

Supporting Information for:

**Direct Patterning of Colloidal Quantum-Dot Thin Films for
Enhanced and Spectrally Selective Out-Coupling of Emission**

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1. Material Synthesis

Chemicals: Cadmium oxide (CdO, 99.999%) was purchased from Strem Chemicals. n-dodecylphosphonic acid (DDPA, 98%) was purchased from Epsilon Chimie. 1-butanol (ACS Grade) was purchased from Merck KGaA. Diphenylphosphine (DPP, 98%), ethanol (96%), hexadecylamine (HDA, 90%), hexane (95%), methanol (99.9%), selenium pellets (99.999%), sulfur (99.5%), trioctylphosphine (TOP, 90% and 97%), trioctylphosphine oxide (TOPO, 90%), 1-octadecene (ODE, 90%), 1-octanethiol (98.5%), octylamine (99%), oleylamine (OAm, 70%), oleic acid (OLA, 90%), and zinc acetate [Zn(ac)₂, 99.99%] were purchased from Sigma.

Cadmium oleate stock and zinc oleate stock were prepared as previously reported¹ and stored in the glovebox for future use.

Preparation of Red-Emitting Core/Shell Quantum Dots: CdSe cores with a lowest energy exciton peak of 579 nm (size approximately 3.8 nm, as determined by Yu *et al.*²) were synthesized following a modified version of a procedure by Reiss *et al.*³ Briefly, 822 mg of CdO (6.4 mmol), 16.2 g of TOPO (42 mmol), 37 g of HDA (153.2 mmol), and 3.215 g of DDPA (12.8 mmol) were combined in a 250 mL 4-neck round-bottom flask and heated to 90 °C under N₂(g). Then, the mixture was degassed 3 times to below 0.1 Torr with stirring at 1000 rpm. The flask was filled with N₂(g) and heated at 320 °C until the solution turned clear. The temperature was then reduced to 260 °C and 8 mL of 1M Se in TOP (97%) solution containing 85 μL of DPP was swiftly injected at 300 rpm. After injection, the stir rate was increased to 1000 rpm and the temperature was maintained at 260 °C. The growth of CdSe nanocrystals was monitored using an UV-visible spectrophotometer (Varian Cary 300, UV-VIS). The reaction was quenched by removing the heating mantle, cooling to 200 °C with an air gun, submerging the flask in a water bath, and adding 40 mL of 1-butanol at 130 °C to prevent solidification. To isolate the product, the reaction mixture was split into 6 centrifuge tubes and methanol was added to reach a total volume of 50 mL in each tube. A precipitate was collected by centrifugation at 4000 rpm for 10 min, redispersed in 20 mL of hexane, and left undisturbed overnight at room temperature (RT). The following day, the mixture was

centrifuged at 4000 rpm for 20 min, the supernatant was transferred to 6 centrifuge tubes, and ethanol was added to precipitate the product. The nanocrystals were isolated by centrifugation at 4000 rpm for 10 min. The precipitate in each tube was dispersed in 4 mL of hexane to be precipitated out once more with ethanol and centrifuged under the same conditions. The nanocrystals were dispersed in a 20 mL of hexane and stored in the dark until further use.

The growth of the CdS/ZnS shell on CdSe nanocrystals was performed following Boldt *et al.*⁴ and as previously reported by our group.¹ Briefly, 100 nmol of CdSe nanocrystals in hexane, 3 mL of ODE, and 3 mL of OAm were combined in a 3-neck 100 mL round-bottom flask and degassed at RT for 1 h. The mixture was then heated at 120 °C for 20 min. The flask was filled with N₂(g) and heated to 305 °C at a rate of 16 °C/min. At 210 °C, two separate syringes containing cadmium oleate (0.22 mmol) and octanethiol (0.26 mmol), each diluted in ODE (final volume of 3 mL), were injected with a syringe pump at a rate of 1.5 mL/h. After injection, the temperature was lowered to 200 °C, 1 mL of degassed OLA was added dropwise, and the mixture was allowed to anneal for 1 h at 200 °C. Subsequently, the temperature was lowered to 120 °C and the reaction mixture was degassed for 30 min. The flask was then filled with N₂(g) and the temperature was raised to 280 °C at a rate of 16 °C/min. At 210 °C, two separate syringes containing zinc oleate (0.24 mmol) and octanethiol (0.48 mmol) each diluted in ODE (final volume of 3 mL) were injected with a syringe pump at a rate of 2.5 mL/h. After injection, the reaction mixture was quickly cooled down to RT. To precipitate and clean the nanocrystals, an equivalent amount of ethanol to reaction-mixture volume was added and centrifuged at 4000 rpm for 10 min. The bright precipitate was dispersed in 4 mL of hexane, 10 mL of ethanol was added, and the mixture was centrifuged under the same conditions. This step was repeated (2 mL of hexane and 5 mL of ethanol). The product was dispersed in a small volume of hexane and stored in the dark until future use. The recipe resulted in core/shell nanocrystals with a lowest energy excitonic absorption peak at 607 nm and an emission peak at 622 nm with a full-width-at-half-maximum (fwhm) of 28 nm.

Preparation of Green-Emitting Core/Shell Quantum Dots: The core/shell CdSe/ZnS nanocrystals with a composition gradient were prepared by modifying a procedure by Bae *et al.*⁵ Briefly, 51.4 mg of CdO (0.4 mmol), 734 mg of Zn(ac)₂ (3.34 mmol), and 2 mL of OLA (6 mmol) were combined in a 3-neck 100 mL round-bottom flask and degassed 3 times under 0.1 Torr. The mixture was heated at 150 °C and degassed for 30 min. Then, the flask was filled with N₂(g), 15 mL of degassed ODE was added and degassed at 120 °C for an additional 5 min. Subsequently, the mixture was heated at 310 °C to form a clear solution. 3 mL of TOP (90%) containing 0.2 mmol Se and 4 mmol S was then swiftly injected into the reaction mixture. The temperature was maintained at 300 °C for 10 min and it was then quickly cooled down to RT. The reaction mixture was transferred to a centrifuge tube, filled with ethanol, vortexed and centrifuged at 4000 rpm for 10 min. This ethanol extraction procedure was repeated (typically 5 times) until a bright pellet was fully precipitated with a clear supernatant. The product was dispersed in 8 mL of hexane and stored in the dark until future use. The recipe resulted in core-shell nanocrystals with a lowest energy excitonic absorption peak at 530 nm and an emission peak at 545 nm.

To grow a ZnS shell on CdSe/ZnS nanocrystals a modified recipe by Boldt *et al.* was followed. Briefly, 100 nmol of CdSe/ZnS nanocrystals in hexane (which was approximated with an absorption cross-section of 517 nm CdSe cores), 3 mL of ODE, 3 mL of OAm, and 1 mL OLA were combined in a 3-neck 100 mL round-bottom flask and degassed at room temperature for 1 h. The mixture was heated to 120 °C for 20 min, switched to N₂(g) and raised to 280 °C at a rate of 16 °C/min. When 210 °C was reached, two separate syringes containing zinc oleate (0.25 mmol) and octanethiol (0.5 mmol), each diluted in ODE (final volume of 3 mL), were injected using a syringe pump at a rate of 2.5 mL/h. After injection, the temperature was lowered to 200 °C and 1 mL of degassed OLA was added dropwise. The reaction annealed at 200 °C for 1 h, and then it was quickly cooled down to RT. The nanocrystals were purified and isolated by precipitation with ethanol and centrifugation at 4000 rpm for 10 min. The resulting bright precipitate was dispersed in 2 mL of hexane 5 mL of ethanol was slowly added, and the mixture was centrifuged once more. This step was repeated (1 mL hexane and 3 mL

ethanol). The product was dispersed in 3 mL of hexane and stored in the dark until future use. The recipe resulted in nanocrystals with a lowest energy excitonic absorption peak at 505 nm and an emission peak at 526 nm with a fwhm of 29 nm.

Preparation of Blue-Emitting Core/Shell Quantum Dots: The core/shell nanocrystals with a composition gradient were prepared by modifying a procedure by Lee *et al.*⁶ Briefly, 128.4 mg of CdO (1 mmol), 1832 mg of Zn(ac)₂ (8.3 mmol), and 7 mL of OLA (22 mmol) were combined in a 3-neck 100 mL round-bottom flask. The mixture was degassed 3 times under 0.1 Torr and at 150 °C for 20 min while stirring at 1000 rpm. The flask was filled with N₂(g), 15 mL of degassed ODE was added, and the mixture was degassed at 120 °C for 10 min. The flask was filled with N₂(g) and heated to 305 °C to obtain a clear solution. At 305 °C, a clear solution consisting of 3 mL of ODE with 1.6 mmol of S prepared inside the glovebox, was swiftly injected into the reaction mixture. After injection, the temperature was maintained at 305 °C for 12 min. Subsequently, a clear solution consisting of 5 mL of OLA with 4 mmol of sulfur prepared in the glovebox, was injected with a syringe pump at a rate of 0.5 mL/min. After injection, the temperature was maintained at 305 °C for 3 h. After annealing, the reaction mixture was quickly cooled down to RT. To precipitate and purify the nanocrystals, the reaction mixture was split into two centrifuge tubes. Then 20 mL of ethanol was added to each tube and centrifuged at 8000 rpm for 10 min. The solid was dispersed in 5 mL of hexane, 1 mL of octylamine was added, and the mixture was sonicated for 5 min. Then, 20 mL of ethanol was added and the mixture was centrifuged at 8000 rpm for 10 min. The cleaning process was repeated 2 times. The particles were cleaned 3 times using a combination of hexane (4 mL) and a mixture of acetone (10 mL) ethanol (20 mL), with a clear supernatant being discarded each time. The particles were dispersed in 5 mL of hexane and stored in the dark until future use. The recipe resulted in core/shell nanocrystals with a lowest energy excitonic absorption peak at 450 nm and an emission peak at 460 nm with a fwhm of 25 nm.

2. Sample Fabrication

Materials: Four-inch diameter, single-side-polished, single-crystalline Si(100) wafers with <0.4 nm root-mean-square (RMS) roughness and thicknesses of either 500 or 1000 μm were purchased from Silicon Valley Microelectronics and diced into 2 x 2 cm square pieces. Octadecyltrichlorosilane (OTS, 96%) was purchased from Merck KGaA. Bicyclohexyl (99%, D79403), carbon tetrachloride (CCl_4 , 99.5%, 289116), chloroform (99.8%, 132950), and sulfuric acid (H_2SO_4 , 95-98%, 258105) were purchased from Sigma. Hydrogen peroxide (H_2O_2 , 30%, AnalaR Normapur) was purchased from VWR. Methyl isobutyl ketone (MIBK, Technic France Micropur, VLSI Grade) and isopropanol (IPA, Technic France Micropur, VLSI Grade) was provided by IBM Zurich's Binnig and Rohrer Nanotechnology Center (BRNC).

Template Fabrication: Si(100) substrates of 2 x 2 cm in size were cleaned using sonication in acetone, isopropanol, and deionized (DI) water and prebaked at 180 $^\circ\text{C}$ for 10 min. Substrates were coated with 200 nm PMMA (AR-P 672.03 950K) and patterns were defined using electron-beam lithography (Vistec, NFL 5). Patterns were developed using MIBK:IPA (1:2 ratio) for 2 min, followed by 1 min in fresh IPA and then 1 min under running DI water. Features 100 nm deep were etched into the Si substrate using deep-reactive-ion etching (Alcatel, AMS-200 I Speeder) at 11.25 mTorr with 60 SCCM C_4F_8 , 40 SCCM SF_6 , a plate power of 80 W, and an inductive-coupled-plasma (ICP) power of 1200 W. The etch rate for these settings was ~ 8 nm/s. The PMMA mask was removed using ultrasonication in acetone, followed by an IPA rinse, and subsequent O_2 plasma at 750 mTorr, 600 SCCM O_2 , and 600 W (PVA-TePla, GIGAbatch 310 M) for 3 min.

Surface Functionalization: Patterned Si substrates were functionalized with octadecyltrichlorosilane (OTS) based self-assembled monolayers following a recipe by Lessel *et al.*⁷ In short, silicon templates were cleaned in a piranha solution (1:1 H_2O_2 , H_2SO_4) for 15 min, submerged in DI water for 5 min, then blow dried with a N_2 gun. In a Teflon container, 150 μL of OTS, 300 μL of CCl_4 , and 10 mL of bicyclohexyl were combined. A beaker of DI water was set to 170 $^\circ\text{C}$ on a hotplate, and the silicon substrate

was quickly passed over the water vapor. Immediately after the thin film of water evaporated, the sample was placed in the Teflon container with OTS for 15 min. Next, to remove non-bound OTS, the samples were thoroughly rinsed with chloroform and subsequently sonicated in a chloroform bath for 2 min. Samples were placed back in the Teflon container with OTS, rinsed and sonicated two more times to complete the process. The resulting hydrophobic surface yields a contact angle of $> 110^\circ$ for unpatterned areas.

Quantum-Dot Deposition: The concentration was determined by taking the optical density of the quantum-dot dispersion with a UV-VIS spectrophotometer at the lowest energy exciton (red = 607 nm, green = 505 nm, blue = 450 nm). For the red-emitting quantum dots, we prepared the cQD dispersion at an optical density of 2.0 (1 cm optical path length). For the green-emitting quantum dots, we prepared the cQD dispersion at an optical density of 6.0. For the blue-emitting quantum dots, we prepared the cQD dispersion at an optical density of 2. All dispersions were prepared using a hexane:octane ratio of 9:1. Then, 35 μL of cQDs was dropcast onto the silicon substrate and allowed to dry, yielding a uniform film approximately 200 nm in thickness. For white light, we mixed 10 μL of red-emitting quantum dots, 30 μL of green-emitting quantum dots, 150 μL of blue-emitting quantum dots, using the before mentioned optical densities with 9:1 hexane:octane ratio. The apparent overexpression of green and blue accommodates for energy-transfer dynamics and the resulting red-shift of spectral features in the film. 35 μL of red-green-blue-emitting (RGB) cQDs was dropcast onto the silicon substrate and dried to yield a uniform film. Template stripping was then performed by placing a drop of epoxy (NOA 61, Norland Products) on the cQD film after drying. The epoxy was allowed to flow towards the edges of the template until only the corners were free, after which it was cured with a 365 nm UV lamp for 30 min. Please note that, although minor percolation of the epoxy into possible void spaces of the cQD film cannot be excluded, no effect on the quality and effective refractive index of the film was observed. After curing, the silicon template was separated from the QD/epoxy/glass stack by placing a razor blade between the silicon template and the glass slide at one of the corners of the template, thereby exposing the patterned cQD film. Templates can be cleaned for future use through ultra-sonication in chloroform for 5 min. The SAM maintains sufficient

quality for 10-15 dropcasts, although best results are generally obtained with freshly prepared SAMs. An O₂ plasma (600W, 10 min) and piranha treatment (1:1 H₂O₂/H₂SO₄, 15 min) can be used to remove the SAM, making the template ready for a new octadecyltrichlorosilane treatment.

3. Atomic Force Microscopy (AFM)

Atomic force microscopy (Bruker FastScan) was performed to characterize the height of the cQD grating structure. Figure S1 shows an atomic force micrograph of a linear grating on a red-emitting quantum-dot film with a pitch of 550 nm. The height of the pattern is consistent with the etch depth of the template, which was set to 100 nm.

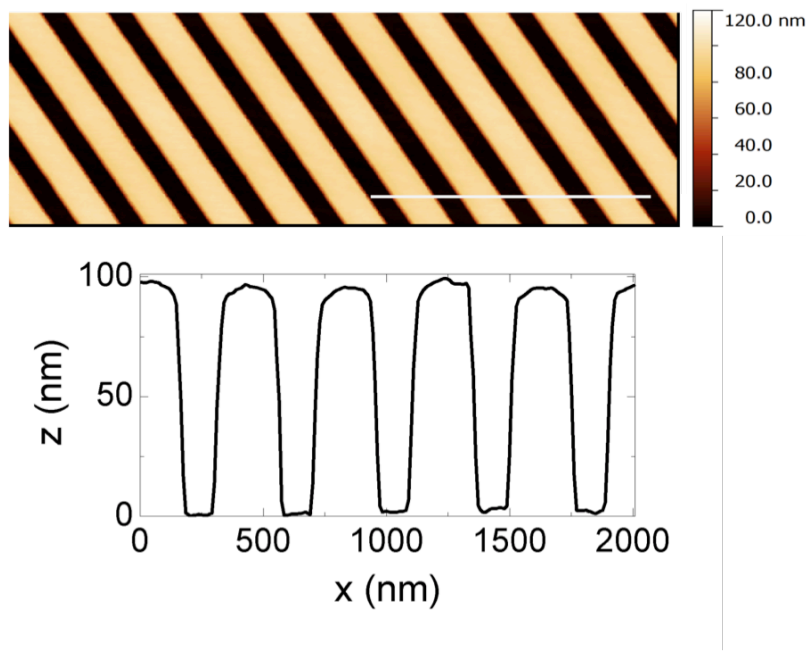


Figure S1. Top: Atomic force micrograph of a cQD linear grating with 400 nm pitch. Bottom: line trace taken perpendicular to the same grating structure.

4. Angular Dependence of Emission for Varying λ_{em}

Figure S2 shows the angle of emission from different circular Bragg gratings for red-, green-, and blue-emitting cQD films as a function of pitch. The measured emission angles can be fit to Equation (1) in the main text, using the effective refractive index of the waveguided mode as the only fitting parameter. We obtain n_{eff} values of 1.58 ± 0.02 , 1.55 ± 0.04 and 1.73 ± 0.02 for the red-, green-, and blue-emitting films, respectively. Note that the n_{eff} value for the red-emitting film that is obtained here is consistent with the one obtained from the fit in Figure 2c in the main text. The effective refractive index of our waveguided modes is a non-trivial quantity that depends sensitively on the geometry of the structured surface, as well as the composition and fill-factor of the cQD film. Generally, the increasing effective refractive index values in the blue wavelength region are consistent with previous reports in literature.⁸

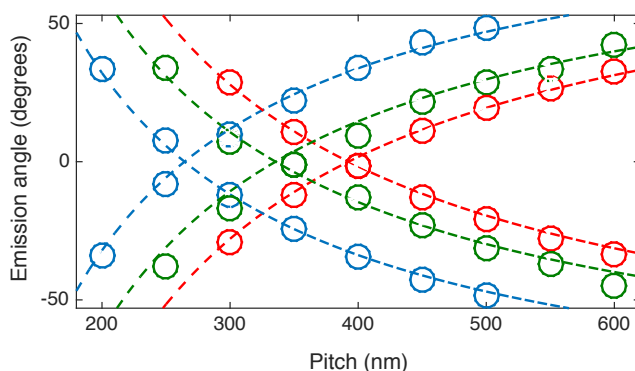


Figure S2. Emission angle with respect to the surface normal for different circular Bragg gratings for red, green, and blue cQD films as a function of the pitch of the grating. Open circles indicate experimental data for three wavelengths with associated uncertainty that is smaller than the symbol size. The dashed lines are fits to equation 1 of the main text.

5. Band structure calculations

Band structure calculations of the patterned cQD films were performed using the MIT Photonic Bands (MPB) package. Using experimentally determined input parameters for the sample geometry (see Figure S3a) and the refractive index of the cQD film ($n = 1.8$), we have simulated the dispersion diagram around the Bragg crossing shown experimentally in Figure 2c of the main text. Using these parameters, both the slope and the crossing point of the mode dispersion were reproduced accurately, as can be seen in Figure S3.

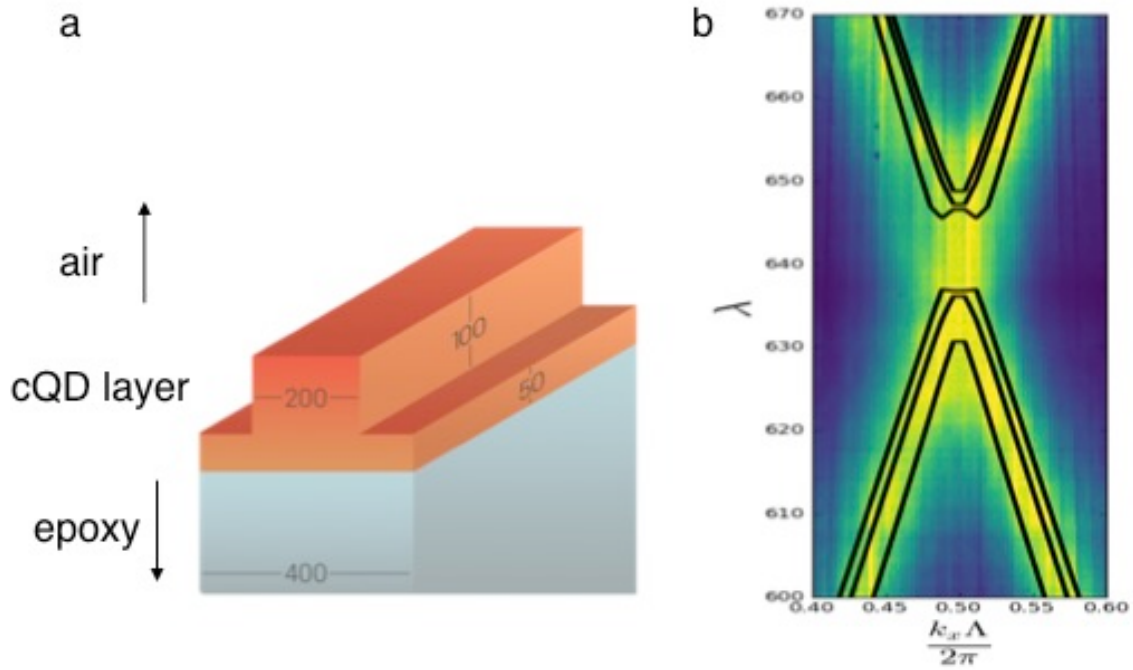


Figure S3 (a) Three dimensional geometry used in the MPB simulation, following experimentally determined parameters. (b) results of the eigenmode dispersion (black lines) superimposed on the experimentally obtained dispersion from k-space measurements described in Figure 2c. For clarity, the experimental data has been normalized at each wavelength.

6. Color Gamut Tuning Through Surface Patterning of Mixed Films

We fabricated bull's-eye gratings with different pitches onto a mixed RGB cQD film to provide color tuning of spontaneous emission through spectrally selective out-coupling (see Figure 5 in the main text). The different patterns shift the color gamut of the out-coupled light from the mixed RGB film. To quantify the tunability of color through the surface patterning, we plot the color coordinates of each spectrum on a International Commission on Illumination (CIE) color map, as shown in Figure S4.

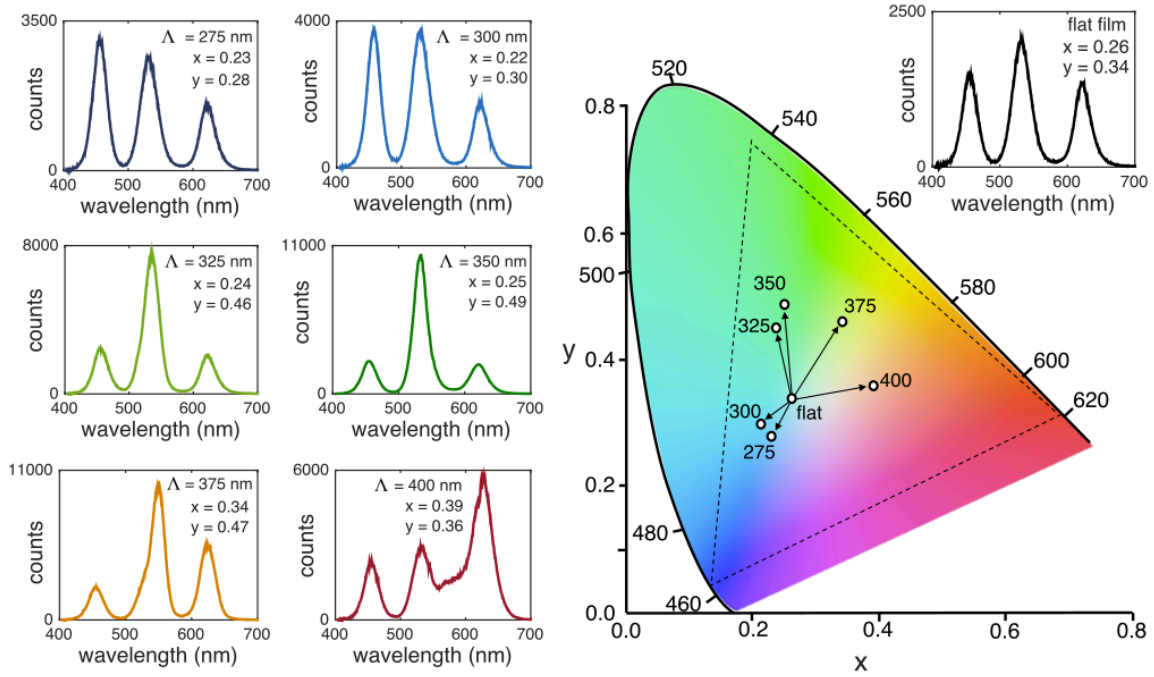


Figure S4. Emission spectra of the unpatterned and patterned RGB-emitting mixed-cQD film recorded using a N.A. = 0.2 objective indicating the CIE x and y values, and CIE color map indicating the tunability of the color gamut of the out-coupled emission.

7. Further enhancement of out-coupling using back reflectors

To demonstrate the compatibility of the direct patterning strategy with conventional light management strategies, we have fabricated template stripped bull's eye gratings on top of a silver back reflector. The back reflector serves to redirect light emitted into the substrate and further improve the hemispherical emission from the front side of the structure. Figure S5 compares the k-space emission map of a red emitting 400 nm pitch bull's eye on top of epoxy/glass (top) with an identical structure on top of epoxy/silver (bottom). The data is compensated for excitation enhancement by normalizing the maps to their respective non-resonant emission at higher angles. To allow comparison of the emission enhancement, both maps are normalized to the overall highest intensity observed for the silver backed bull's eye structure. The use of a back reflector results in a further enhancement of the peak emission intensity by $\sim 35\%$.

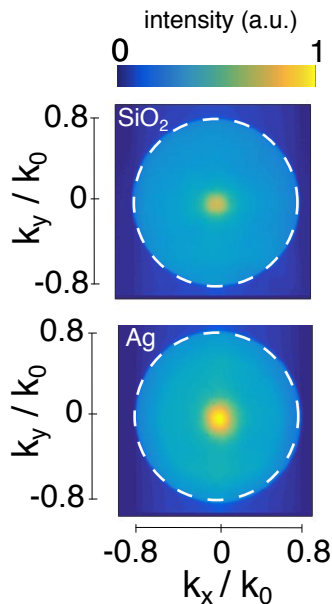


Figure S5. Normalized k-space color maps of fluorescent emission from identical red-emitting bull's-eye gratings with (bottom) and without (top) silver back reflector ($\Lambda = 400$ nm). Dashed white lines indicate the numerical aperture of the objective (N.A. = 0.8).

Supplementary References

- (1) Kress, S. J. P.; Antolinez, F. V.; Richner, P.; Jayanti, S. V.; Kim, D. K.; Prins, F.; Riedinger, A.; Fischer, M. P. C.; Meyer, S.; McPeak, K. M.; et al. Wedge Waveguides and Resonators for Quantum Plasmonics. *Nano Lett.* **2015**, *15* (9), 6267.
- (2) Yu, W. W.; Qu, L.; Guo, W.; Peng, X. Experimental Determination of the Extinction Coefficient of CdTe, CdSe, and CdS Nanocrystals. *Chem. Mater.* **2003**, *15* (14), 2854.
- (3) Reiss, P.; Bleuse, J.; Pron, A. Highly Luminescent CdSe/ZnSe Core/Shell Nanocrystals of Low Size Dispersion. *Nano Lett.* **2002**, *2* (7), 781.
- (4) Boldt, K.; Kirkwood, N.; Beane, G. A.; Mulvaney, P. Synthesis of Highly Luminescent and Photo-Stable, Graded Shell CdSe/Cd X Zn 1– X S Nanoparticles by In Situ Alloying. *Chem. Mater.* **2013**, *25* (23), 4731.
- (5) Bae, W. K.; Char, K.; Hur, H.; Lee, S. Single-Step Synthesis of Quantum Dots with Chemical Composition Gradients. *Chem. Mater.* **2008**, *20* (2), 531.
- (6) Lee, K.-H.; Lee, J.-H.; Song, W.-S.; Ko, H.; Lee, C.; Lee, J.-H.; Yang, H. Highly Efficient, Color-Pure, Color-Stable Blue Quantum Dot Light-Emitting Devices. *ACS Nano* **2013**, *7* (8), 7295.
- (7) Lessel, M.; Bäumchen, O.; Klos, M.; Hähl, H.; Fetzer, R.; Paulus, M.; Seemann, R.; Jacobs, K. Self-Assembled Silane Monolayers: An Efficient Step-by-Step Recipe for High-Quality, Low Energy Surfaces. *Surf. Interface Anal.* **2015**, *47* (5), 557.
- (8) Diroll, B. T.; Gauding, E. A.; Kagan, C. R.; Murray, C. B. Spectrally-Resolved Dielectric Functions of Solution-Cast Quantum Dot Thin Films. *Chem. Mater.* **2015**, *27* (18), 6463.