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High-performance inverted quantum dot light-emitting diodes with conductive zirconium acetylacetonate interlayers

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Experimental section

Materials.

CdSe-CdZnS core-shell red QDs were provided by Najing technology Co., Ltd. Spiro-NPB and HATCN were purchased from Lumtec. Polyethylenimine, ethoxylated (PEIE, 80%, Mw = 70,000 g/mol), zinc acetate hydrate (>98%) and magnesium acetate hydrate were purchased from Sigma Aldrich. The $\text{Zr}(\text{acac})_4$ powder with a purity of 98% and tetramethylammonium hydroxide (TMAH, 98%) were purchased from Alfa-Aesar. Octane (extra dry, >99%), ethanol (extra dry, 99.5%) and 2-ethanolamine (99%) were purchased from Acros. Dimethyl sulphoxide (DMSO, HPLC grade), 2-methoxyethanol and ethyl acetate (HPLC grade) were purchased from J&K Chemical Ltd.

Colloidal $\text{Zn}_{0.9}\text{Mg}_{0.1}\text{O}$ nanoparticles were synthesized by a low-temperature solution-precipitation method¹ with some modifications. Briefly, a DMSO solution (30 mL) of zinc acetate hydrate (2.7 mmol) and magnesium acetate hydrate (0.3 mmol) were mixed with an ethanol solution (10 mL) of TMAH (5 mmol) and stirred for 1 h under air circumstance to form $\text{Zn}_{0.9}\text{Mg}_{0.1}\text{O}$ nanoparticles. Then $\text{Zn}_{0.9}\text{Mg}_{0.1}\text{O}$ nanoparticles were purified by adding ethyl acetate and re-dispersed in ethanol. The solutions were filtered with 0.22 μm PTFE filter before use.

Device fabrication.

Patterned indium tin oxide (ITO) glass substrates were cleaned sequentially using acetone, deionized water, and ethanol, and then treated for 10 min under oxygen plasma. Then, the ITO glass substrates were transferred into a nitrogen-filled glove box ($\text{O}_2 < 1$ p.p.m., $\text{H}_2\text{O} < 1$ p.p.m.). PEIE solutions (in ethanol 0.5 mg/ml) were spin-coated onto ITO glass substrates at 4,000 rpm for 45 s. Next $\text{Zn}_{0.9}\text{Mg}_{0.1}\text{O}$ nanoparticles (in ethanol, 30 mg/mL) were deposited onto the PEIE modified ITO-glass substrate and annealed at 120 $^{\circ}\text{C}$ for 30 min. Then $\text{Zr}(\text{acac})_4$ solution (6.0 mg/mL) and PEIE solution (2.0 mg/mL) were prepared by adding the powder into the anhydrous ethanol and stirred overnight. The interlayers were prepared by spin-coating the solution onto the $\text{Zn}_{0.9}\text{Mg}_{0.1}\text{O}$ layers at 4000 rpm for 45 s, followed by annealing at 80 $^{\circ}\text{C}$ for 30 min. Finally, QDs (in octane, 15 mg/mL) were spin-coated onto $\text{Zr}(\text{acac})_4$ layer at 2000 rpm for 30 s, no additional thermal annealing process was performed. After completion of the solution processing, the substrates were transferred to a vacuum chamber with a base pressure of 2×10^{-7} Torr for deposition of top organic films and Al electrodes.

Characterizations.

The transmittance spectra of ITO/Zn_{0.9}Mg_{0.1}O and ITO/Zn_{0.9}Mg_{0.1}O /Zr(acac)₄ samples were measured using an Agilent Cary 5000 spectrophotometer. The PL spectrum of the QDs was measured by using an Edinburgh Instruments FLS920 spectrometer. The time-resolved fluorescence spectrum was obtained using an Edinburgh Instruments FLS920 fluorescence spectrometer by the time-correlated single-photon counting method. The samples were excited by a 405nm pulsed diode laser (EPL-405). The absolute PL QYs of the QD samples were measured using a home-built system consisting of a Xenon lamp, optical fiber, a QE65000 spectrometer (Ocean Optics) and an integrating sphere.² The samples for interfacial exciton quenching experiments were prepared by deposition of the oxide nanocrystal films onto quartz substrates, followed by deposition of the Zr(acac)₄ and spin coating a monolayer of QDs. Then the samples were encapsulated in a glove-box by covering glass slides using ultraviolet-curable resin.

AFM and kelvin probe force microscopy (KPFM) measurements were performed on a Cypher S Atomic Force Microscope. The thicknesses of the Zr(acac)₄ and the PEIE films, which were prepared on annealed ITO/ZnMgO substrate, were measured using Stylus Profiler (KLA Tencor P-7) and AFM.

XPS and UPS analysis were recorded on a Thermo ESCALAB-250Xi spectrometer in an ultrahigh vacuum chamber with a vacuum < 10⁻¹⁰ Torr. He I (21.22 eV) radiation line from a discharge lamp, with an experimental resolution of 0.1 eV, was used in the UPS measurements. Zr(acac)₄ powder samples for XPS measurements were prepared by pressing the powder into thin sheets about 1 cm in diameter and ~1 mm in thickness through a powder tablet press. Zr(acac)₄ films were prepared by spin-coating 6 mg/ml Zr(acac)₄ ethanol on ITO/ZnMgO substrate and annealed at 80 °C for 30 min.

FTIR characterizations were measured with a Thermo Fisher IS50 equipped with a Smart SAGA reflectance accessory. Film sample was prepared using 10 mg/ml Zr(acac)₄ ethanol solution spread onto CaF₂ substrates to form smooth films, followed by annealing at 80 °C for 30 min.

Device performance (I-V-L curves, EQE&PCE) were measured by a system consisting of a Keithley 2400 source meter and an integration sphere (FOIS-1) coupled with a QE-Pro spectrometer (Ocean Optics). QLEDs were placed on top of the integration sphere and only forward light emission could be collected.

The stability of QLEDs were characterized under ambient conditions (temperature 21~24 °C and relative humidity: 40~60%) by using an aging system design by Guangzhou New Vision Opto-Electronic Technology Co., Ltd.

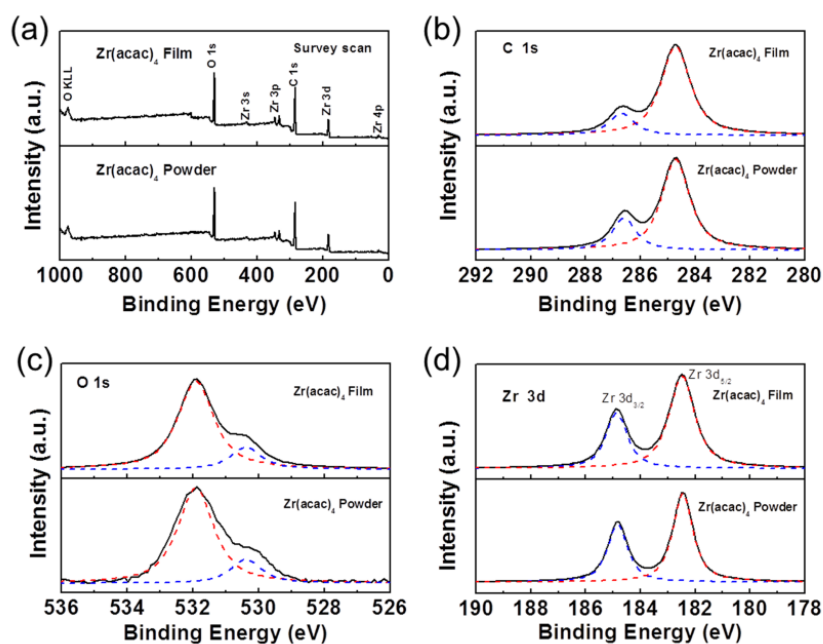


Fig. S1 XPS spectrum of $\text{Zr}(\text{acac})_4$ film (~ 10 nm) and powder (tableting) on quartz substrate. (a) survey scan, (b) C 1s, (c) O 1s, and (d) Zr 3d core level spectra.

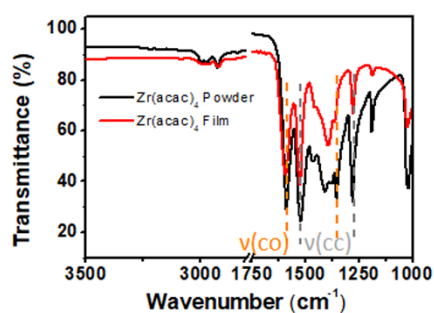


Fig. S2 FTIR spectrums of $\text{Zr}(\text{acac})_4$ powder and annealed (80 °C) $\text{Zr}(\text{acac})_4$ film.

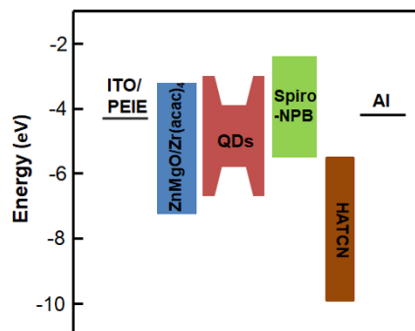


Fig. S3 Flat-band energy diagram of the inverted QLED.

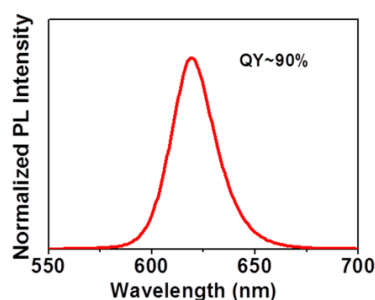


Fig. S4 PL spectrum of the CdSe-CdZnS core-shell QDs in solution (n-octane).

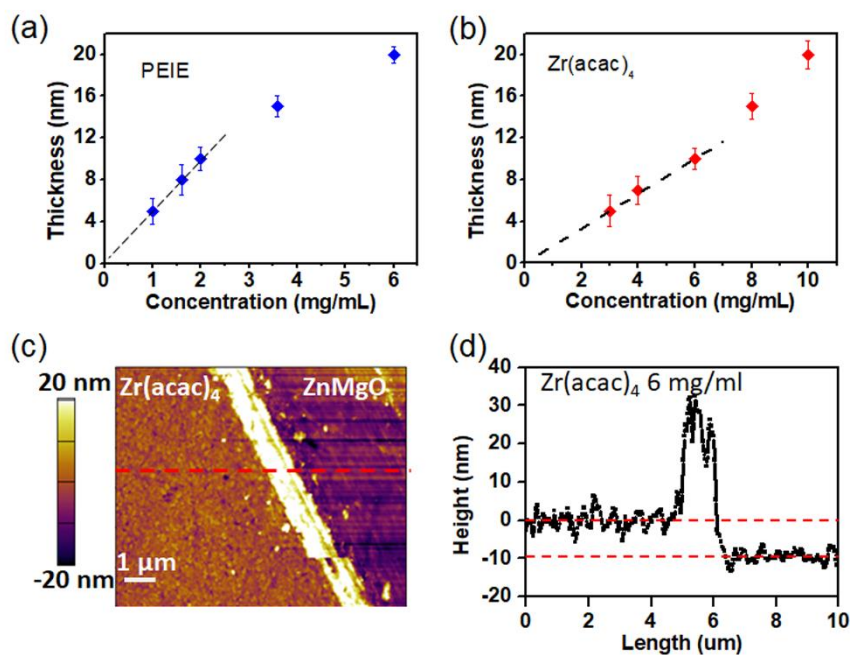


Fig. S5 Thickness characterizations of the PEIE and the $Zr(acac)_4$ films. Concentration dependent thicknesses of (a) the PEIE and (b) the $Zr(acac)_4$ films measured by Stylus Profiler. (c) AFM height topography image of 6 mg/ml $Zr(acac)_4$ spin-coated on ITO/ $Zn_{0.9}Mg_{0.1}O$ and (d) the extracted line-scan profile (red dashed line in c).

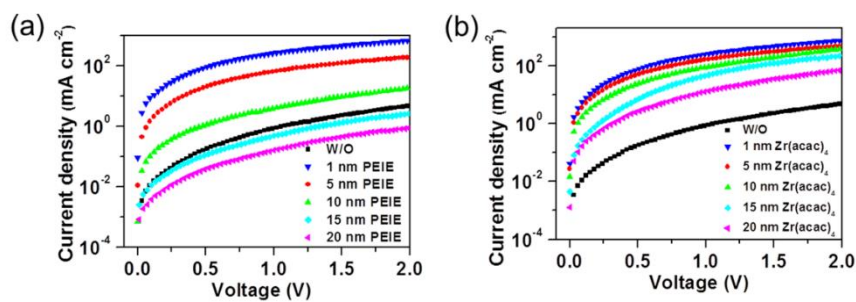


Fig. S6 J-V curves for the electron-only devices (ITO/Al/Zn_{0.9}Mg_{0.1}O (60 nm)/interlayer/QDs (20 nm)/Al). (a) PEIE and (b) Zr(acac)₄ layers with different thicknesses were inserted as interlayers.

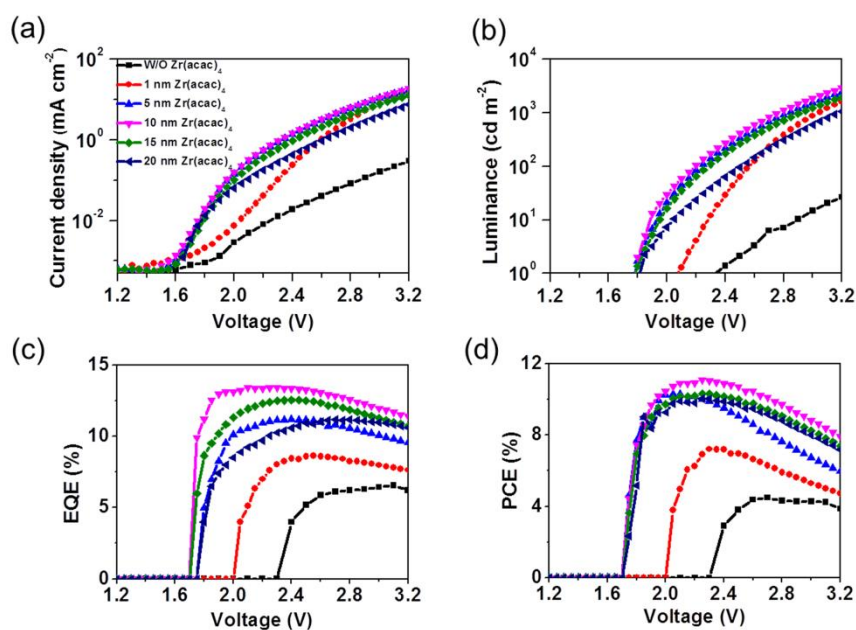


Fig. S7 (a) Current density, (b) luminance, (c) EQE and (d) PCE versus voltage characteristics of the devices with different Zr(acac)₄ interlayer thicknesses. Device structure: PEIE coated ITO/Zn_{0.9}Mg_{0.1}O (~60 nm)/Zr(acac)₄ (1, 5, 10, 15, 20 nm)/QDs (~20 nm)/Spiro-NPB (~65 nm)/HATCN (~15 nm)/Al (~100 nm).

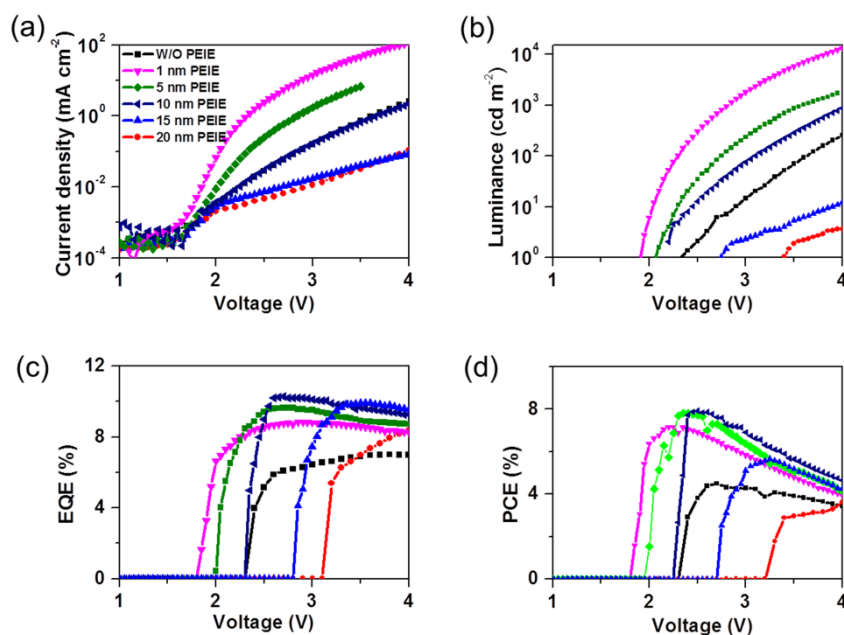


Fig. S8 (a) Current density, (b) luminance, (c) EQE and (d) PCE versus voltage characteristics of the devices with different PEIE interlayer thicknesses. Device structure: PEIE coated ITO/ $\text{Zn}_{0.9}\text{Mg}_{0.1}\text{O}$ (~60 nm)/PEIE (1, 5, 10, 15, 20 nm)/QDs (~20 nm)/Spiro-NPB (~65 nm)/HATCN (~15 nm)/Al (~100 nm).

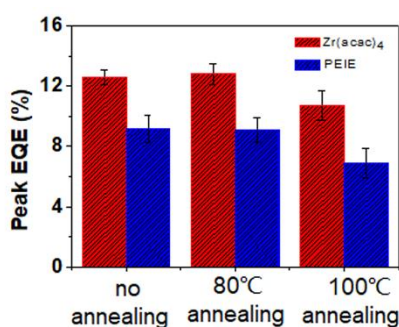


Fig. S9 Peak EQE of QLEDs with 10 nm PEIE or $\text{Zr}(\text{acac})_4$ interlayer without post-fabrication thermal annealing and with post-fabrication thermal annealing at 80 °C or 100 °C for an hour.

References:

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- 2 J. C. deMello, H. F. Wittmann and R. H. Friend, Adv. Mater., 1997, **9**, 230.