https://dx.doi.org/10.1016/j.matt.2022.04.028

Ambipolar-Transport Wide-Bandgap Perovskite Interlayer for Organic Photovoltaics with over 18% Efficiency

Cenqi Yan,[1] *Jiangsheng Yu,*[1]*Yuhao Li,*[2] *Patrick W. K. Fong,*[1] *Ran Ding,*[3]*Kuan Liu,*[1] *Hao Xia,*[1]*Zhiwei Ren,*[1]*Xinhui Lu,*[2] *Jianhua Hao,*[3] *and Gang Li**[1,4]

[1]Department of Electronic and Information Engineering, Research Institute for Smart Energy (RISE), The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China

E-mail: gang.w.li@polyu.edu.hk

[2]Department of Physics, The Chinese University of Hong Kong, New Territories, Hong Kong, China

[3]Department of Applied Physics, The Hong Kong Polytechnic University, Hung Hom, Hong Kong, China

[4]Lead Contact

ABSTRACT:

Anode interface layers (AILs) are of vital importance to the performance of organic photovoltaics (OPVs). Herein, $MAPbBr_3$ is firstly demonstrated as effective solution-processed AIL, featuring a 2.3-eV bandgap and high hole and electron mobility. PM6:BO-4Cl based on unannealed device with the $MAPbBr_3$ AIL exhibits an encouraging efficiency of 15.5%. F4TCNQ is further doped into $MAPbBr_3$ to increase work function and passivate defects, boosting the efficiency to 17.3%. Likewise, the unannealed devices based on PM6:BTP-eC9:$PC_{71}BM$ achieved a high efficiency of 18.3% with $MAPbBr_3$/F4TCNQ AIL. The ambipolar ability of $MAPbBr_3$ in OPVs was further proved by inverted devices. Therefore, $MAPbBr_3$ successfully serves multiple functions: a down-conversion layer, an energy donor, and a textured seeding layer influencing BHJ morphology. This finding successfully demonstrates the practicability of wide-bandgap perovskite materials as highly promising OPV interfacial materials.

Introduction

Solution-processed organic photovoltaics (OPVs) are an emerging PV technology that combines benefits in flexibility, lightweight form factor, tunable color, and transparency.[1-4]OPV is also abundant and versatile in materials, and viable with large-area fabrication. In the previous fifteen years, the OPV performance in the laboratory has undergone intriguing advancement–from 4% to approaching 20% power conversion efficiency (PCE).[5-22]Towards OPV commercialization, application-specific requirements on efficiency, stability, and printability should be met.[23, 24]

Typically, single-junction OPVs comprise a bulk-heterojunction active layer sandwiched between an anode and a cathode. Excitons generated by the photo-active materials under illumination diffuse to the donor-acceptor interface and separate into free holes and electrons, which are collected by the corresponding electrodes afterward. The optimization of the interface between the electrode and the active layer is very critical to the device performance.[25, 26]Interface engineering can modify the work function of the electrode, reduce the recombination of interfacial charges. Interface engineering can also physically modulate the surface of ITO, passivate the surface defects and pinholes, and impact the morphology evolution of the bulk-heterojunction (BHJ) layer atop the interface since it is critically correlated with the surface energy and surface texture of the seeding layers.[27]

Anode interface layer (AIL) preferably increases the work function of the ITO anode, blocks electrons, physically modulates the ITO surface, and regulates the active-layer morphology. Notwithstanding the importance of AILs, the development of anode interface materials lags far behind that of photoactive materials. Only PEDOT:PSS and inorganic p-type transition metal oxides or sulfides (e.g. MoO_3 and WO_3) are extensively utilized in OPVs. The acidity and hygroscopicity characteristics of PEDOT:PSS raise the stability issue, as PEDOT: PSS can corrode the ITO anode, make the In ions diffuse into PEDOT: PSS and the active layer, and absorb moisture from the air. The inorganic AILs typically need vacuum thermal evaporation and have strict requirement on thickness (typically < 10 nm) to realize high efficiency, which is incompatible with scalable processing.

Hybrid organic-inorganic perovskites (HOIPs), such as methylammonium lead iodide ($FAPbI_3$), have achieved certified PCE surpassing 25% in single-junction photovoltaic devices. The scientific community focuses on the narrow-bandgap and medium-bandgap HOIPs, leaving the wide-bandgap hybrid perovskite less studied. Recently, the Adachi group utilized thermal evaporated $MAPbCl_3$ to construct an extraordinarily thick transport layer for organic light-emitting diode (OLEDs). Owing to the high carrier mobilities and high visible light transparency, the thickness of the $MAPbCl_3$ layer is enlarged to 2,000 nm via co-evaporation of MACl and $PbCl_2$ without requiring high voltage and without reducing either internal electroluminescence quantum efficiency or operational durability.[28] Based on our previous exploration of perovskite solar cells,[29] we realized the wide-bandgap solution-processed HOIPs are of intriguing properties and very promising potential as OPV interlayers. First, the energy levels and bandgaps of solution-processed HOIPs can be tailored by varying the composition of halide, metal, and A-cation. The intermediate compositions with a mixture of different halides, metals, or A-cations form perovskite crystalline alloys with intermediate bandgaps, which allows the continuous bandgap tuning from 1.2 to over 3.0 eV. Second, wide-bandgap HOIPs show superior carrier transport properties with long electron-hole diffusion lengths and carrier lifetimes. Besides, the ambipolar carrier transport characteristics endow HOIPs with the potential to shape interconnecting layers in tandems. Third, wide-bandgap $MAPbBr_{3-X}Cl_X$ ($0 \leq X \leq 3$) crystallizes in the same way - the perovskite phase forms a solid film directly from the colloidal solution state, which improved the alloying and phase stability compared with $MAPbI_{3-X}Br_X$ ($0 < X < 3$) systems.[30]

These considerations stimulated our exploitation of wide-bandgap HOIPs as interlayer materials of OPVs. We selected the wide-bandgap $MAPbBr_3$ as the AIL,[31] which exhibits a wide optical bandgap of 2.3 eV with an absorption onset of 539 nm, an electron conductivity of 5.88×10^{-3} S m^{-1}, good ambipolar transport capability with a hole mobility of 1.74 $cm^2V^{-1}S^{-1}$, and electron mobility of 2.04 $cm^2V^{-1}S^{-1}$(**Figure S1**).[32]As a result, the conventional device with the structure of ITO/$MAPbBr_3$/PM6:BO-4Cl/PFNBr/Ag (without thermal annealing of active layer) exhibited an encouraging PCE of 15.5%, with a V_{OC} of 0.82V, a J_{SC} of 26.0 mA cm^{-2}, and an FF of 72.6%. The efficient Förster energy transfer between interface and donor is firstly observed. F4TCNQ is further doped into $MAPbBr_3$ to increase the work function and passivate the defects, boosting the PCE to 17.3%, along with a V_{OC} of 0.84V, a J_{SC} of 26.5 mA cm^{-2}, and an FF of 77.6%. Notably, the device performance shows insensitivity to the thickness of $MAPbBr_3$, which is of importance to the up-scaling processing. The ambipolar transporting ability of $MAPbBr_3$ was clearly shown by the unannealed device with a structure of ITO/$MAPbBr_3$/Naphen-DPO/PM6:BO-4Cl/MoO_3/Ag, which offers a PCE of 8.75%, along with a V_{OC} of 0.59V, a J_{SC} of 25.8 mAcm^{-2}, and an FF of 57.3%. We also utilized the PM6:BTP-eC9:$PC_{71}BM$ ternary system and PM6:PY-IT all polymer system to study the universality of the $MAPbBr_3$ interfacial layer. The unannealed devices based on PM6:BTP-eC9:$PC_{71}BM$and PM6:PY-IT incorporating the $MAPbBr_3$(14 nm)/F4TCNQ AIL exhibited high PCEs of 18.3% and 15.1%, excelling the unannealed counterparts bearing the PEDOT:PSS AIL (17.4% and 14.2%). Our investigation shows that the solution-processed $MAPbBr_3$ is multifunctional and versatile in improving OPVs, serves as (a) ambipolar hole/electron transporting layer, (b) down-conversion layer that absorbs light in the range of 300-530 nm and reemits light in the range of 500-570 nm to boost J_{SC}, as well as (c) a textured interface layer that increases the crystallinity of the active layer.[27]

RESULTS AND DISCUSSION

We investigated the optical and transport properties of the $MAPbBr_3$ film. From the steady-state absorption measurement, $MAPbBr_3$ showed an absorption onset of 539 nm and an optical bandgap of 2.3 eV (**Figure 1a and S2**). Space charge limited current (SCLC) analysis based on electron-only devices with the structure of ITO/SnO_2/$MAPbBr_3$/$PC_{61}BM$/Au and hole-only devices with the structure of ITO/PEDOT:PSS/$MAPbBr_3$/MoO_3/Au was carried out to estimate the electron and hole mobilities, electron and hole trap densities, respectively (**Figure 1b** and **1c**). The trap-filled limit voltage (V_{TFL}) determined as the onset voltage of TFL regime (n>3) can be used to calculate trap density (N_t) with the equation:

$$N_t = 2\varepsilon_0\varepsilon_r V_{TFL}/qL^2$$

in which ε_0 is the vacuum permittivity, ε_r is the relative permittivity of perovskite, which can be taken as the value of 28.7 for $MAPbBr_3$, and L is the thickness of the perovskite film. The $MAPbBr_3$ perovskite film exhibited electron trap density of 1.7×10^{16} cm^{-3}, and hole trap density of 1.05×10^{16} cm^{-3}. Charge transport property in the perovskite films can be estimated in the trap-free regime (n=2)[33]with the equation:

$$J = (9\mu_e\varepsilon_0\varepsilon_r V^2)/8L^3$$

$MAPbBr_3$ exhibited high and balanced hole and electron mobilities of 1.74 and 2.04 $cm^2V^{-1}S^{-1}$ in the vertical direction, which agreed with the former reports.

Ultraviolet photoelectron spectroscopy (UPS) displays the photoemission cut-off, from which the work function of the surface is extracted. As shown in **Figure 1d**, the PEDOT:PSS/ITO and $MAPbBr_3$/ITO exhibited large work function (WF) of 5.2 and 5.0 eV, respectively. Kelvin probe force microscope (KPFM) has been extensively used to measure the contact potential differences (CPD) between a conducting atomic force microscopy (AFM) tip and a sample, and allows to map the work function of the sample. KPFM was used here to probe the work function difference of PEDOT:PSS/ITO and $MAPbBr_3$/ITO (**Figure 1e**). At the same color scale, the contact potential difference between the KPFM tip and the $MAPbBr_3$ surface is estimated as -463 mV in the dark, and that between the KPFM tip and PEDOT:PSS surface is estimated as -600 mV, which is in line with the UPS result. According to the X-ray photoelectron spectroscopy (XPS) characterization, the Pb 4f 7/2 and Pb 4f 5/2 peaks (at 138.4 and 143.3 eV) observed in the $MAPbBr_3$ perovskite were shifted to the direction with larger binding energy by 0.2 eV in the $MAPbBr_3$/F4TCNQ perovskite, indicative of the supramolecular interactions between the Lewis bases F4TCNQ and $MAPbBr_3$ (**Figure S3**).

Table 1. Photovoltaic parameters of unannealed OPV devices with the structure of ITO/AIL/PM6:BO-4Cl/PFNBr/Ag.

AIL	V_{OC} (V)	J_{SC} (mA cm^{-2})	calc. J_{SC} (mA cm^{-2})	FF (%)	PCE$^{a)}$ (%)
14 nm $MAPbBr_3$	0.82	26.0	24.9	72.6	15.5 (15.2±0.2)
7 nm $MAPbBr_3$/F4TCNQ	0.83	26.1	25.0	72.2	15.5 (15.2±0.2)
14 nm $MAPbBr_3$/F4TCNQ	0.84	26.5	25.2	77.6	17.3 (16.8±0.3)
30 nm $MAPbBr_3$/F4TCNQ	0.83	25.9	25.0	77.3	16.6 (16.2±0.2)
45 nm $MAPbBr_3$/F4TCNQ	0.83	25.7	24.7	73.2	15.5 (14.9±0.3)
60 nm $MAPbBr_3$/F4TCNQ	0.81	25.4	24.2	72.0	14.8 (14.3±0.3)
30 nm PEDOT:PSS	0.84	25.2	24.1	74.0	15.6 (15.5±0.1)
w/o AIL	0.68	22.5	23.7	59.2	9.09 (7.58±1.20)

$^{a)}$ Average value of 12 devices in parentheses.

Devices were fabricated based on conventional structures of ITO/AIL/PM6:BO-4Cl[34]/PFNBr/Ag using non-halogen solvent[35] (o-xylene) and no thermal annealing step for all the active layers. (In this paper, the unannealed device means its active layer does not undergo thermal annealing treatment). **Figure S4** showed the UV-vis absorption spectra of PM6 and BO-4Cl. **Figure S5** showed the energy level distribution of related interfacial and active-layer materials. The current density versus voltage (*J*-*V*) characteristics were shown in **Figure 2a** and the key parameters of OPVs were summarized in **Table 1**. The unannealed control devices without AIL exhibited a champion PCE of 9.09%, accompanied with a V_{OC} of 0.68V, a J_{SC} of 22.5 mA/cm^2, and an FF of 59.2%. Besides, these AIL-free devices exhibited poor repeatability of efficiency. The unannealed control devices with PEDOT:PSS AIL displayed a PCE of 15.6%, with a V_{OC} of 0.84V, a J_{SC} of 25.2 mAcm^{-2}, and an FF of 74.0%. The experimental devices with $MAPbBr_3$ (14 nm) exhibited a comparable performance, affording a similar PCE of 15.5%, slightly lower V_{OC} of 0.82V and FF of 72.6%, and a higher J_{SC} of 26.0 mA cm^{-2}. We then adopted F4TCNQ to modify the $MAPbBr_3$layer with favorable band alignment, which was expected to facilitate the extraction of holes from $MAPbBr_3$ to ITO electrode.[36] F4-TCNQ is also shown to increase the WF of the $MAPbBr_3$/ITO substrate, which is confirmed by the UPS and KPFM characterization (**Figure 1d** and **1e**). Meanwhile, F4TCNQ improves the hole mobility of MAPbBr3 from 1.74 to 2.49 $cm^2V^{-1}S^{-1}$, and the electron mobility from 2.04 to 2.88 $cm^2V^{-1}S^{-1}$ (**Figure S6-7**). After F4TCNQ doping, the device performance was successfully boosted to 17.3%, with a V_{OC} of 0.84V, a J_{SC} of 26.5 $mAcm^{-2}$ and an FF of 77.6%. Notably, even when the thickness of $MAPbBr_3$ interlayer is increased to 60 nm, the device still demonstrated a PCE of 14.8%, a V_{OC} of 0.81V, a J_{SC} of 25.4 $mAcm^{-2}$, and an FF of 72.0%. The OPV device exhibited excellent tolerance to the thickness of $MAPbBr_3$ due to the high hole mobility of $MAPbBr_3$, which is valuable for industrial fabrication. **Table S1** summarized photovoltaic parameters of annealed devices. After thermal annealing, the device with $MAPbBr_3$/F4TCNQ also exhibits a higher PCE of 17.5% than the counterpart with PEDOT:PSS (16.9%) (**Figure S8-9**). The stability of OPV devices with PEDOT:PSS and $MAPbBr_3$/F4TCNQ were also studied. These two kinds of devices exhibited comparable thermal stability; they both retained approximately 60-70% after 200 hours' thermal annealing at 80 °C in the glove box filled with N_2 (**Figure S10**).

The EQE characterization was carried out to evaluate the accuracy of J_{SC} measured from the *J-V* curves (**Figure 2b**). The OPV devices based on PEDOT:PSS and $MAPbBr_3$ AILs both exhibited high EQE response in the wavelength of 500-800 nm. The devices with $MAPbBr_3$ (7-30 nm) all presented higher EQE peaks at wavelength <400 nm (~70% at 380 nm) than the devices with PEDOT:PSS AIL (~62% at 380 nm) (**Figure 2c**). Such an interesting phenomenon encouraged us to further study how the $MAPbBr_3$ AIL contributed to the EQE in the short wavelength. The steady-state PL spectra of PM6 and $MAPbBr_3$ pure films, and PM6/$MAPbBr_3$ films (excited at 450 nm) were therefore plotted in **Figure 2d**. As for the $MAPbBr_3$ pure film, the PL Peak intensified with the increased thickness. The PL spectrum of the $MAPbBr_3$ pure film, featuring sharp peak at 526 nm, strongly overlapped the absorption of PM6 and afforded the possibility of energy transfer from $MAPbBr_3$ to PM6. In the $MAPbBr_3$/PM6 film, the emission of $MAPbBr_3$ was entirely quenched by PM6 while that of PM6 showed some enhancement, indicating effective Förster resonance energy transfer from $MAPbBr_3$ to PM6. In the $MAPbBr_3$/PM6 composite film, the enhancement of PM6 peak became more obvious with the increasing thickness of $MAPbBr_3$. This phenomenon soundly proved that the wide-bandgap $MAPbBr_3$ can efficiently transfer energy to PM6, which accounted for the increased EQE response in the short wavelength for OPVs with $MAPbBr_3$. We also designed the device structure of ITO/PEDOT:PSS/$MAPbBr_3$/PM6/PFNBr/Ag to check if there existed charge transfer between PM6 and $MAPbBr_3$. The corresponding device showed an extremely small J_{SC} of 0.025 mAcm^{-2}, indicative of negligible charge transfer between them (**Figure 2e**).

To probe hole extraction of OPVs with different AILs, the photocurrent density (J_{ph})-effective voltage (V_{eff}) relationships were investigated (**Figure 2f**). $J_{ph}= J_L - J_D$ and $V_{eff} = V_0 - V_{appl}$, where V_{appl} represents the applied voltage, V_0 refers to the voltage value when $J_{ph} = 0$. When V_{eff} reaches a high value (> 2.3V), the generated excitons are assumed to be fully collected, and J_{ph} is equal to saturated current density (J_{sat}). The J_{SC}/J_{sat} and J_{max}/J_{sat} can be calculated to evaluate exciton dissociation (η_{diss}) and charge collection (η_{coll}) efficiency. The champion devices incorporating PEDOT:PSS, $MAPbBr_3$ (14 nm) and $MAPbBr_3$(14 nm) /F4TCNQ interlayers exhibited η_{diss}/η_{coll} of 98.1%/88.2%, 96.4%/84.5%, and 98.2%/90.3%, respectively. These results showed that the F4TCNQ doping can effectively improve the efficiency of charge collection, and devices with the F4TCNQ doped $MAPbBr_3$ AIL have comparable or even higher charge collection efficiency than controls with PEDOT:PSS.

To decipher the effect of replacing PEDOT:PSS with $MAPbBr_3$ in charge recombination, the power-law relation ($J \propto P_{light}^{\alpha}$) was used to fit J_{SC} as a function of the incident light intensity in the corresponding devices. A value of α equal to 1 means the ideal case where all the free carriers are swept out and collected at the electrodes before recombination. The devices with PEDOT:PSS, $MAPbBr_3$ and F4TCNQ doped $MAPbBr_3$ exhibited α values of

0.98, 0.98, and 0.99, indicative of negligible bimolecular recombination losses for all the devices (**Figure 2g**). To analyze the trap-assisted Shockley-Read-Hall (SRH) recombination, V_{OC} as a function of the incident light intensity was measured. The data were fitted according to the equation $V_{OC} \propto nkT/q \ln(P_{light})$, where k, T, and q are the Boltzmann constant, the temperature in kelvin, and elementary charge, respectively. The parameter n is generally in the range of 1-2 and reflects the presence of carrier traps across the active layer or at the interfaces. A value of n equal to 1 means the ideal case where the trap-assisted recombination does not exist. The fitted data derived n values of 1.17, 1.45 and 1.11, for devices with PEDOT:PSS, $MAPbBr_3$, and $MAPbBr_3$/F4TCNQ (**Figure 2h**). These results revealed that the doping of F4TCNQ effectively reduced trap-assisted recombination, which accounted for the PCE enhancement from 15.5% to 17.3%.

Contact angle (CA) measurement and atomic force microscopy (AFM) were performed to study the surface energy (γ) and surface morphology of $MAPbBr_3$ and PEDOT:PSS film on ITO substrates. The contact angle of $MAPbBr_3$ and PEDOT:PSS were shown in **Figure 3a**, **S11-12**.

According to Wu model,[37, 38] the $MAPbBr_3$ thin film exhibited surface tension of 61.6 mNm^{-1} with γ^d of 13.5 mN m^{-1} and γ^P of 48.1 mNm^{-1}. By contrast, the PEDOT:PSS interface exhibited surface tension of 71.9 mN m^{-1} with γ^d of 13.9 mN $m^{-1}$and γ^P of 58.0 mN m^{-1}. Atomic force microscope (AFM) is one of the most widely used tools for surface morphology characterization, providing the basic information of surface morphology, mainly the surface topography with high spatial resolution within 10 nm. As **Figure 3b** shows, the PEDOT:PSS interlayer showed a uniform and flat surface with a R_q of 1.64 nm, whereas the $MAPbBr_3$ layer showed a coarse surface with a larger R_q of 5.37 nm. This kind of pattern might be advantageous for broadband light trapping over the full solar spectral range, and did not have bad influence on FF. The upper surfaces of PM6:BO-4Cl system solution-deposited on the PEDOT:PSS and $MAPbBr_3$ AILs exhibited similar roughness of 1.48 and 1.71 nm.

AFM only probes the surface information of the active layer, while the inward donor/acceptor configuration is pivotal for device performance. Grazing incidence wide-angle X-ray scattering (GIWAXS) was therefore adopted to investigate crystalline structures on the molecular scale, including information of the distance of the lamellar layers, π-π stacking, and crystalline coherence length (CCL).[39-41]The 2D diffraction patterns and 1D line-cuts were depicted in **Figures 3c**, **3d** and **S13-17**, and the extracted data of GIWAXS in-plane peaks and out-of-plane peaks were summarized in **Tables S2** and **S3**. The Si/PEDOT:PSS sample only showed very weak scatter ring. By contrast, the Si/$MAPbBr_3$ sample displayed two peaks at q_r=1.07 Å^{-1} ($d \approx$ 5.87 Å), and 1.51 Å^{-1} ($d \approx$ 4.16 Å), and a peak at q=1.51 Å^{-1} ($d \approx$ 4.16 Å), in the direction of an angle of 45° relative to the substrate. The $MAPbBr_3$thin film showed very strong orientation, which obviously varied from the $MAPbBr_3$thick film.[30]The PM6 neat film exhibits a weak π-π peak at $q_z\approx$ 1.70 Å^{-1} ($d \approx$ 3.69 Å) and an obvious lamellar peak at $q_z\approx$ 0.326 Å^{-1} ($d \approx$ 19.3 Å), 0.663 Å^{-1} ($d \approx$ 9.47 Å), 0.954 Å^{-1} ($d \approx$ 6.58 Å). The PM6 neat film also exhibited a lamellar peak at $q_r\approx$ 0.273Å^{-1} ($d \approx$ 23.0 Å) along the in-plane (IP) direction. The BO-4Cl neat film displayed a preferential face-on orientation, with a strong π-π peak at $q_z\approx$ 1.79 Å^{-1} ($d \approx$3.51 Å), and diffraction peaks at $q_r\approx$ 0.396 Å^{-1} ($d \approx$ 15.9Å) and $q_z \approx$ 0.590 Å^{-1} ($d \approx$ 10.6 Å). The PEDOT:PSS/PM6:BO-4Cl film showed lamellar peaks at $q_r\approx$ 0.296 Å^{-1} ($d \approx$ 21.2Å) and $q_z\approx$ 0.315 Å^{-1} ($d \approx$ 20.0Å), and π-π peak at $q_z\approx$ 1.74 Å^{-1} ($d \approx$ 3.62Å). By comparison, the $MAPbBr_3$/PM6:BO-4Cl film exhibited lamellar peaks at $q_r\approx$ 0.299 Å^{-1} (d $\approx$ 21.0 Å) and $q_z\approx$ 0.320 Å^{-1} (d $\approx$19.6 Å), and π-π peak at $q_z\approx$ 1.76 Å^{-1} (d $\approx$ 3.57Å), indicative of the tighter packing of PM6:BO-4Cl on the $MAPbBr_3$ interlayer. Along the IP direction, the $MAPbBr_3$/PM6:BO-4Cl film also displayed broad peaks at 1.06 and 1.50 Å^{-1}, which belongs to the characteristics of $MAPbBr_3$ film. The combined characteristics of PM6:BO-4Cl and $MAPbBr_3$ therein imply the rough interface between $MAPbBr_3$ and PM6:BO-4Cl, which is in accord with the AFM result. To quantitatively discuss the morphology evolution, the CCL of the π–π peak was estimated by the equation CCL $=1.8\pi/\mathrm{FWHM}$, where FWHM referred to the full width at half maximum of the peak in the intensity profile. The CCL of π-π peak of PM6:BO-4Cl atop PEDOT:PSS interface was 21.0 Å, slightly smaller than that of PM6:BO-4Cl atop MAPbBr$_3$ interface (23.0 Å), indicating the coarse MAPbBr$_3$ film facilitated the aggregation of active-layer materials, and probably served as the crystalline seeding.

Ambipolar transport fuels many interesting prospects at both fundamental and technological levels to organic electronics society. Ambipolar transistors, for example, in which holes and electrons transport concurrently within a semiconducting channel, are finding new uses in lighting, display, memory, and neuromorphic computers for artificial intelligence. The MAPbBr$_3$ layer's ambipolar transporting nature may allow it to operate as a cathode interface layer (CIL) in OPVs, which we investigated using an inverted configuration.[43]

Table 2. Photovoltaic parameters of unannealed OPV devices with the structure of ITO/ cathode interface layer (CIL)/PM6: BO-4Cl/MoO$_3$/Ag.

CIL	V_{OC} (V)	J_{SC} (mA cm^{-2})	calc. J_{SC} (mA cm^{-2})	FF (%)	PCE$^{a)}$ (%)
w/o CIL	0.15	17.4	17.4	31.0	0.799 (0.750±0.021)
50 nm MAPbBr$_3$/Naphen-DPO	0.59	25.8	24.8	57.3	8.75 (8.42±0.13)
Naphen-DPO	0.80	25.6	24.7	68.8	14.2 (13.8±0.2)

a) Average value of 12 devices in parentheses.

Table 3. Photovoltaic parameters of unannealed OPV devices with the structure of ITO/AIL/active layer/PFNBr/Ag.

Active Layer	AIL	V_{OC} (V)	J_{SC} (mA cm^{-2})	calc. J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
PM6:PY-IT	PEDOT:PSS	0.93	22.0	21.1	69.2	14.2 (14.0±0.1)
PM6: PY-IT	14 nm MAPbBr$_3$/F4TCNQ	0.93	22.7	21.6	71.1	15.1 (14.7±0.2)
PM6:BTP-eC9:PC$_{71}$BM	PEDOT:PSS	0.86	26.5	25.3	76.6	17.4 (17.1±0.2)
PM6:BTP-eC9:PC$_{71}$BM	14 nm MAPbBr$_3$/F4TCNQ	0.86	26.7	25.9	79.5	18.3 (17.9±0.2)

a) Average value of 12 devices in parentheses.

The inverted devices featuring the architecture of ITO/MAPbBr$_3$/PM6:BO-4Cl/MoO$_3$/Ag displayed negligible J_{SC} and PCE, which was because (a) the high-WF MAPbBr$_3$ cannot form energy level alignment with the LUMO level of BO-4Cl, and (b) MAPbBr$_3$ and MoO$_3$ have similar WF, which forms a hole-only device (**Figure S18**). The control inverted device with the structure of ITO/PM6:BO-4Cl/MoO_3/Ag exhibited a V_{OC} of 0.15V, a J_{SC} of 17.4 mA cm^{-2}, an FF of 31.0%, and a PCE of 0.799% (**Table 2**). The poor performance is ascribed to the mismatch of the work function of ITO and the LUMO level of BO-4Cl. Therefore, a very thin Naphen-DPO layer was inserted between $MAPbBr_3$ and the PM6:BO-4Cl active layer to facilitate electron collection. The corresponding device with the architecture of ITO/$MAPbBr_3$ (*ca.* 50 nm)/Naphen-DPO/PM6:BO-4Cl/MoO_3/Ag exhibited a PCE of 8.75%, along with a V_{OC} of 0.59V, a J_{SC} of 25.8 $mAcm^{-2}$ and an FF of 57.3%. (**Figure 4a-b, S19**) The results showed clearly that $MAPbBr_3$ can effectively transport electrons in OPV as long as the energy level aligns and thus electron extraction is efficient. This proved the ambipolar ability of $MAPbBr_3$ in OPV, in which it allowed both electron and hole transports, in opposite directions.

To demonstrate the universality of the $MAPbBr_3$ interfacial layer in OPVs, we also utilized the PM6:BTP-eC9[44]:$PC_{71}BM$ ternary system and PM6:PY-IT[45] all polymer system to construct the corresponding conventional device. (**Table 3**, **Figure 4c-d**) The unannealed device with the structure of ITO/PEDOT:PSS/PM6:BTP-eC9:$PC_{71}BM$/PFNBr/Ag exhibited a PCE of 17.4%, a V_{OC} of 0.86V, an FF of 76.6%, and a J_{SC} of 26.5 mA cm^{-2}. By comparison, the unannealed experimental device incorporating the architecture of ITO/$MAPbBr_3$(14 nm)/F4TCNQ/PM6:BTP-eC9:$PC_{71}BM$/PFNBr/Ag successfully demonstrated a high PCE of 18.3%, accompanied with a V_{OC} of 0.86V, an FF of 79.5%, and a J_{SC} of 26.7 mA cm^{-2}. It is noteworthy this efficiency is among the highest for the devices without thermal annealing. As for the PM6:PY-IT all polymer system, the unannealed device incorporating the $MAPbBr_3$(14 nm)/F4TCNQ AIL exhibited a high PCE of 15.1%, excelling the unannealed counterpart bearing the PEDOT:PSS AIL (14.2%).

CONCLUSION

To summarize, we first successfully demonstrated one of the solution-processed wide-bandgap perovskites ($MAPbBr_3$, E_g=2.3 eV) as the anode interfacial layer for highly-efficient conventional OPV device with an encouraging efficiency of 15.5%. F4TCNQ doping of $MAPbBr_3$ increased the work function, passivated the defects, and thereby boosted the efficiency to 17.3%. Parallelly, the unannealed device based on PM6:BTP-eC9:$PC_{71}BM$ and PM6:PY-IT incorporating the $MAPbBr_3$(14 nm)/F4TCNQ AIL afforded high efficiencies of 18.3% and 15.1%, exceeding the unannealed controls bearing the PEDOT:PSS AIL (17.4% and 14.2%). The efficiency of 18.3% is among the highest for the devices without thermal annealing. The ambipolar ability of $MAPbBr_3$ in OPVs was proved by inverted devices. The $MAPbBr_3$ interface layer therefore serves multiple purposes: novel ambipolar OPV hole/electron transporting layer, a down-conversion layer, an energy donor, and a textured layer to influence the active-layer morphology. Considering the myriad of methods reported to modulate the optoelectronic property of perovskite, this work provides a unique perspective on designing high-performing and cost-effective interlayers for organic photovoltaics.

EXPERIMENTAL PROCEDURES

Resource availability

Lead contact

Further information and requests for resources and materials should be directed to and will be fulfilled by the Lead Contact: Gang Li (gang.w.li@polyu.edu.hk)

Materials availability

This work does not generate new materials.

Data and code availability

This work does not generate program and coding.

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at xxx.

ACKNOWLEDGEMENTS

G. Li thanks the support from Research Grants Council of Hong Kong (Project Nos 15221320, C5037-18G), Shenzhen Science and Technology Innovation Commission (Project No. JCYJ20170413154602102), National Science Foundation of China (51961165102) and Sir Sze-yuen Chung Endowed Professorship (8-8480) provided by the Hong Kong Polytechnic University. X. Lu thanks the Research Grants Council of Hong Kong (General Research Fund No. 14314216). J. Yu thanks the support from the Hong Kong Scholars Program (XJ2020042). We thank Prof. He Yan and Ruijie Ma for contact angle measurement and thank Qiong Liang for XRD measurement.

AUTHOR CONTRIBUTIONS

G. L. and C. Y. proposed the idea. C. Y. fabricated devices. C. Y. and J. Y. completed the draft. Y. L. and X. L. did the GIWAXS and GISAXS measurements. P. F. performed in-situ absorption measurements. R. D. and J. H. performed KPFM measurements. K. L., H. X., and Z. R. performed correlated analysis. G. L. revised the draft and supervised the work.

DECLARATION OF INTERESTS

The authors declare no competing interests.

Figure 1. Basic optoelectronic properties of $MAPbBr_3$.
(a) The UV-vis absorption spectrum of $MAPbBr_3$. (b) The dark current density- voltage curve of hole-only device with a structure of ITO/PEDOT:PSS/$MAPbBr_3$/MoO_3/Au. (c) The dark current density-voltage curve of electron-only device with a structure of ITO/SnO_2/$MAPbBr_3$/$PC_{61}BM$/Au. (d) The UPS spectra of $MAPbBr_3$, $MAPbBr_3$/F4TCNQ and PEDOT:PSS on ITO substrates. (e) The KPFM images of $MAPbBr_3$, $MAPbBr_3$/F4TCNQ and PEDOT:PSS on ITO substrates (1.5 μm × 1.5 μm).

Figure 2. Comparison between devices with PEDOT:PSS, $MAPbBr_3$ and $MAPbBr_3$/F4TCNQ anode interface layers.
The *J-V* curve (a) and EQE spectra (b) of devices with the structures of ITO/PM6:BO-4Cl/PFNBr/Ag, ITO/PEDOT:PSS/PM6:BO-4Cl/PFNBr/Ag, ITO/$MAPbBr_3$/PM6:BO-4Cl/PFNBr/Ag, and ITO/$MAPbBr_3$/F4TCNQ/PM6:BO-4Cl/PFNBr/Ag. (c) The EQE difference between devices with the structures of ITO/PEDOT:PSS/PM6:BO-4Cl/PFNBr/Ag and ITO/$MAPbBr_3$(14 nm)/F4TCNQ/PM6:BO-4Cl/PFNBr/Ag. (d) The PL spectra of $MAPbBr_3$, PM6 and $MAPbBr_3$/PM6 on ITO substrates. (λ_{ex}=450 nm) (e) The *J-V* curve of devices with the structures of ITO/PEDOT:PSS/$MAPbBr_3$/PM6/PFNBr/Ag. (f) Photocurrent density (J_{ph})

versus effective voltage (V_{eff}) curves of devices with structures of ITO/PEDOT:PSS/PM6:BO-4Cl/PFNBr/Ag, ITO/$MAPbBr_3$(14 nm)/PM6:BO-4Cl/PFNBr/Ag, and ITO/$MAPbBr_3$(14 nm)/F4TCNQ/ PM6:BO-4Cl/PFNBr/Ag. Light intensity dependence of (g) J_{SC} and (h) V_{OC} of devices with the structures of ITO/PEDOT:PSS/PM6:BO-4Cl/PFNBr/Ag, ITO/$MAPbBr_3$(14 nm)/PM6:BO-4Cl/PFNBr/Ag, and ITO/$MAPbBr_3$(14 nm)/F4TCNQ/PM6:BO-4Cl/PFNBr/Ag.

Figure 3. Contact angle measurement of anode interfacial layers and morphology characterization of anode interfacial interlayers and active layers.
(a) The contact angles of H_2O and ethylene glycol (GL) on the PEDOT:PSS and $MAPbBr_3$ substrates. (b) The AFM height images (1μm ×1μm), (c) The 2D GIWAXS patterns, and (d) The GIWAXS profiles along the out-of-plane (OOP) and in-plane (IP) directions of PEDOT, $MAPbBr_3$, PEDOT:PSS/PM6:BO-4Cl, and $MAPbBr_3$/PM6:BO-4Cl.

Figure 4. Photovoltaic properties of inverted devices based on PM6:BO-4Cl and conventional devices based on PM6:PY-IT and PM6:BTP-eC9:$PC_{71}BM$. (a) The *J-V* curve and (b) the EQE spectra of the devices with the structure of ITO/PM6:BO-4Cl/MoO_3/Ag, ITO/$MAPbBr_3$/Naphen-DPO/PM6:BO-4Cl/MoO_3/Ag, and ITO/Naphen-DPO/PM6:BO-4Cl/MoO_3/Ag.(c) The *J-V* curve and(d) EQE spectra of devices with the structures of ITO/PEDOT:PSS/PM6:PY-IT/PFNBr/Ag, ITO/$MAPbBr_3$(14nm)/F4TCNQ/PM6:PY-IT/PFNBr/Ag, ITO/PEDOT:PSS/PM6:BTP-eC9:$PC_{71}BM$/PFNBr/Ag, and ITO/$MAPbBr_3$(14nm)/F4TCNQ/PM6:BTP-eC9:$PC_{71}BM$/PFNBr/Ag.

References

1. Yan, C., Barlow, S., Wang, Z., Yan, H., Jen, A. K. Y., Marder, S. R., Zhan, X. (2018). Non-fullerene acceptors for organic solar cells. *Nat. Rev. Mater.3,* 18003.
2. Li, G., Chang, W.-H., Yang, Y. (2017). Low-bandgap conjugated polymers enabling solution-processable tandem solar cells. *Nat. Rev. Mater.2*, 17043.
3. Cheng, P., Li, G., Zhan, X., Yang, Y. (2018). Next-generation organic photovoltaics based on non-fullerene acceptors. *Nat. Photon. 12*, 131-142.
4. Cheng, P., Yang, Y. (2020). Narrowing the Band Gap: The Key to High-Performance Organic Photovoltaics. *Acc. Chem. Res. 53*, 1218-1228.
5. Bi, P., Zhang, S., Chen, Z., Xu, Y., Cui, Y., Zhang, T., Ren, J., Qin, J., Hong, L., Hao, X., Hou, J. (2021). Reduced non-radiative charge recombination enables organic photovoltaic cell approaching 19% efficiency. *Joule5*, 1-12.
6. Li, C., Zhou, J., Song, J., Xu, J., Zhang, H., Zhang, X., Guo, J., Zhu, L., Wei, D., Han, G.,et al. (2021). Non-fullerene acceptors with branched side chains and improved molecular packing to exceed 18% efficiency in organic solar cells. *Nat. Energy 6*, 605-613.
7. Cai, Y., Li, Y., Wang, R., Wu, H., Chen, Z., Zhang, J., Ma, Z., Hao, X., Zhao, Y., Zhang, C.,et al. (2021). A Well-Mixed Phase Formed by Two Compatible Non-Fullerene Acceptors Enables Ternary Organic Solar Cells with Efficiency over 18.6%. *Adv. Mater. 33*, 2101733.
8. Wang, J., Zheng, Z., Zu, Y., Wang, Y., Liu, X., Zhang, S., Zhang, M., Hou, J., (2021). A Tandem Organic Photovoltaic Cell with 19.6% Efficiency Enabled by Light Distribution Control. *Adv. Mater. 33*, 2102787.
9. Meng, L., Zhang, Y., Wan, X., Li, C., Zhang, X., Wang, Y., Ke, X., Xiao, Z., Ding, L., Xia, R.,*et al*. (2018). Organic and solution-processed tandem solar cells with 17.3% efficiency. *Science 361*, 1094-1098.

10. Qin, J., Zhang, L., Zuo, C., Xiao, Z., Yuan, Y., Yang, S., Hao, F., Cheng, M., Sun, K., Bao, Q.,et al. (2021).A chlorinated copolymer donor demonstrates a 18.13% power conversion efficiency. *J. Semicond. 42*, 010501.

11. Lin, Y., Nugraha, M. I., Firdaus, Y., Scaccabarozzi, A. D., Aniés, F., Emwas, A.-H., Yengel, E., Zheng, X., Liu, J., Wahyudi, W., et al. (2020).A Simple n-Dopant Derived from Diquat Boosts the Efficiency of Organic Solar Cells to 18.3%. *ACS Energy Lett. 5* , 3663-3671.

12. Lv, J., Tang, H., Huang, J., Yan, C., Liu, K., Yang, Q., Hu, D., Singh, R., Lee, J., Lu, S.,et al. (2021). Additive-induced miscibility regulation and hierarchical morphology enable 17.5% binary organic solar cells. *Energy Environ. Sci. 14*, 3044-3052.

13. Zhu, C., Yuan, J., Cai, F., Meng, L., Zhang, H., Chen, H., Li, J., Qiu, B., Peng, H., Chen, S.,et al. (2020). Tuning the electron-deficient core of a non-fullerene acceptor to achieve over 17% efficiency in a single-junction organic solar cell. *Energy Environ. Sci. 13*, 2459-2466.

14. Zhang, Z., Li, Y., Cai, G., Zhang, Y., Lu, X., Lin, Y. (2020). Selenium Heterocyclic Electron Acceptor with Small Urbach Energy for As-Cast High-Performance Organic Solar Cells. *J. Am. Chem. Soc. 142*, 18741-18745.

15. Zhan, L., Li, S., Xia, X., Li, Y., Lu, X., Zuo, L., Shi, M., Chen, H. (2021). Layer-by-Layer Processed Ternary Organic Photovoltaics with Efficiency over 18%. *Adv. Mater.33*, 2007231.

16. Ma, X., Zeng, A., Gao, J., Hu, Z., Xu, C., Son, J. H., Jeong, S. Y., Zhang, C., Li, M., Wang, K.,et al. (2020). Approaching 18% efficiency of ternary organic photovoltaics with wide bandgap polymer donor and well compatible Y6 : Y6-1O as acceptor. *Natl. Sci. Rev. 8*, nwaa305.

17. Yang, C., An, Q. S., Bai, H. R., Zhi, H. F., Ryu, H. S., Mahmood, A., Zhao, X., Zhang, S. W., Woo, H. Y., Wang, J. L. (2021). A Synergistic Strategy of Manipulating the Number of Selenophene Units and Dissymmetric Central Core of Small Molecular Acceptors Enables Polymer Solar Cells with 17.5% Efficiency. *Angew. Chem. In. Ed. 60*, 19241-19252.

18. Jiang, K., Zhang, J., Peng, Z., Lin, F., Wu, S., Li, Z., Chen, Y., Yan, H., Ade, H., Zhu, Z.,et al. (2021). Pseudo-bilayer architecture enables high-performance organic solar cells with enhanced exciton diffusion length. *Nat. Commun. 12*, 468.

19. Liu, T., Yang, T., Ma, R., Zhan, L., Luo, Z., Zhang, G., Li, Y., Gao, K., Xiao, Y., Yu, J.,et al. (2021). 16% efficiency all-polymer organic solar cells enabled by a finely tuned morphology via the design of ternary blend. *Joule 5*, 914-930.

20. Li, G., Shrotriya, V., Huang, J., Yao, Y., Moriarty, T., Emery, K., Yang, Y. (2005). High-efficiency solution processable polymer photovoltaic cells by self-organization of polymer blends. *Nat. Mater. 4*, 864-868.

21. Liu, S., Yuan, J., Deng, W., Luo, M., Xie, Y., Liang, Q., Zou, Y., He, Z., Wu, H., Cao, Y. (2020). High-efficiency organic solar cells with low non-radiative recombination loss and low energetic disorder. *Nat. Photon. 14*, 300-305.

22. Zhang, M., Zhu, L., Hao, T., Zhou, G., Qiu, C., Zhao, Z., Hartmann, N., Xiao, B., Zou, Y., Feng, W.,et al. (2021). High-Efficiency Organic Photovoltaics using Eutectic Acceptor Fibrils to Achieve Current Amplification. *Adv. Mater. 33*, 2007177.

23. Sun, R., Wu, Q., Guo, J., Wang, T., Wu, Y., Qiu, B., Luo, Z., Yang, W., Hu, Z., Guo, J.,et al. (2020). A Layer-by-Layer Architecture for Printable Organic Solar Cells Overcoming the Scaling Lag of Module Efficiency. *Joule4, 407*-419.

24. Yang, W., Wang, W., Wang, Y., Sun, R., Guo, J., Li, H., Shi, M., Guo, J., Wu, Y., Wang, T.,et al. (2021). Balancing the efficiency, stability, and cost potential for organic solar cells via a new figure of merit. *Joule 5*, 1209-1230.

25. Xu, B., Hou, J.(2018). Solution-Processable Conjugated Polymers as Anode Interfacial Layer Materials for Organic Solar Cells. *Adv. Energy Mater. 8*, 1800022.

26. Xu, H. T., Yuan, F., Zhou, D., Liao, X. F., Chen, L., Chen, Y. W. (2020). Hole transport layers for organic solar cells: recent progress and prospects.*J. Mater. Chem. A 8,* 11478-11492.

27. Yu, J., Xi, Y., Chueh, C.-C., Xu, J.-Q., Zhong, H., Lin, F., Jo, S. B., Pozzo, L. D., Tang, W., Jen, A. K. Y. (2017). Boosting performance of inverted organic solar cells by using a planar coronene based electron-transporting layer. *Nano Energy 39*, 454-460.

28. Matsushima, T., Bencheikh, F., Komino, T., Leyden, M. R., Sandanayaka, A. S. D., Qin, C., Adachi, C. (2019). High performance from extraordinarily thick organic light-emitting diodes. *Nature*, *572,* 502-506.

29. Yang, G., Ren, Z., Liu, K., Qin, M., Deng, W., Zhang, H., Wang, H., Liang, J., Ye, F., Liang, Q.,et al. (2021). Stable and low-photovoltage-loss perovskite solar cells by multifunctional passivation. *Nat. Photon. 15*, 681-689.

30. Tang, M.-C., Dang, H. X., Lee, S., Barrit, D., Munir, R., Wang, K., Li, R., Smilgies, D.-M., De Wolf, S., Kim, et al. (2021). Wide and Tunable Bandgap MAPbBr3−xClx Hybrid Perovskites with Enhanced Phase Stability: In Situ Investigation and Photovoltaic Devices. *Solar RRL 5,* 2000718.

31. Wang, K.-H., Li, L.-C., Shellaiah, M., Wen Sun, K. (2017). Structural and Photophysical Properties of Methylammonium Lead Tribromide ($MAPbBr_3$) Single Crystals. *Sci. Rep. 7,* 13643.

32. Musiienko, A., Moravec, P., Grill, R., Praus, P., Vasylchenko, I., Pekarek, J., Tisdale, J., Ridzonova, K., Belas, E., Landová, L., et al. (2019). Deep levels, charge transport and mixed conductivity in organometallic halide perovskites. *Energy Environ. Sci. 12* (4), 1413-1425.

33. Peng, J., Chen, Y., Zheng, K., Pullerits, T., Liang, Z. (2017). Insights into charge carrier dynamics in organo-metal halide perovskites: from neat films to solar cells. *Chem. Soc. Rev. 46*, 5714-5729.

34. Cui, Y., Yao, H., Hong, L., Zhang, T., Tang, Y., Lin, B., Xian, K., Gao, B., An, C., Bi, P.,et al. (2019). Organic photovoltaic cell with 17% efficiency and superior processability. *Natl. Sci. Rev. 7*, 1239-1246.

35. Ma, R., Yang, T., Xiao, Y., Liu, T., Zhang, G., Luo, Z., Li, G., Lu, X., Yan, H., Tang, B. (2021). Air-Processed Efficient Organic Solar Cells from Aromatic Hydrocarbon Solvent without Solvent Additive or Post-Treatment: Insights into Solvent Effect on Morphology. *Energy Environ. Mater. 2,* 12226.

36. Wu, W.-Q., Wang, Q., Fang, Y., Shao, Y., Tang, S., Deng, Y., Lu, H., Liu, Y., Li, T., Yang, Z.,et al. (2018). Molecular doping enabled scalable blading of efficient hole-transport-layer-free perovskite solar cells. *Nat. Commun. 9,* 1625.

37. Wu, S. (1971). Calculation of interfacial tension in polymer systems. *J. Polym. Sci. Part C Polym. Symp. 34*, 19-30.

38. Wu, S. (1973). Polar and Nonpolar Interactions in Adhesion. *J. Adhes. 5*, 39-55.

39. Mai, J., Lu, H., Lau, T.-K., Peng, S.-H., Hsu, C.-S., Hua, W., Zhao, N., Xiao, X., Lu, X. (2017). High efficiency ternary organic solar cell with morphology-compatible polymers. *J. Mater. Chem. A 5*, 11739-11745.

40. Mai, J., Lau, T.-K., Li, J., Peng, S.-H., Hsu, C.-S., Jeng, U. S., Zeng, J., Zhao, N., Xiao, X., Lu, X. (2016). Understanding Morphology Compatibility for High-Performance Ternary Organic Solar Cells. *Chem. Mater. 28,* 6186-6195.

41. Mai, J., Xiao, Y., Zhou, G., Wang, J., Zhu, J., Zhao, N., Zhan, X., Lu, X. (2018) Hidden Structure Ordering Along Backbone of Fused-Ring Electron Acceptors Enhanced by Ternary Bulk Heterojunction. *Adv. Mater. 30,* 1802888.

42. Fong, P. W.-K., Hu, H., Ren, Z., Liu, K., Cui, L., Bi, T., Liang, Q., Wu, Z., Hao, J., Li, G. (2021). Printing High-Efficiency Perovskite Solar Cells in High-Humidity Ambient Environment—An In Situ Guided Investigation. *Adv. Sci. 8,* 2003359.

43. Li, G., Chu, C.-W., Shrotriya, V., Huang, J., Yang, Y. (2006). Efficient inverted polymer solar cells. *Appl. Phys. Lett. 88*, 253503.

44. Cui, Y., Yao, H., Zhang, J., Xian, K., Zhang, T., Hong, L., Wang, Y., Xu, Y., Ma, K., An, C.,et al. (2020). Single-Junction Organic Photovoltaic Cells with Approaching 18% Efficiency. *Adv. Mater. 32*, 1908205.

45. Luo, Z., Liu, T., Ma, R., Xiao, Y., Zhan, L., Zhang, G., Sun, H., Ni, F., Chai, G., Wang, J.,et al. (2020). Precisely Controlling the Position of Bromine on the End Group Enables Well-Regular Polymer Acceptors for All-Polymer Solar Cells with Efficiencies over 15%. *Adv. Mater. 32*, 2005942.