Supplementary Materials for

All-solution processed inverted green quantum dot light-emitting diodes with concurrent high efficiency and long lifetime

Zhiwen Yang[1,†], Qianqian Wu[2,†], Gongli Lin[1,†], Xiaochuan Zhou[1], Weijie Wu[1], Xuyong Yang[2,*], Jianhua Zhang[2,*] and Wanwan Li[1,*]

1. State Key Lab of Metal Matrix Composites, School of Materials Science and Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, P. R. China

2. Key Laboratory of Advanced Display and System Applications of Ministry of Education, Shanghai University, Shanghai 200072, China

Corresponding authors: wwli@sjtu.edu.cn (Wanwan Li), yangxy@shu.edu.cn (Xuyong Yang), jhzhang@shu.edu.cn (Jianhua Zhang)

EXPERIMENTAL SECTION

Chemicals. Cadmium acetate (anhydrous, 99.995%), zinc acetate (trace metals basis, 99.99%), zinc oxide (ZnO, 99.99%, powder), sulfur (S, 99.98%, powder), trioctylphosphine (TOP, 97%), 1-octadecene (ODE, technical grade, 90%), oleic acid (OA, 90%), oleylamine (OLAM, 70%), and 1-octanethiol (OT, ⩾98.5%) were purchased from Sigma-Aldrich. Selenium (Se, 99.99%, powder), hexane (analytical grade) and acetone (analytical grade) were obtained from Beijing Chemical Reagent Ltd, China. 1-octane (96%) was purchased from Aladdin.

Synthesis of Zn-oleate as Zinc precursor. ZnO (1.562 g, 19.19 mmol), oleic acid (18 mL), and 1-octadecene (45 mL) were combined in a 100 mL 3-neck flask and heated to 120 °C, first under a nitrogen atmosphere and then for 30 min under vacuum. The temperature was then raised to 310 °C for 10 min to obtain a colorless clear solution, which was cooled to 150 °C for use.

Synthesis of Zn-OLA as Zinc precursor. Zinc acetate (2.048 g, 11.16 mmol) and oleylamine (40 mL) were combined in a 100 mL 3-neck flask and heated to 120 °C to obtain a colorless clear solution, which was then cooled to room temperature for use.

Preparation of S-OLA. Sulfur (450 mg, 14.03 mmol) was dissolved in 30 mL of OLA at room temperature.

Synthesis of the CdSeZnS, CdSeZnS/ZnS, and CdSeZnS/ZnS/ZnS QDs. To synthesize CdSeZnS QDs, a 100 mL 3-neck flask containing a mixture of cadmium acetate (32.27 mg, 0.14 mmol), ZnO (416.25 mg, 5.11 mmol), and oleic acid (11.25 mL) was heated to 150 °C in an atmosphere rendered inert via Ar purging, and then degassed for 30 minutes while maintaining the temperature. Then 15 mL 1-ODE was added into the flask under Ar and the mixture was heated to 290 °C. An injection of 2.3 mL Top-Se/S (2.5 mmol Se powder and 2.5 mmol S powder dissolved in 2.3 mL

TOP) was quickly added to the flask, and the reaction was allowed to proceed for 8 minutes. To form the first ZnS shell coating, the temperature was raised to 310 °C, and a mixture of 9 mL of the prepared Zn-oleate and 0.9 mL 1-octanethiol was injected into the flask at a rate of 6 mL/h. Following the injection, the reaction was annealed for 30 min at 310 °C. The second ZnS shell coating was achieved by lowering the reaction temperature to 290 °C and adding dropwise a solution of 3 mL Zn-OLA or 4mL S-OLA and 21 mL 1-ODE. The solution was annealed for 3 min before it was injected with 4 mL of OA. After the reaction completed, the solution was cooled to room temperature and the resulting QDs were purified with acetone and hexane. The QDs were then redispersed in 1-octane before they were tested in QLED applications.

Synthesis of ZnO nanoparticles. Colloidal ZnO nanoparticles were synthesized as follows: First, 5.5 mmol tetramethylammonium hydroxide was dissolved in 10 mL ethanol. Then the solution was added dropwise into a dimethyl sulfoxide (30 mL) solution of anhydrous zinc acetate (3 mmol), which was then stirred for 2 h under ambient conditions. Next, the ZnO nanoparticles were purified with excess ethyl acetate. Finally, the resulting ZnO nanoparticles were redispersed in ethanol and stored in a refrigerator for later use.

Fabrication of the QLEDs. The ITO-coated glass substrates (Rs ≈ 15 Ω sq^{-1}) were sequentially cleaned via ultrasonication in deionized water, acetone, and ethanol for 30 min each. The substrates were baked dry and transferred into a N_2-filled glove box for spin-coating. The ZnO nanoparticles, which form the electron transport layers, were spin-coated onto the substrates at 2000 rpm and baked at 150 °C for 30 min. The EML was deposited by spin-coating green QDs in 1-octane (10 mg/mL) at 4000 rpm and subsequently baking at 90 °C for 20 min. The PEIE layer was spin-coated at 5000

rpm for 40 s on the EML, and then baked at 110 °C for 10 min. The hole transport layer consisting of poly-TPD (Solaris Chem, Inc.) in chlorobenzene (10 mg/mL) was spin-coated at 3000 rpm for 30 s and baked at 120 °C for 20 min. A 5 mg/mL solution of PMA in isopropanol was spin-coated onto the sample and annealed at 100 °C for 10 min. Finally, a 100 nm thick layer of Al was thermally evaporated at about 2×10^{-4} Pa. The effective area of the devices was 4 mm^2.

PL intensity measurement for a single QD. The as-prepared QDs were dispersed in toluene at a concentration appropriate for single particle optical characterization and then spin-coated onto a clean coverslip at 2000 rpm to form a solid film. All of the optical experiments were performed in a standard atmosphere. Optical experiments on single particles were conducted using a homemade wide-field fluorescence microscope modeled after the Olympus IX73. A 450 nm CW diode laser provided the excitation light, and the laser power density was about 2 W/cm^2. The fluorescence signal was collected by a dry microscope objective (Olympus LUCPlanFI 40×, NA=0.6) and detected by an EMCCD camera (iXon Ultra 888, Andor) after passing through a 473 nm (BLP01-473R-25, Semrock) long-pass filter. The exposure time was set to 500 ms.

Characterizations. UV-vis absorption was measured using a UV-2550 Shimadzu UV-vis spectrophotometer and PL spectra were measured by a RF-5301PC Shimadzu spectrofluorophotometer at room temperature. TEM imaging was performed using a JEOL-JEM 2010 electron microscope with an accelerating voltage of 200 kV. High-resolution TEM images were obtained with a JEM-100CX transmission electron microscope. The X-ray diffraction patterns were recorded by an Ultima IV X-ray diffractometer. The PLQYs and time decay dynamics data were measured using an Edinburgh FLS920 PL spectrometer. UPS data were acquired using an ESCALAB

250Xi (Thermo) system. The *J-L-V* and *CE-EQE-L* characteristics were measured by a Keithley 2400 source meter and PR-670 Spectra Colorimeter. The film thicknesses were quantified by a Tencor Alpha-Step 500 step profiler and a Seiko instrument SPA 400 AFM system. The lifetime measurements of the QLEDs were conducted using a ZJZCL-1 OLED aging lifespan test instrument.

SUPPORTING TABLES

Table S1. Comparison of our device properties with other all-solution processed inverted QLEDs.

Emitting layer	Color of QD-LED	PL λ max (nm)	EL λ max (nm)	EL FWHM(nm)	PL QY (%)	Peak EQE(%)	Peak CE (cd A^{-1})	Peak PE (lm W^{-1})	Max.L (cd m^{-2})	CIE coordinates	T_{50} @ 100 cd m^{-2}	Refs
CdSe@ZnS/ZnS/ZnS	green	523	524	21	>85	25.04	96.42	33.36	70650	(0.155, 0.787)	4943.6	This work
CdSe/CdS/ZnS	green	537	/	23	/	0.88	2.81	1.08	32370	(0.27, 0.71)	/	[1]
CdSe/CdS/ZnS	green	/	528	21	>90	15.6	65.3	29.3	110205	(0.157, 0.786)	/	[2]
CdZnSeS/ZnS/oleic acid	green	525	538	23	80	13.65	57.06	11.72	>100000	/	/	[3]
CdSe/CdS/ZnS	green	520	523	34	/	13.8	35.4	33.5	>10000	/	/	[4]
CdSe@ZnS/ZnS	green	/	527	23	88-90	11.6	48.9	/	100000	/	/	[5]
CdSe@ZnS/ZnS	green	524	525	20	90	24	89.8	/	72814	(0.13, 0.79)	/	[6]
CdSe/ZnS	green	/	528	29	/	5.29	21.4	/	80000	/	/	[7]
CdSe/ZnS/oleic acid	green	/	534	27	/	21.18	91.24	38.22	46430	/	222	[8]
CdSe/CdS/ZnS	red	634	/	37	/	1.3	0.69	0.52	12510	(0.69, 0.31)	/	[1]
/	red	/	618	28	/	12.7	22.1	/	98000	/	260	[7]
CdSe/ZnS/oleic acid	red	/	624	32	/	20.74	30.16	11.84	68100	/	127	[8]
CdSe-ZnS	red	612	633	/	/	0.18	0.51	0.2	2900	(0.68, 0.32)	/	[9]
CdSe/CdS/ZnS	red	624	630	/	82.7	2.72	4.1	2.03	16290	/	/	[10]
CdSe/ZnS/CdZnS	red	/	622	24	/	3.1	4.9	4.26	75444	/	/	[11]
CdS/ZnS	blue	441	/	27	/	/	0.06	0.04	249	(0.18, 0.07)	/	[1]
/	blue	/	454	21	/	5.99	1.99	/	41400	/	/	[7]
ZnCdS/ZnS	blue	/	456	21	/	8.38	2.67	1.05	1708	/	30	[8]

PL, photoluminescence; EL, electroluminescence; FWHM, full widths at half maximum; QD, quantum dot; QY, quantum yield; EQE, external quantum efficiency; CE, current efficiency; PE, power efficiency.

SUPPORTING FIGURES

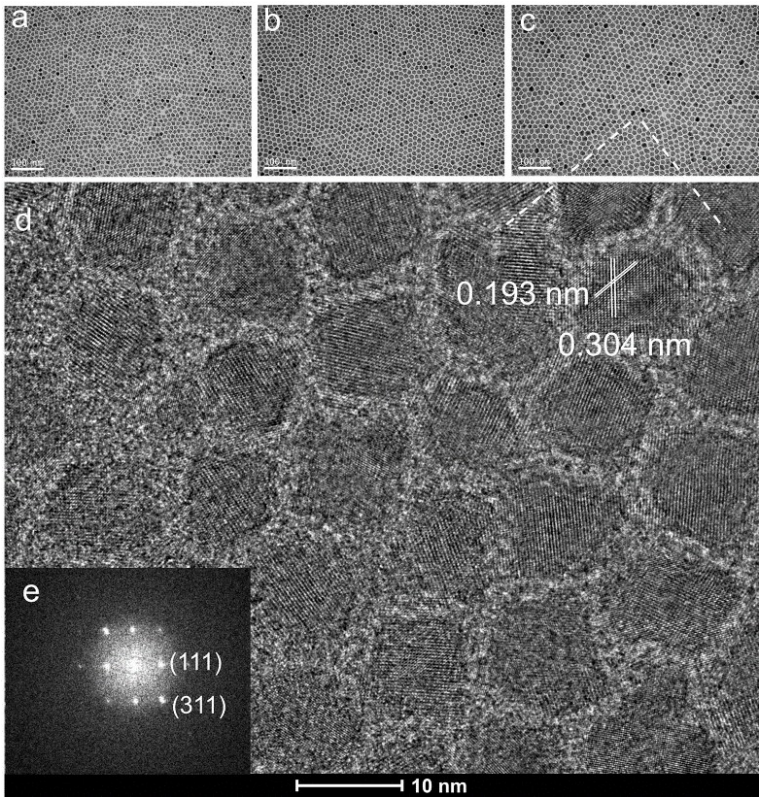

Figure S1. TEM images of (a) C, (b) C/S, and (c) C/S/S QDs. (d) High-resolution TEM image and (e) diffraction patterns of C/S/S QDs.

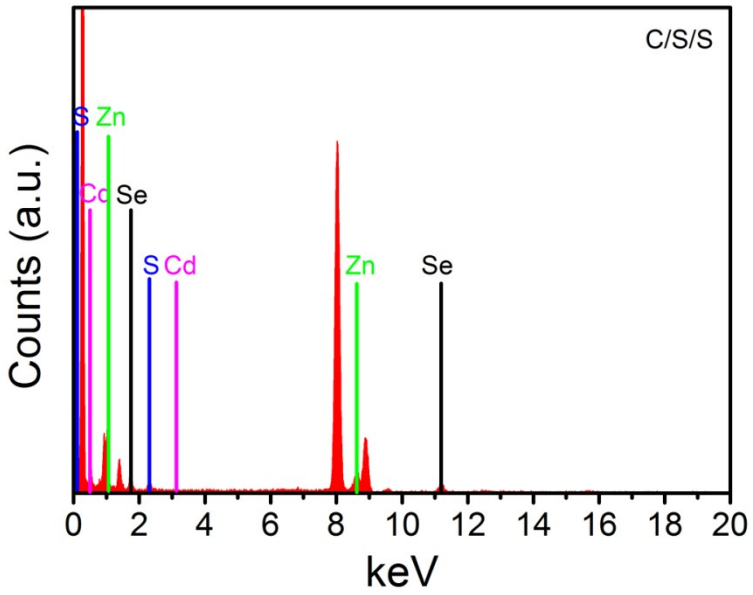

Figure S2. EDS spectrum of C/S/S QDs. The calculated molar proportions of elements in the QDs are: 1.22 ± 1.08% Cd, 51.63 ± 8.19% Zn, 27.75 ± 6.13% Se, and 19.44 ± 4.75% S.

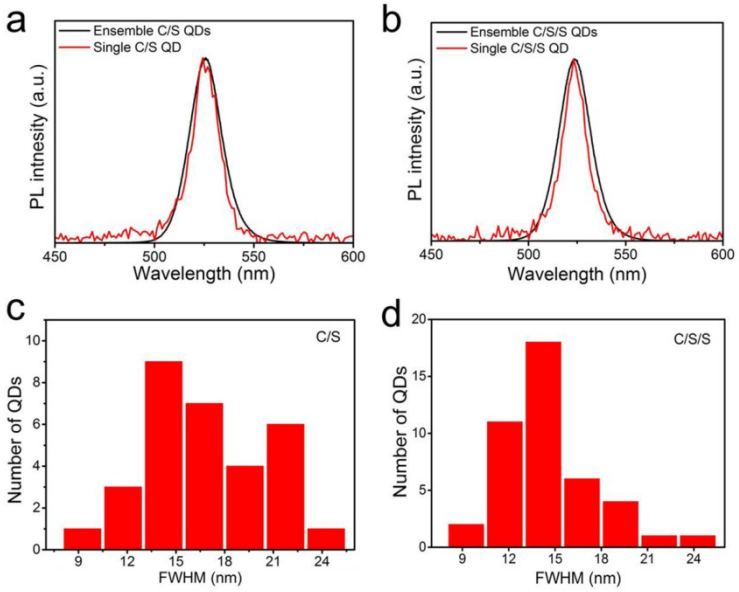

Figure S3. The photoluminescence spectra of (a) single C/S QD and ensemble C/S QDs, and (b) single C/S/S QD and ensemble C/S/S QDs. Histograms of FWHM for single (c) C/S QDs and (d) C/S/S QDs.

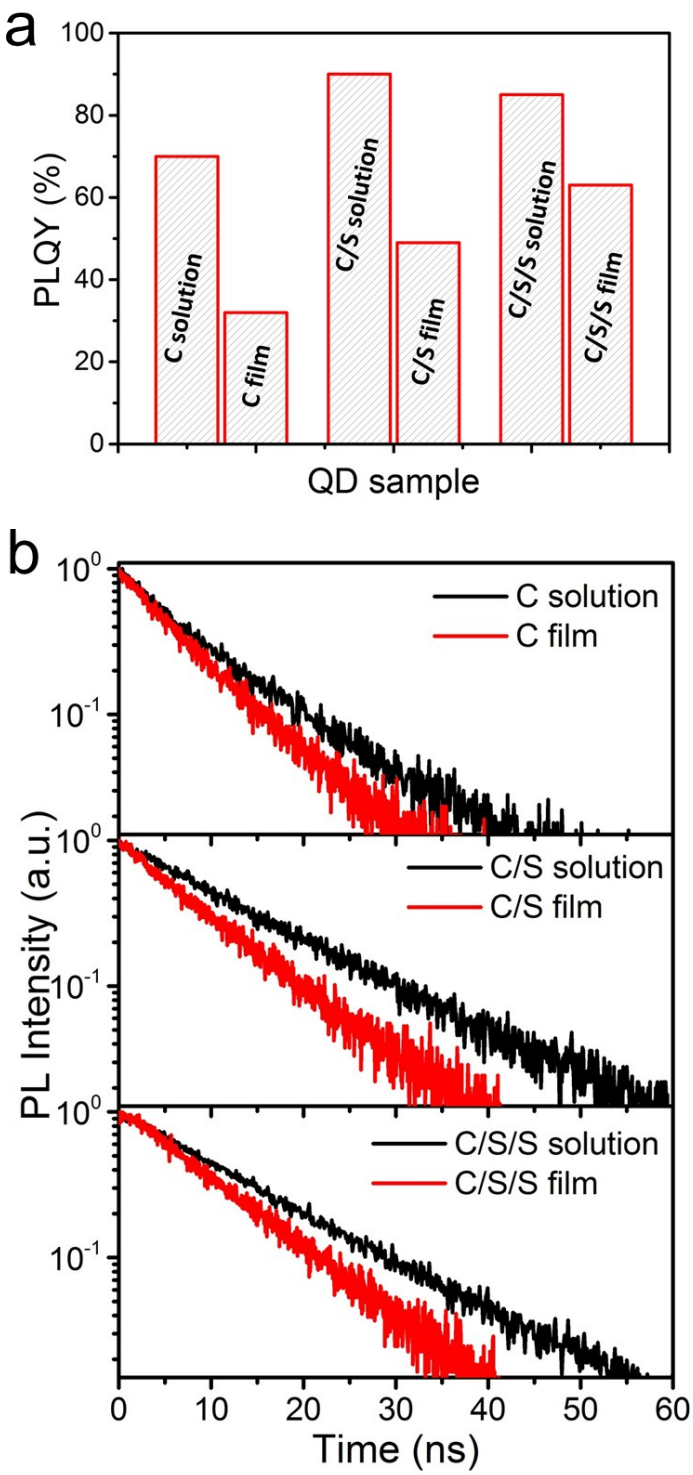

Figure S4. (a) PLQYs and (b) PL lifetimes of C, C/S, and C/S/S QDs in the solution and solid film.

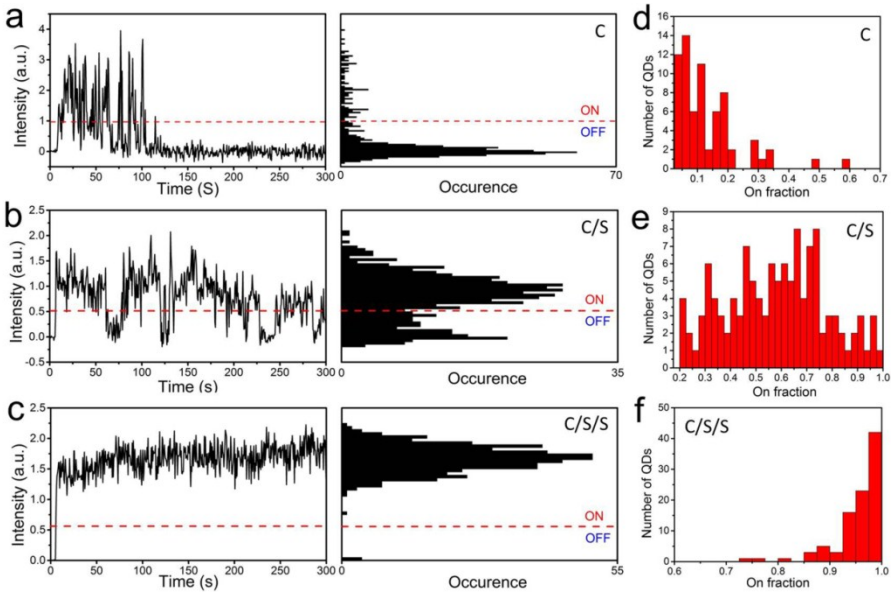

Figure S5. Representative photoluminescence blinking traces and distributions of intensities in the traces for single (a) C, (b) C/S, and (c) C/S/S QDs. (d-f) Histograms of the ON time fraction for C, C/S, and C/S/S QDs.

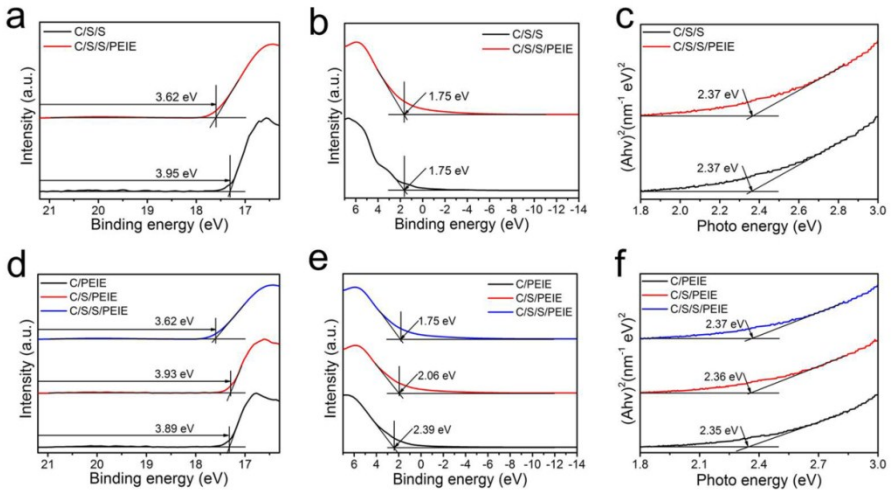

Figure S6. (a) UPS spectra of secondary-electron cut-off regions and (b) valence band edge regions of the C/S/S QD films with and without PEIE. (C) Dependence of $(Ahv)^2$ of C/S/S QD films on the incident photon energy (hv). (d) UPS spectra of secondary-electron cut-off regions and (e) valence band edge regions of the C, C/S, and C/S/S QD films. (f) Dependence of $(Ahv)^2$ of C, C/S, and C/S/S QD films upon the incident photon energy (hv).

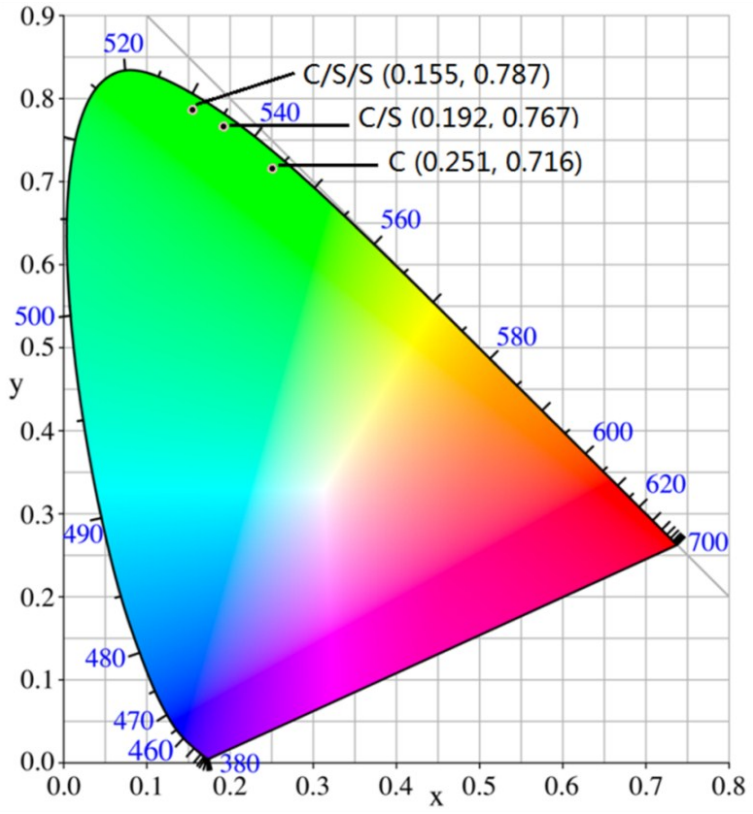

Figure S7. CIE color coordinates corresponding to C, C/S, and C/S/S QDs-based QLEDs.

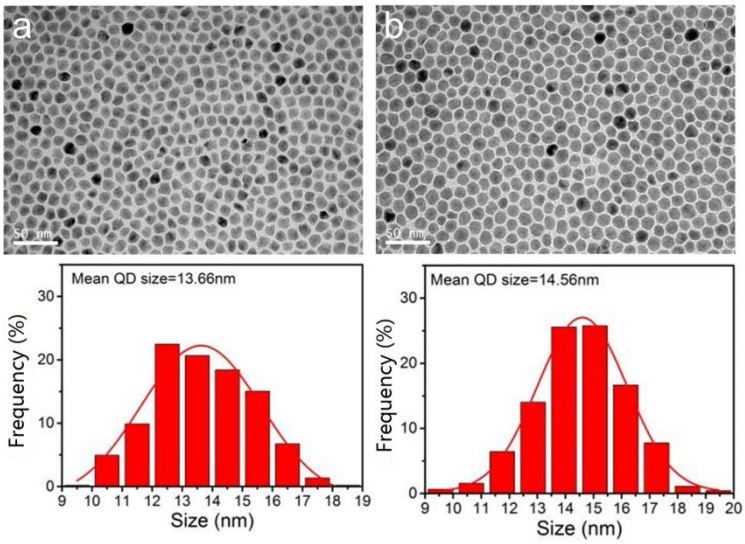

Figure S8. TEM images and size distribution histograms of (a) C/S-OT and (b) C/S-OLAS QDs.

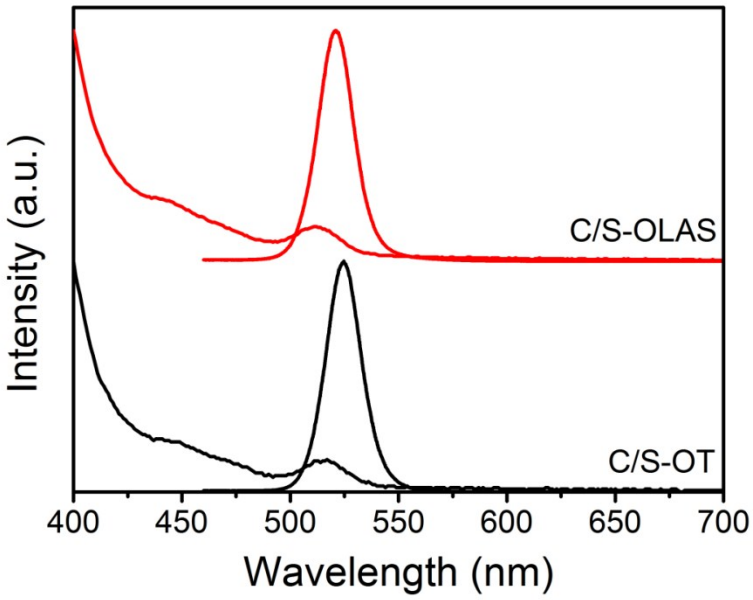

Figure S9. The absorption and photoluminescence spectra of C/S-OT and C/S-OLAS QDs.

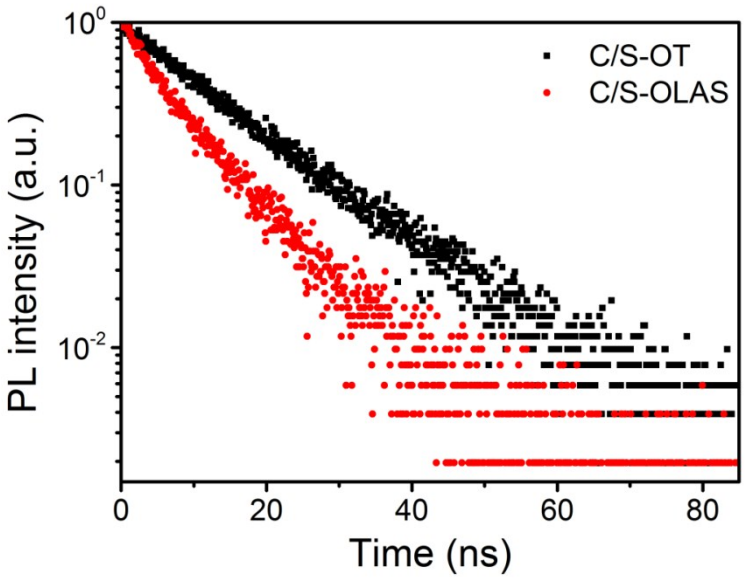

Figure S10. PL lifetime of C/S-OT and C/S-OLAS QDs.

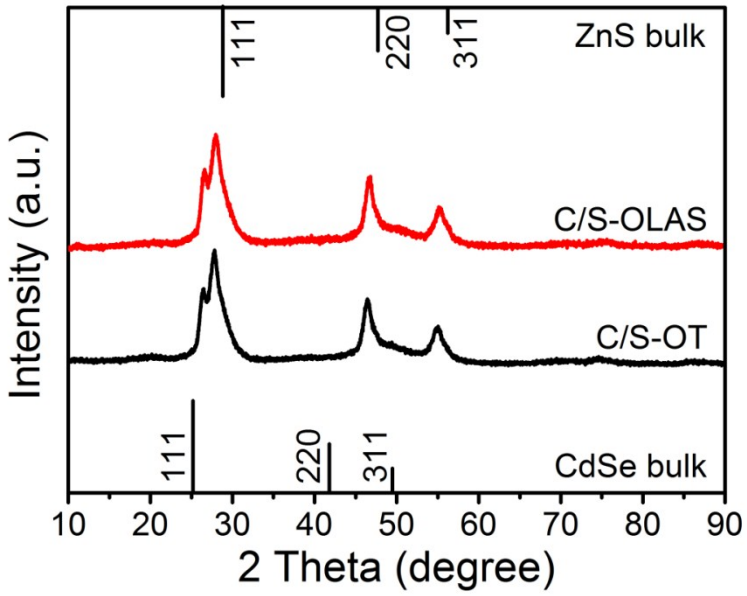

Figure S11. XRD patterns of C/S-OT and C/S-OLAS QDs.

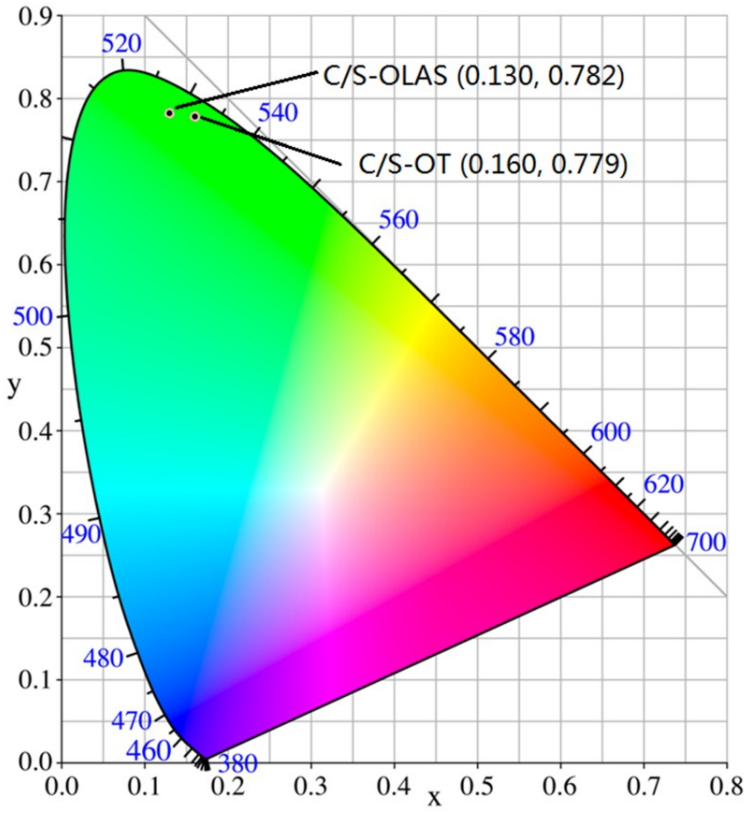

Figure S12. CIE color coordinates corresponding to C/S-OT and C/S-OLAS QDs-based QLEDs.

References

[1] A. Castan, H.-M. Kim, J. Jang, *ACS Appl. Mater. Interfaces* **2014**, 6, 2508.

[2] D. Kim, Y. Fu, S. Kim, W. Lee, K.-H. Lee, H. K. Chung, H.-J. Lee, H. Yang, H. Chae, *ACS Nano* **2017**, 11, 1982.

[3] H. Zhang, X. Sun, S. Chen, *Adv. Funct. Mater.* **2017**, 27, 1700610.

[4] H.-M. Kim, J. Kim, S.-Y. Cho, J. Jang, *ACS Appl. Mater. Interfaces* **2017**, *9*, 38678.

[5] Y. Fu, D. Kim, H. Moon, H. Yang, H. Chae, *J. Mater. Chem. C* **2017**, *5*, 522

[6] Y. Fu, W. Jiang, D. Kim, W. Lee, H. Chae, *ACS Appl. Mater. Interfaces* **2018**, *10*, 17295.

[7] Y. Liu, C. Jiang, C. Song, J. Wang, L. Mu, Z. He, Z. Zhong, Y. Cun, C. Mai, J. Wang, J. Peng, Y. Cao, *ACS Nano* **2018**, *12*, 1564.

[8] F. Cao, D. Zhao, P. Shen, J. Wu, H. Wang, Q. Wu, F. Wang, X. Yang, *Adv. Opt. Mater.* **2018**, *6*, 1800652.

[9] D. I. Son, H. H. Kim, D. K. Hwang, S. Kwon, W. K. Choi, *J. Mater. Chem. C* **2014**, *2*, 510.

[10] H. Zhang, H. Li, X. Sun, S. Chen, *ACS Appl. Mater. Interfaces* **2016**, *8*, 5493.

[11] M. A. Triana, H. Chen, D. Zhang, R. J. Camargo, T. Zhai, S. Duhm, Y. Dong, *J. Mater. Chem. C* **2018**, *6*, 7487.