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Achieving over 18% Efficiency Organic Solar Cell Enabled by a ZnO-Based Hybrid Electron Transport Layer with an Operational Lifetime up to 5 Years

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Abstract: Although organic solar cells (OSCs) have delivered an impressive power conversion efficiency (PCE) of over 19%, most of them demonstrated rather limited stability. So far, there are hardly any effective and universal strategies to improve stability of state-ofthe-art OSCs. Herein, we developed a hybrid electrontransport layer (ETL) in inverted OSCs using ZnO and a new modifying agent (NMA), and significantly improved the stability and PCEs for all the tested devices. In particular, when applied in the D18:N3 system, its inverted OSC exhibits so far the highest PCE (18.20%) among inverted single-junction OSCs, demonstrating an extrapolated T₈₀ lifetime of 7572 h (equivalent to 5 years under outdoor exposure). This is the first report with T80 over 5000 h among OSCs with over 18% PCE. Furthermore, a high PCE of 16.12% can be realized even in a large-area device (1 cm²). This hybrid ETL strategy provides a strong stimulus for highly prospective commercialization of OSCs.

Introduction

Organic solar cells (OSCs) have demonstrated tremendous potential for converting solar energy with considerable competitiveness for commercial applications, because of

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their remarkable merits, such as being lightweight, and their transparency and flexibility.^[1-4] Whether OSCs can emerge as a truly practical application hinges on the combination of high efficiency, high stability and low cost.^[5,6] Although impressive PCEs over 19% have been reported for state-ofthe-art OSCs,^[7-11] most of them demonstrated limited stability and short lifetime. Partially, this might be that most of them adopt a conventional device structure as ITO/holetransport layer (HTL)/bulk heterojunction (BHJ)/ETL/metal electrode,^[7-15] and PEDOT: PSS has been selected as the most frequently used HTL material.^[7-13,15] Although PE-DOT: PSS holds many advantages as HTL, for example, high optical transparency in a wide range, adjustable conductivity, and well-matched work function (W_F) with most donor molecules,^[16,17] its several critical shortcomings cannot be ignored, especially in the aspects of stability: i) PEDOT: PSS can corrode ITO anode, leading to migration of In ions into the active layer;^[18] ii) PEDOT chains with positive charges can react with electronegative end groups in most non-fullerene acceptors;^[19] iii) PEDOT: PSS always absorbs moisture and oxygen inevitably.^[20,21] This is probably one of the most important reasons why the devices with PEDOT:PSS exhibit overall low stability and short lifetime.^[16] While attempts have been made to address this issue, the outcome for the stability performance using conventional architecture so far has not been very successful.^[14,19,22]

In contrast, inverted devices fabricated with the structure of ITO/ETL/BHJ/HTL/metal electrode have attracted considerable interest. These exhibited rather promising stability results^[23-27] and are promising for the solution-based roll-toroll printing industry.^[28,29] But it is rather regrettable that the PCEs of the above-stable systems reported so far are relatively low. Another striking point is that almost all the state-of-the-art OSC systems with high PCEs adopt the conventional architecture,^[7-15] and their inverted ones show much lower performance.^[26,30] This situation clearly creates an urgent and important need to design and fabricate OSCs with inverted architecture demonstrating both high performance and stability. In inverted OSC devices, the most popular ETL material has been ZnO, and the main reasons are that this inorganic material demonstrates quite some advantages such as good electron mobility, high optical transparency in the visible region and stable chemical structure composition.^[31,32] But one of the most challenging issues for this material is its photoinduced catalysis, which

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leads to the downgraded stability of OSCs.^[23,33,34] So, to apply ZnO for stable OSCs, this challenge must also be addressed.

With all these issues for both stable and high-performance OSCs, one strategy would be to develop inverted OSCs using state-of-the-art active materials (for high performance) and ZnO, but importantly with both the issues of low PCE and ZnO's photo-catalysis (for high stability) solved. Following this strategy, in this work, we designed and synthesized an organic molecule named 2-(3-(dimethpropyl)-1,3-dioxo-2,3-dihydro-1H-benzo[de]vlamino) isoquinoline-6,7-dicarboxylic acid (NMA) as a ZnO modifying material (Figure 1a). Note that NMA has carboxylic acid groups at one end, designed for strong coupling with the surface of ZnO to deactivate the photoinduced catalysis of ZnO.^[35] Its main backbone has a large fused aromatic unit derived from naphthalene diimide (NDI), beneficial for electron transport/hoping.^[36,37] Furthermore, the amine and alkyl groups at the other end of this molecule would endow it with high miscibility with organic active layer materials on its top.

As a result, when using this molecule as the modifying material and combined it with ZnO together to form a hybrid ETL, the tested typical five systems of state-of-theart materials using inverted OSC architecture all demonstrated simultaneously improved stability and performance. In particularly, a significantly improved PCE of 18.20 % was achieved for the inverted device of D18:N3 enabled by the hybrid ETL. This is the highest PCE among inverted singlejunction OSCs so far. Most importantly, with this top performance, the devices based on the hybrid ETL maintained 95.4% of its initial PCE after 1500 h illumination. The T₈₀ lifetime was extrapolated and determined to be 7572 h (equivalent to 5 years' operational lifetime under outdoor exposure), which is the first report achieving T_{80} over 5000 h among OSCs with over 18 % PCE. A high PCE of 16.12 % can also be realized even in large-area device of 1 cm². Mechanism studies revealed that the main reasons for such improvement of both performance and stability include: i) compressed mismatch at the interface of the electron acceptor material and our new hybrid ETL; ii) supppressed capacity of ZnO's catalysis; iii) more optimal vertical phase separation of active layer, iv) accelerated charge extraction speed, prolonged carrier lifetime and decreased charge recombination. We believe our strategy and the results represent an important forward step towards the materialization of OSCs' future commercialization and would also promote studies for OSCs with both high performance and stability.

Results and Discussion

The structure of modifying material NMA is shown in Figure 1a. Theoretical calculation based on the density functional theory (DFT) at the B3LYP/6-31G* level was firstly carried out to get the information of frontier molecular orbitals (FMOs) of NMA. As displayed in



Figure 1. a) Illustration of the inverted device structure utilized in this work. Chemical structure, optimal geometric conformation and dipole moment orientation of NMA. b) Operation stability test of devices under MPP tracking with continuous illumination of 100 mW cm⁻² provided by LED arrays. c) Optimal current density–voltage (*J*–V) curves of the device based on ZnO or ZnO/NMA as the ETL under the illumination of AM 1.5G. Inset: PCE distributions counted by 25 devices. d) The statistical figure of PCE vs. T₈₀ counting the OSCs reported with a T₈₀ lifetime over 1000 h. e) Optimal current density–voltage (*J*–V) curves of the 1 cm² device based on ITO/ZnO/NMA/D18:N3/MoO_x/Ag under the illumination of AM 1.5G.

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Figure S1, the HOMO of NMA mainly distributes in the electron-rich amine side chain, and the LUMO is mainly distributed in the electron-poor aromatic backbone. The electron-state density distributions in FMOs lead to an intramolecular dipole moment of 3.07 Debye (Figure 1a). When processed in common polar solvents, the existence of an intramolecular dipole moment makes it easy to form an interfacial dipole, which could be beneficial to the charge extraction and transfer at the interface between charge transport layers and active layer.^[37,38] In view of these merits, we then combined NMA with ZnO as a new hybrid ETL.

With this hybrid ETL of ZnO/NMA at hand, D18:N3, one of the high-performance OSC systems^[39] (see chemical structure in Figure S2) was selected to fabricate devices with an inverted structure as ITO/ETL/D18:N3/MoO_x/Ag, where devices with ETL of both bare ZnO and the hybrid ETL were fabricated. Then these devices were evaluated for their operational stability and PCEs following the standard protocol.^[23,40] For operational stability test, devices were placed under continuous 1 sun illumination simulated by LED arrays (see light spectrum in Figure S3) under max power point (MPP) tracking in a nitrogen-filled glovebox. As shown in Figure 1b, while devices based on bare ZnO had already degraded 20% of the initial PCEs within 300 h, the devices based on the hybrid ETL maintained 95.4% of its initial PCE after 1500 h illumination and still present a steady-state. The plots of $V_{\rm oc}$, $J_{\rm sc}$ and FF vs. time with continuous illumination were displayed in Figure S4. Table S1 gave the specific retention rates of $V_{\rm oc}$, $J_{\rm sc}$ and FF. Then, we can extrapolate T_{80} lifetime of the devices by fitting the linearly decaying part and a value of 7572 h of $T_{\rm 80}$ lifetime was determined (Figure S5). Furthermore, with the estimating an average intensity (1500 kWh/(m²year) of solar irradiance outdoor for China,^[24] the operational lifetime under outdoor exposure is equivalent to over 5 years, much longer than the majority OSC systems so far.^[5,6]

Importantly, besides remarkable stability achieved, much higher PCEs of the dedicated inverted devices of ZnO/NMA were also observed. For example, for the inverted D18:N3 devices using the hybrid ETL, simultaneously enhanced V_{oc} (from 0.856 to 0.864 V), J_{sc} (from 26.55 to 27.23 mA cm⁻²) and FF (from 73.2% to 77.3%) endow devices with a clear improved PCE from 16.64% to 18.20%, which is the highest value among inverted singlejunction OSCs till now. The plots of the *J*–V curves are provided in Figure 1c, with PCE distributions as inset.

Details of photovoltaic parameters are summarized in Table 1. We then summarized OSCs reported in the literatures with T₈₀ lifetime over 1000 h (Figure 1d and Table S2). It can be seen that this is the first report achieving T_{80} over 5000 h among OSCs with over 18 % PCE. We then calculated effective lifetime energy yield (LEY) of OSCs in Table S2, to evaluate OSCs' potential of practical application considering both performance and stability. Assuming the degradation of PCE from the beginning to T_{80} is a linear decay, we got the corresponding LEY based on the equation of LEY = $\int_0^{T_{80}} PCE(t) dt$ following the literature^[41,42] and summarized them in Table S2. It can be seen that the devices demonstrated in this work is among the top five OSC systems based on LEY values. These results demonstrate the superiority of NMA of promoting devices' efficiency and stability simultaneously. Moreover, a high PCE of 16.12% can also be realized even in the large-area device of 1 cm² enabled in hybrid ETL/D18:N3 system, which is among the most efficient OSCs with device area of 1 cm² (Figure 1e and Table S3).

To understand the reasons for the simultaneously improved stability and efficiency enabled by the hybrid ETL, mechanism studies were performed. We first investigated the surface properties difference of ZnO before and after modification with NMA. X-ray photoelectron spectra (XPS) measurement was carried out firstly. Compared with that without modification, the region of the C1s core level (Figure 2a) can be split into four peaks, with new peaks at 284.8 eV (for C-H and C-C bond), 286.0 eV (for C-N bond), 288.2 eV (for N-C=O group) and 289.2 eV (for COO⁻ group),^[35,43] corresponding to the chemical structure of NMA. Note that weak peaks at 284.8 and 288.5 eV before modification should be assigned to the ubiquitous "adventitious" carbon and carbonate.^[44] On the other hand, after modification, a 0.2 eV shift of peaks at the Zn 2p core level towards lower energy was observed (Figure 2b), indicating a change of ZnO layer's nature that oxygen defects were largely reduced.^[45,46] Figure 2c displays the XPS at O 1s core level. After modification, the signal of lattice oxygen of ZnO was still centered at 530.1 eV,^[26] but importantly the signal of defect oxygen of ZnO shifted from 531.8 to 531.6 eV with a 0.2 eV change. Moreover, the peak intensity of lattice oxygen increased, but that for defect oxygen decreased. The stoichiometric ratio of lattice oxygen to defect oxygen are 0.83 and 1.89 before and after modification calculated from corresponding peak areas, respectively, which strongly

Table 1: Photovoltaic parameters of optimized inverted OSCs utilizing D18:N3 as active layer and based on ZnO or ZnO/NMA as the ETL under the illumination of AM 1.5G (100 mW cm⁻²).^[a]

ETL/Active layer	<i>V</i> _{oc} [V]	\int_{sc} [mA cm ⁻²]	$\int_{sc}^{cal} \left[mA cm^{-2} \right]^{[b]}$	FF [%]	PCE [%]
ZnO/D18:N3	0.856 (0.855±0.004)	26.55 (26.12±0.45)	25.92	73.2 (73.5±0.9)	16.64 (16.40±0.20)
ZnO/NMA/D18:N3	0.864 (0.864±0.003)	27.23 (27.48±0.40)	26.82	77.3 (75.6±0.8)	18.20 (17.95±0.18)

[a] Optimal results and statistical results are listed outside of parentheses and in parentheses, respectively. The average parameters were calculated from 25 independent devices. [b] Current densities calculated from EQE curves.



Figure 2. XPS for ZnO before and after modification with NMA for C 1s core level (a), Zn 2p core level (b) and O 1s core level (c). The UV/Vis absorption spectra of N3 coated upon glass/ZnO (d) and glass/ZnO/NMA (e) with different exposure time under continuous UV illumination in ambient conditions. The insets are photos of films under corresponding illumination time. f) Energy level diagrams of ZnO and ZnO/NMA. E_{vac} and E_{F} represent vacuum level and Fermi level, respectively.

reveals the function of NMA as defect oxygen inhibitor of ZnO,^[26,47] consistent with the above results observed from Zn 2p peaks. In addition, after modification, signals at 531.1 and 532.4 eV emerged, ascribed to the COO⁻ and the N–C=O group of NMA, consistent with the XPS for neat NMA film (Figure S6). XRD analysis has also been carried out for both ZnO films with and without NMA modification, no clear diffraction peak or difference was observed, in line with the literature.^[48]

It has been widely reported that ZnO can catalyze the decomposition of acceptors of OSCs induced by ultraviolet light, and defect oxygen of ZnO plays a key role.^[23,33,34] As aforementioned, by modifying NMA on a ZnO film, a lower content of defect oxygen was achieved, which should help prevent acceptors from being decomposed. To study the decomposition behavior of the acceptors under UV light before and after modification, we tested the stability of the acceptor molecule N3 under continuous UV illumination $(365 \text{ nm}, 40 \text{ mW cm}^{-2})$. As shown in Figure 2d, the N3 film coated upon glass/ZnO exhibited rather poor stability, where its absorption strength decreased quickly as time went on and became almost colorless ultimately in merely 30 h. On the contrary, when coated onto glass/ZnO/NMA, rather high stability of N3 film was achieved without any observed decay of the absorption intensity in the same period (Figure 2e), which clearly verified the much-reduced photocatalytic activity of ZnO after modification with NMA. On the other hand, carboxylic acid groups of NMA ensure strong coupling with the surface of ZnO to form a protector in space, blocking the reaction between photogenerated holes^[49] (in ZnO) and active layer materials effectively. These results could unravel the cause of muchenhanced operational stability and the prolonged $T_{\rm 80}$ lifetime of the devices with hybrid ETL.

Ultraviolet photoelectron spectroscopy (UPS) using a He I discharge lamp (21.22 eV) was then conducted. As illustrated in Figure S7, the secondary electron cutoff (E_{Cutoff}) edges with and without modification with NMA are 17.33 and 17.45 eV, respectively, and the gap between E_F and the highest occupied state (HOS) with and without modification with NMA are 3.41 and 3.47 eV, respectively. Thus, the valence band maximum (VBM) and WF before and after the modification are -7.24/3.77 eV and -7.30/ 3.89 eV, respectively. The increased WF likely benefits from a downward intramolecular dipole^[35] caused by the electrondonating amine side chain and the electron-withdrawing carboxyl group. On the other hand, optical band gaps of ZnO and ZnO/NMA are 3.53 and 3.43 eV (Figure S8), respectively. Thus, the conduction band minimum (CBM) can be estimated from the VBM and optical band gap and is determined to be -3.71 and -3.87 eV for ZnO and ZnO/ NMA, respectively (Figure 2f). At the same time, the CBM (LUMO) value of N3 was obtained from its UPS and UV-Vis spectrum (Figure S9, S10) and determined to be -3.79 eV. That the LUMO of N3 is lower than the CBM of the ZnO film is unfavorable to electron hopping in inverted devices. Herein, with this hybrid ETL, a cascade alignment of CBM between N3 and hybrid ETL was achieved with a rather small mismatch of 0.08 eV at the interface of them (Figure S11 and Table S4). Such a small energy level mismatch at the BHJ/ETL interface can also help sweep out defects and trap and avoid charge accumulation in space.^[35]

Dynamic measurements enable us to explore the exciton dissociation process, charge transport properties and recom-

bination behaviors of optimized devices. External quantum efficiency (EQE) was conducted first. Devices with hybrid ETL achieved a higher EQE response in the wide range from 300 to 1000 nm (Figure S12). The EQE offset (Figure S13) can give direct insight into the difference. The integral current density value obtained from EQE curves was improved from 25.92 to 26.82 mA cm⁻² by employing the hybrid ETL, likely due to promoted exciton dissociation at the interface between the ETL and active layer, and responsible for improved J_{sc} .^[50] Figure 3a exhibits curves of photocurrent density $(J_{\rm ph})$ with respect to effective bias, which corresponds to the results observed from EQE spectra. Dissociation probabilities P (E,T) were improved in devices with hybrid ETL from 94.8% to 96.5% (for the short-circuit condition) and from 81.9% to 86.8% (for the maximal power output condition), compared with that of bare ZnO-based devices. Figure 3b shows the J-V characteristics of OSCs under dark conditions, in which a reduced leakage current under a reverse bias voltage and an enhanced rectification ratio of devices enabled by the hybrid ETL were clearly observed, corresponding to an improved carrier injection registered process from active layer to the ETL.^[51]

Electrochemical impedance spectroscopy (EIS) measurements were performed to investigate the interface resistance, with a bias voltage equal to $V_{\rm oc}$ of the corresponding devices. Nyquist plots are depicted in Figure 3c, fitted by an equivalent-circuit model (ECM) referencing previous work.^[52] Under ECM, series resistances ($R_{\rm series}$) and interfacial resistance ($R_{\rm surface}$) are 56.7 and 54.1 Ω for the devices

based on ZnO, and 44.1 and 31.5Ω for devices based on ZnO/NMA film, respectively. Simultaneously reduced R_{series} and R_{surface} after modification demonstrates fewer interfacial defects and better contact between the active layer and ETL, which should suppress charge recombination further. $^{[53,54]}$ To verify this, the dependence of the $J_{\rm sc}$ and $V_{\rm oc}$ on light intensity was examined (Figure S14 and Figure 3d). After modification, the exponent α of the equation $J_{sc} \propto P^{\alpha}$ is closer to 1 (0.987 vs. 0.984) in $J_{sc} \sim P_{light}$ curves, and the slope is closer to 1 kT/q (1.26 vs. 1.40 kT/q) in $V_{oc} \sim P_{light}$ curves, which proves that bimolecular and trap-assisted recombination decreased in the hybrid ETL-based devices.[55,56] Transient photovoltage (TPV) and transient photocurrent (TPC) measurements were carried out to understand the influence of decreased recombination behavior and are displayed in Figure S15 and Figure 3e. After modification, the charge extraction speed is accelerated to 1.68 times (0.28 vs. 0.47 µs), and the carrier lifetime is prolonged to 1.72 times (88.8 vs. 51.5 µs). These dynamic study results are consistent with the observed significantly improved FF and J_{sc} of devices using the hybrid ETL.^[57]

As known, the built-in electric field reflects the internal electric field state of the device, impacting the drifting of charge towards the corresponding electrode and often deciding the upper limit of open-circuit voltage.^[50] Figure 3f displays the *C*–*V* characteristics of the devices with bare ZnO and hybrid ETL, from which the built-in voltage ($V_{\rm bi}$) was evaluated by utilizing the Mott–Schottky analysis.^[58] A larger value of $V_{\rm bi}$ in devices based on the hybrid ETL than that based on ZnO (0.748 vs. 0.735 V) corresponds to a



Figure 3. a) Photocurrent density versus effective voltage $(J_{ph}-V_{eff})$ characteristics for the devices based on ZnO or the hybrid ETL. b) J-V characteristics in the dark of devices based on ZnO or the hybrid ETL. c) Nyquist plots of devices based on ZnO or the hybrid ETL. Inset: The equivalent-circuit model employed for fitting of EIS data. d) V_{oc} values of the photovoltaic devices versus light intensity. e) Transient photocurrent measurements of devices based on ZnO or the hybrid ETL analyzed by a one order exponential decline model. f) Mott–Schottky fitting to the capacitance–potential plots of the devices based on ZnO or the hybrid ETL.

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superior built-in electric field. On the other hand, as reported by Tang,^[59,60] augmented $V_{\rm bi}$ obtained by regulating the carrier transport layer in devices will decrease undesired diffusion to the "wrong" electrode, which will further lead to suppressed non-radiative recombination. We then carried out electroluminescence external quantum efficiency (EQE_{EL}) measurement to explore this. As shown in Figure S16, the device based on the hybrid ETL yielded a higher EQE_{EL} of 1.20×10^{-4} than that of a bare ZnO-based device (6.75×10^{-5}), and corresponded to a much lower energy loss of non-radiative recombination (calculated according to $-kT \ln(EQE_{EL})$) of 0.232 eV than that of bare ZnO (0.247 eV). The enhanced $V_{\rm bi}$ and reduced non-radiative recombination should account for the improved $V_{\rm oc}$ and FF after modification of ZnO with NMA.^[35,50]

In addition to changing the contact barrier, another important role of the modification layer in OSCs is to tune the surface energy of the interface and modulate the active layer morphology. Thus, we subsequently analyzed the active layer morphology coated upon ZnO or ZnO/NMA. Molecular dynamics simulation (details are in Supporting Information) was first carried out to investigate the surface molecule adsorption properties. As depicted in Figure S17, the adsorption energy (E_{ads}) of N3 and D18 on the surface of the ZnO film is $-147.9 \text{ kJ} \text{ mol}^{-1}$ ($E_{ads(ZnO/N3)}$) and $-108.4 \text{ kJ mol}^{-1}$ ($E_{\text{ads}(\text{ZnO/D18})}$), respectively. E_{ads} of N3 and D18 on the surface of the ZnO/NMA film is $-566.2 \text{ kJ mol}^{-1}$ $(E_{ads(ZnO/NMA/N3)})$ and $-292.2 \text{ kJ mol}^{-1}$ $(E_{ads(ZnO/NMA/D18)})$, respectively. The ratio of $E_{\rm ads\,(ZnO/NMA/N3)}$ to $E_{\rm ads\,(ZnO/NMA/D18)}$ is much larger than the ratio of $E_{\rm ads(ZnO/N3)}$ to $E_{\rm ads(ZnO/D18)}$ (1.9 vs. 1.4), which should promote the acceptor N3 to segregate more likely at the BHJ-ETL interface. In order to confirm this, we studied the surface properties of the interface layer before and after modification. First, as shown in Figure S18, the surfaces of ZnO and ZnO/NMA film are both smooth and uniform. Next, the contact angles of ZnO, ZnO/NMA, D18 and N3 films based on water and glycerol were tested (Figure S19 and Table S5), based on which surface tension (γ) values were calculated following Wu's model.^[61] The surface tension of the ZnO/NMA film is smaller than that of the ZnO film (36.52 vs. 66.72 mNm^{-1}) and is closer to that of the N3 and D18 films. Such a change of the ETL surface from hydrophilic to hydrophobic is due to the wellconjugated naphthalene unit and alkyl chain of NMA, which is likely also beneficial to achieve better contact between the ETL and active layer. Furthermore, the surface tension of ZnO/NMA is closer to that of N3 (compared with D18), indicating that N3 more likely attempts to gather at the bottom (close to the cathode of the device).^[35]

To further verify the difference in vertical phase distribution of the D18:N3 layer for the devices using bare ZnO and hybrid ETL, time-of-flight secondary ion mass spectrometry (TOF-SIMS) was carried out, where CN^- acted as an indicator of the component N3, and F^- represents the total component of BHJ. Hence, the ratio of CN^- intensity to F^- intensity could partially represent the amount of N3 at a specific location/height in the vertical direction. The CN^- and F^- intensity, together with CN^-/F^- variation are plotted in Figure 4a,b. Notably, with the hybrid

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ETL, a higher CN⁻/F ratio was exhibited in the region near the bottom of the ETL (2.89 vs. 1.26), revealing a N3 accumulated distribution happening near the cathode^[15,62] consistent with the result of theoretical calculations and the surface tension analysis above. To provide more in-depth information, film-depth-dependent light absorption spectra (FLAS) of the BHJ based on ZnO and ZnO/NMA films were carried out. The experimental and numerical simulation methods were conducted following previous reports.^[63,64] The absorption peaks located from 500 to 600 nm in Figure 4c,d are mainly attributed to D18, and the absorption around 800 nm is mainly ascribed to N3. With this, the component content distributions along the vertical direction were obtained and are illustrated in Figure 4e, f. It can be observed clearly that the content of N3 at the bottom in the hybrid ETL-based devices is larger, which guaranteed a more favorable vertical phase separation (depicted in Figure 4g,h). On the other hand, grazing-incident wideangle X-ray scattering (GIWAXS), atomic force microscopy (AFM) and transmission electron microscopy (TEM) were conducted to further study the microscopic morphology of the active layer upon ZnO and ZnO/NMA (Figure S20 and S21, Table S6). D18:N3 upon ZnO and ZnO/NMA both adopt a face-on orientation, with nearly the same location of the (100) diffraction peak around 0.30 Å^{-1} (d spacing: 20.94 Å) in the in-plane direction and a π - π stacking (010) diffraction peak around 1.73 Å⁻¹ (d spacing: 3.63 Å) in the outof-plane direction. However, a slightly larger crystal coherence length (CCL) of both (010) (36.48 vs. 35.12 Å) and (100) diffraction peaks (62.14 vs. 58.18 Å) was delivered for that upon the ZnO/NMA film, which is beneficial for charge transport. From AFM images, both flat and uniform surfaces of D18:N3 films upon ZnO/NMA and ZnO were observed with approximate roughness values of 0.725 and 0.761 nm, respectively. According to TEM images, a better continuous phase separation of D18:N3 with clearer nanoscale fibrillar structure was achieved upon ZnO/NMA. The well-modulated morphology could explain the reduced charge accumulation, faster extraction process and inhibited recombination behavior, responsible for improved performance with the hybrid ETL.

With the exciting results for the top performance of the D18:N3 active material, four other typical systems (PM6:Y6:PC₇₁BM; PM6:L8-BO; PM6:F-2Cl and $PCE10:PC_{71}BM$) in inverted devices were selected to explore the generality of our hybrid ETL approach (see chemical structures in Figure S22). With the hybrid ETL, all the PCEs have been enhanced significantly together with simultaneously enhanced $V_{\rm oc}$, $J_{\rm sc}$ and FF (Figure 5, Table 2 and Figure S23). More importantly, besides such performance improvement, operational stability was also enhanced for all devices utilizing the hybrid ETL. PCEs' degradations vs. time are shown in Figure 5, and plots of V_{oc} , J_{sc} and FF vs. time are shown in Figures S24-S27. Specific retention rates of V_{oc} , J_{sc} , FF and PCE are summarized in Table S7. It can be seen clearly that by employing the hybrid ETL, the enhanced operation stability comes from concurrently increased stability of V_{oc} , J_{sc} and FF, which is in alignment with the results in the above D18:N3 system. With the





Figure 4. a) Relative TOF-SIMS ion intensity of F^- (blue diamonds and line) and CN^- (red balls and line), and CN^-/F^- intensity ratio (green triangles and line) as a function of t/t_{max} in the BHJ coated upon ZnO (a) or ZnO/NMA (b), where "t" is specific sputtering time and t_{max} is total sputtering time. Film-depth-dependent light absorption spectra of the photoactive layer for ZnO/D18:N3 (c) and ZnO/NMA/D18:N3 (d). Distribution of the donor and the acceptor in the photoactive layer coated upon ZnO (e) and ZnO/NMA (f) along the vertical direction as obtained from the real-time absorption spectra. Schematic illustrations of composition gradient of photoactive layer coated upon ZnO (g) and ZnO/NMA (h). The blue fibers represent D18 blocks and the orange bricks represent N3 blocks.

positive results of our hybrid ETL for these typical and state-of-the-art systems, while further studies are needed for other systems to have a conclusion, it is likely similar results could be achieved following the same strategy by designing similar modifying agents such as derivatives of NMA.

It should be noted that, in addition to operation stability, thermal stability of OSCs is another crucial aspect for commercial application.^[65] Thus, we examined the thermal stability of these two types of devices with bare ZnO and the hybrid ETL by a continuous thermal stress of 85 °C

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under dark conditions. Importantly, all the above-mentioned five systems exhibited much enhanced thermal stability (Figure S28) when employing the hybrid ETL. As indicated from previous reports,^[66-68] the active layer morphology will change induced by heat, and will further change the interface adhesion between the active layer and carrier transport layers. This will further create barriers and defects that are unfavorable to charge transport and extraction, leading to performance deterioration eventually. As mentioned above, compared with bare ZnO, the surface energies of the



Figure 5. Optimal current density–voltage (*J*–V) curve of the device with ZnO or the hybrid ETL as the ETL under the illumination of AM 1.5G (100 mW cm⁻²) based on PM6:Y6:PC₇₁BM (a); PM6:L8-BO (c); PM6:F-2Cl (e) and PCE10:PC₇₁BM (g). Operation stability test of devices with ZnO or the hybrid ETL as the ETL under MPP tracking with continuous illumination of 100 mW cm⁻² provided by LED arrays at 23–27 °C in N₂ atmosphere based on PM6:Y6:PC₇₁BM (b); PM6:L8-BO (d); PM6:F-2Cl (f) and PCE10:PC₇₁BM (h).

interface between the active layer and the hybrid ETL match better. This will decrease the driving force for the active layer's morphology relaxation,^[24] which could provide the reasons for the improved thermal stability for all the tested systems.

Conclusion

An organic modifying material of ZnO was designed and synthesized, and when combined with ZnO as a hybrid ETL to fabricate inverted OSCs devices, both significantly enhanced performance and stability were achieved for all tested typical devices. For example, the device with D18:N3 as the active layer offered a PCE of 18.20% and an

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extrapolated T_{80} lifetime of 7572 h, equivalent to an operational lifetime up to 5 years under outdoor exposure. This is among the best results for OSCs, when considering both performance and stability together. The main reasons for such dual-improvement include: i) NMA reduced the content of defect oxygen on the surface of the ZnO film and suppressed ZnO's capacity for photo-catalysis; ii) the energy barrier at the ETL/N3 interface was reduced and hence decreased the charge accumulation and recombination; iii) a more optimal vertical phase separation of the active layer has formed. These excellent results and the generality of our approach demonstrate a high feasibility for broad applications for other state-of-the-art OSC systems and the potential of practical commercialization of OSCs.

Table 2:	Photovoltaic p	parameters of	OSCs under	the illumination	of AM 1.5G	(100 mW cm ⁻²	²). ^[a]
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Active layer	ETL	V _{oc} [V]	$J_{\rm sc}$ [mA cm ⁻²]	$J_{\rm sc}^{\rm cal} [{ m mA}{ m cm}^{-2}]^{[b]}$	FF [%]	PCE [%]
PM6:Y6:PC ₇₁ BM	ZnO	0.831 (0.830±0.001)	26.71 (26.17±0.45)	26.11	72.9 (72.7±0.6)	16.19 (15.80±0.27)
	ZnO/NMA	0.838 (0.837±0.003)	27.56 (27.77±0.31)	26.80	75.4 (74.0±0.9)	17.41 (17.19±0.11)
PM6:L8-BO	ZnO	0.875 (0.875±0.002)	25.93 (25.82±0.34)	25.08	75.9 (73.3±1.6)	17.21 (16.54±0.36)
	ZnO/NMA	0.880 (0.879±0.003)	26.04 (26.07±0.19)	25.36	77.2 (75.7±0.9)	17.68 (17.35±0.19)
PM6:F-2Cl	ZnO	0.902 (0.885±0.005)	19.96 (19.70±0.40)	19.52	74.9 (74.3±0.9)	13.48 (13.12±0.25)
	ZnO/NMA	0.905 (0.906±0.006)	20.34 (20.41±0.31)	19.76	76.5 (75.3 ± 0.8)	14.07 (13.93 ± 0.13)
PCE10: PC ₇₁ BM	ZnO	0.800 (0.801±0.001)	17.49 (17.12±0.28)	17.07	63.8 (63.6±1.6)	8.93 (8.72±0.14)
	ZnO/NMA	0.804 (0.800±0.005)	17.72 (17.58±0.36)	17.30	67.5 (66.5±0.7)	9.62 (9.36±0.17)

[a] Optimal results and statistical results are listed outside of parentheses and in parentheses, respectively. The average parameters were calculated from 10 independent devices. [b] Current densities calculated from EQE curves.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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