SOLAR CELLS

Improved charge extraction in inverted perovskite solar cells with dual-site-binding ligands

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Inverted (pin) perovskite solar cells (PSCs) afford improved operating stability in comparison to their nip counterparts but have lagged in power conversion efficiency (PCE). The energetic losses responsible for this PCE deficit in pin PSCs occur primarily at the interfaces between the perovskite and the charge-transport layers. Additive and surface treatments that use passivating ligands usually bind to a single active binding site: This dense packing of electrically resistive passivants perpendicular to the charge-transport layers limit the PCE of pin cells (Fig. 1). Alternative small-molecule binders, such as benzenesulfonate (BZS) ligands and their derivatives, have been used as ETL interlayers in pin PSCs, which do not rely on p-type dopants in their hole-transporting layers (ETL) (13–15). To enable strong binding with the perovskite, we focused on available sulfonates (27–29), with the length of the side chain expected to lie parallel to the perovskite surface (Conf-perp; Fig. 1B) and another in which the ligands were oriented perpendicular to the perovskite surface (Conf-perp; Fig. 1C). Although Conf-perp was more energetically favorable for BZS and 4CH3-BZS, Conf-perp was energetically more favorable for 4CI-BZS because of the additional Pb2+ surface binding. We also investigated the effects of ligand orientation on charge transfer at the perovskite-ETL interface by examining fullerene (C60), which is widely used as an ETL in pin PSCs and is known to induce energetic losses in devices (21, 22, 34, 35). Analysis of the calculated charge density difference (Fig. 1E and fig. S1) showed that 4CI-BZS has a notably stronger binding energy than the C60 layer [adsorption (Eads) = −0.85 eV] in contrast to BZS (Eads = −0.46 eV) and 4CH3-BZS (Eads = −0.39 eV) (36). Fracture energy (Gf) results show that 4CI-BZS increases the mechanical strength of the perovskite-C60 interface (Fig. S2) (37).

Ligand-perovskite binding characterization

To explore interactions between perovskite and BZS ligands, we began by adding each ligand directly into the precursor solutions and spin-coating Cs0.05FA0.85MA0.1PbI3 perovskite thin films, where FA is formamidinium and MA is methylamine. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) of untreated (control) and treated films showed that BZS, 4CH3-BZS, and 4CI-BZS were all concentrated near the top (ETL-facing) surface of the perovskite film (Fig. S3). This result, combined with x-ray diffraction (XRD) patterns of control and treated perovskite films that showed no discernable peak-shifting after treatment (Fig. S4), indicated that the ligands did not enter the lattice but rather diffused toward the top surface during film crystallization. Scanning electron microscopy (SEM) images of perovskite films with additives are presented in fig. S5 and illustrate that the perovskite films (both additives and controls) exhibit substantially uniform morphology.

We used x-ray photoelectron spectroscopy (XPS) to check for possible evidence of interaction between the additives and perovskite. We observed a shift of the Pb 4f XPS peaks to a lower binding energy for each treated film compared with the peaks of controls (Fig. 2A).
We saw evidence of interaction between Cl and Pb in 4Cl-BZS–treated perovskite from both XPS spectra (Fig. 2B) and nuclear magnetic resonance spectra (fig. S6).

Optoelectronic characterization of perovskite films and device stacks
To evaluate the passivation efficacy of each ligand, we studied photoluminescence (PL) of neat control and treated perovskite films. We observed an increase in PL quantum yield (PLQY) for each of the treated films and the full device stack (Fig. 2C), with 4Cl-BZS exhibiting a twofold increase in PLQY (41%) compared with control films (20%), which corresponded to a projected 20-mV increase in quasi-Fermi level splitting (QFLS). The PLQY of full-device stacks [FTO/SAMs/perovskite/C60, where FTO is fluorinate tin oxide and SAMs (self-assembled monolayers) are mixtures of 2PACz and Me-4PACz] revealed a substantial improvement after 4Cl-BZS treatment—5% for 4Cl-BZS compared with 0.6% for the control, corresponding to 1.17 and 1.1 V in QFLS for 4Cl-BZS and the control device, respectively. This improvement was consistent with reduced interface losses. Time-resolved photoluminescence (TRPL) revealed a similar increase in carrier lifetimes after treatment. Specifically, 4Cl-BZS–treated films exhibited a weighted-average lifetime of

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**Fig. 1.** DFT studies of ligand binding and predicted orientation. (A) Structure and electrostatic potential of BZS, 4CH₃-BZS, and 4Cl-BZS ligands. (B) Atomic structures of ligand adsorbed in a perpendicular orientation (Conf-perp) on the perovskite surface. (C) Atomic structures of ligand adsorbed in a planar or parallel orientation (Conf-para) on the perovskite surface. (D) Formation energy difference between parallel and perpendicular ligand-surface orientations \(E_{\text{Conf-para}} - E_{\text{Conf-perp}}\). (E) The adsorption energies \(E_{\text{ads}}\) of C60 with different molecules (BZS, 4CH₃-BZS, and 4Cl-BZS) adsorbed on the perovskite surface.
3.0 μs compared with 0.6 μs for the control film (Fig. 2D and table S1).

We fabricated partial and full perovskite/ETL device stacks to probe interface recombination and charge transfer. First, we conducted TRPL measurements of perovskite/C$_{60}$ stacks, wherein decay was dictated by non-radiative surface-bulk recombination (monoeponential decay), radiative recombination (second-order decay), and charge extraction effects, which could be distinguished if the time constants for each process differed sufficiently (38). The first interval at shorter times was dominated by the transfer of electrons from the bulk into the C$_{60}$, and the second interval at longer delay times was dominated by interfacial recombination (39). The sharp drop in emission for 4Cl-BZS/C$_{60}$ indicated efficient electron transfer at the interface, and the longer second-order decay time was indicative of a reduced trap density compared with BZS and 4CH$_3$-BZS (fig. S7). This effect of this reduction was especially evident in fits to the TRPL traces to compute the differential lifetime as $\tau = -d \ln(\phi(t))/dt$ (Fig. 2E), where $\phi(t)$ is the time-dependent PL photon flux, because the sharpness of the rise implied the speed of the electron transfer from perovskite to C$_{60}$.

Transient photocurrent measurements of full device stacks in which we used mixed SAMs as the hole-transport layer (see methods) revealed a similar trend. Both BZS and 4CH$_3$-BZS resulted in slower photocurrent decay, whereas 4Cl-BZS treatment led to faster photocurrent decay (Fig. 2F). This observation suggested that electron extraction became more efficient. Ultraviolet photoelectron spectroscopy (UPS) revealed an increased conduction band offset with C$_{60}$ that was caused by a Fermi-level upshift after BZS and 4CH$_3$-BZS treatment, whereas 4Cl-BZS caused a Fermi-level downshift and reduced conduction band offset (figs. S8 and S9). This trend was further confirmed by kelvin probe force microscopy (KPFM) measurements (fig. S10 and table S2) and DFT calculations (fig. S11).

Inverted perovskite solar cells
Using 4Cl-BZS-treated perovskite, we fabricated inverted PSCs with the structure FTO/SAMs/perovskite/C$_{60}$/SnO$_2$/Ag (Fig. 3A). The thickness of the perovskite layer was 900 nm. Control devices had a PCE of 24%, whereas the 4Cl-BZS–treated devices exhibited a PCE of 26.3% (fig. S12). Analysis of device statistics for both control and 4Cl-BZS–treated PSCs revealed a substantial enhancement in PCE, primarily by increased open-circuit voltage ($V_{OC}$). Additionally, 4Cl-BZS–treated PSCs showed a much higher FF compared with BZS- and 4CH$_3$-BZS–treated PSCs. We attribute this improvement in FF to enhanced charge extraction in 4Cl-BZS–treated PSCs (Fig. 3B and figs. S13 and S14).

We also evaluated the effectiveness of the additive change with a stronger or weaker donating group, namely 4F-BZS, 4Br-BZS, and 4I-BZS. Notably, 4F-BZS exhibits a more-negative averaged electrostatic potential, whereas 4I-BZS displays a more-positive averaged electrostatic potential (fig. S15). We posit that a stronger donating group, such as Cl or F, is beneficial in providing dual-site defect passivation. Because 4F-BZS, 4Cl-BZS, and 4I-BZS are not readily available, we used the structurally similar molecules 4-fluorobenzenesulfonic acid (4F-BZSA) and 4-iodobenzenesulfonic acid (4I-BZSA) in our devices (fig. S16). Notably, treatments with 4F-BZSA resulted in comparable PCE as in the
case of 4Cl-BZS, and 4I-BZSA also showed an improved PCE compared with controls.

We then added the bimolecular surface passivation (BMP) approach, based on 3-(methylthio) propylamine hydroiodide (3MTPAI) and propane-1,3 diammonium iodide (PDAI2), reported in (8). This strategy has been reported to provide a combination of chemical and field-effect passivation (see methods). The PLQY of full-device stacks (FTO/SAMs/perovskite/BMP/C60) indicated a further improvement after the BMP treatment (fig. S17). The combined treatment increased the PCE of 4Cl-BZS-treated devices from 26.3 to 26.9% and featured a $V_{OC}$ of 1.18 V, FF of 86.2%, and short-circuit current density ($J_{SC}$) of 26.4 mA cm$^{-2}$ (Fig. 3C).

The bandgap of the pin PSCs was taken from external quantum efficiency measurements as 1.53 eV (figs. S19 and S20). We sent devices with active areas of 0.05 and 1.04 cm$^2$ to a National Renewable Energy Laboratory (NREL)-accredited independent photovoltaic calibration laboratory (Newport) for certification. The devices achieved certified stabilized quasi-steady state (QSS) PCEs of 26.15 and 24.74%, respectively (Fig. 3, D and E, and figs. S21 and S22). These reported pin PCEs surpass the record nip device performance reported in recent years (Fig. 3E and tables S3 and S4).

Next, we sought to test the thermal stability of the 4Cl-BZS-treated PSCs following protocols established by the International Summit on Organic Photovoltaic Stability (ISOS).
mixed halide devices as well as 1.25-eV narrow-bandgap mixed Pb-Sn PSCs, which are compositions of interest in all-perovskite tandem solar cells. In each case, we observed an increase in PCE after 4Cl-BZS treatment (fig. S24).

REFERENCES AND NOTES
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Competing interests: B.C., H.C., and E.H.S. are filing a patent based on this work. The other authors declare no competing interests.

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SUPPLEMENTARY MATERIALS
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Materials and Methods
Figs. S1 to S24
Tables S1 to S5
References (40–54)
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