Supporting Information

Partially Pyridine-Functionalized Quantum Dots for Efficient Red, Green, and Blue Light-Emitting Diodes

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Experimental

Materials: QDs (NANOSQUARE INC.), zinc acetate hydrate (Sigma-Aldrich), tetramethylammonium hydroxide (Sigma-Aldrich), ethyl acetate (JUNSEI), 2-ethanolamine (Sigma-Aldrich), and pyridine (Sigma-Aldrich).

Synthesis of ZnO nanoparticles: Colloidal ZnO nanoparticles were synthesized according to a previously reported method with a few modifications. Zinc acetate hydrate was dissolved in dimethyl sulfoxide and mixed with tetramethylammonium hydroxide in ethanol (molar ratio, 1:1.8) and stirred overnight at room temperature. Then, the ZnO nanoparticles were precipitated by adding ethyl acetate as an antisolvent. The precipitate was redispersed in alcohol (methanol or ethanol) and 2-ethanolamine was added as surface ligands for the ZnO nanoparticles. After the washing step to remove excess ligands, ZnO nanoparticles were redispersed in ethanol at an appropriate concentration.

Fabrication of QD-LED devices: The patterned ITO glass substrates were successively cleaned with acetone, methanol, and water. For obtaining the ZnO layer, a suspension of ZnO nanoparticle in ethanol (50 mg/ml) was spin-coated at 2000 rpm onto the ITO-coated glass substrates after filtering through a 0.1-μm PTFE filter and then baked at 100 °C for 30 min. After that, the QD suspension in toluene (20 mg/ml) was spin-coated at 4000 rpm and annealed at 80 °C for 30 min under nitrogen environment. For surface ligand exchange, liquid pyridine was dropped onto the QD layer and spin-dried. Then, the film was washed with methanol and annealed at 80 °C for 30 min under nitrogen environment. Subsequently, 4,4′,4″-tris-(carbazol-9-yl)triphenylamine (TCTA), MoO₃, and Ag layers were successively deposited by a thermal evaporation method. The fabricated inverted bottom-emission QD-LEDs were encapsulated by
a glass cap with a moisture absorbent using a UV-curable epoxy resin. The emission area of the devices was $2 \times 2 \text{ mm}^2$.

**Measurements and characterizations:** The absorbance was measured on a UV/VIS/NIR spectrometer (PerkinElmer Lambda 750), and a NICOLET 6700 spectrometer was employed to record the Fourier transform infrared (FTIR) spectra. A Cs-corrected scanning transmission electron microscopy (TEM) by ZEOL was used to acquire the cross-sectional images of the QD-LEDs. TEM samples were prepared by focused ion beam (FIB) micromachining. UPS spectra were recorded on a Micro X-Ray/UV Photoelectron Spectrometer (AXIS NOVA, Ultra DLD) with a He I (21.2 eV) UV source. The Photoluminescence (PL) and Time-resolved PL were measured by HORIBA Fluorog3 with TCSPC (time-correlated single photon counting). The excitation light source was 374 nm pulsed laser diode. The current density-voltage-luminance (J-V-L) characteristics of the QD-LEDs were determined using a Keithley-238 source-measure unit, and Konica Minolta spectroradiometer (Model CS-2000) at room temperature in a dark room.
Figure S1. Normalized absorption spectra and photoluminescence spectra of red(R)-, green(G)-, and blue(B)-emitting quantum dots in the colloidal states.
Figure S2. (a) Photoluminescence (PL), (b) PL-decay dynamics of QD films with original surface ligand (QD, black circle) and partial pyridine ligand (QD/pyridine, red diamond).

Table S1. The fitting parameters of PL decay curves for QD and QD/pyridine films.

<table>
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<tr>
<th>Sample</th>
<th>$\tau_1$ [ns]</th>
<th>$\tau_2$ [ns]</th>
<th>$B_1$</th>
<th>$B_2$</th>
<th>$R_1$</th>
<th>$R_2$</th>
<th>$A$</th>
<th>$\chi^2$</th>
<th>$\tau_{average}$ [ns]</th>
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<td>QD</td>
<td>9.95</td>
<td>25.66</td>
<td>5583.89</td>
<td>3187.26</td>
<td>0.6366</td>
<td>0.3634</td>
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<td>QD/pyridine</td>
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<td>29.98</td>
<td>5542.69</td>
<td>2457.29</td>
<td>0.6928</td>
<td>0.3072</td>
<td>1800.45</td>
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The PL decay curves were fitted to a bi-exponential function.

$I(t) = A + B_1 \cdot e^{(-t/\tau_1)} + B_2 \cdot e^{(-t/\tau_2)}$, $R_i$ is the relative ratio factor which is calculated by $R_i = B_i / (B_1 + B_2)$. $\tau_{average}$ is the average lifetime which was calculated according to $\tau_{average} = R_1 \tau_1 + R_2 \tau_2$. 
Figure S3. Absorption spectrum of ZnO nanoparticles in EtOH. The estimated optical band gap is 3.42 eV.
Figure S4. Ultraviolet photoelectron spectra of (a) red-, (b) green-, and (c) blue-emitting quantum dot films.

Table S2. Determination of the Fermi levels and HOMO levels for red (R)-, green (G)-, and blue (B)-emitting quantum dots (QDs) from the ultraviolet photoelectron spectroscopy data.

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<tr>
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<td></td>
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<tr>
<td>$</td>
<td>E_F</td>
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<tr>
<td>$</td>
<td>E_F</td>
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<tr>
<td>$E_{HOMO}$</td>
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<td>-2.7 eV - 5.1 eV</td>
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Figure S5. Current density-voltage (J-V) characteristics of hole-only devices based on QDs with original surface ligand (QD, black circle) and partial pyridine ligand (QD/pyridine, red diamond)
Figure S6. Current density-voltage-luminance (J-V-L) characteristics of the (a) conventional QD-LEDs for QDs with original surface ligands (QD) and partially pyridine-functionalized QDs (QD/pyridine), (c) inverted QD-LEDs for QDs with original surface ligands (QD) and pyridine functionalized QDs in solution states (QD-pyridine). Current efficiency and power efficiency as a function of current density for (b) conventional QD-LEDs for QDs with original surface ligands (QD) and partially pyridine-functionalized QDs (QD/pyridine), (d) inverted QD-LEDs for QDs with original surface ligands (QD) and pyridine functionalized QDs in solution states (QD-pyridine).