, Y. B. Shen, R. Österbacka, G. L. Grancini and C. Q. Ma, *Adv. Mater.*, 2022, **35**, 2207656.
- 217.R. D. Chavan, B. Bonczak, J. Kruszynska, A. Mahapatra, M. Ans, J. Nawrocki, K. Nikiforow, P. Yadav, J. Paczesny, F. Sadegh, M. Unal, S. Akin and D. Prochowicz, *Chem. Mater.*, 2023, **35**, 8309-8320.
- 218.P. Q. Song, E. L. Hou, Y. M. Liang, J. F. Luo, L. Q. Xie, J. H. Qiu, C. B. Tian and Z. H. Wei, *Adv. Funct. Mater.*, 2023, **33**, 2303841.