Steering perovskite precursor solutions for multijunction photovoltaics

Shuaifeng Hu,*,[†,a,b] Junke Wang,[†,a] Pei Zhao,[a,c] Jorge Pascual,[b,d] Jianan Wang,[e,f] Florine Rombach,[a] Akash Dasgupta,[a] Wentao Liu,[b] Minh Anh Truong,[b] He Zhu,[e,f] Manuel Kober-Czerny,[a] James N. Drysdale,[a] Joel A. Smith,[a] Zhongcheng Yuan,[a] Guus J. W. Aalbers,[g] Nick R. M. Schipper,[g] Jin Yao,[h] Kyohei Nakano,[i] Silver-Hamill Turren-Cruz,[b,j] André Dallmann,[k] M. Greyson Christoforo,[a] James M. Ball,[a] David P. McMeekin,[a] Karl-Augustin Zaininger,[a] Zonghao Liu,[e,f] Nakita K. Noel,[a] Keisuke Tajima,[i] Wei Chen,[e,f] Masahiro Ehara,[c] René A. J. Janssen,[g,l] Atsushi Wakamiya,*,[b] and Henry J. Snaith*,[a]

[a]Clarendon Laboratory, Department of Physics, University of Oxford, Oxford OX1 3PU, U.K.

[b]Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan.

[c]Research Center for Computational Science, Institute for Molecular Science, Okazaki, 444-8585, Japan.

[d]Polymat, University of the Basque Country UPV/EHU, 20018 Donostia-San Sebastian, Spain.

[e]Wuhan National Laboratory for Optoelectronics, Huazhong University of Science and Technology (HUST), Luoyu Road 1037, Wuhan, 430074, China.

[f]Optics Valley Laboratory, Hubei 430074, China.

[g]Molecular Materials and Nanosystems and Institute for Complex Molecular Systems, Eindhoven University of Technology, P.O. Box 513, 5600 MB, Eindhoven, The Netherlands.

[h]National Thin Film Cluster Facility for Advanced Functional Materials, Department of Physics, University of Oxford, Oxford OX1 3PU, U.K.

[i]RIKEN Center for Emergent Matter Science (CEMS), Wako, Saitama 351-0198, Japan.

[j]Instituto de Ciencia de los Materiales (ICMUV), Universitat de Valencia, 46980 Paterna, Spain.

[k]Humboldt Universität zu Berlin, Institut für Chemie, AG NMR, Germany.

[l]Dutch Institute for Fundamental Energy Research, Eindhoven, The Netherlands.

[†]These authors contributed equally.

Main

Multijunction photovoltaics (PVs) are gaining prominence owing to their superior capability of achieving power conversion efficiencies (PCEs) beyond the radiative limit of single-junction cells[1,2], where improving narrow bandgap tin–lead perovskites (E_g: ~1.25 eV) is critical for thin-film devices[3]. For all-perovskite double- and multi-junction cells, further advancement is largely hindered by the challenging but necessary tin–lead perovskite material, due to the facile oxidation of Sn(II) to Sn(IV) and the difficult-to-control crystallisation dynamics[4]. The field has extensively investigated suppressing Sn(II) oxidation using various additives[5] or non-oxidizing solvents[6] and improving the performance through surface modifications[3,7-9]. In contrast, studies on precursor solution chemistry and their impacts on the crystallisation process and film properties are limited. We have previously found that an amino acid salt glycine hydrochloride could preferentially accumulate at the bottom interface, improving device hole extraction[10]. This strategy has been widely adopted for fabricating efficient single-junction and tandem cells[3], while understanding the core mechanism and how to further adapt this approach to make further gains is underexplored. To understand the role of amino acid salts further and decouple the effect of functional groups from a solution chemistry perspective, herein, we select three structurally similar molecules that individually contain ammonium, carboxyl, or both motifs on a single molecule, i.e., phenethylammonium chloride (PEA), 3-phenylpropionic acid (PPA), and L-phenylalanine hydrochloride (PhA), respectively (**Figure 1a**).
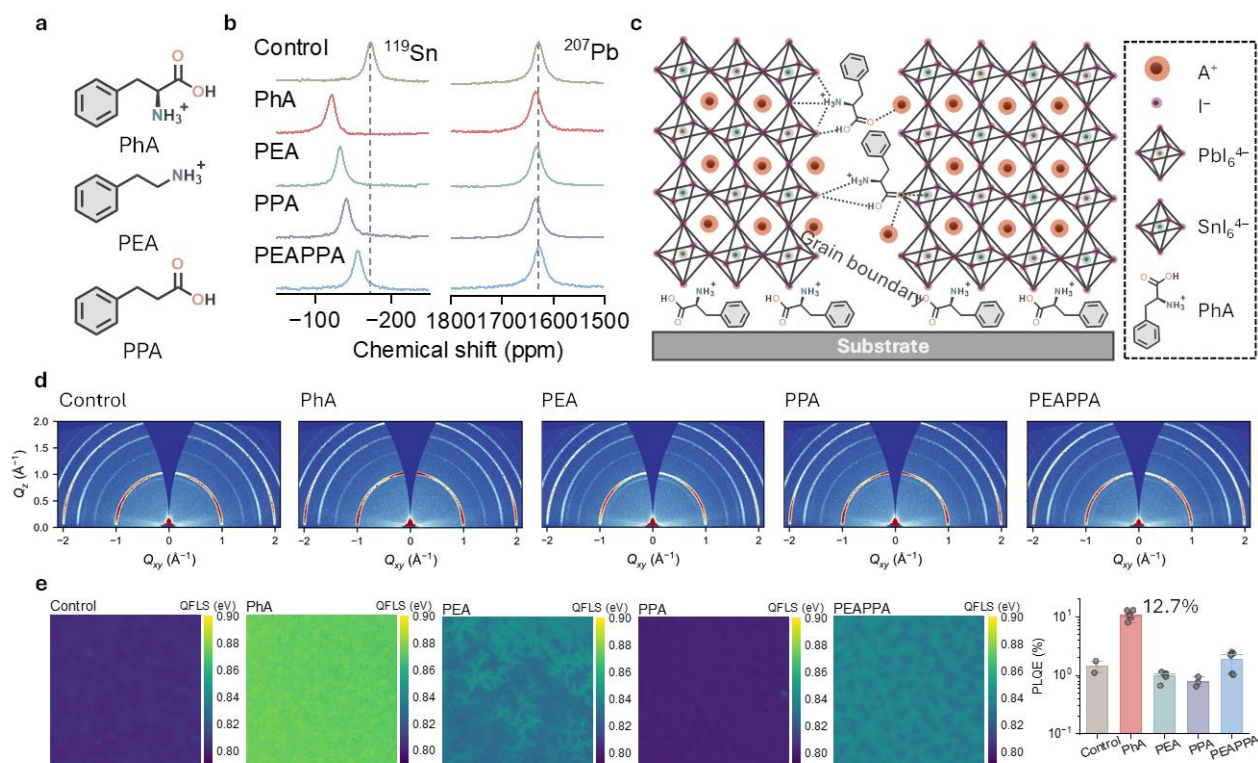
Figure 1. a, Chemical structures of the molecules. **b,** ^{119}Sn- and ^{207}Pb-NMR spectra showing Sn(II) and Pb(II) signals in perovskite precursor solutions containing different additives. **c,** Schematic illustration for the location and impact of PhA in the as-crystalised perovskite films. **d,** 2D GIWAXS patterns of perovskite films. **e,** QFLS mapping calculated from 2 mm × 2 mm PLQE images and PLQE of the perovskite films recorded at V_{OC} conditions under illumination (equivalent to 1 sun intensity for a 1.26 eV bandgap).

With a focus on understanding the chemistry of tin–lead perovskite precursor solutions, we, for the first time, find that Sn(II) species dominate interactions with precursors and additives (**Figures 1b, c**) and uncover the exclusive role of carboxylic acid in regulating solution colloidal properties and film crystallisation (**Figure 1d**), and ammonium in improving film optoelectronic properties (**Figure 1e**). Materials that combine these two function groups, amino acid salts, considerably improve the semiconducting quality and homogeneity of perovskite films, surpassing the effect of the individual functional groups when introduced as part of separate molecules. Our enhanced tin–lead perovskite layer allows us to fabricate solar cells with PCEs of 23.9, 29.7 (certified 29.26%, by Shanghai Institute of Microsystem and Information Technology (SIMIT) in China), and 28.7% for single-, double-, and

triple-junction devices, respectively (**Figures 2a, b, and c**), with the best open-circuit voltage of 0.91, 2.22, and 3.46 V, respectively. Our 1-cm^2 double- and triple-junction devices show PCEs of 28.4% (1-cm^2 triple-junction cell certified at 27.28%, by the National Institute of Advanced Industrial Science and Technology (AIST) in Japan) (**Figure 2d**). Further optical simulation suggests a potential PCE value of 34.4% for the triple-junction cells based on our current design (**Figures 2e and f**). Encapsulated triple-junction cells maintain 80% of their initial efficiencies after 860 h maximum power point tracking in ambient (**Figure 2g**). We further fabricate quadruple-junction devices and obtain PCEs of 27.9% with the highest open-circuit voltage of 4.94 V, representing the first report on all-perovskite thin film devices with the junction number up to four. Overall, our work sets the benchmark for all-perovskite multijunction PVs (**Figure 3**) and reveals a pathway towards triple- and quadruple-junction cells, which hold high-efficiency potentials and offer low electrical power losses in large area cells and modules, owing to the low current densities and high operating voltages. In addition, our work also demonstrates that the PCE of large-area triple-junction cells closely matches the efficiency of double-junction cells. We expect to see triple- and/or quadruple-junction cells lead the efficiency race for thin-film tandem perovskite-containing devices shortly, with researchers adopting the protocols we have outlined here.
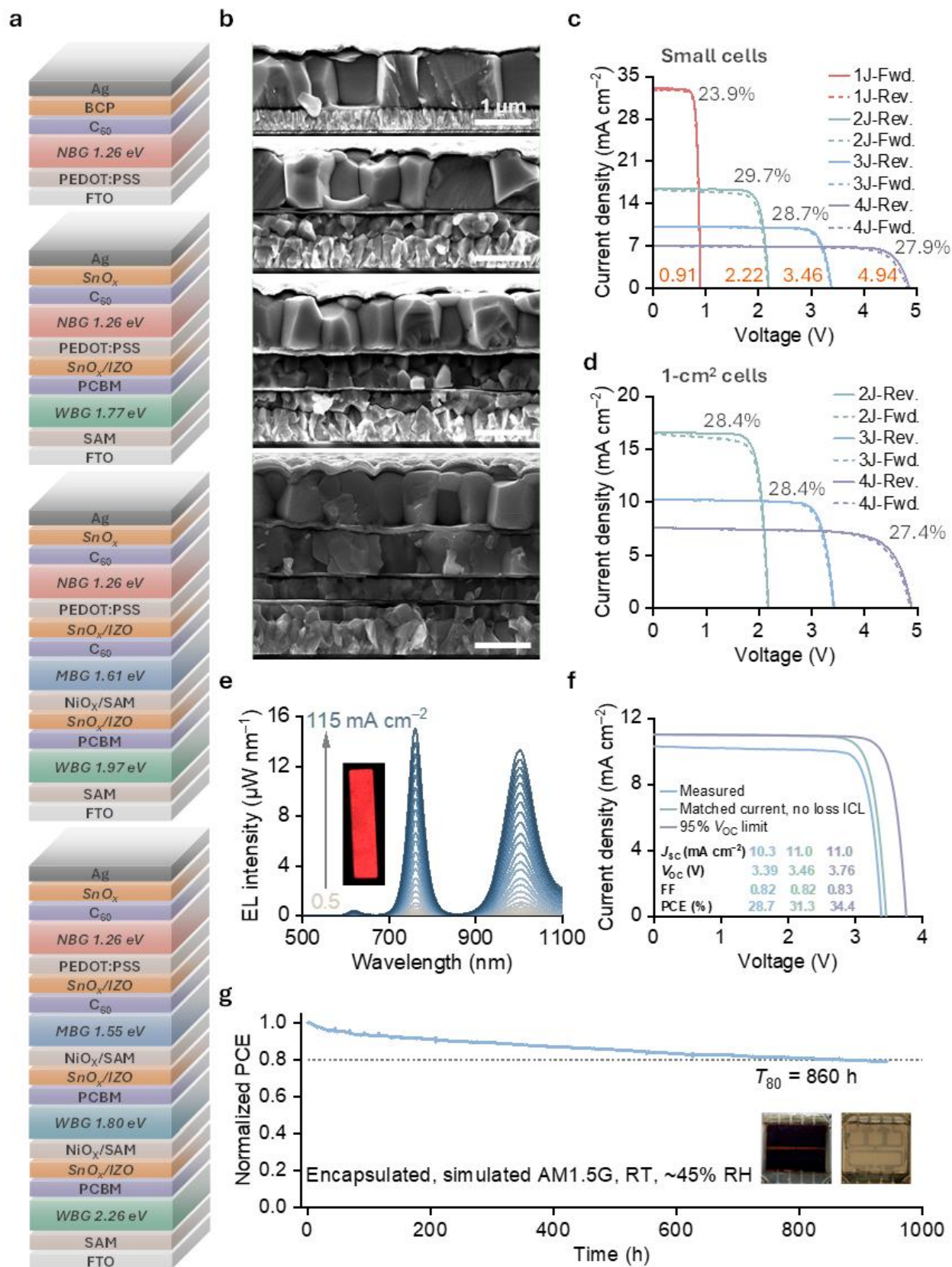
Figure 2. a, Device configuration (top to bottom), **b,** cross-sectional SEM images (top to bottom, scale

bar: 1 μm), *J–V* curves of **c,** small and **d,** 1-cm^2 cells of optimised single (1J)-, double (2J)-, triple (3J)-, and quadruple (4J)-junction cells. **e,** EQE$_{EL}$ spectra of one representative triple-junction cell measured as a function of injected current density ranging from 0.5 to 115 mA cm^{-2}. **f,** Experimental and reconstructed *J–V* curves of the triple-junction device from the simulated EQE at different optical conditions and assuming a V_{OC} of 95% detailed-balance limit is achieved in each subcell. **g,** MPP tracking stability of an encapsulated triple-junction device.
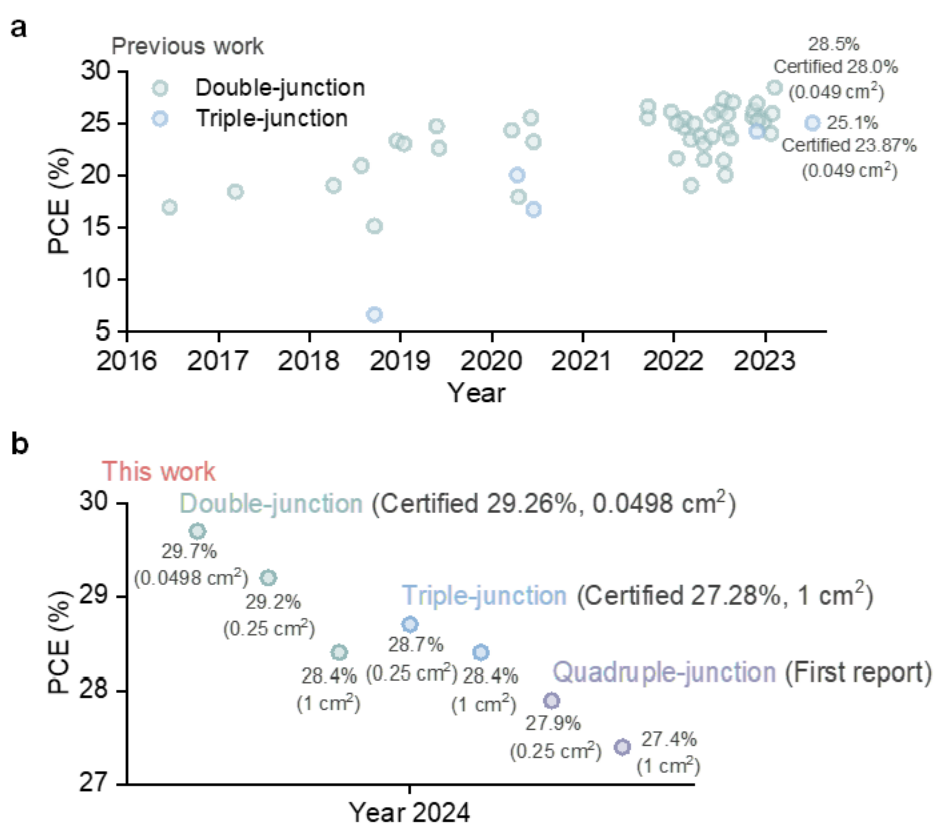

Figure 3. Efficiency progress of all-perovskite tandem solar cells with the data collected from **a,** the previously published results[3] (the record power conversion efficiency (PCE) values are given[11,12].) and **b,** our current work[13,14]. The active area of the devices is provided in brackets.

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