Surface Organic Ligands-Passivated Quantum Dots: Toward High-Performance Light-Emitting Diodes with Long Lifetime

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MATERIALS AND METHODS

Materials. Titanium dioxide (99%), PVK (average molecular weight 25,000-100,000 g mol^{-1}), and silicon dioxide (99%) were purchased from Sigma Aldrich. Zinc acetate dehydrate (99%) was purchased from Xilong Chemical Co., Ltd (Guangdong China), potassium hydroxide was acquired from Tianjin Chemical Reagent Factory (Tianjin China), chlorobenzene (99.8%) was purchased from Sigma Aldrich, and normal butanol (99%) was purchased from Alfa-Aesar. Methanol (99%) was obtained from Sinopharm Chemical Reagents (Shanghai China). The red emitting core-shell CdSe-ZnS QDs were provided by Mesolight Inc., had sizes of 10-13 nm, and surface ligands were replaced the conventional oleic acid (OA) ligands on the as-synthesized QDs with shorter chain ligands (DDT or OT). All materials were used as received without any further purification.

Synthesis of QDs.

A mixture of CdO (1 mmol), ZnO (20 mmol), oleic acid (50 mmol), and 1-octadecene (150 mmol) was loaded into a 250 mL three-necked flask and heated to 300 ℃ under nitrogen to obtain a colorless, clear solution. The mixture was heated to 310 ℃. A certain amount of the stock solution for Se and S precursors prepared by Se powder (40 mmol), S powder (40 mmol), and tri-n-octylphosphine (40 mL) was added, and the reactions were kept at 310 ℃ for 30 min. The reaction mixture was then kept at 240 ℃, 15 mmol of 1-dodecanethiol and 10 mmol of the as-prepared stock solution for the Zn precursor another 5 mL of the as-prepared stock solution for the S precursor were swiftly injected into the reaction flask; the reaction was kept for more than 30 min. At the end, the heating was removed to stop the reaction and allow the flask to cool to room temperature. By comparison, QDs capped with OT ligands were synthesized by the same procedure during the growth of a ZnS outer shell.

Synthesis of ZnMgO NPs.

The ZnMgO NPs were synthesized by the reported method under ambient conditions with some modification[1]. For a typical synthesis of the ZnMgO solution, an ethanol solution of potassium hydroxide (0.4 mmol) was dropwise added into a three-neck flask, in which 17 mmol zinc acetate dehydrate and 3 mmol magnesium acetate were dissolved in a mixture of 120 mL dimethyl sulfoxide and 120 mL ethanol previously.

The solution was kept stirring vigorously for 3 hours after the end of dropwise addition, and then ZnMgO NPs were washed and redisperse by using ethyl acetate and ethanol, respectively.

Characterizations. The cross-sectional Scanning Electron Microscope (SEM) measurements were performed on a field emission scanning electron microscopy instrument (S4800, Hitachi). ^{1}H NMR spectra were recorded on a Bruker AVANCE 400 MHz spectrometer. For standard samples, about 10 mg of QDs was dissolved in $CDCl_3$ (~0.8 mL) for ^{1}H NMR measurement. Transmission electron microscopy (TEM) images were recorded with a transmission electron microscope (JEM-2100F, JEOL) operating at 200 kV. The PL spectra were measured with a fluorescence spectrophotometer (F-7000, Hitachi) at an excitation wavelength of 360 nm. The UV-vis absorption spectrum of the QD solution was obtained using a spectrophotometer (UV-3100PC, Hitachi). The fluorescence lifetimes were measured using a time-corrected single-photon counting system (FLS920, Edinburgh). Absolute fluorescent quantum yield measurements were performed using a calibrated integrating sphere on the Edinburgh FLS920 spectrometer. The thickness of the films was calibrated using a surface profiler (XP-1, Ambios). The current density-voltage (J-V) characteristics of the devices were determined using a computer-controlled source meter (2611, Keithley). The EL spectra and luminance of the QLEDs were obtained using a well-calibrated spectroradiometer (PR 705, Photo Research) and cross-checked with a luminance meter (LS-110, Konica Minolta). All QLED characterizations were conducted at room temperature in ambient air atmosphere.

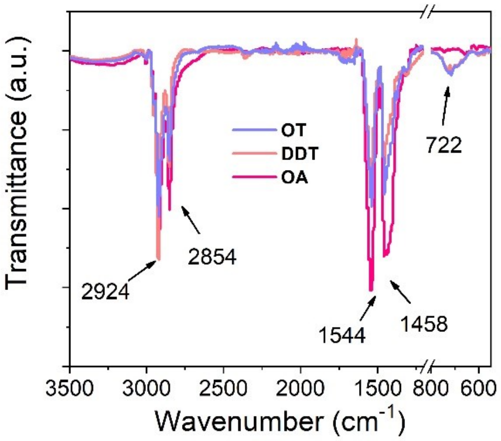


Figure S1. The FTIR spectra of OT-QD and DDT-QD film.

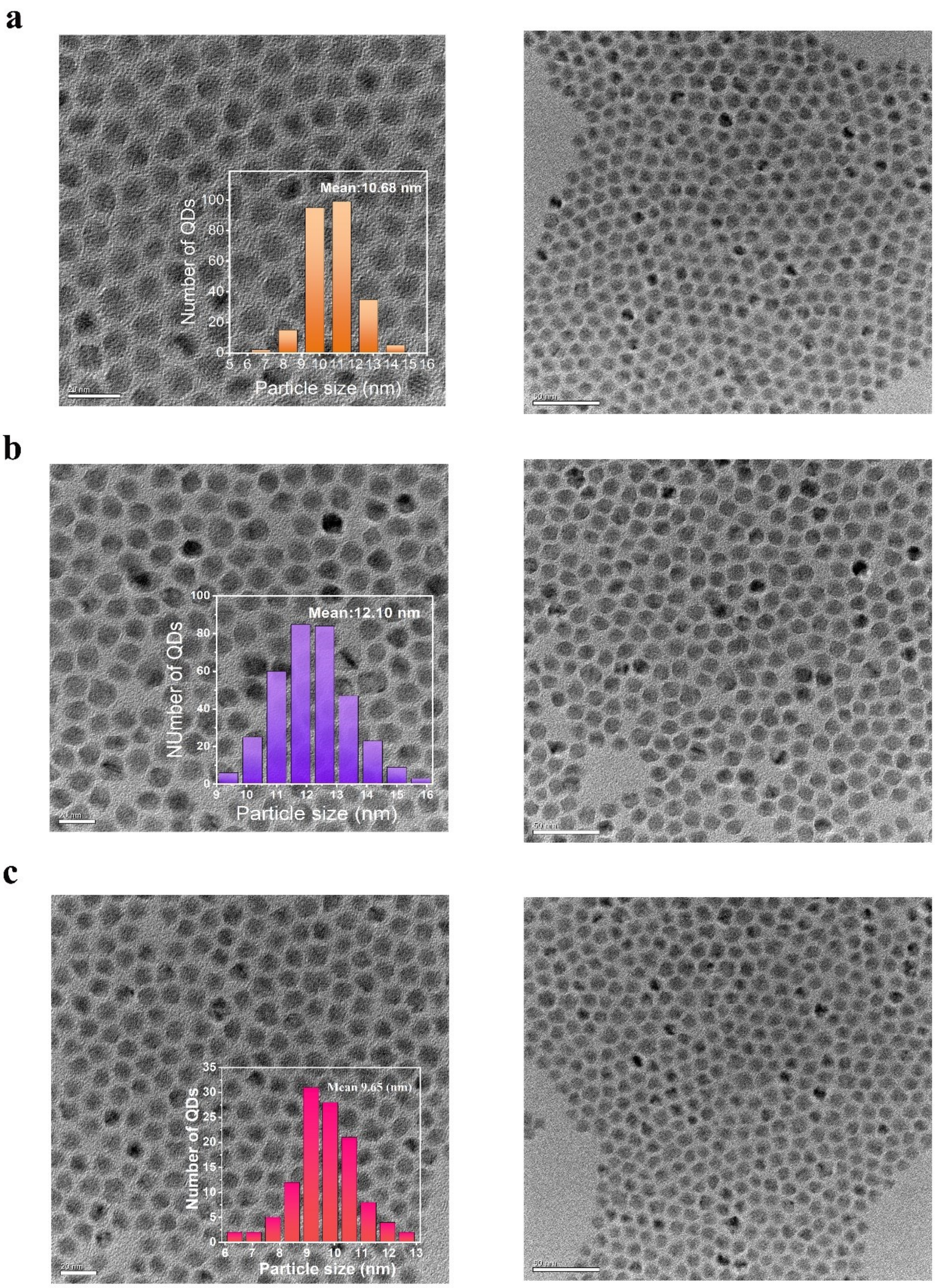


Figure S2. TEM images of (a) DDT-QD film, (b) OT-QD film and (c) OA-QD film with scale bar 20 and 50 nm. Inset: corresponding size distribution.

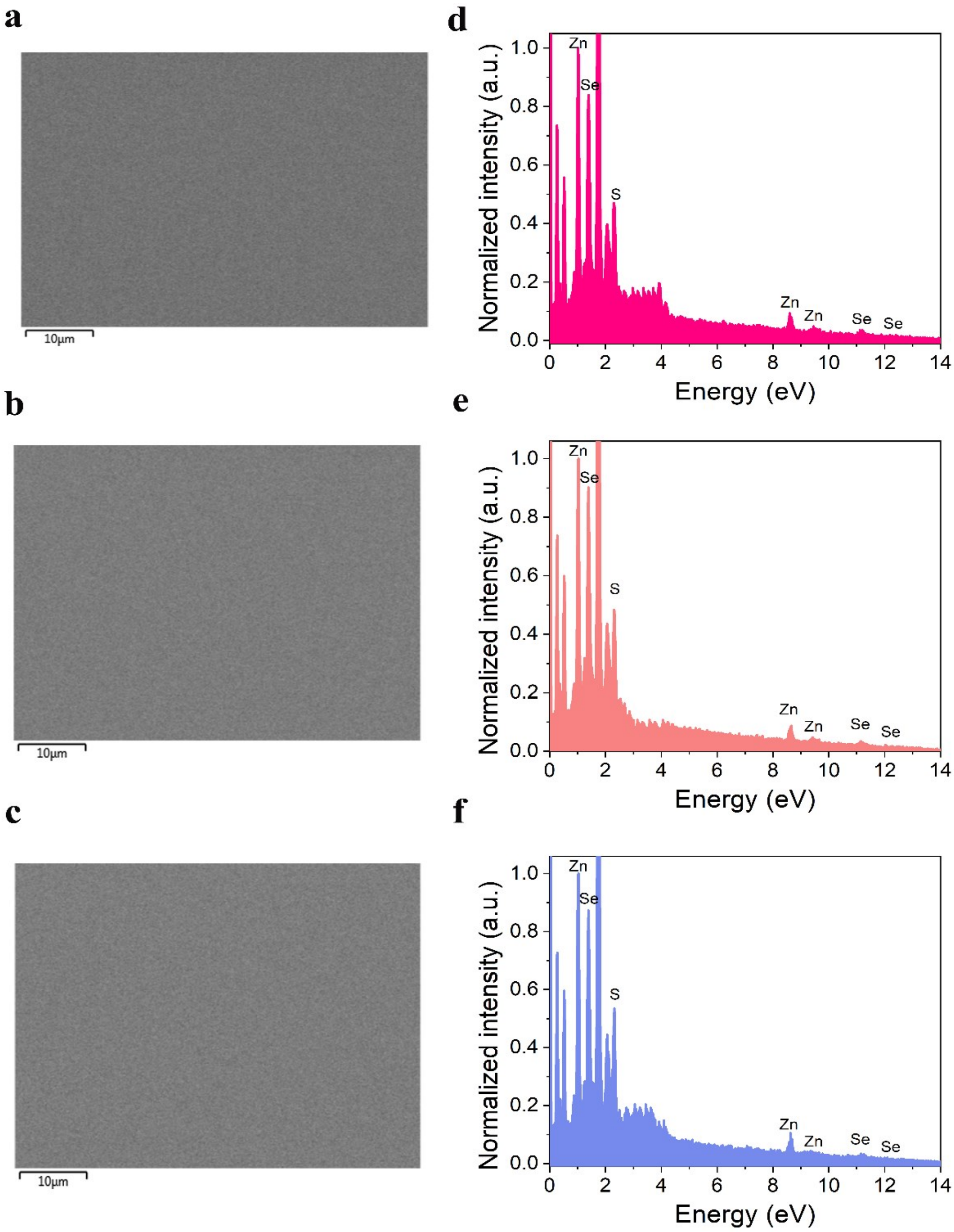


Figure S3. EDS elemental maps of (a) OA-QD, (b) DDT-QD and (c) OT-QD. Corresponding EDS spectra for (d) OA-QD, (e) DDT-QD and (f) OT-QD.

Table S1. Element content of Cd, Se, Zn and S in OA-QD, (e) DDT-QD and (f) OT-QD from EDS measurement.

Element (atomic %)	Cd	Se	S	Zn	Total
OA-QD	9.45	31.86	27.50	31.19 .88	100
DDT-QD	10.48	30.77	28.32	30.44 .93	100
OT-QD	11.42	33.21	27.66	27.70 .1	100

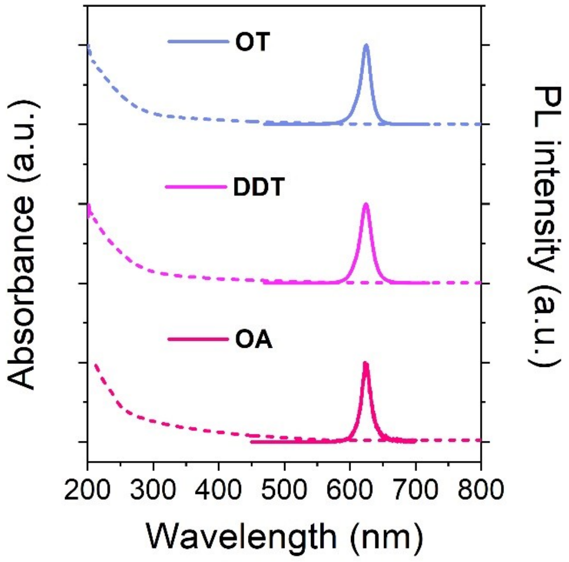


Figure S4. UV-abs spectroscopy and PL spectra of QDs with different surface ligands.

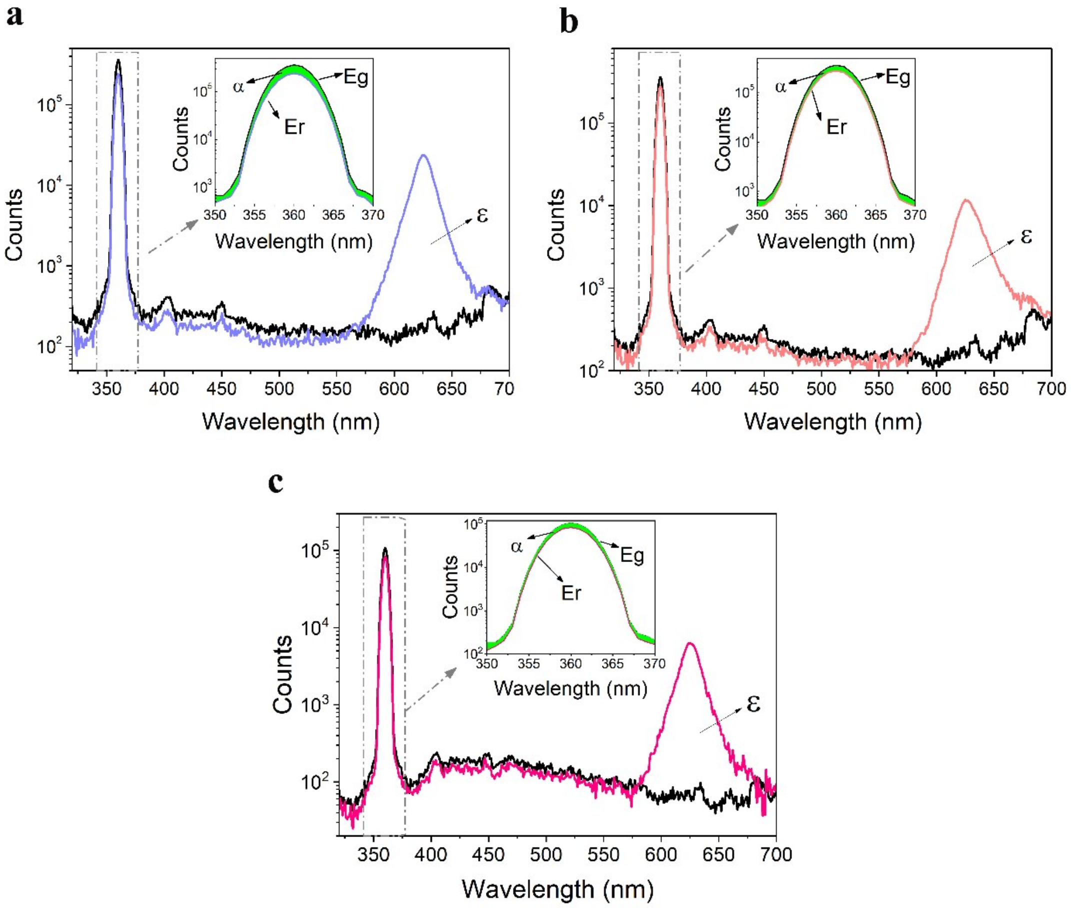


Figure S5. Excitation spectra and emission spectra of QDs film collected by Edinburgh FLS920 spectrometer with a calibrated integrating sphere: (a) OT-QD film, (b) DDT-QD film and (c) OA-QD film. The inset figure is the magnification of excitation line and emission spectrum.

The excitation spectra are obtained with an excitation wavelength of 360 nm. As shown in Figure S5 the Eg is the excited light (reference), Er is the excited light (sample). The luminescence light of sample is obtained in emission spectra. The number of photons absorbed by sample, α, is determined by excited light (reference) and excited light (sample). And the ε number of photons emitted as photoluminescence from sample. Thus, the $PL\ QY = \frac{\varepsilon}{\alpha} \times 100\%$.

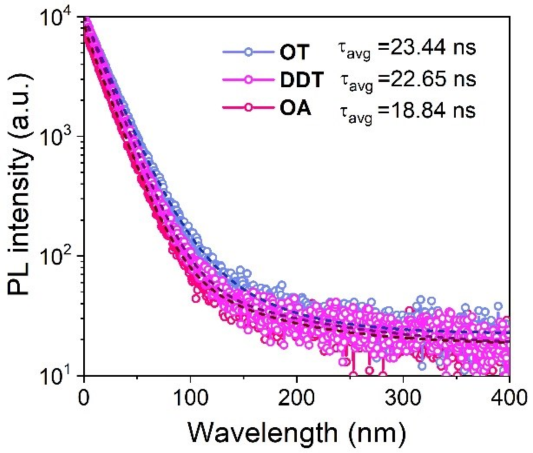


Figure S6. Evolution of PL decay curves of DDT-QD, OT-QD and OA-QD solution.

Table S2. Fitted results of PL exponential decay of red QDs.

QDs	A_1	τ_1 (ns)	A_2	τ_2 (ns)
DDT-QDs	10028.32125	18.69357	78.28305	109.29794
OT-QDs	9759.31959	20.07129	330.52454	57.87892
OA-QDs	2258.99801	1.46145	8160.1684	18.44939

The decay of PL intensity of QDs can be fitted with a double exponential formula:

$$y = y_0 + A_1 e^{-x/t_1} + A_2 e^{-x/t_2} \tag{1}$$

And avenge lifetime is calculate from the following equation:

$$\tau_{\mathrm{avg}} = \frac{\sum_{i=1}^{n} A_i \tau_i^2}{\sum_{i=1}^{n} A_i \tau_i} \tag{2}$$

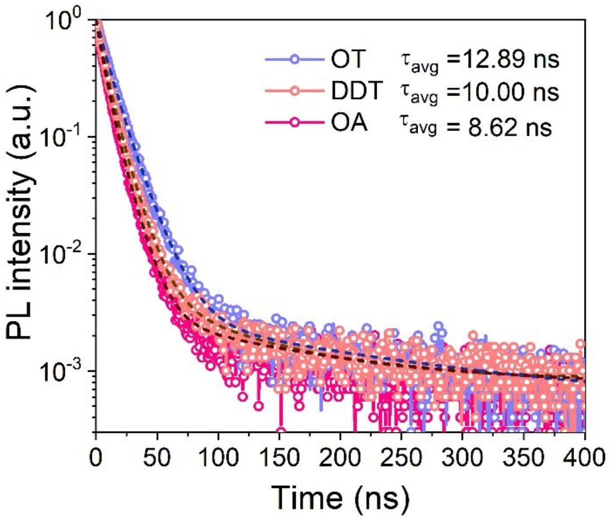
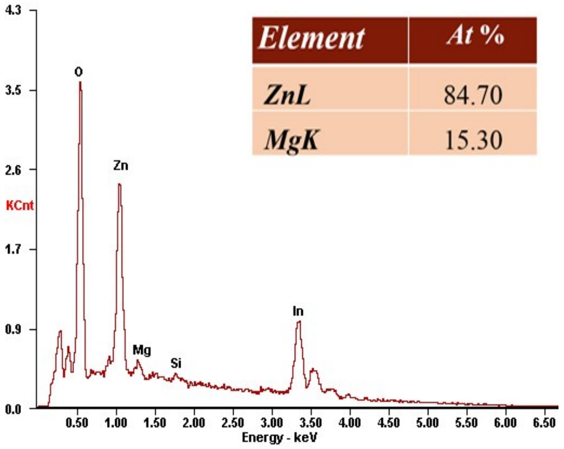


Figure S7. Evolution of time-resolved PL decay curves of DDT-QD, OT-QD and OA-QD film.



Element	*At %*
ZnL	84.70
MgK	15.30

Figure S8. The EDX spectrum of ZnMgO NP film.

The composition of Mg in ZnO NPs was researched from energy dispersive spectroscopy (EDS). The tested sample is glass/ITO/ZnMgO NPs, the peak of indium element came from the ITO substrate. As shown in Figure S7, mass fraction of doped percentage of Mg in ZnO NPs is ~6%, and atom fraction of Mg in ZnO NPs is 15%, so the used interlayer is the $Zn_{0.85}Mg_{0.15}O$ NP film.

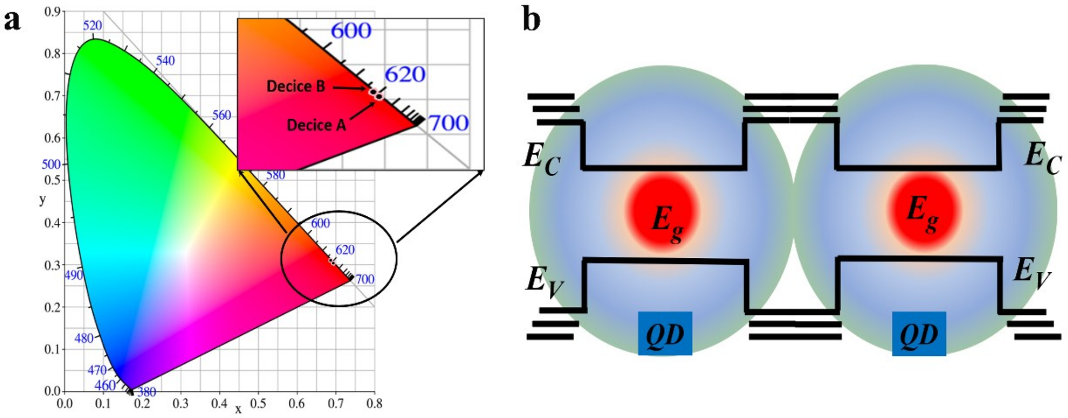


Figure S9. (a) CIE 1931 color coordinates of device A and B. (b) A schematic of a QD and its energy levels, with the core/shell/ligands represented by the red/sky blue/green part.

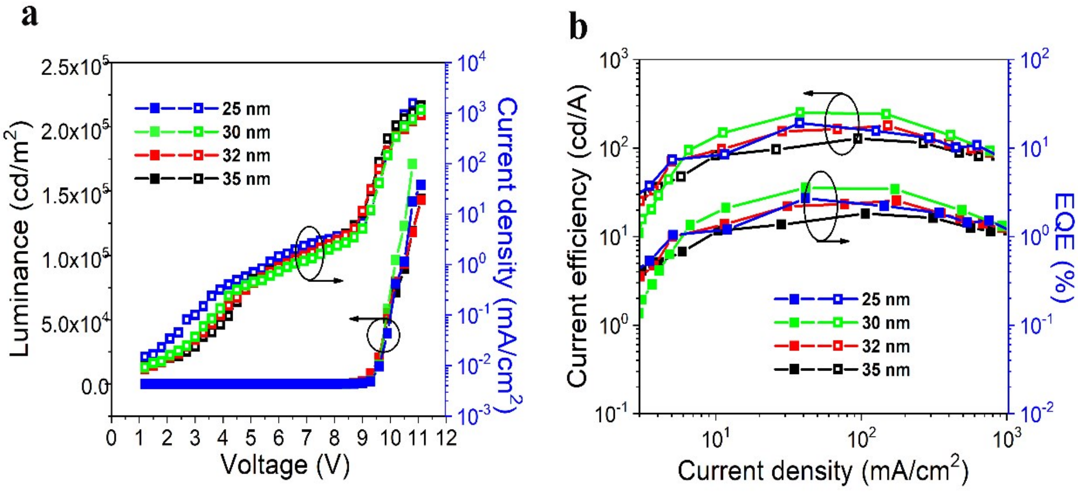


Figure S10. EL performances of QLEDs with different thickness of ZnMgO layer. (a) L−V−J characteristics of QLEDs. (b) CE properties as a function of voltage.

Table S3. Summary of EQE at L of 10000 cd/m^2, maximum CE (CE_{max}), maximum EQE (EQE_{max}) and maximum L(L_{max}) of OT based QLEDs with different thickness ETL.

Thickness of ETL	CE_{max} (cd/A)	EQE @ L of 10000 cd/m^2	EQE_{max} (%)	L_{max} (cd/m^2)
25 nm	27.0	18.3	19.1	155000

30 nm	35.5	20.1	25.1	171000
32 nm	25.4	15.8	17.9	143000
35 nm	18.2	11.5	12.8	144000

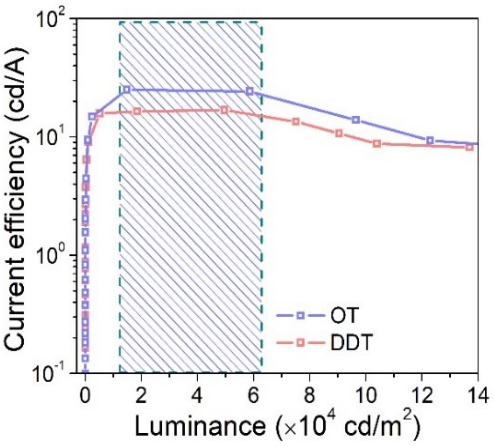


Figure S11. CE and EQE curves as a function of luminance for device A and B.

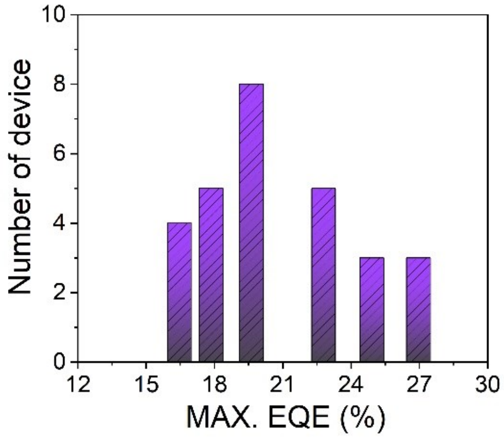


Figure S12. Histogram of peak EQEs measured from 28 red devices.

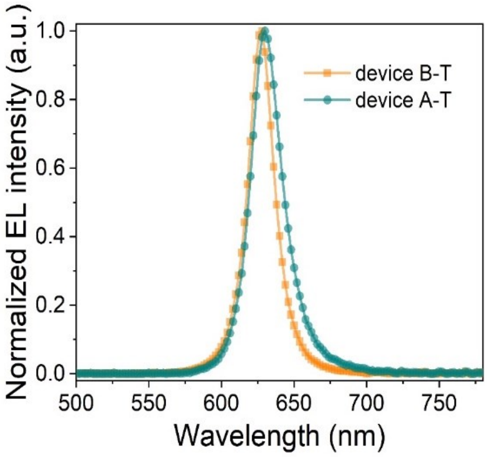


Figure S13. Normalized EL spectra of device A-T and device B-T.

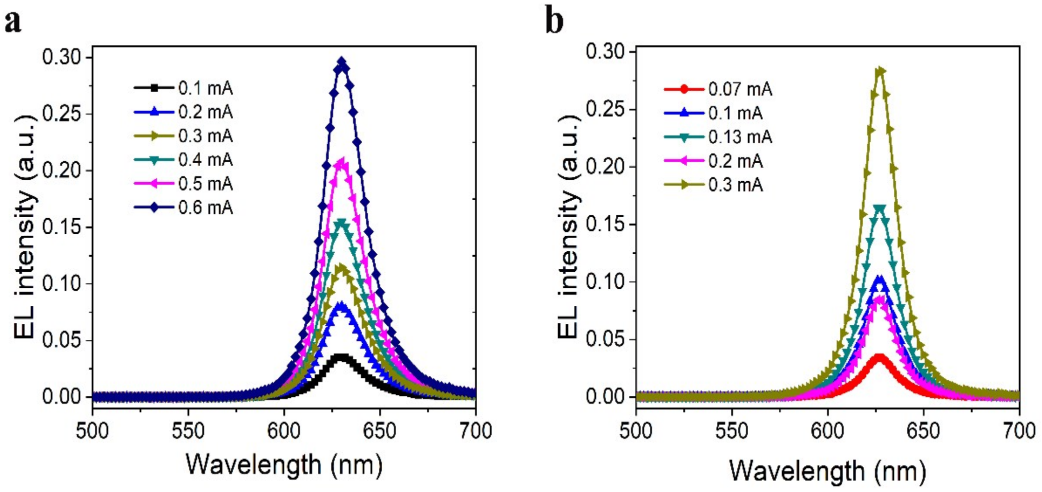


Figure S14. EL spectra of QLEDs at different current density: (a) device A and (b) device B.

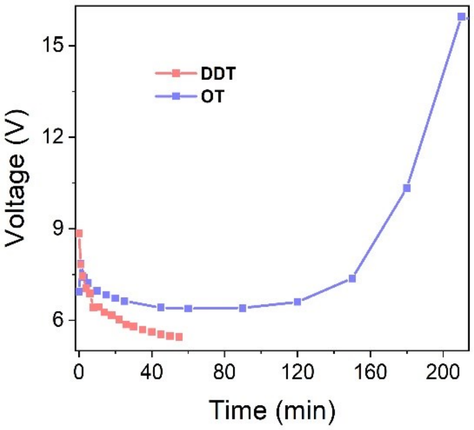


Figure S15. The operational lifetime characteristics of QLEDs.

Lifetime test was conducted under accelerated conditions to shorten the testing period, as widely used and accepted for OLED devices. The T_{50} lifetime of QLEDs at various luminance were measured. The lifetime at low luminance, L_L, can be extrapolated based on the lifetime of the same device operated at high luminance, L_H, following the equation below:

$$T50_L = T50_H \cdot (\frac{L_H}{L_L})^A$$

The acceleration factor, A, for OLEDs usually ranges from 1.6 to 2. In our devices, for example, we test QLEDs at two different luminance of 81100 and 145000 cd/m^2, and Then the A factor was calculated to be 1.83. So the T_{50} lifetime at a display-relevant luminance of 100 cd/m^2, for device A can be extrapolated by the equation above to be 421000 hours (based on 120 mins @ 81100 cd/m^2), and for device B can be extrapolated to be 123000 hours (based on 55 mins @ 83900 cd/m^2).

References:

1. Kim, J. H.; Han, C. Y.; Lee, K. H.; An, K. S.; Song, W.; Kim, J.; Min, S. O.; Do, Y. R.; Yang, H., Performance Improvement of Quantum Dot-Light-Emitting Diodes Enabled by an Alloyed ZnMgO Nanoparticle Electron Transport Layer. *Chem. Mater.* **2015,** *27* (1), 197-204.