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Supplementary Information

Positive Aging in InP-based QD-LEDs Encapsulated with Epoxy: Role of Thiol Molecules and Post-Annealing Treatment

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Experimental

Materials

A Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS Al4083) was purchased from Heraeus. Poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(4,4'-(N-(p-butylphenyl)) diphenylamine)] (TFB) was purchased from American Dye Source, Inc. Zinc acetate dihydrate ($Zn(Ac)_2 \cdot 2H_2O$) (ACS reagent, ≥98%), magnesium acetate tetrahydrate ($Mg(Ac)_2 \cdot 4H_2O$) (ACS reagent, ≥99%), tetramethylammonium hydroxide pentahydrate ($TMAH \cdot 5H_2O$) (≥97%), pentaerythritol tetrakis(3-mercaptopropionate) (PETMP), pentaerythritol tetraacrylate (PETA), molybdenum(VI) oxide (ACS reagent, ≥99.5%), aluminum (evaporation slug, 99.999%), chlorobenzene (anhydrous, ≥99%) , octane (anhydrous, ≥99%), dimethyl sulfoxide (DMSO) (ACS reagent, ≥99.9%) were purchased from Sigma-Aldrich. Ethyl alcohol (anhydrous, ≥99%) was purchased from DAEJUNG. Norland Optical Adhesive 68 (NOA68) was purchased from Norland Products.

Fabrication of QD-LEDs

The QD-LEDs were fabricated on glass substrates covered with indium tin oxide (ITO) with a sheet resistance of 10 Ω per square. The substrates were cleaned by ultrasonication in acetone and isopropanol for 30 min each. Prior to deposition, the substrates were underwent UV-ozone for 15 min. PEDOT:PSS solution (filtered through a 0.45 μm PVDF filter) was spin-coated on top of the substrates using a multistep of 500 rpm for 3 s and 5000 rpm for 30 s and then baked at 120 ℃ for 5 min under atmospheric conditions. The PEDOT:PSS-coated substrates were then moved into an N_2-filled glovebox and baked at 210 ℃ for 15 min. Next, 8 mg/ml of TFB dispersed in chlorobenzene (filtered through a 0.45 μm PTFE filter) was spin-coated at 3000 rpm and baked at 180 ℃ for 30 min. Subsequently, QDs dispersed in octane at a concentration of 30 mg/ml were spin-coated at 2000 rpm for 30 s on top of the TFB film and baked at 100 ℃ for 30 min. $Zn_{0.85}Mg_{0.15}O$ NPs, dispersed in ethanol at a concentration of 60 mg/ml, were spin-coated at 3000 rpm for 30 s and baked at 100 ℃ for 30 min. Finally, an Al electrode was deposited through thermal evaporation with a shadow mask at a deposition rate of 1–1.3 Å/s under a high vacuum pressure (1–2×10^{-6} Torr). After device fabrication, the devices were encapsulated using UV-curable epoxy resin. The epoxy-encapsulated QD-LEDs were annealed at 25 ℃, 80 ℃, and 100 ℃.

Fabrication of single carrier devices

A hole-only device (HOD) was fabricated with a structure of ITO/PEDOT:PSS/TFB/QD/MoO_x/Al/epoxy. The layers from ITO to QD were then fabricated using the same method as the QD-LEDs. MoO_x as the electron blocking layer and Al as the electrode were deposited through thermal evaporation with a shadow mask at deposition rates of 0.4–0.6 and 1–1.3 Å/s, respectively. An electron-only-device (EOD) was fabricated with a structure of ITO/ZnMgO/QD/ZnMgO/Al/epoxy. Each layer was fabricated using the same fabrication method as that of QD-LEDs.

Synthesis of $Zn_{0.85}Mg_{0.15}O$ NPs

$Zn_{0.85}Mg_{0.15}O$ NPs were synthesized using a solution-precipitation method [1]. Zinc acetate dihydrate (2.55 mmol) and magnesium acetate tetrahydrate (0.45 mmol) dissolved in DMSO (30 ml) were prepared in a three-neck flask and vigorously stirred for 30 min. TMAH (5 mmol) dissolved in ethanol (10 ml) was then added dropwise to the flask for 20 min, and the mixture was stirred for 1 h. Next, the $Zn_{0.85}Mg_{0.15}O$ NPs were washed twice with acetone and redispersed in ethanol for use.

Characterization

The current–voltage (I–V) curves of the QD-LEDs were measured using a Keithley 2602A system source meter. The luminance and EL spectra of the QD-LEDs were measured using a PR-670 spectrometer. The PL spectra were measured using a HORIBA Fluoromax-Plus, and the TRPL spectra were measured using a time-correlated single-photon counting (TCSPC) module with an excitation wavelength of 375 nm. XPS analysis was performed using a ThermoFisher Scientific NEXSA. In order to investigate the chemical changes of the ZnMgO layer before and after epoxy encapsulation through XPS, we coated QDs and ZnMgO on a silicon wafer and selectively applied epoxy to a portion of the surface. The samples were manufactured and stored within a nitrogen-filled glove box, and during XPS measurements, analysis was conducted at the boundary where the epoxy-coated layer was present. The capacitance–voltage characteristics were measured at a frequency of 10 kHz and an amplitude of 300 mV using an S3000 Electrical Parameter Analyzer. The EQE was calculated from the current density, luminance, and EL spectra of the QD-LEDs, which were assumed to be Lambertian emission.

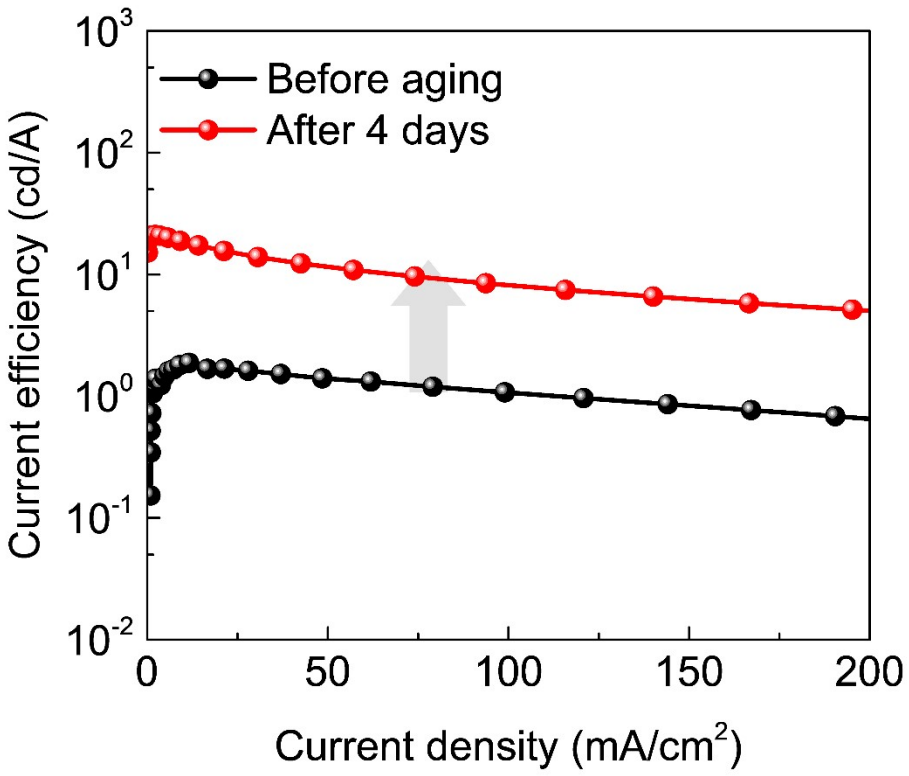

Fig. S1. Current efficiency-current density characteristics of QD-LEDs before and after aging.

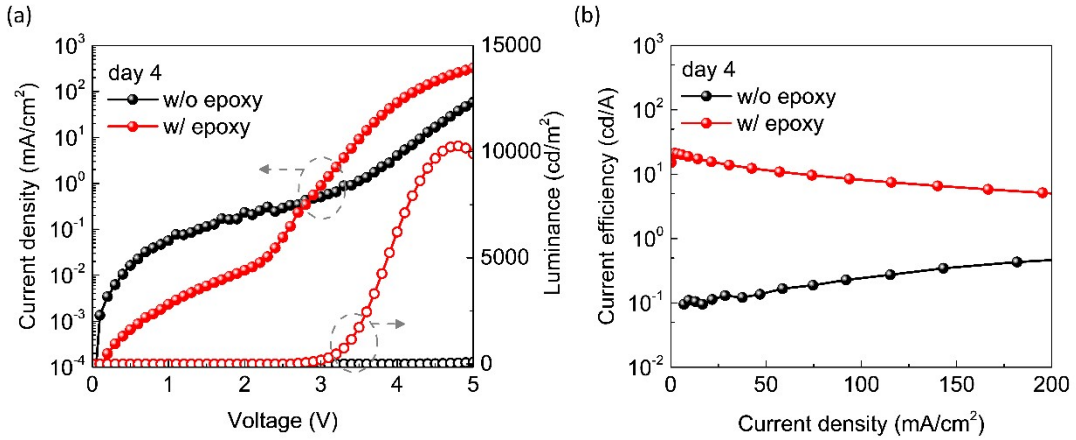

Fig. S2. (a) Current density-voltage-luminance and (b) Current efficiency-current density characteristics of QD-LEDs without and with epoxy after 4 days stored in glove box.

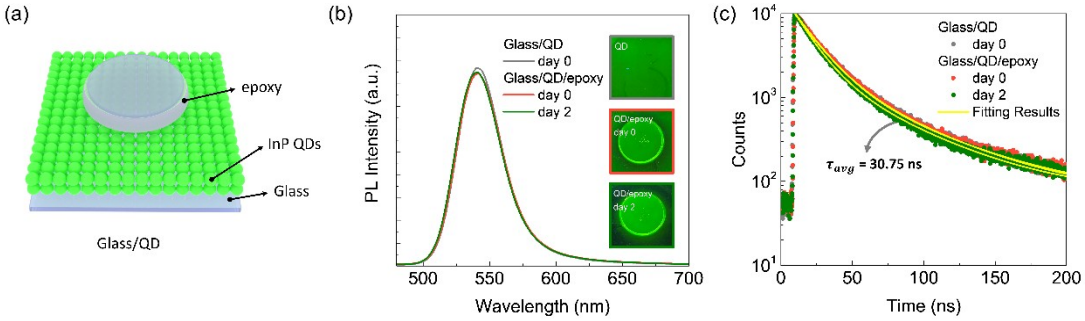

Fig. S3. (a) Schematics of Glass/QD structure. (b) PL intensity and (c) TRPL decay profiles at different aging times.

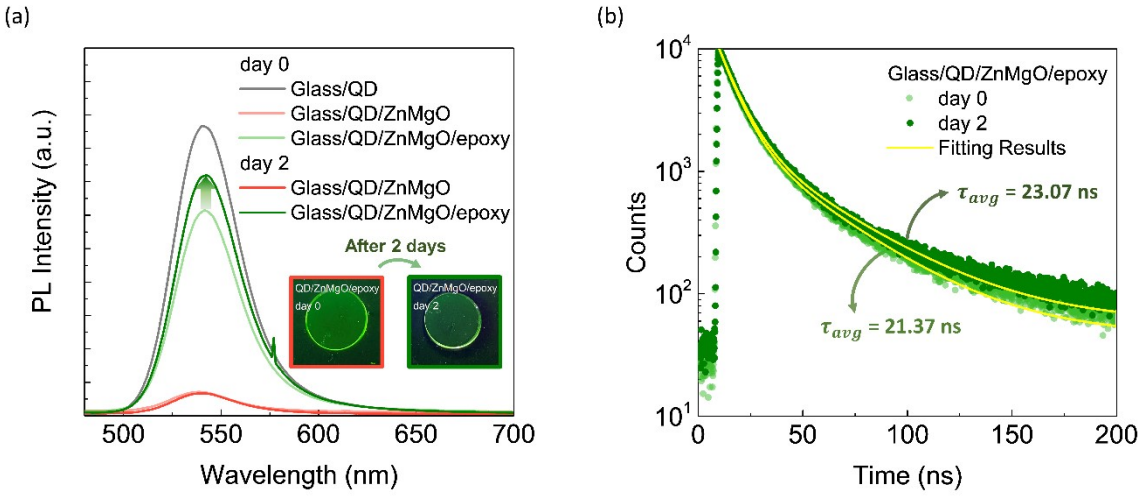

Fig. S4. (a) PL intensity and (b) TRPL decay profiles of Glass/QD/ZnMgO/without or with epoxy at different aging time.

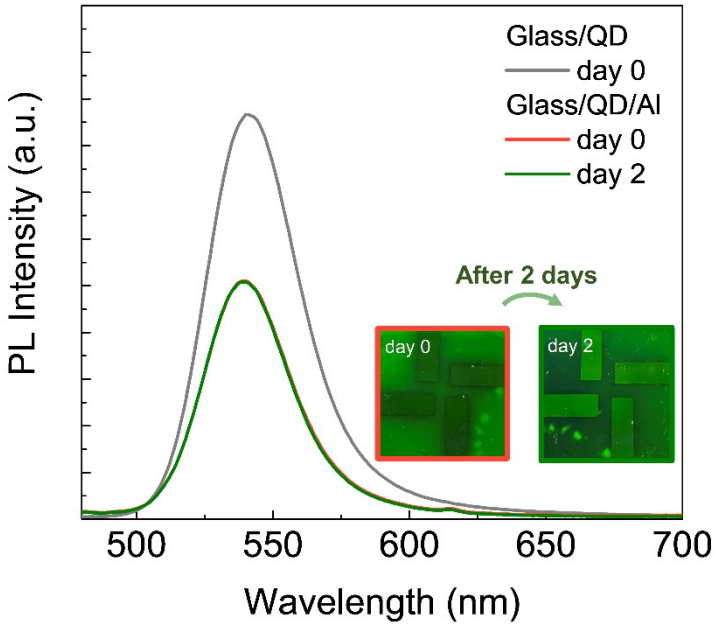

Fig. S5. PL intensity of Glass/QD/Al at different aging time.

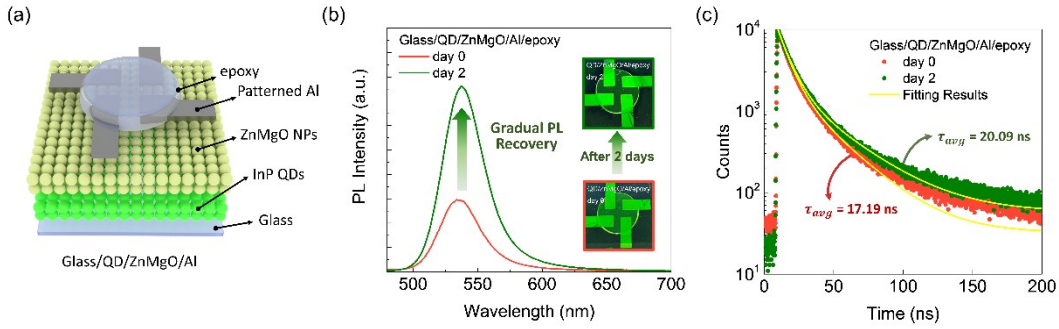

Fig. S6. (a) Glass/QD/ZnMgO/Al/epoxy structure. (b) PL intensity and (c) TRPL decay profiles at different aging time.

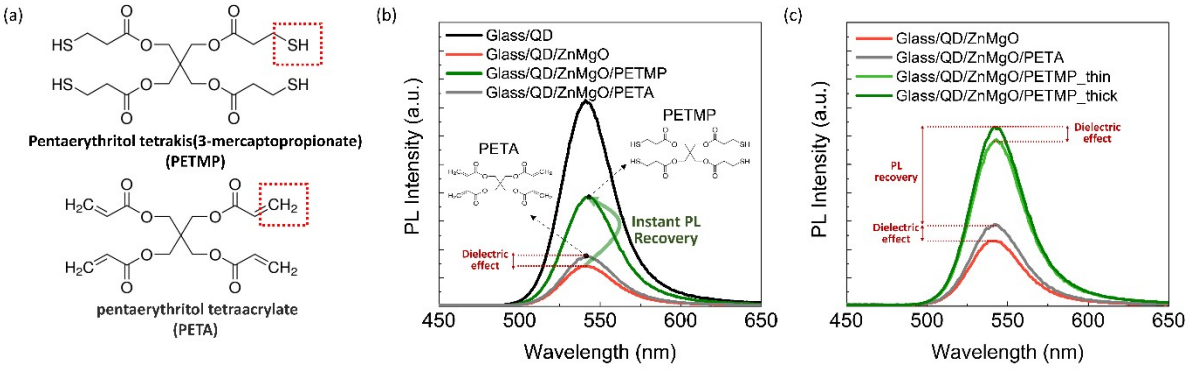

Fig. S7. (a) Structures of PETMP and PETA. (b) PL intensity of Glass/QD/ZnMgO/PETMP and PETA. (c) PL intensity of Glass/QD/ZnMgO/thin and thick PETMP.

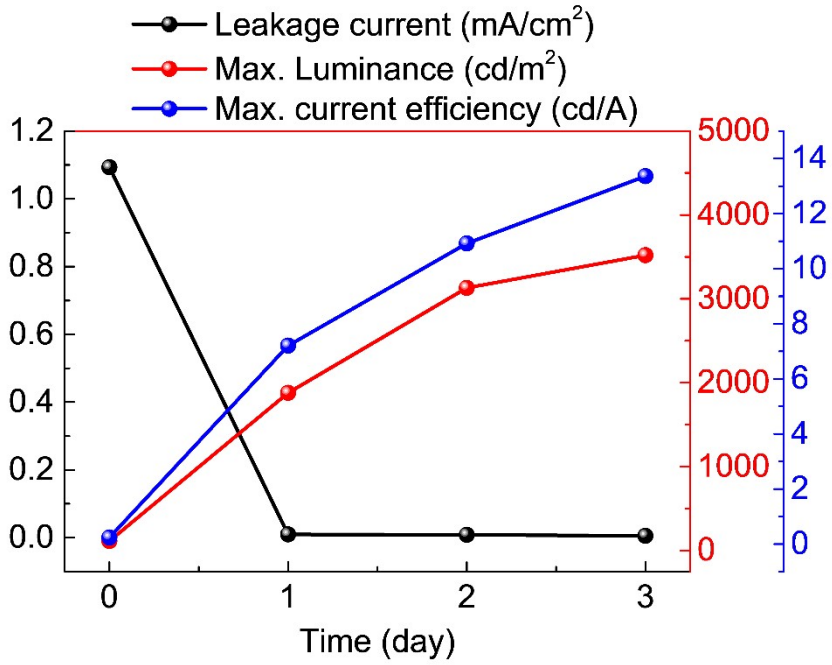

Fig. S8. Comparison of leakage current (at 1.0V), maximum luminance and maximum current efficiency of QD-LED at the different aging time.

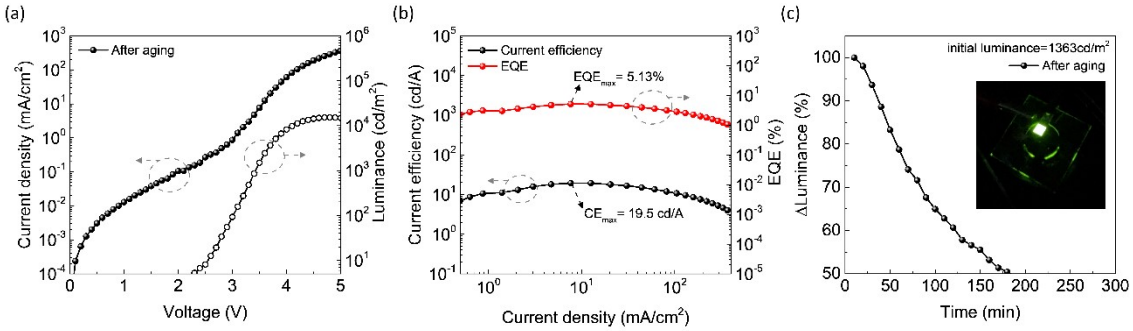

Fig. S9. (a) Current density-voltage-luminance, (b) current efficiency-current density-EQE and (c) operational lifetime characteristics of QD-LEDs after undergoing the optimal aging process.

	L_{max} [cd/m^2]	CE_{max} [cd/A]	PE_{max} [lm/W]	EQE_{max} [%]
day 0	114.2	0.236	0.165	0.06
day 1	1880	7.205	7.592	1.87
day 2	3131	11.106	11.247	3.33
day 3	3520	13.363	13.171	3.41

Table S1. EL performance of the QD-LED as the aging time increases day by day.

References

1 M. Chrzanowski, G. Zatryb, P. Sitarek, A. Podhorodecki, *ACS Appl. Mater. Interfaces,* 2021, **13**, 20305–20312.