

Supporting Information

**Bi-Inorganic-ligands Coordinated Colloidal
Quantum Dot Ink**

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EXPERIMENTAL SECTION

Materials: N-methylformamide (NMF, Aladdin, 99%), hexane (Greagent, 97%), acetonitrile (Aladdin, 99.8%), aqueous ammonium sulfide ((NH₄)₂S, Macklin, 20% in H₂O), ethylene glycol (Sigma-Aldrich, 99.5%), cadmium oxide (CdO, Aladdin, 99.99%), zinc acetate (Zn(AC)₂, Macklin, 99.99%), KOH (Adamas, 85%), sulfur (S, Macklin, 99.99%), selenium (Se, Aladdin, 99.99%), trioctylphosphine (TOP, Sigma-Aldrich, 97%), oleic acid (OA, Aladdin, AR), and 1-octadecene (ODE, Aladdin, 90%) were used as received. Other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd.

Processing of NiO layers: The precursor solution was prepared according to a previously reported procedure.¹ For the precursor solution, equimolar quantities of nickel(II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O) and ethylenediamine were added to an ethylene glycol solution. The 1 M solution was stirred at 70 °C for 3 h. Thin films were prepared by spin coating 160 μL of the precursor on ITO substrates at 1500 rpm for 90 s. Samples were then transported to a muffle furnace and annealed at 300 °C for 1 h.

Synthesis of CdSe@ZnS QDs: QDs with chemical composition gradients were prepared by a single-step synthesis.² In detail, 0.2 mmol CdO and 4 mmol Zn(AC)₂ were placed in a 100 mL round flask containing 5 mL OA and 15 mL ODE and then degassed for 60 min at 100 °C. The N₂-protected precursor was heated to 300 °C to yield a clear solution. Then, a solution of 0.4 mmol Se and

3.5 mmol S dissolved in 2 mL TOP at 100 °C was quickly injected into the flask. The reaction was held at 300 °C for 5 min to form chemical-composition-gradient CdSe@ZnS QDs, and then the growth of the QDs was terminated by cooling the solution down to room temperature by a N₂ purge, followed by the washing process three times using hexane and ethanol. Finally, the purified QDs were dispersed in hexane.

Ligand exchange: For QD-OS, 4 mL of CdSe@ZnS QDs in hexane (2 mg/mL) was added to an equal volume of 0.03~0.04 M KOH/NMF. The mixture was stirred at room temperature for 10 min and then washed three times with hexane. Next, 15 mL acetonitrile was added to precipitate the QDs, which were subsequently redispersed in 0.5 mL BA with the addition of 5 µL (NH₄)₂S. For QD-OT, 0.2 ml 1-octanethiol was added in 1ml of CdSe@ZnS QDs in hexane (20 mg/ml). The mixture was stirred at room temperature for 30 min. Then, ethanol was used to precipitate QDs, followed by adding 0.6ml hexane to form QD-OT colloid.

Synthesis of ZnO nanoparticles: ZnO nanoparticles were synthesized via a simple, low-temperature method.³ Zn(AC)₂·2H₂O (5.90g) was dissolved in 250 mL methanol at 60 °C. Afterward, a solution of 2.96 g KOH in 130 mL methanol was added to the Zn(AC)₂·2H₂O solution within 10 min under continuous stirring. After 2 h and 15 min, the solution was cooled down and stored overnight to precipitate the product. The liquid was removed, and the precipitate was

washed twice with methanol (50 mL). The washed precipitate was treated with chlorobenzene to dissolve the nanoparticles.

Al₂O₃ precursor: The Al₂O₃ precursor solution was prepared under ambient conditions. 1 g of anhydrous aluminum chloride was added into 10 ml of acetic acid. The solution was stirred at 100°C for 10 min to let the aluminum chloride fully react. The synthesized aluminum acetate is a translucent white colloid which was separated from the solution by centrifugation. Al₂O₃ precursor solution was prepared by dissolving 15 mg of freshly prepared aluminum acetate colloid in 5 ml of isopropanol.

Device fabrication: The patterned ITO substrates were sequentially cleaned by ultrasonication in soap water, acetone, deionized water and isopropanol for 30 min each. The NiO layer was spin coated on the plasma-treated ITO substrates and then UVO treated for 9 min before spin coating with the QDs. The Al₂O₃ layer was spin coated on the NiO layer with 3000 rpm/s 30s and annealed at 60 °C for 10 min. The ligand-exchanged QDs layer was deposited on the Al₂O₃ layer by spin coating the QDs dispersion at 3000 rpm for 30 s and annealing at 200 °C for 30 min. The QD-OA and QD-OT layer was deposited under the same process and annealed at 60 °C for 30 min. After that, the ZnO layer was deposited on a QDs layer via spin coating at 6000 rpm for 30 s by using a 10 mg/mL chlorobenzene solution, followed by annealing at 60 °C for 5 min. Finally, an Al contact (100 nm) was thermally deposited under a base pressure

of 2×10^{-7} Torr using an Angstrom Engineering deposition system. All of the precursors were filtered with 0.2- μm PTFE filters before the spin-coating process. One point to emphasize is that all active layer deposition techniques were carried out under ambient conditions.

Materials characterization: PL spectra were recorded with a HORIBA FL-3 instrument. A Quanta-Phi integrating sphere was implemented according to the published standard method for calculating PL QY.⁴ The settings were as follows: an excitation wavelength of 375 nm, excitation and emission bandwidths of 5 nm, step increments of 0.5 nm and integration time of 0.3 s. FTIR spectra were recorded in transmission mode on a PerkinElmer Spectrum 10 instrument. TGA spectra were conducted using a PerkinElmer TGA 8000 at a heating rate of 10 °C/min under N_2 . Both FTIR and TGA samples were prepared by applying a vacuum to the QDs samples at 60 °C. Abs spectra of the QDs solution were measured by an Agilent Cary5000 UV-visible spectrophotometer. TEM images were recorded using a JEOL JEM-2100 Plus electron microscope operated at 200 kV. TEM samples were prepared by dropping the QDs solution on a copper grid and drying in air. ^1H NMR results were tested using an AVANCE III HD500 from BRUKER. All XPS spectra were obtained from a Thermo Fisher ESCALAB 250XI spectrometer.⁵ All spectra were corrected using the baseline of the C 1s peak at 284.8 eV.

Device characterization: The EL spectra and luminance (L)–current density (J)–

voltage (V) characteristics were collected by using a Keithley 2400 source and a PR-655 Spectra Scan spectrophotometer (Photo Research) in air and at room temperature.

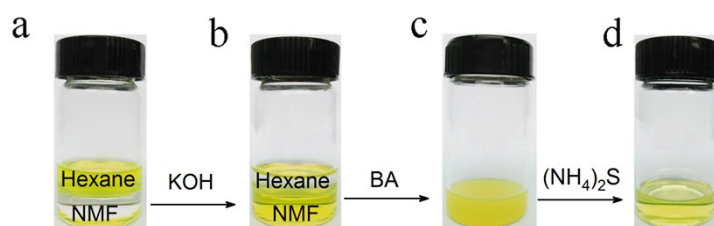


Figure S1. CdSe@ZnS QDs before (a) and after (b) phase transfer. (c) Hydroxy capped QDs dissolved in BA. (d) Turbid liquid becomes clear when adding $(\text{NH}_4)_2\text{S}$.

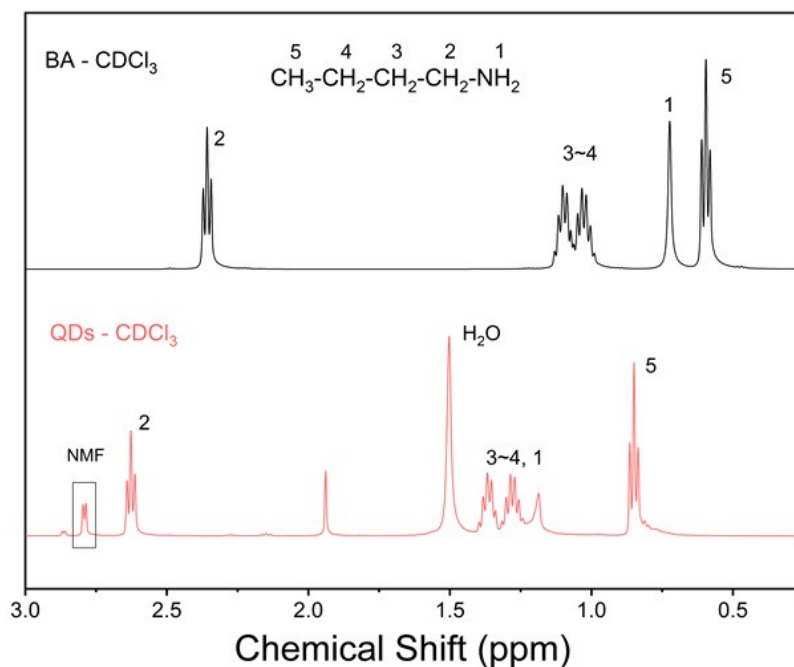


Figure S2. ^1H NMR of BA solvent and QDs colloid.

Details of **Figure S2**:

Sample of BA-CDCl_3 is prepared by adding butylamine into chloroform-d. Sample of QDs-CDCl_3 is prepared by dissolving QD-OS colloid (after ligand exchange) in chloroform-d.

Peaks of butylamine move to the low field from the high field, indicating the weaker shielding effect due to the protonation of amine units. The charged ammonium could bond on QDs through electrostatic interaction, which has been demonstrated by Vladimir Sayevich *et al.*⁶

Table S1. Atomic ratio of QDs films coated by NMF(QD-OH) and BA(QD-OS).

	O-OH	O-SO _x ⁻	Zn	O/Zn	OH/Zn
QD-OH	33.78%	12.17%	54.05%	85%	62.5%
QD-OS	47.92%	0	52.08%	92%	92%

The ratio is calculated from high-resolution XPS spectra.

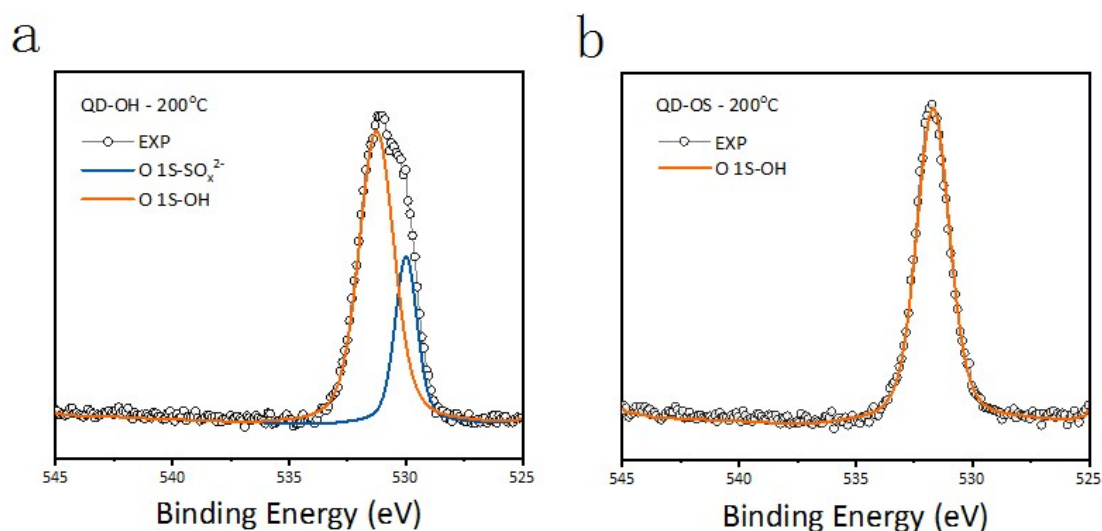


Figure S3. High-resolution O 1S XPS spectra of QDs film (a) QD-OH (b) QD-OS. EXP is the original data.

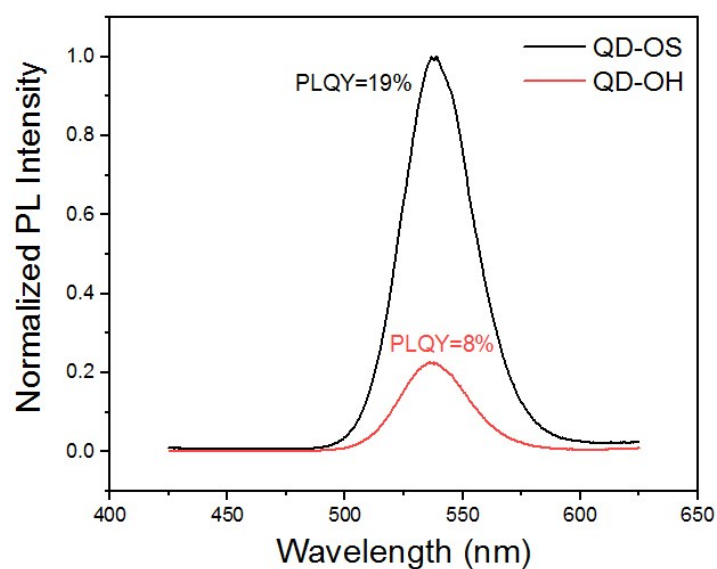


Figure S4. PL intensity and PL QY of QD-OH and QD-OS.

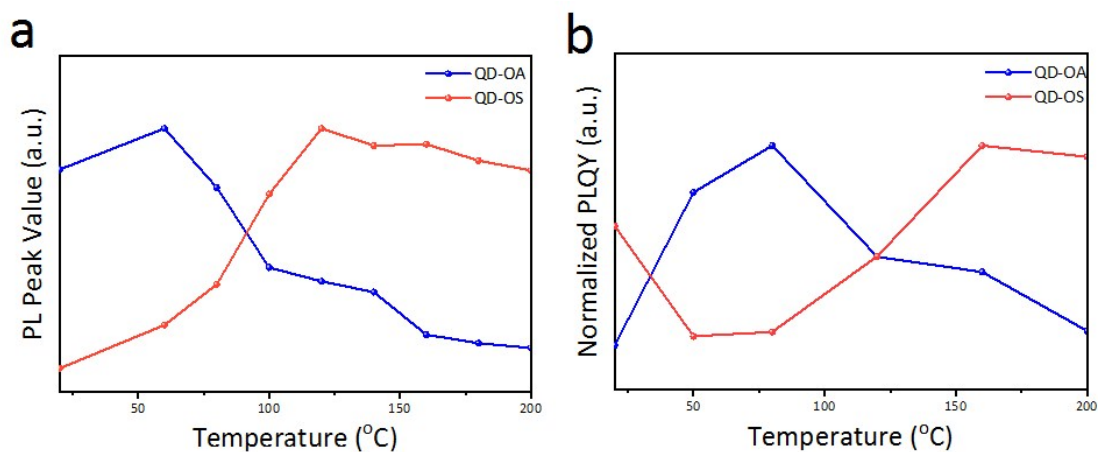


Figure S5. PL peak intensity (a) and PL QY (b) with different annealing temperature.

Table S2. PL QY of QDs films with different annealing temperature.

	20 °C	50 °C	80 °C	120 °C	160 °C	200 °C
QDs-OA	21.2%	51.7%	61.0%	38.8%	35.8%	24.0%
QDs-OS	13.9%	7.1%	7.3%	12.1%	19%	18.3%

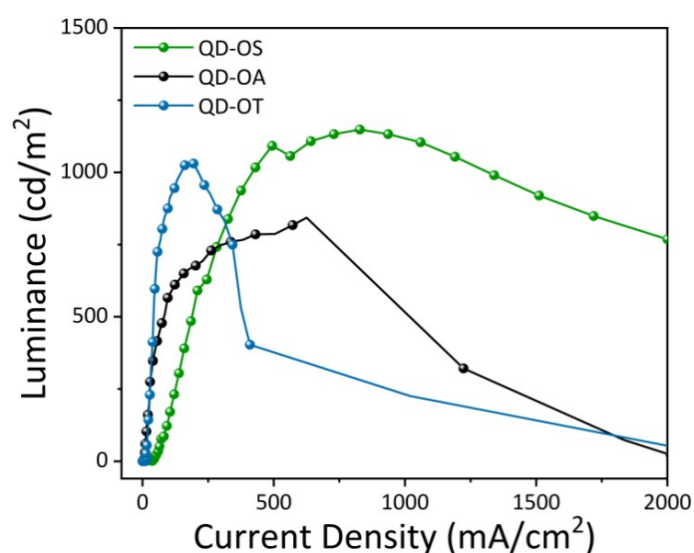


Figure S6. Luminance – current density plot of QLED based on QD-OS, QD-OA and QD-OT.

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