Quantum-dot light-emitting diodes (QLEDs) promise a new generation of high-performance, large-area, and cost-effective electroluminescent devices for both display and solid-state lighting technologies. However, a positive ageing process is generally required to improve device performance for state-of-the-art QLEDs. Here, it is revealed that the in situ reactions induced by organic acids in the commonly used encapsulation acrylic resin lead to positive ageing and, most importantly, the progression of in situ reactions inevitably results in negative ageing, i.e., deterioration of device performance after long-term shelf storage. In-depth mechanism studies focusing on the correlations between the in situ chemical reactions and the shelf-ageing behaviors of QLEDs inspire the design of an electron-transporting bilayer, which delivers both improved electrical conductivity and suppressed interfacial exciton quenching. This material innovation enables red QLEDs exhibiting negligible changes of external quantum efficiency (>20.0%) and ultralong operational lifetime (T95: 5500 h at 1000 nits) after storage for 180 days. This work provides design principles for oxide electron-transporting layers to realize shelf-stable and high-operational-performance QLEDs, representing a new starting point for both fundamental studies and practical applications.

This work targets shelf stability, a must for the commercialization of QLEDs. Shelf stability is currently overlooked in the QLED field. Up to now, there is no report demonstrating QLEDs with both high operational performance and long shelf lifetime.

Remarkably, a so-called positive ageing behavior, i.e., improvements in device performance including efficiency, electrical conductance, and operational lifetime after short storage time of within several days, is generally observed for the state-of-the-art QLEDs. This phenomenon implies poor shelf stability of the QLEDs, albeit in a positive way. The origin of positive ageing behavior is still under debate. Most importantly, as we demonstrated below, in the long run, the QLEDs benefiting from the positive ageing behaviors would inevitably undergo gradual deterioration of device performance, which we refer to as negative ageing. These facts indicate that the general practice of employing positive ageing to improve QLED performance is unacceptable for practical applications. The poor shelf stability of the state-of-the-art QLEDs urgently calls for solutions.

Here, we carry out in-depth mechanism studies to reveal for the first time the correlations between the in situ chemical reactions and the shelf ageing behaviors of QLEDs. The resulting understanding inspires us to design a new device structure of...
bilateral oxide ETLs consisting of optical ZnO and conductive ZnO. The material-based innovation enables shelf-stable, high-efficiency, and ultralong-operational-lifetime QLEDs.

We use red QLEDs with the hybrid structure (Figure 1a) as a model system. The devices consist of multilayers of indium tin oxide (ITO) anode/poly(ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS, ≈ 35 nm)/poly(9,9-dioctylfluorene-co-N-(4-(3-methylpropyl))diphenylamine) (TFB, ≈ 45 nm)/QDs (≈ 15 nm)/Zn$_{0.9}$Mg$_{0.1}$O (≈ 60 nm)/silver cathode. CdSe/CdZnSe/ZnSeS core–shell–shell QDs (Figure S1, Supporting Information) capping with electrochemically stable tri-n-octylphosphine ligands and possessing a photoluminescence quantum yield (PL QY) of ≈90% (in solution) are used as emitters. PEDOT:PSS, TFB, and Zn$_{0.9}$Mg$_{0.1}$O nanocrystals (Figure S2, Supporting Information) are used as the hole-injection layer, the hole-transporting layer, and the ETL, respectively. The devices were encapsulated using a UV-curable acrylic resin (LOCTITE 3492), and stored in a nitrogen-filled glovebox. We note that the UV-curable acrylic resins are one of the most widely used encapsulation materials for electronic and optoelectronic devices.[23,25]

The red QLEDs show positive ageing within short storage time (typically within seven days). The corresponding characteristics include the increase of EQEs and current densities, and the decrease of turn-on voltages (Figure 1b–d). For a typical fresh device, the peak EQE, the current density at 4.0 V and the operational lifetime at 10 000 cd m$^{-2}$ for devices shelf-aged for 1 day (top), 21 days (middle), and 70 days (bottom), respectively. Inset: the corresponding electroluminescence images. Scale bar: 1 mm.

Figure 1. Positive ageing and negative ageing of the red QLEDs. a) Device structure. b) J–L–V characteristics, and c) the corresponding EQE–V relationships for the encapsulated devices stored for 0 (fresh device), 1, 21, and 70 days in a nitrogen-filled glovebox. d) Shelf-ageing time-dependent peak EQEs, current densities at 4.0 V, and turn-on voltages. e) Histograms of $T_{95}$ operational lifetime at 10 000 cd m$^{-2}$ for devices shelf-aged for 1 day (top), 21 days (middle), and 70 days (bottom), respectively. Inset: the corresponding electroluminescence images. Scale bar: 1 mm.
The shelf-ageing behaviors of the unencapsulated red QLEDs and the acid-treated red QLEDs. a) $J$–$V$ characteristics of the unencapsulated devices stored for 0 (fresh device), 1, and 7 days in a nitrogen-filled glovebox. b) $J$–$V$ characteristics, and c) the corresponding EQE–$V$ relationships for the QLEDs treated with two acids for 1 day. d) Dependence of peak EQEs, current densities at 4.0 V and turn-on voltages of the isobutyric-acid-treated devices stored for 0 (fresh device), 1, and 7 days in a nitrogen-filled glovebox. b) relationships $J$ characteristics, and c) the corresponding EQE–$V$–$L$ characteristics of the unencapsulated devices stored for 0 (fresh device), 1, and 7 days in a nitrogen-filled glovebox. Biological ageing of the red QLEDs is also evidenced by the elongating storage time results in negative ageing of QLEDs (Figure 1b–d). Negative ageing is characterized by the decrease of EQEs and current densities and the increase of turn-on voltages. For example, the devices stored for 21 days exhibit a peak EQE of 17.9%, a current density of 20.5 mA cm$^{-2}$ and a turn-on voltage of 1.8 V (Figure 1d). Extending the storage time to 70 days, these parameters change to 13.2%, 3.2 mA cm$^{-2}$, and 2.1 V, respectively (Figure 1d). Another important feature of negative ageing is the developments of non-emissive areas, i.e., dark spots. Temporal evolution of the electroluminescence images (Inset of Figure 1e and Figure S3, Supporting Information) indicates the emergence of dark spots after $\approx$14 days of storage. The dark spots spread to $\approx$50% of the total device area after 70 days of storage.

Negative ageing of the QLEDs is also evidenced by the gradual deterioration of the operational lifetime. We quantify the operational lifetime of QLEDs by using an empirical equation, $(L_0)^n \times T_{50} = \text{constant}$,[26] where $L_0$ and $n$ are the initial brightness and acceleration factor, respectively. The acceleration factor, $n$ is determined to be $\approx$1.8 by fitting the $T_{50}$ values at various $L_0$ of $>5000$ cd m$^{-2}$ (typically measured at constant driving current densities of $>25.0$ mA cm$^{-2}$, Figure S4, Supporting Information). The average $T_{50}$ operational lifetimes at an $L_0$ of 10000 cd m$^{-2}$ for the QLEDs stored for 1, 21, and 70 days are decreased from $\approx$90 to $\approx$23 h and $\approx$2 h, respectively (Figure 1e and Figure S5, Supporting Information). We note that a sudden failure of QLEDs is frequently observed in the long-term operational stability measurements of $>500$ h (Figure S6, Supporting Information), which is in line with the previous report on the positive aged QLEDs.[12] For this reason, the measured $T_{50}$ lifetime at $L_0$ of $<5000$ cd m$^{-2}$ are lower than the values extrapolated based on the data measured at higher $L_0$ (Figure S4, Supporting Information).

To understand the shelf ageing of the red QLEDs, we investigated unencapsulated devices stored in a glovebox. Surprisingly the current density–luminance–voltage ($J$–$L$–$V$) and EQE–$V$ curves of the unencapsulated devices are nearly identical after seven days of shelf ageing (Figure 2a and Figure S7, Supporting Information). The absence of shelf-ageing for the devices stored in the glovebox led us to believe that the UV-curable acrylic resin results in the abnormal ageing effects, motivating us to identify its compositions. Gas chromatography–mass spectroscopy characterizations show that the main compositions are acrylic acid, $N,N$-dimethylacrylamide, and isobornyl acrylate with a molar ratio of 1:30:10 (Table S1, Supporting Information). In order to understand the critical component(s) in the acrylic resin causing the ageing effect, three sets of unencapsulated QLEDs were separately stored at room temperature for one day in a nitrogen atmosphere with a saturated vapor density of pure compound of acrylic acid, $N,N$-dimethylacrylamide, or isobornyl acrylate (see Experimental Section for details). The $N,N$-dimethylacrylamide treated devices and the isobornyl-acrylate treated devices show negligible changes (Figure S8, Supporting Information). The acrylic-acid treated devices show positive ageing behaviors similar to those of the devices encapsulated by the acrylic resin (Figure 2b,c). The peak EQEs increase from 13.9 to 19.1%, accompanied by increases of the current densities by approximately one order of magnitude and a reduction of the turn-on voltage from 2.1 to 1.7 V.

The above control experiments suggest that the component of acrylic acid, which is a commonly used additive in the acrylic resin,[27] is responsible for the changes of the red QLEDs during shelf ageing. To test the general impacts of organic acids, unencapsulated QLEDs were treated by isobutyric acid, a saturated organic acid. As shown in Figure 2b–d,
and Figure S9, Supporting Information, the devices show positive ageing behaviors after being exposed to a saturated vapor density of isobutyric acid in a nitrogen atmosphere for one day. Extending the exposure time to seven days leads to negative ageing characteristics, including a decrease of the peak EQE from 19.7 to 14.3%, a reduction of the current density at 4.0 V from 36.0 to 1.4 mA cm\(^{-2}\), an increase of the turn-on voltage from 1.7 to 2.2 V, a decrease of the \(L_0\) operational lifetimes at an \(L_0\) of 10000 cd m\(^{-2}\) from 72 to 5 h and spreading of the dark-spot area (Figure S9, Supporting Information). At this point, we conclude that the vapors of organic acids induce the abnormal shelf-ageing behaviors of the QLEDs.

We investigate the molecular mechanisms of the organic acid-induced in situ reactions, focusing on their correlations with the shelf-ageing behaviors of the red QLEDs. To this end, various devices or films are treated by the vapor of isobutyric acid at room temperature to mimic the in situ reactions during the shelf ageing of the red QLEDs. Isobutyric acid is selected because it is a saturated organic acid with a relatively low saturated vapor pressure,\(^{[28]}\) offering good control of the in situ reactions.

Our previous studies on the operation of the red QLEDs follows the pathway of\(^{[29]}\)

\[
\text{QD} \rightarrow \text{QD}^+ + \text{h} \rightarrow \text{QD}^+ + \text{h} \rightarrow \text{QD}^+ + \text{QD} + \text{photon}
\]

Exciton generation is initiated by electron injection (followed by charge-confinement-enabled hole injection)\(^{[29]}\) and exciton recombination is largely affected by the QD/ETL interfaces.\(^{[37]}\) Based on these understanding, we propose that two factors, increase of electron injection and suppression of interfacial exciton quenching, contribute to the positive ageing of the red QLEDs. The following experiments demonstrate that both factors can be well correlated to the organic acid-induced in situ reactions.

First, the organic acid leads to interdiffusion of silver, the cathode metal, into the oxide ETLs. X-ray photoelectron spectroscopy (XPS) depth analyses show that placing an unencapsulated QLED in a nitrogen atmosphere with a saturated vapor density of isobutyric acid for one day results in broadening of the silver/oxide interfacial layer from 30 nm (≈ density of isobutyric acid for one day results in broadening of the silver/oxide interfacial layer from 30 nm (≈ density of isobutyric acid for one day results in broadening of the silver/oxide interfacial layer from 30 nm (≈ density of isobutyric acid for one day results in broadening of the silver/oxide interfacial layer from 30 nm (≈ density of isobutyric acid for one day results in broadening of the silver/oxide interfacial layer from 30 nm (≈ density of isobutyric acid for one day results in broadening of the silver/oxide interfacial layer from 30 nm) to 60 nm in thickness (Figure 3a).

At this stage, the interdiffusion of silver into oxide ETLs greatly increases electron conductivity. This can be evidenced by the electrical measurements on electron-only devices of ITO/aluminium/Zn0.9Mg0.1O nanocrystals film (150 nm)/silver. After the 1-day acid treatment, the current density at 1.0 V increases from 6.4 to 432.4 mA cm\(^{-2}\) (Figure 3b). This result agrees well with the increase of current densities and the reduction of turn-on voltages of the red QLEDs in the positive ageing stage.

Second, the organic acid modifies the surfaces of the Zn0.9Mg0.1O nanocrystals. The Zn0.9Mg0.1O nanocrystals are synthesized by hydrolysis of zinc acetate, resulting in large densities of acetate groups and hydroxide groups on the surfaces.\(^{[30,33]}\) The organic acids readily react with the surface hydroxyl groups. This scenario is verified by spectroscopic analyses on the Zn0.9Mg0.1O films treated by isobutyric acid. Results show that a mild acid treatment, i.e., reacting a film of Zn0.9Mg0.1O nanocrystals (≈60 nm in thickness) with a limited amount (≈10\(^{-7}\) mol) of isobutyric acid (see Experimental Section for details), causes minimal changes on the absorption of the oxide-nanocrystal film (Figure S10, Supporting Information). Meanwhile, Fourier transform infrared spectroscopy measurements (Figure 3c) show that the reaction between the free isobutyric acid and the surface hydroxyl groups substantially increases the density of the surface carboxylate groups.

The mild acid treatment effectively suppresses exciton quenching at the QD/oxide interface (Figure 3d). The pristine red QD film (a monolayer of QDs) shows a PL QY of 75% and an average PL lifetime of 13.0 ns. Depositing a layer of Zn0.9Mg0.1O nanocrystals onto the QD monolayer causes significant interfacial exciton quenching, as characterized by a lower PL QY of 51% and a shorter average PL lifetime of 8.5 ns. A mild isobutyric acid treatment on the QD film contacting the Zn0.9Mg0.1O layer increases the PL QY and the average PL lifetime to 74% and 12.8 ns, respectively. Furthermore, our control experiments show that acid treatment on a pristine QD film does not cause any change to the optical properties (Figure S11, Supporting Information). These results allow us to conclude that the mild organic-acid treatment suppresses exciton quenching by modifying the QD/oxide interfacial interactions, instead of passivating the non-radiative recombination centers in the QD films. The suppression of interfacial exciton quenching is in line with the enhancements of device EQEs in the positive ageing stage.

Progression of the organic acid-induced in situ reactions causes the negative ageing of QLEDs. A cross-sectional sample of a red QLED subjected to the isobutyric acid treatment for seven days was analyzed by aberration-corrected scanning transmission electron microscopy (STEM). High-angle annular dark-field (HAADF) observations reveal severe corrosion of the silver cathode and formation of voids at the cathode/ETL interface (Figure 3e). Degradation of the silver cathode is also evidenced by the drastically increased surface roughness observed in atomic force microscopy characterizations (Figure S12, Supporting Information). Regarding the reaction between the Zn0.9Mg0.1O films and isobutyric acid, increasing the amounts of acid causes the gradual conversion of the conductive films of oxide nanocrystals to metal carboxylate salts (Figure 3f and Figure S10, Supporting Information), which are insulators. Furthermore, the by-product of this reaction is water, which is readily being detected by a trace moisture analyzer (Figure 3g and Figure S13, Supporting Information). For an encapsulated device, the progression of this reaction would cause in situ accumulation of water, which may further trigger other in situ chemical reactions during device storage or in situ electro-chemical reactions during device operation.\(^{[26,32–36]}\) Combining the consequences of degradation of the silver cathode, conversion of oxide ETLs to insulating metal carboxylates and in situ accumulation of water would inevitably lead to negative ageing of the red QLEDs.

The above mechanism studies indicate that realizing shelf-stable QLEDs with high operational performance should reserve the benefits of the acid-induced in situ reactions at the positive ageing stage, i.e., enhanced electron conduction and suppressed interfacial exciton quenching while eliminating the harm caused by the in situ reactions at the negative ageing stage. Both electron conduction and interfacial exciton quenching can be modulated by controlling the properties of
Figure 3. Acid-induced in situ reactions and their impacts. a) XPS depth analyses showing the relative atomic ratios of silver and zinc for the ITO/Zn$_{0.9}$Mg$_{0.1}$O/silver samples before (black) and after (blue) the 1-day acid treatment. The widths of the silver/Zn$_{0.9}$Mg$_{0.1}$O interfacial layer are defined by the depth of $\approx 90\%$ ($\approx 10\%$) of silver (zinc) changing to $\approx 90\%$ ($\approx 10\%$) of zinc (silver). b) J-V curves of the electron-only devices (ITO/aluminium/Zn$_{0.9}$Mg$_{0.1}$O nanocrystals (150 nm)/silver) before and after the 1-day acid treatment. c) Fourier transform infrared spectra of a Zn$_{0.9}$Mg$_{0.1}$O film (deposited onto a CaF$_2$ substrate) before and after the mild acid treatment. Vibration bands of the carboxylate groups are labeled as $\nu_{\text{COO}}$. d) Time-resolved PL decay for the pristine QD film, the QD/Zn$_{0.9}$Mg$_{0.1}$O film, and the mild acid-treated QD/Zn$_{0.9}$Mg$_{0.1}$O film deposited on quartz substrates. Inset showing the corresponding absolute PL QYs. e) A cross-sectional STEM image of a red QLED exposed in a nitrogen atmosphere with a saturated vapor density of isobutyric acid for seven days. Scale bar: 100 nm. Inset is a color-mixed elemental mapping image measured by energy-dispersive X-ray spectroscopy, showing a pinhole formed at the cathode/oxide interface. f) Absorbance (at 300 nm, extracted from the spectra shown in Figure S10, Supporting Information) of the Zn$_{0.9}$Mg$_{0.1}$O films (deposited onto quartz substrates) reacted with different amounts of isobutyric acid. g) Time-dependent water content showing a significant increase of water content in 12 min when isobutyric acid is injected into a sealed glass bottle containing Zn$_{0.9}$Mg$_{0.1}$O films (see Figure S13, Supporting Information, for detailed experimental setup). The water contents in the sealed glass bottle containing only the Zn$_{0.9}$Mg$_{0.1}$O films or only the isobutyric acid are also shown.
the oxide ETLs. In this regard, we designed two types of ZnO nanocrystals, namely optical ZnO (O-ZnO), which is responsible for suppressing interfacial exciton quenching, and conductive ZnO (C-ZnO), which is responsible for improving electron conductivity.

For the rational design of O-ZnO nanocrystals, we investigated the mechanism of exciton quenching at the QD/oxide interface by combining nanosecond transient absorption (TA) (Figure 4a) and time-resolved (TR) PL (Figure 4b) measurements. For the CdSe-based QDs, TA signal at the band-edge position probes the conduction-band electrons in QDs with negligible contributions from the valence-band holes while TR-PL is sensitive to both electrons and holes, i.e., excitons in QDs.\(^{[37,38]}\) Therefore, both electron-transfer and hole-transfer quenching pathways lead to faster PL decay while only electron-transfer pathways yield faster TA decay kinetics. Comparing with the pristine QD films, QD films contacting the Zn\(_{0.9}\)Mg\(_{0.1}\)O layers show a longer TA kinetics but a shorter TRPL kinetics (Figure 4a,b). The results indicate nonradiative quenching of holes but not electrons in QDs by Zn\(_{0.9}\)Mg\(_{0.1}\)O. The photoinduced interfacial charge-transfer process, i.e., hole transfer from QDs to the Zn\(_{0.9}\)Mg\(_{0.1}\)O layers, is likely to be affected by the electronic properties of the oxide-nanocrystal films.\(^{[39,40]}\)

This fact motivates us to exploit quantum confinement effects to modulate the electronic structure of the oxide nanocrystals.

We adopt a reaction system based on the hydrolysis reactions of zinc acetate and lithium hydroxide (LiOH) for the syntheses of O-ZnO nanocrystals.\(^{[41,42]}\) We find that adjusting the concentrations of LiOH in the reaction solution results in good size control of the as-synthesized ZnO nanocrystals in the range of

**Figure 4.** Design of C-ZnO and O-ZnO. a) Normalized bleaching kinetics at 2.0 eV (the first exciton absorption peak of QDs) for the QD/Zn\(_{0.9}\)Mg\(_{0.1}\)O film, the QD/O-ZnO film, and the QD film. b) The corresponding time-resolved PL decay for the QD/Zn\(_{0.9}\)Mg\(_{0.1}\)O film, the QD/O-ZnO film, and the QD film. c) A typical TEM image of the O-ZnO nanocrystals showing the sizes of 2.1 ± 0.4 nm. Scar bar: 20 nm. d) Absorption and PL spectra of the O-ZnO nanocrystals and the Zn\(_{0.9}\)Mg\(_{0.1}\)O nanocrystals in solution. Inset showing the photograph of the colloids of the oxide nanocrystals under UV irradiation (365 nm). e) A typical TEM image of the C-ZnO nanocrystals showing the size of 6.2 ± 0.6 nm. Scar bar: 20 nm. f) J–V curves for the electron-only devices (ITO/aluminium/oxide nanocrystals (150 nm)/silver) based on the C-ZnO nanocrystals or the Zn\(_{0.9}\)Mg\(_{0.1}\)O nanocrystals.
≈2.1 nm to ≈6.2 nm (Figure S14, Supporting Information). The ZnO nanocrystals with the smallest average size of ≈2.1 nm (Figure 4c) are selected because of the pronounced quantum confinement effects. Furthermore, a magnesium-acetate (MgAc₂) surface-modification method (see Experimental Section for details) is developed to inhibit the post-synthesis ripening processes, leading to colloids of O-ZnO nanocrystals that are stable for months (Figure S15, Supporting Information). The colloid of O-ZnO nanocrystals shows a first excitonic absorption peak at ≈295 nm and an intragap PL peak at ≈480 nm (Figure 4d), both of which are blueshifted comparing with those of the colloid of Zn₀.₉Mg₀.₁O nanocrystals. On contrary to the QD/Zn₀.₉Mg₀.₁O sample, TA and TR-PL measurements on the QD/O-ZnO sample show identical decay kinetics to those of the pristine QD films (Figure 4a,b), indicating that the hole-transfer channels are blocked. As a result, the interfacial exciton quenching is minimized and the sample of a monolayer of QDs contacting an O-ZnO film shows a high PLQY of 74%.

Regarding C-ZnO, we show that the conductance of the films consisting of ZnO nanocrystals is highly dependent on the sizes of the nanocrystals. Electron-only devices of ITO/alu-minium/ZnO film (150 nm)/silver using oxide nanocrystals with different average sizes of 2.1 to 6.2 nm were fabricated. Electrical measurements show that the current densities can be varied by three orders of magnitude (Figure S16, Supporting Information). Thus, the ZnO nanocrystals with the largest average size, 6.2 nm (Figure 4e), which is significantly larger than that of the Zn₀.₉Mg₀.₁O nanocrystals (≈3.5 nm, Figure S2, Supporting Information), is selected as C-ZnO. Consequently, films based on the C-ZnO nanocrystals demonstrate electrical conductance two orders of magnitude larger than that of the films based on the Zn₀.₉Mg₀.₁O nanocrystals (Figure 4f).

We design a bilayered ETLs comprising of O-ZnO layers and C-ZnO layers for red QLEDs. Devices with a structure (Figure 5a) of ITO/PEDOT:PSS (≈35 nm)/TFB (≈45 nm)/CdSe/CdZnSe/ZnSeS core–shell–shell QDs (≈15 nm)/O-ZnO

![Figure 5. Shelf-stable red QLEDs with bilayered oxide ETLs. a) A STEM-HAADF image of a cross-sectional sample showing the device structure. Scale bar: 50 nm. b) J–L–V characteristics, and c) the corresponding EQE–L relationships of a fresh device and a device shelf-aged for 180 days. Inset of (c): an electroluminescence image of a device shelf-aged for 180 days. Scale bar: 1 mm. d) Stability data of a fresh device and a shelf-aged device (180 days) driven at a constant-current mode. e) Long-time (≥1000 h) stability data of the two QLEDs measured at a L₀ of 2700 and 11 800 cd m⁻², respectively. f) Histograms of T₉₅ operational lifetime at 1000 cd m⁻² measured from 20 fresh devices and 20 shelf-aged devices (100 days).](https://www.advancedsciencenews.com/doi/10.1002/adma.202001088)
(≈15 nm)/C-ZnO (≈45 nm)/Ag (≈100 nm) were fabricated and stored in a nitrogen-filled glovebox without encapsulation. In this structure, the O-ZnO layer is in contact with the red QDs to minimize interfacial exciton quenching and the C-ZnO layer is in contact with the silver cathode, offering efficient electron transport.

The red QLEDs demonstrate excellent optoelectronic characteristics. The fresh device exhibits a sub-bandgap turn-on voltage of 1.7 V. At a voltage of 4.0 V, the current density reaches 1018 mA cm\(^{-2}\) (Figure 5b), which are higher than that of the positive aged devices with Zn\(_{0.9}\)Mg\(_{0.1}\)O ETLs (Figure 1b). The fresh device demonstrates a peak EQE of 20.1% and high EQEs of >19.0% in a wide brightness range of 100–15000 cd m\(^{-2}\) (Figure 5c).

Control devices of using the O-ZnO films or the C-ZnO films as ETLs were fabricated. \(J–L–V\) and EQE–\(L\) characteristics of the two set of devices (Figure S17, Supporting Information) indicate that the current density of the QLEDs with O-ZnO ETLs is two orders of magnitude lower than that of devices with bilayered ETLs and the QLEDs with C-ZnO ETLs exhibit a peak EQE of ≈12%, lower than that of the devices with bilayered ETLs. The results demonstrate the advantages of the bilayered ZnO ETLs, i.e., simultaneously offering efficient electron transport and suppressed interfacial exciton quenching.

We highlight that the red QLEDs with bilayered oxide ETLs demonstrate both outstanding shelf stability and ultra-long operational lifetime. The \(J–L–V\) and EQE–\(L\) characteristics of a device are almost identical after 180 days of shelf-ageing (Figure 5b,c). No dark spots are observed for the shelf-aged device (Inset of Figure 5c and Figure S18, Supporting Information). Both a fresh QLED and a 180-day shelf-aged QLED exhibit a long \(T_{95}\) operational lifetime of 52 h at ≈13300 cd m\(^{-2}\) (Figure 5d). Remarkably, no sudden failure is observed for all stability measurements of the QLEDs of up to ≈1400 h (Figure 5e). The data of log\(_{10}\) show linear dependence on log\(_{10}\) in a wide range of \(L^\star\) ranging from ≈2000 to ≈13000 cd m\(^{-2}\) (Figure S19, Supporting Information). Statistically, the average \(T_{95}\) operational lifetime at 1000 cd m\(^{-2}\) for both the fresh QLEDs and the shelf-aged (for 100 days) QLEDs is determined to be ≈5500 h (Figure 5f).

Specifically, the red QLEDs with bilayered ETLs were encapsulated by acids-free epoxy resin (LOCTITE 3335), and stored in an air atmosphere. The fresh devices and the shelf-aged devices (100 days) show excellent and nearly identical operational performance, i.e., a turn-on voltage of 1.7 V, a luminance of >20000 cd m\(^{-2}\) at 4.0 V, a peak EQE of >20.0%, and a \(T_{95}\) operational lifetime of 57 h at ≈12800 cd m\(^{-2}\) (Figure S20, Supporting Information). The results indicate that combining our design of the bilayered oxide ETLs with the currently available encapsulation techniques can realize air-stable devices with high operational performance, which are critical for practical applications.

Finally, we show that the strategy of bilayer oxide ETLs is readily extended to QLEDs with other types of QD emitters. Green-emitting CdZnSe–ZnS core–shell QDs (PL peak: 522 nm) with a high PL QY of ≈90% (in solution) were used as an example. Applying the device structure with the bilayered O-ZnO/C-ZnO ETLs leads to QLEDs with a peak EQE of ≈18.0% and a \(T_{95}\) operational lifetime of ≈100 h at ≈10500 cd m\(^{-2}\) (Figure S21, Supporting Information). Most importantly, the devices show negligible changes after shelf-ageing for 100 days, demonstrating outstanding shelf stability.

In summary, our work addresses shelf stability, a critical but overlooked challenge for QLEDs. State-of-the-art QLEDs exhibit high efficiency, long operational lifetime, and, however, poor shelf stability. At the fundamental level, we show that shelf ageing of the state-of-the-art QLEDs, both positive ageing and negative ageing, is originated from acid-induced in situ reactions. The mechanisms of shelf ageing are different from those of the intensively investigated operational degradation processes of QLEDs, which are mostly associated with chemical or electrochemical reactions induced by the injected charges. To eliminate the use of acidic encapsulation resin, we design the C-ZnO/O-ZnO bilayered ETLs, providing a material solution to simultaneously achieve improved electrical conductance and suppressed interfacial excitons quenching. This conceptually new ETL results in unprecedented shelf-stable red QLEDs with high operational performance. Furthermore, comparing with the state-of-the-art QLEDs which exhibit storage-time dependent characteristics, our shelf-stable devices offer a simplified model system ideal for fundamental mechanism studies. Our shelf-stable and high-performance devices represent a new starting point for the development of QLEDs.

**Experimental Section**

**Synthesis of the Zn\(_{0.9}\)Mg\(_{0.1}\)O, O-ZnO, and C-ZnO Nanoparticles:** The Zn\(_{0.9}\)Mg\(_{0.1}\)O nanoparticles were prepared by a solution-precipitation process reported in the literature with some modifications. Typically, a solution of Zn(CH\(_3\)COO\(_2\)) \(_{2}\) (2.7 mmol) and Mg(CH\(_3\)COO\(_2\)) \(_{2}\) (0.3 mmol) in DMSO (30 mL) were mixed with a solution of TMAH (5 mmol) in ethanol (10 mL). The mixture was stirred for 1 h under ambient conditions.

For a typical synthesis of the C-ZnO nanoparticles, a solution of Zn(CH\(_3\)COO\(_2\)) \(_{2}\) (1 mmol) in DMSO (10 mL) was mixed with a solution of LiOH (1 mmol) in ethanol (40 mL). The mixture was stirred for 1 h under ambient conditions.

For a typical synthesis of the O-ZnO nanoparticles, a solution of Zn(CH\(_3\)COO\(_2\)) \(_{2}\) (1 mmol) in DMSO (10 mL) was mixed with a solution of LiOH (4 mmol) in ethanol (40 mL). The mixture was stirred for 1 h under ambient conditions. Then, a solution of acetic acid (2 mmol) in ethanol (2 mL) was introduced into the reaction solution to neutralize the excess LiOH. Next, a solution of Mg(CH\(_3\)COO\(_2\)) \(_{2}\) (0.5 mmol) in DMSO (5 mL) was added to prevent the ripening of the oxide nanoparticles. All oxide nanoparticles were precipitated by adding ethyl acetate and further purified by dispersing/precipitating twice using the combination of ethanol/ethyl acetate. The resultant oxide nanocrystals were redissolved in ethanol and filtered (0.22 µm PTFE filter) before use.

**Device Fabrication:** PEDOT:PSS solutions (Baytron PVP Al 4083, filtered through a 0.22 µm N66 filter) were spin coated onto ITO-coated glass substrates at 3500 r.p.m. for 40 s and baked at 150 °C for 30 min in air. The PEDOT:PSS-coated substrates were treated by oxygen plasma for 4 min before transferred into a nitrogen-filled glovebox (O\(_2\) < 1 ppm, H\(_2\)O < 1 ppm). TFB (in chlorobenzene, 12 mg mL\(^{-1}\)), QDs (in octane, 15 mg mL\(^{-1}\)), and Zn\(_{0.9}\)Mg\(_{0.1}\)O nanoparticles (in ethanol, 30 mg mL\(^{-1}\)) were layer-by-layer deposited by spin coating at 2000 r.p.m. for 45 s. The TFB layers were baked at 150 °C for 30 min before the deposition of the QD layers. For the QLEDs with bilayered O-ZnO/C-ZnO ETLs, the O-ZnO nanoparticles (in ethanol, 8 mg mL\(^{-1}\)) and the C-ZnO nanoparticles (in ethanol, 20 mg mL\(^{-1}\)) were layer-by-layer deposited onto the QD layers. The O-ZnO layers were baked at 80 °C for 30 min before the deposition of the C-ZnO layers. No further annealing treatment was
applied after deposition of the Zn$_{0.9}$Mg$_{0.1}$O or C-ZnO layers. Finally, silver electrodes (100 nm) were deposited through a shadow mask using a thermal evaporation system (Trovato 300C) under a base pressure of $\approx 3 \times 10^{-7}$ Torr. The device area defined by the overlapping of the ITO and silver electrodes is 4 mm$^2$. UV-curable resins (LOCTITE 3492 or LOCTITE 3335) were used to encapsulate the devices by covering glass slides in a glovebox.

Acid Treatment on the Unencapsulated QLEDs or the Electron-Only Devices: The devices were placed onto a rack and then sealed in a glass bottle (100 mL) containing pure acid liquid (0.5 mL) for a fixed period. Treatment of the devices with N,N-dimethylacylamide and isobornyl acrylate followed the same procedure, except the acid is replaced by N,N-dimethylacrylamide and isobornyl acrylate liquid. All procedures were conducted at room temperature in a nitrogen-filled glovebox.

Mild Acid Treatment on the Zn$_{0.9}$Mg$_{0.1}$O Films: Films of Zn$_{0.9}$Mg$_{0.1}$O nanocrystals or QD/Zn$_{0.9}$Mg$_{0.1}$O nanocrystals were sealed in a glass slide in a glovebox. LOCTITE 3335) were used to encapsulate the devices by covering glass slides in a glovebox.

Materials and characterization techniques are provided in the Supporting Information.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Keywords
electron-transporting bilayers, in situ chemical reactions, light-emitting diodes, quantum dots, shelf stability

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