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Improved performance and stability in quantum dot solar cells through band alignment engineering

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Solution processing is a promising route for the realization of low-cost, large-area, flexible, and light-weight photovoltaic devices with short energy payback time and high specific power. However, solar cells based on solution-processed organic, inorganic, and hybrid materials reported thus far generally suffer from poor air stability, require an inert-atmosphere processing environment, or necessitate high temperature processing¹, all of which increase manufacturing complexities and costs. Simultaneously fulfilling the goals of high efficiency, low-temperature fabrication conditions, and good atmospheric stability remains a major technical challenge, which may be addressed, as we demonstrate here, with the development of room-temperature solution-processed ZnO/PbS quantum dot (QD) solar cells. By engineering the band alignment of the QD layers through the use of different ligand treatments, a certified efficiency of 8.55% has been reached. Furthermore, the performance of unencapsulated devices remains unchanged for over 150 days of storage in air. This material system introduces a new approach towards the goal of high-performance air-stable solar cells compatible with simple solution processes and deposition on flexible substrates.

Near-infrared PbS QDs composed of earth-abundant elements² have emerged as promising candidates for photovoltaic applications because of a tunable energy bandgap that covers the optimal bandgap range for single and multi-junction solar cells¹. The QD surface ligands^{3–7} and the photovoltaic device architecture^{8–17} play crucial roles in determining the optoelectronic properties of QD solar cells. Advances in QD surface passivation, particularly

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Author Contributions

C.M.C and M.G.B. conceived and designed the project. C.M.C. performed most of the experiments and data analysis with some technical assistance from P.R.B. P.R.B. and C.M.C. performed UPS measurements and their analysis. All authors discussed the results. C.M.C. wrote the manuscript with contributions from all authors.

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through the use of halide ions as inorganic ligands⁴, have led to rapid improvements in QD solar cell power conversion efficiencies to 7%^{5,15,16} as a result of a lower density of trapped carriers than in their organic ligands counterparts⁴. In addition, recent studies have demonstrated the ability to control the band edge energies of QD films through ligand exchange^{18–20}. However, fabrication of these recent QD devices requires high-temperature annealing (>500°C) of the TiO₂ window layer^{5,16} or two different processing atmospheres, including an inert gas environment¹⁵. Although good stability has been claimed, the devices still show performance degradation to ~85% of their original efficiencies within one week even under inert atmosphere^{5,16}. Here, we demonstrate ZnO/PbS solar cells in which the PbS QD and ZnO nanocrystals are both solution-processed in air and at room temperature. We demonstrate a device architecture that employs layers of QDs treated with different ligands for different functions by utilizing their relative band alignment—a layer of inorganic-ligand-passivated QDs serves as the main light-absorbing layer and a layer of organic-ligand-passivated QDs serves as an electron-blocking/hole-extraction layer. The devices show significant improvements in power conversion efficiency and long-term air-stability, as compared to previously reported devices.

Fig. 1a shows the schematics of the device structures employed in this work. Oleic-acid-capped PbS QDs with the first exciton absorption peak at $\lambda=901\text{nm}$ in solution (Fig. S1) are used to fabricate the thin films. Tetrabutylammonium iodide (TBAI) and 1,2-ethanedithiol (EDT) are used as the inorganic and organic ligands for solid-state ligand exchange. After solid-state ligand exchange, the first exciton absorption peak shifts to $\lambda\sim 935\text{nm}$, which corresponds to an optical bandgap $E_g=1.33\text{ eV}$. We find that PbS QD films treated with TBAI (PbS-TBAI) exhibit superior air stability compared to PbS QDs treated with EDT (PbS-EDT) (Fig. S2). PbS-TBAI-only devices also show a higher short-circuit current density (J_{SC}), while PbS-EDT-only devices show a higher open circuit voltage (V_{OC}) (Fig. S3).

The J-V characteristics of photovoltaic devices with Au anodes are shown in Fig. 1b. The device consisting of 12 PbS-TBAI layers (corresponding to ~220 nm thick film) shows a power conversion efficiency of $6.0\pm 0.4\%$, which is higher than the previously reported TiO₂/PbS-TBAI devices consisting of PbS QDs with an additional solution phase CdCl₂ treatment and MoO₃/Au/Ag anode⁴. Although PbS-EDT-only devices show a lower J_{SC} than PbS-TBAI-only device, replacing the top-most 2 PbS-TBAI layers with 2 PbS-EDT layers significantly improves the J_{SC} , V_{OC} , and fill factor (FF), resulting in a ~35% improvement in power conversion efficiency to $8.2\pm 0.6\%$ with a 9.2% lab-champion device (Table 1).

We attribute the improvement in efficiency to the band offsets between the two PbS QD layers which effectively block electron flow to the anode while facilitating hole extraction. We use ultraviolet photoelectron spectroscopy (UPS) to determine the band edge energies with respect to vacuum in PbS QD films (Fig. 2a). PbS-TBAI exhibits a deeper work function of 4.77 eV (i.e. $E_F=-4.77\text{ eV}$ with respect to vacuum, where E_F is the Fermi level energy) than PbS-EDT. We attribute the difference in their work functions to the difference between the Pb-halide anion and the Pb-thiol-carbon interactions, which give rise to different surface dipole moments as is discussed elsewhere²⁰. In addition, the difference

between the Fermi level and valence band edge (E_V) in PbS-TBAI is greater ($E_F - E_V = 0.82$ eV) than that in PbS-EDT ($E_F - E_V = 0.63$ eV). According to the individually determined band positions, the large conduction band offset (0.68 eV) between PbS-TBAI and PbS-EDT should block electron flow from the PbS-TBAI layer to the PbS-EDT layer. However, since the interactions between the PbS-TBAI and the PbS-EDT layers can affect the interfacial band bending, the actual band offsets in the device must be measured directly.

To determine the band alignment at the PbS-TBAI/PbS-EDT interface, we performed UPS measurements on PbS-TBAI films covered with different thicknesses of PbS-EDT (see Supplementary Information for the spectra and more details). As shown in Fig. 2a, as the thickness of the PbS-EDT layer increases, the Fermi level with respect to vacuum shifts to shallower energy levels and reaches saturation when the thickness of the PbS-EDT layer exceeds 13.5 nm. The shift indicates the formation of an interfacial dipole, which results in a reduction of the work function and a downward vacuum level shift at the interface. Moreover, the difference between the Fermi level and the valence band edge decreases with increasing PbS-EDT layer thickness. The energy level alignment at the PbS-TBAI/PbS-EDT interface deduced from the thickness-dependent UPS data is plotted in Fig. 2b.

The band alignment demonstrates the role of the PbS-EDT layer as an electron-blocking/hole-extraction layer between the PbS-TBAI layer and the anode, which leads to an improved photocurrent collection efficiency and enhanced device performance in the PbS-TBAI/PbS-EDT devices. In the PbS-TBAI-only device, electron flow from PbS-TBAI to the anode, which is in the opposite direction to the photocurrent, and interfacial recombination at the PbS/anode interface are possible loss mechanisms (Fig. 2c). In the PbS-TBAI/PbS-EDT device, the conduction band offset between the PbS-TBAI and PbS-EDT layers provides an energy barrier that prevents photogenerated electrons from flowing to the PbS-EDT layer, while the valence band offset provides an additional driving force for the flow of photogenerated holes to the PbS-EDT layer. The insertion of the PbS-EDT layer not only prevents electron flow from PbS-TBAI to the anode but may also reduce surface recombination of photogenerated electrons and holes at the PbS-TBAI/anode interface.

The interfacial band bending makes an additional minor contribution to the improved J_{SC} . The band bending at the PbS-TBAI/PbS-EDT interface implies the formation of a depletion region adjacent to this junction, which effectively extends the overall depletion width in the PbS-TBAI light-absorbing layer. This effect is similar to that in previously reported graded-doping devices^{15,16} where control of carrier concentrations through ligand exchange extends the depletion region, but there without altering the band edge positions of the PbS QD layers¹⁶. The extension of the depletion region in those graded-doping devices accounts for a marginal increase (<5%) in J_{SC} compared to ungraded devices^{15,16}.

In our study, the PbS-TBAI/PbS-EDT devices typically show ~20% improvements in J_{SC} compared to PbS-TBAI-only devices (Fig. S14). As shown in Fig. 1c, the PbS-TBAI/PbS-EDT device exhibits a higher external quantum efficiency (EQE) than that in the PbS-TBAI-only device at longer wavelengths. Long-wavelength photons have longer penetration depths due to the smaller absorption coefficients. Therefore, a higher fraction of long-wavelength photons are absorbed deeper in the film relative to the short-wavelength photons whose

absorption is predominantly close to the ZnO/PbS-TBAI interface (Fig. S16). The improvement in EQE at longer-wavelengths clearly indicates a better photocurrent collection efficiency especially in the region close to the PbS-TBAI/PbS-EDT interface, consistent with the proposed mechanisms. The J_{SC} calculated by integrating the EQE spectra with AM1.5G solar spectrum for PbS-TBAI-only and PbS-TBAI/PbS-EDT devices are 21.0 and 23.7 mA/cm², respectively, which show good agreement with the measured J_{SC} (20.7 ± 1.1 and 25.3 ± 1.1 mA/cm²).

The device stability is found to depend to a greater extent on the interface and band alignment between the QDs and anodes than on the bulk QD layer itself. Fig. 3 compares the evolution of solar cell performance parameters with air storage time in devices with Au and MoO₃/Au anodes, where the MoO₃ is the commonly used hole-extraction layer in PbS-based and other organic photovoltaic devices^{21–24}. Both PbS-TBAI and PbS-TBAI/PbS-EDT devices with Au anodes show stable performance compared to their counterparts with MoO₃/Au anodes. In contrast, devices with MoO₃/Au anodes developed S-shape J-V characteristics after air-exposure (Fig. S8), consistent with the development of a Schottky barrier at the anode^{23–25}. This effect significantly reduces the FF and device performance, limiting air stability.

The mechanism through which MoO₃ acts as the hole-extraction layer is the electron transfer from its deep-lying conduction band or from gap states to the active layer^{22–24}. However, the positions of these states strongly depend on the stoichiometry, environment, and deposition conditions^{22,26}. It has been shown that briefly exposing MoO₃ film deposited under vacuum to oxygen can decrease its work function by more than 1 eV to 5.5 eV²⁷. Exposing MoO₃ to humid air can decrease its work function even further²⁸. The S-shaped J-V characteristics in devices with a MoO₃ anode are most likely due to unfavorable band alignment between PbS and air-exposed MoO₃. We note that the air-exposure time in which this effect becomes significant varies from batch to batch of fabricated devices as a result of uncontrolled humidity in ambient storage conditions. In contrast, the performance of devices without a MoO₃ interfacial layer remains unchanged, implying that the PbS-TBAI absorber layers are functionally insensitive to oxygen and moisture during storage.

We also note that devices generally show an initial increase in V_{OC} and FF after air-exposure regardless of the active layer (PbS-TBAI, PbS-EDT, or PbS-TBAI/PbS-EDT) and anode materials (MoO₃/Al, MoO₃/Au, or Au). The ZnO/PbS films are fabricated and stored in air overnight before being transferred to a glovebox for anode deposition. The performance increases during the first hour of air-exposure after evaporation of the metal electrodes (Fig. S9). Therefore, further oxidation of the PbS QDs is unlikely to explain the performance enhancement. The origin of this initial increase in performance as a result of short air exposure is still under investigation.

The devices with Au anodes exhibit excellent long-term storage stability in air for over 150 days without any encapsulation (Fig. 4a). During the course of the stability assessment, devices are stored in air in the dark without humidity control but with some exposure to ambient light during sample transfer to the glovebox for testing. Devices have also been tested in air (Fig S10) and do not show any degradation in performance after testing in air.

An unencapsulated device was sent to an accredited laboratory (Newport Corp.) after 37 days of air-storage. This device tested in air under standard AM1.5G condition shows a power conversion efficiency of $8.55 \pm 0.18\%$ (Fig. 4b and Fig. S10), which represents the highest certified efficiency to date for colloidal QD photovoltaic devices. To the best of our knowledge, it is also the highest certified efficiency to date for any room-temperature solution-processed solar cell. Another device certified after 131 days of air-storage shows a comparable efficiency of $8.19 \pm 0.17\%$ and the highest FF (66.7%) in QD solar cells to date (Fig. S13).

In summary, we have demonstrated high-performance quantum dot solar cell through the engineering of band alignment at QD/QD and QD/anode interfaces. These solar cells are processed at room temperature and in air. Furthermore, they exhibit excellent air-storage stability. Our results indicate that (i) using inorganic-ligand-passivated QDs as the light-absorbing layer and (ii) removal of the MoO_3 interfacial layer are essential to achieving air-stability. Compared to other solution-processed solar cells, the present limiting factor of our device is the relatively low V_{OC} , where qV_{OC} is less than half of the optical bandgap. We suspect that elucidating the origin of the low V_{OC} , optimizing combinations of ligands and QD sizes, and further improving surface passivation via solution-phase treatments will result in continued efficiency improvements. The simplicity of the room temperature fabrication processes in ambient conditions and the robustness of the devices to ambient conditions provide advantages compared to other solution-processed solar cells. Greater understanding of the QD optoelectronic properties and further progress in materials development could lead to a generation of air-stable, solution-processable QD based solar cells.

METHODS

Synthesis of colloidal PbS QDs

The synthesis of oleic-acid-capped PbS QD with a first absorption peak at $\lambda=901$ nm was adapted from the literature^{11,29}. Lead acetate (11.38 g) was dissolved in 21 mL of oleic acid and 300 mL of 1-octadecene at 100 °C. The solution was degassed overnight and then heated to 150 °C under nitrogen. The sulfur precursor was prepared separately by mixing 3.15 mL of hexamethyldisilathiane and 150 mL of 1-octadecene. The reaction was initiated by rapid injection of the sulfur precursor into the lead precursor solution. After synthesis, the solution was transferred into a nitrogen-filled glovebox. QDs were purified by adding a mixture of methanol and butanol followed by centrifugation. The extracted QDs were re-dispersed in hexane and stored in the glovebox. For device fabrication, PbS QDs were further precipitated twice with a mixture of butanol/ethanol and acetone, respectively, and then re-dispersed in octane (50 mg/ml).

Synthesis of ZnO nanoparticles

ZnO nanoparticles were synthesized according to the literature³⁰. Zinc acetate dihydrate (2.95 g) was dissolved in 125 mL of methanol at 60 °C. Potassium hydroxide (1.48 g) was dissolved in 65 mL of methanol. The potassium hydroxide solution was slowly added to the zinc acetate solution and the solution was kept stirring at 60 °C for 2.5 hours. ZnO nanocrystals were extracted by centrifugation and then washed twice by methanol followed

by centrifugation. Finally, 10 ml of chloroform was added to the precipitates and the solution was filtered with a 0.45 μ m filter.

Device fabrication

Patterned ITO substrates (Thin Film Device Inc.) were cleaned with solvents and then treated with oxygen-plasma. ZnO layers (120nm) were fabricated by spin-coating a solution of ZnO nanoparticles onto ITO substrates. PbS QD layers were fabricated by layer-by-layer spin-coating. For each layer, \sim 10 μ L of PbS solution was spin-cast onto the substrate at 2500 rpm for 15 s. A TBAI solution (10mg/ml in methanol) was then applied to the substrate for 30 s followed by three rinse-spin steps with methanol. For PbS-EDT layers, an EDT solution (0.02 vol% in acetonitrile) and acetonitrile were used. All the spin-coating steps were performed under ambient condition and room light at room temperature. The thickness of each PbS-TBAI and PbS-EDT layer is about 18 nm and 23 nm, respectively, as determined by a profilometer (Veeco Dektak 6M). The films were stored in air overnight and then transferred to a nitrogen-filled glovebox for electrode evaporation. MoO₃ (Alfa) (25 nm thick), Al or Au electrode (100 nm thick) were thermally evaporated onto the films through shadow masks at a base pressure 10⁻⁶ mbar. The nominal device areas are defined by the overlap of the anode and cathode to be 1.24 mm². Larger-area devices (5.44 mm²) have also been fabricated and show similar performance (Fig. S12 and S13). For certification of the larger area device, a 3 mm² mask was attached to the device to define the device area.

Device characterization

Current-voltage characteristics were recorded by using a Keithley 2636A source-meter under simulated solar light illuminations (1-Sun, 100 mW/cm²) generated by a Newport 96000 solar simulator equipped with an AM1.5G filter. The light intensity was calibrated with a Newport 91150V reference cell before each measurement. The error in efficiency measurements is estimated to be below 7%. EQE measurements were conducted under chopped monochromatic lights from an optical fiber in an underfilled geometry without bias illumination. The light source was provided by coupling the white light from a xenon lamp (Thermo Oriel 66921) through a monochromator into the optical fiber and the photocurrent was recorded by using a lock-in amplifier (Stanford Research System SR830). Both current-voltage and EQE measurements were performed under an inert-atmosphere unless stated otherwise. Devices were stored in ambient air between each measurement.

UPS

PbS-TBAI and PbS-EDT samples for UPS measurements were fabricated in air by six layer-by-layer spin-coating steps to obtain \sim 110nm thick PbS films on glass/Cr(10nm)/Au(80nm) substrates. For PbS-EDT-thickness dependent UPS, a diluted PbS solution (10 mg/mL) was used to obtain the thinner PbS-EDT layers on PbS-TBAI films. The samples were then stored in air overnight before UPS measurements. UPS measurements were performed in an ultra high vacuum chamber (10⁻¹⁰ mbar) with a He(I) (21.2 eV) discharge lamp. Carbon tape was used to make electrical contact between the Cr/Au anode and the sample plate. A $-$ 5.0V bias was applied to the sample to accurately determine the low-kinetic energy photoelectron cut-off. Photoelectrons were collected at 0 $^{\circ}$ from normal and the spectra were recorded using an electron spectrometer (Omicron). The conduction band edge energies

were calculated by adding the optical bandgap energy of 1.33 eV determined by the first exciton absorption peak in the QD thin films to the valence band edge energies. The E_F-E_V values have an error bar of ± 0.02 eV resulting from curve fitting.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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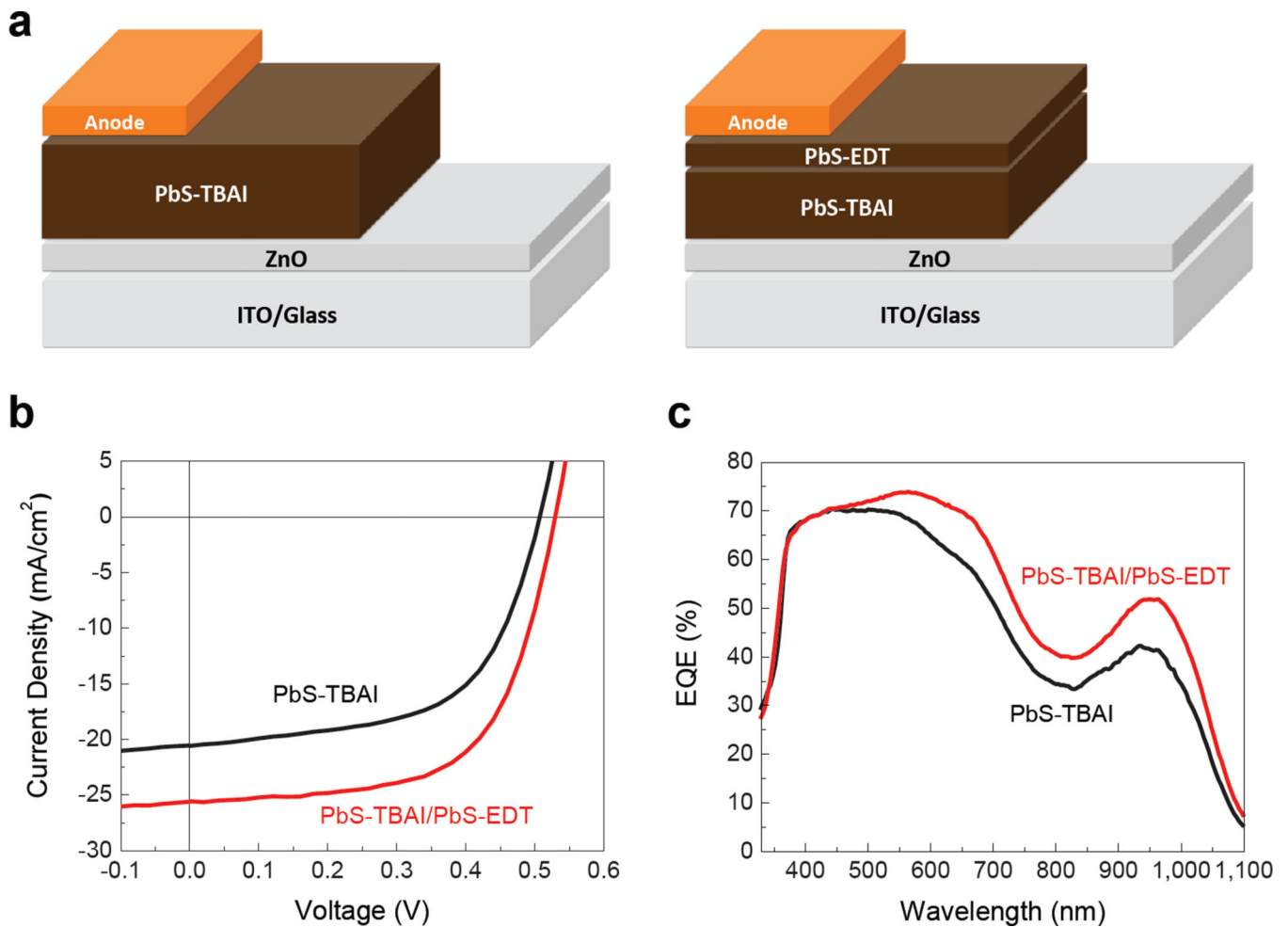


Figure 1. Photovoltaic device architectures and performance

a, Device architectures. **b**, Representative J-V characteristics of devices with Au anodes under simulated AM1.5G irradiation (100 mW/cm²). The PbS-TBAI device consists of 12 layers of PbS-TBAI and the PbS-TBAI/PbS-EDT device consists of 10 layers of PbS-TBAI and 2 layers of PbS-EDT. **c**, EQE spectra.

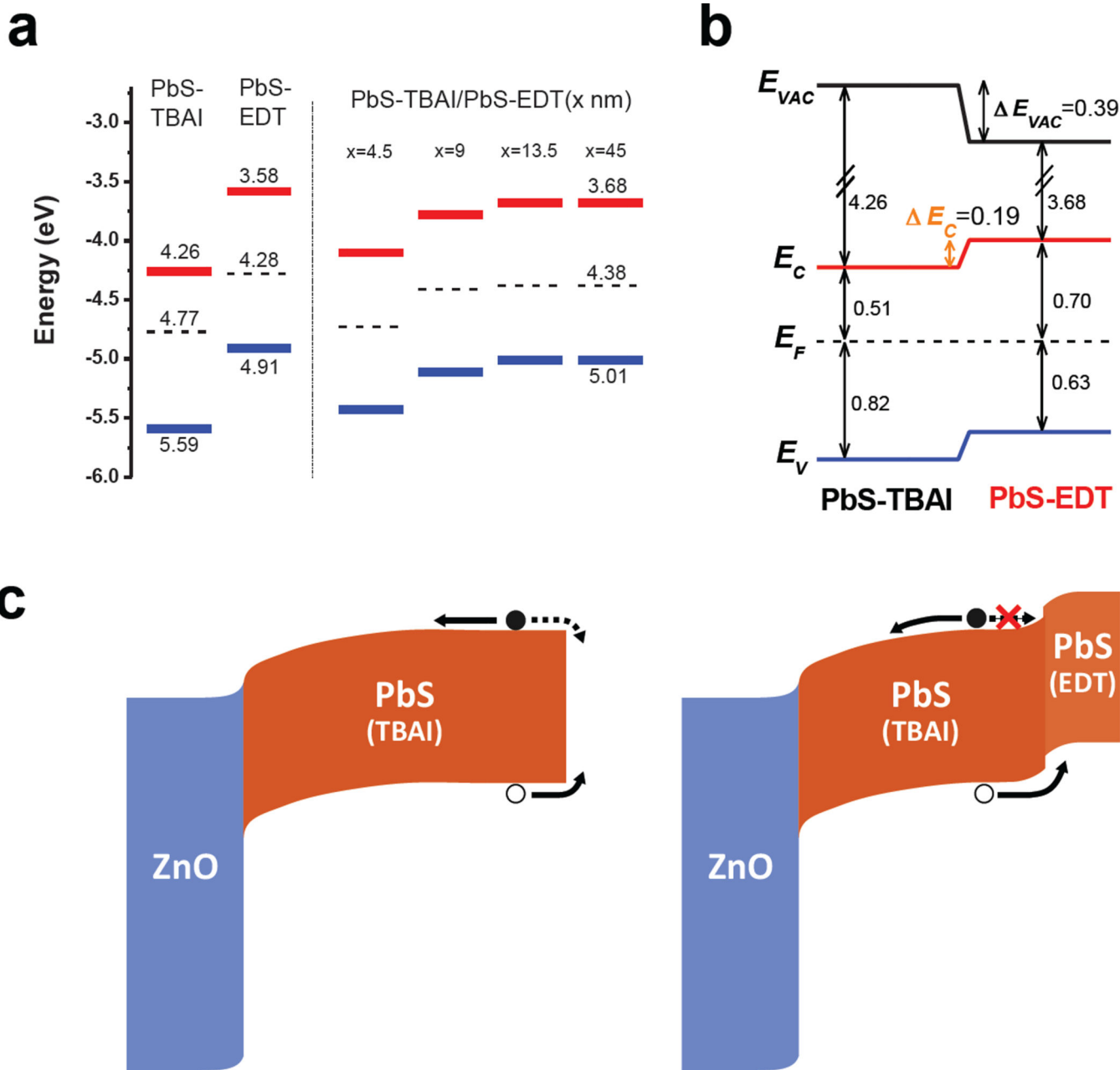


Figure 2. Energy level diagrams of PbS QDs and photovoltaic devices containing the QDs
a, Energy levels with respect to vacuum for PbS-TBAI, PbS-EDT, and PbS-TBAI films covered with different thicknesses of PbS-EDT layers. The Fermi levels (E_F , dashed line) and valence band edges (E_V , blue lines) were determined by UPS. The conduction band edges (E_C , red lines) were calculated by adding the optical bandgap energy of 1.33 eV, as determined from the first exciton absorption peak in the QD thin films, to E_V . **b**, Schematic energy level alignment at PbS-TBAI and PbS-EDT interfaces deduced from UPS. E_{VAC} : vacuum level. **c**, Schematic illustration of band bending in ZnO/PbS-TBAI and ZnO/PbS-TBAI/PbS-EDT devices at short-circuit conditions.

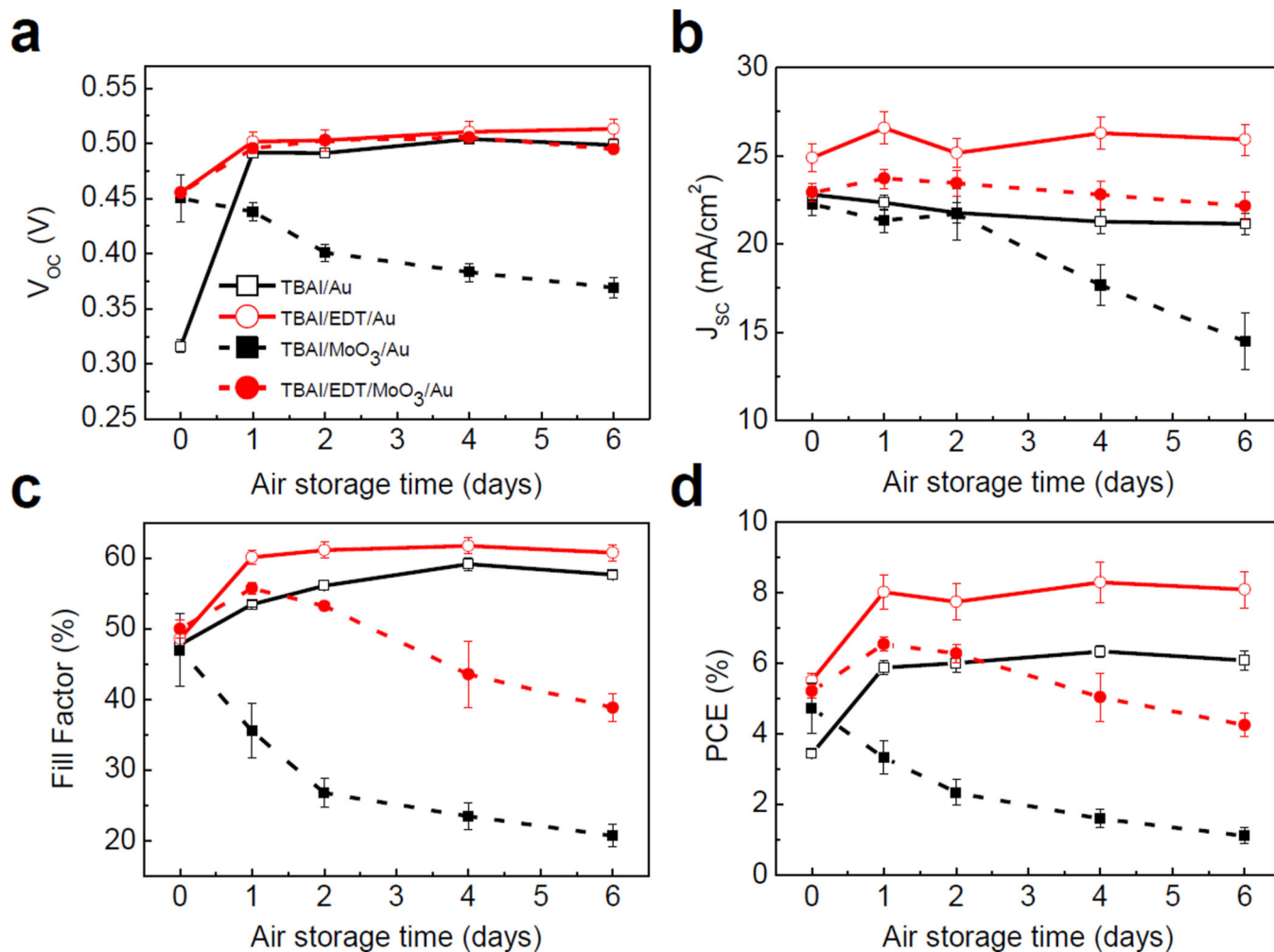


Figure 3. Evolution of photovoltaic parameters with air storage time in devices with Au and MoO₃/Au anodes

a, V_{OC} . **b**, J_{SC} . **c**, FF. **d**, power conversion efficiency (PCE). Measurements were performed in a nitrogen-filled glovebox. Day 0 denotes measurements performed after anode evaporation in vacuum. Between each measurement, the unencapsulated devices were stored in air without any humidity control. The average (symbols) and standard deviation (error bars) were calculated based on a sample of between 6 and 9 devices on the same substrate.

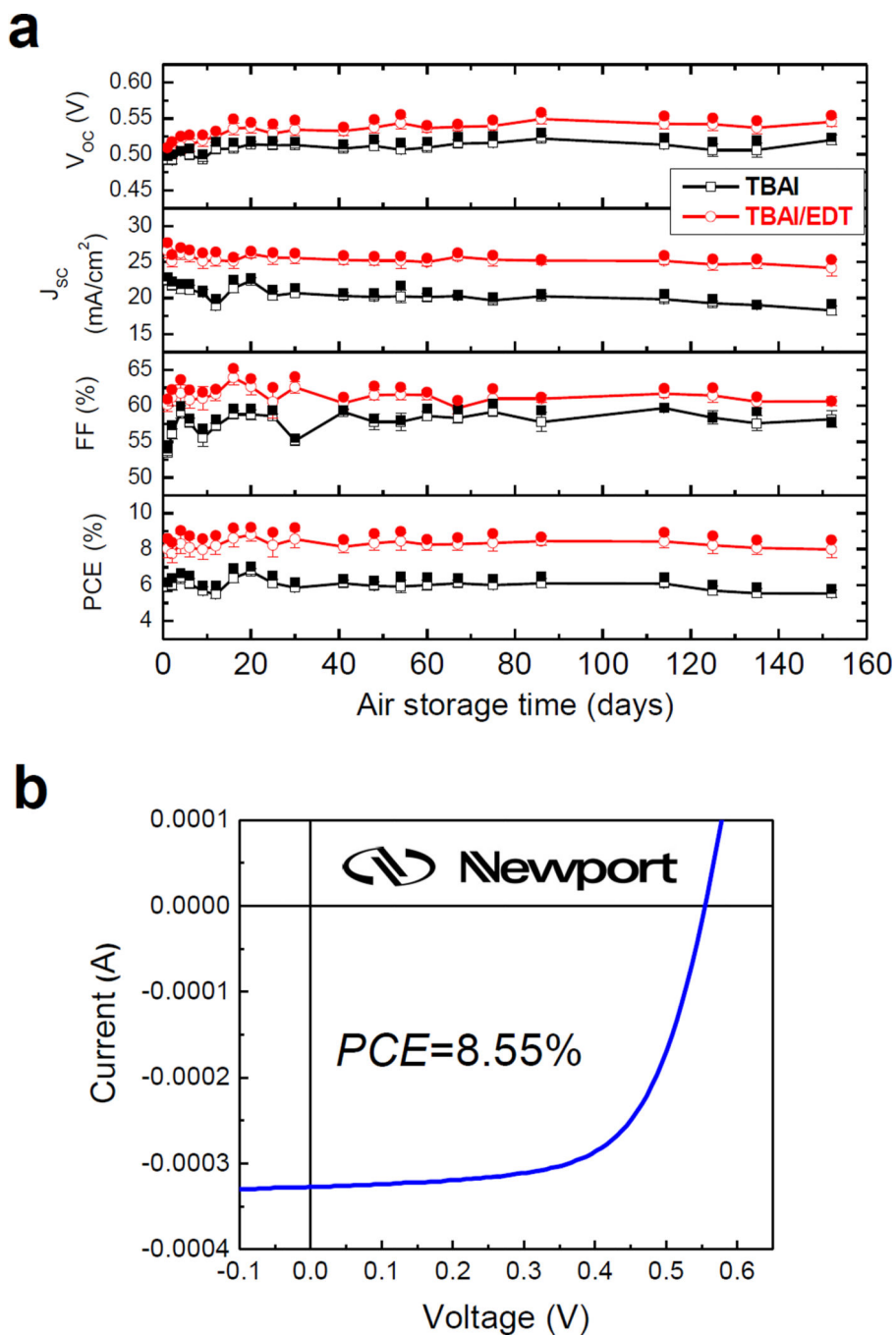


Figure 4. Long-term stability assessment of unencapsulated devices with Au anodes
a, Evolution of photovoltaic parameters of PbS-TBAI (black) and PbS-TBAI/PbS-EDT (red) devices. Open symbols represent the average values and solid symbols represent the values for the best-performing device. **b**, Device performance of a PbS-TBAI/PbS-EDT device certified by an accredited laboratory after 37 days of air-storage.

Table 1

Solar cell performance parameters.

	V_{OC} (V)	J_{SC} (mA/cm²)	FF (%)	PCE (%)
PbS-TBAI *	0.506±0.009 (0.519)	20.7±1.1 (22.8)	57.7±1.9 (59.6)	6.0±0.4 (7.0)
PbS-TBAI/PbS-EDT *	0.525±0.016 (0.544)	25.3±1.1 (26.5)	61.6±1.3 (63.8)	8.2±0.6 (9.2)
PbS-TBAI/PbS-EDT certified **	0.5546±0.0055	24.2±0.7	63.8±1.3	8.55±0.18

The numbers in parentheses represent the values obtained for the best-performing cell.

* To account for experimental errors, the reported averages and deviations are for samples of between 6 and 9 devices on the same substrate from measurements performed in between 1 and 75 days of air-exposure.

** Error bars: quoted uncertainties with an approximately 95% level of confidence.