

Supporting Information

Inkjet-printed aligned quantum rod enhancement films for their application in liquid crystal displays

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Synthesis and characterization of CdSe/CdS quantum rods (QRs). Red-emitting QRs were produced with a rod-in-rod CdSe/CdS structure. For the synthesis of rod-like CdSe seeds, we used the procedure described by Peng et al¹, with minor modifications. 204 mg of CdO, 973 mg of hexadecylphosphonic acid, and 1.85 g of trioctylphosphine oxide were mixed together and heated under vacuum to 150 °C. After an hour, the system was repeatedly degassed by means of filling with N₂ and evacuation (5 times). Then, the reaction mixture was heated to 380 °C until complete dissolution of CdO (app. 10 min), and the temperature was set at 320 °C. Thoroughly degassed solution of Se (63 mg) in a mixture of tributylphosphine (190 mg), trioctylphosphine (1.45 g) and toluene (0.3 g) was rapidly injected upon vigorous stirring, and the mixture was rapidly cooled with air flow to 250 °C. 0.45 ml of solution of Se (97 mg) in trioctylphosphine (1.0 g) was added dropwise within 5 min, and after 7 min the reaction was terminated by fast cooling (removing of heating mantle and addition of 5 ml of cold toluene). The obtained solution was mixed with 10 ml of degassed methanol (HPLC grade) at room temperature, and the white-yellowish precipitate was separated by centrifugation and thoroughly washed with benzene (15 ml) upon sonication, following by centrifugation. The last step was repeated 3 times; the combined benzene solution was concentrated to 10 ml under vacuum and mixed with 15 ml of methanol. The precipitate formed was separated by centrifugation, dissolved in 3 ml of benzene and evaporated under nitrogen flow at 50 °C, providing app. 130 mg of dark-red solid material containing CdSe seeds, which were coated with the CdS shell following previously reported protocol². Dimensions and optical properties of the resulting core/shell rod-in-rod QRs are given in Table S1. Green-emitting QRs of a dot-in-rod CdSe/CdS structure were synthesized according to the previously reported protocol². Their dimensions and optical properties are given in Table SI1.

TEM images of the both kinds of QRs along with corresponding size distributions are provided in Fig. S1a,b. Fig. S1c,d shows absorption and emission spectra of QRs.

Fluorescence anisotropy of the red-emitting rod-in-rod CdSe/CdS QRs is higher than green dot-in-rod QRs (Fig. S1e), in accordance with previous reports³.

Both kinds of QRs were covered with a combination of dendritic ligand 1 and hexylphosphonic acid in the molar ratio 1:4 (Fig. S2), following the previous published procedure⁴. To achieve this, prolonged heating of the solution of as-synthesized QRs with an excess of the ligand mixture in 1,2,4-trichlorobenzene at 160 °C in inert atmosphere was applied, and the obtained QRs were thoroughly washed by means of precipitation-dissolution sequence (3 times). The presence of new ligands at the QRs surface has been confirmed by FTIR spectroscopy, as exemplified in Fig. S3 for the red-emitting QRs.

Formulation of inkjet inks for QREF. Inkjet inks were made to achieve the best possible solubility of the liquid crystal monomer, and at the same time to provide stable colloidal suspension of QRs. Fig. S4a shows photographs of QR solutions in different solvents, with and without additions of liquid crystal monomer (LCM). At the beginning, all solvents provide homogeneous colloidal solutions of QRs. However, after 15 h of storage (Fig. S4b), QRs experience precipitation in 1,2,4-trichlorobenzene (TCB) solution without LCM (Fig. S4b-i). For the solutions with LCM (Fig. S4b-ii), only chlorobenzene (CB), 1,2-dichlorobenzene (DCB) and their mixtures provide good colloidal stability of QRs. Hence, only CB, DCB and their mixtures are used to prepare the inks for QREF printing.

Inkjet printing of QREFs on photoaligned substrates and optimization of waveform.

The inkjet ink has been filled into a printer cartridge, which was placed onto cartridge holder with 10pl nozzle. As the inverse Ohnesorge number for the prepared ink was >14 , the jetting waveform was modified from the usual waveform by using multistep negative section to provide better jetting conditions, as shown in Fig. S5. Formation of droplets from individual nozzles has been checked by a droplet watcher using interfaced computer by setting a particular value of voltage for the waveform applied for jetting. Fig. S6 shows droplet watcher images for different inkjet ink formulations used for the QREF printing with 5 step negative

section. It can be observed that the low-viscosity solvents such as toluene, xylene, and chlorobenzene produce small satellite droplets behind the main droplet, while other inks generate droplets with slight or no satellites. The inks with 50% and 60% v/v CB in DCB still show small satellite drop near to main drop.

Optical quality of the fabricated QREF.

A backlight module for LCD has been fabricated using QREF with blue backlight. Fig. S7a shows the schematic for the QREF equipped backlight unit with LCD. Fig. S7b shows the glued red and green QREF illuminated by a blue laser. The color coordinates (u, v) for red and green color are (0.5302, 0.5204) and (0.1315, 0.5789), respectively. The QREF provides an optical density of 0.6 for 450 nm blue light. The power for blue backlight is 0.416 W, which converts to the white light of power 0.174W by QREF. The total output power of ~0.0139mW has been obtained after the LCD, showing a power efficiency of ~8% for QREF backlight. Fig. S7c, d show images of LCD prototype using QREF backlight.

Fig. S8 shows the schematic diagram for the measurement of polarization properties of QREF emission. Here the QREF is illuminated with a blue laser of 450nm and optical fiber connected with a spectrometer is used to collect the light from the QREF through a polarizer.

Table S1. Dimensions and optical properties of QRs

Material	Mean Length, <i>nm</i>	Standard Deviation, <i>nm</i> (%)	Mean Diameter, <i>nm</i>	Standard Deviation, <i>nm</i> (%)	Mean Aspect Ratio	Max. λ_{em} , <i>nm</i>	FWHM <i>nm</i>	PLQY, %
Red QR	38	4.1 (10.7)	5.6	0.7 (12.5)	6.8	627	39	72
Green QR	25	2.2 (8.8)	5.7	0.6 (10.5)	4.4	562	26	51

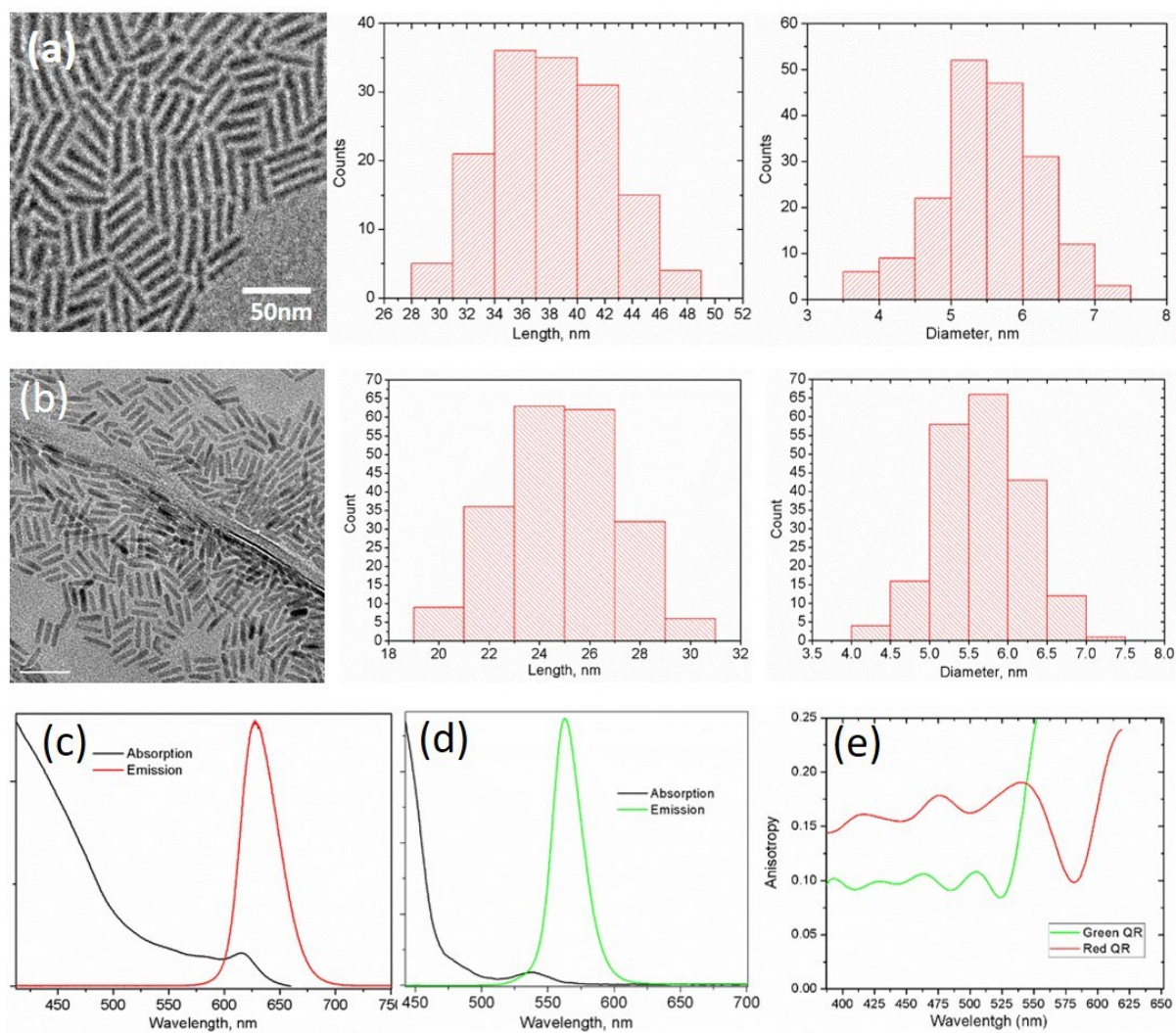


Figure S1. TEM images and length/diameter distributions of a) red-emitting QRs and b) green-emitting QRs. Absorption and emission spectra of c) red-emitting and d) green-emitting QRs. (e) Fluorescence anisotropy for both samples.

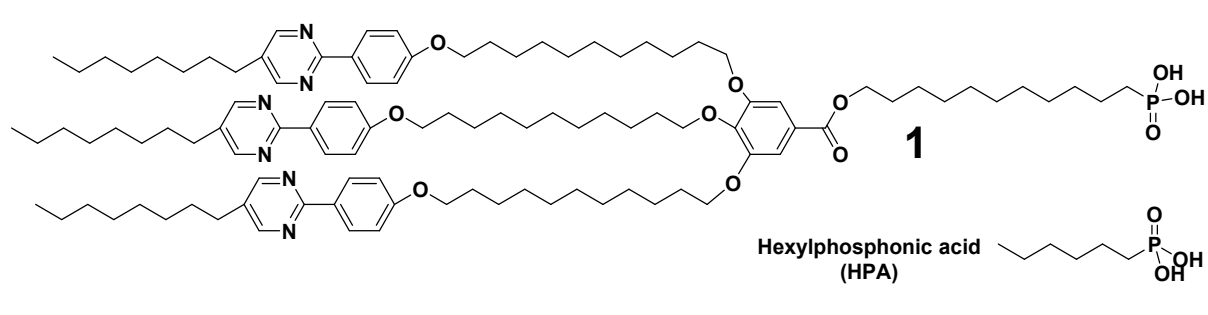


Figure S2. Chemical structures of new ligands used for QRs.

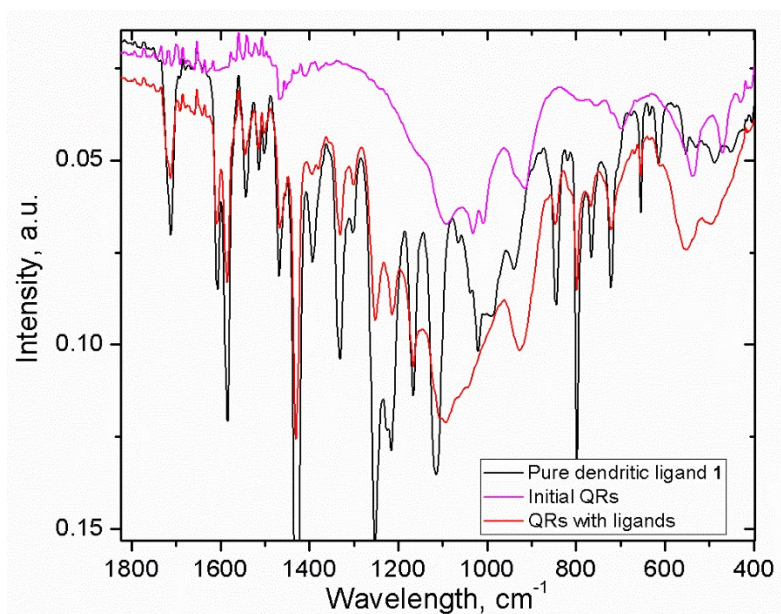


Figure S3. Monitoring of ligand exchange by FTIR spectroscopy for the red-emitting QRs.

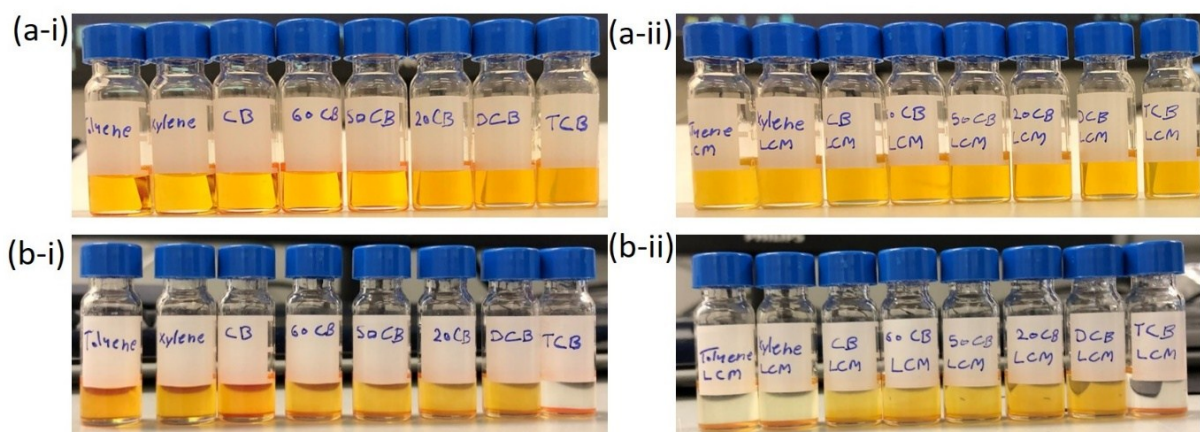


Figure S4. Photographs of QR solutions in different solvents, namely from left to right: toluene, xylene, CB, 60wt% of CB in DCB, 50wt% of CB in DCB, 20wt% of CB in DCB, DCB, and TCB taken a) immediately after preparation and (b) after 15 h of storage. Rows (i) are solutions without LCM, and rows (ii) are solutions with LCM.

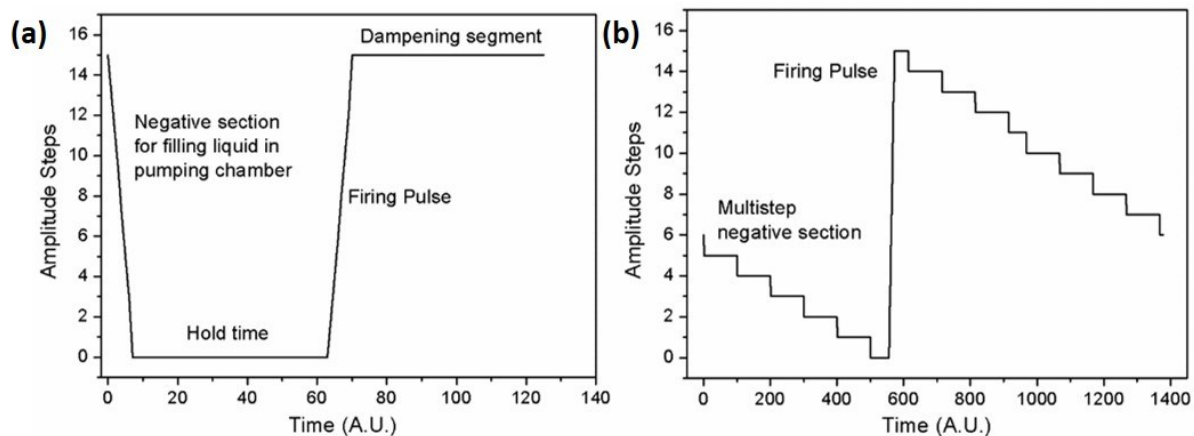


Figure S5. a) The waveform for an ideal ink. b) The modified waveform for the low viscosity ink.

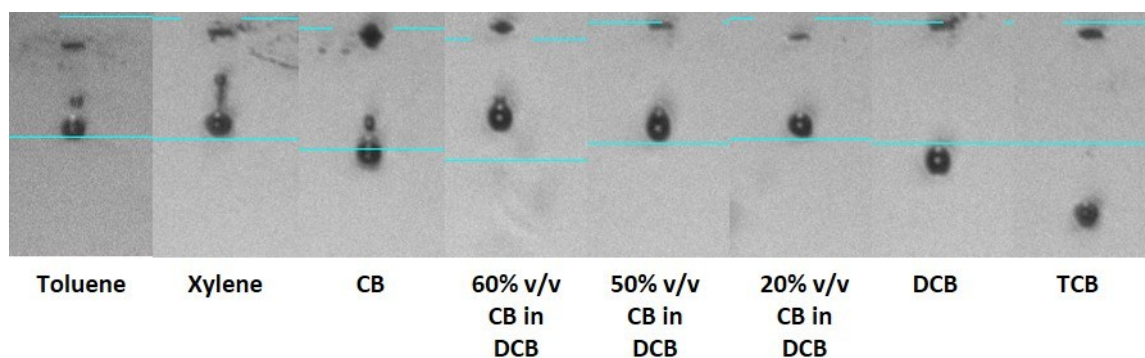


Figure S6. Droplet watcher images for different QR ink formulations with 5 step jetting waveform.

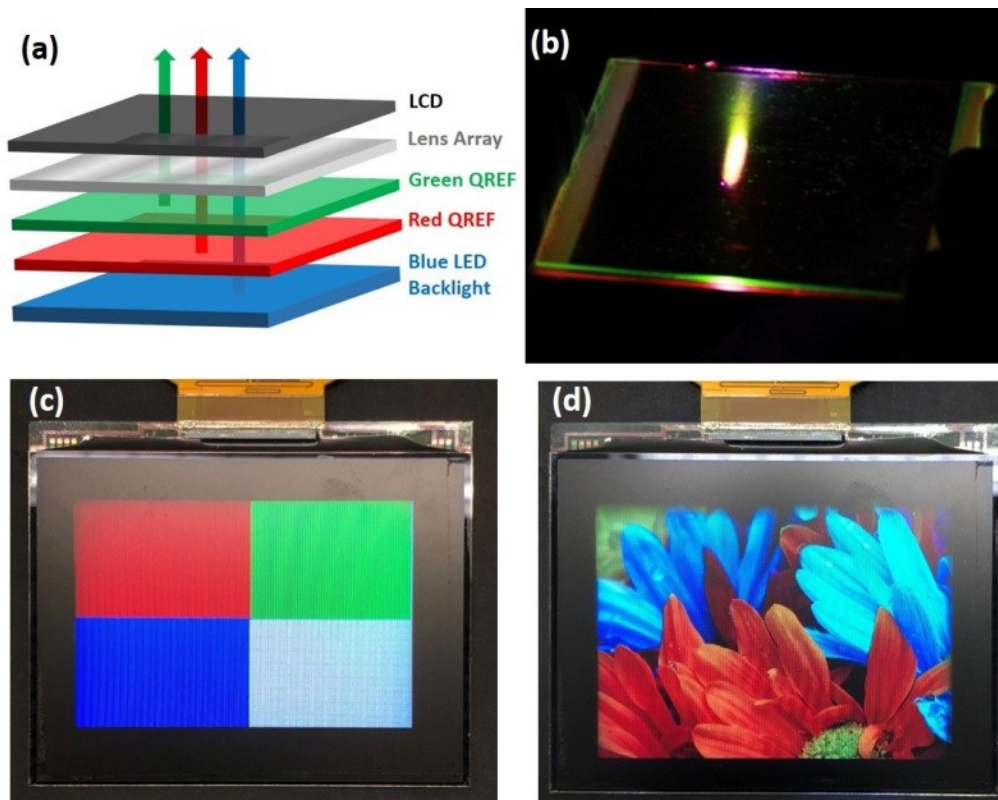


Figure S7. a) Schematics of the QREF backlight assembly with LCD. b) Combined red and green QREF films irradiated by blue laser. c, d) Images of LCD prototypes with different color images utilizing QREFs as the backlight component.

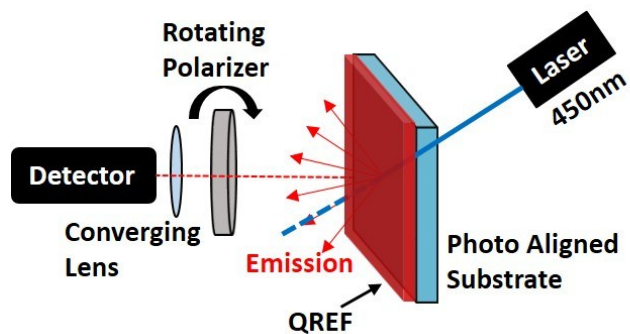


Figure S8. Optical setup used for the measurement of polarized QREF emission.

References

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