Direct Patterning of Colloidal Quantum Dots with Adaptable Dual-Ligand Surface

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Abstract

Colloidal quantum dots (QDs) stand at the forefront of a variety of photonic applications given their narrow spectral bandwidth and near-unity luminescence efficiency. Integrating desired forms of QD films into photonic systems without compromising their optical or transport characteristics is the key to bridging the gap between expectations and outcomes. Here, we devise a dual-ligand passivation system comprising photocrosslinkable ligands and dispersing ligands to enable QDs to be universally compatible with solution-based patterning techniques. The successful control on the structure of both ligands allows multiscale, direct patterning of the dual-ligand QDs on various substrates via commercialized photolithography (i-line) or inkjet printing systems without compromising the optical properties of QDs or the optoelectronic performances of the devices implementing them. Our approach offers a versatile way of creating various structures of luminescent QDs in a cost-effective and non-destructive manner, and thus enables the implementation of QDs in a range of photonic applications.

Main

Colloidal quantum dots (QDs) are promising materials for use in next-generation light sources due to their wide-ranging bandgap tunability, narrow spectral bandwidths, and near-unity luminescence quantum yields (QY)\(^1\)–\(^5\). Together with the capability of cost-effective solution processing, QDs have become the key light-emissive materials for information displays\(^3\),\(^5\)–\(^7\). The patterned QD down-conversion layer on blue light-emitting diodes (LEDs) renders high-color reproduction and ultra-high image quality in full-color displays\(^8\),\(^9\). Likewise, a laterally patterned array consisting of red, green, and blue (RGB) QD-LEDs, in which QDs convert electrically pumped charge carriers into photons, allows for excellent color gamut and brightness as well as light-weight, thin, and flexible form factors\(^10\)–\(^13\), which are suited for wearable near-eye displays for virtual reality (VR) and augmented reality (AR) devices. For these “mixed-reality” applications, the QD deposition process should enable the patterning of RGB QDs (or RG QDs along with the bank) into a few micrometer sub-pixels over a large area with high-precision and high-fidelity\(^14\),\(^15\). At the same time, the process should not disrupt the optical and transport characteristics of QDs and adjacent functional layers. Moreover, from a practical standpoint, it poses great benefit if one can use equipment that are already deployed in display device manufacturing steps for the patterning process. Thus, there is a clear need for a method that enables non-destructive direct patterning of QDs via photolithography.

Photolithography is a well-established fabrication process to create micro to sub-micrometer-scale patterns over a large area on desired substrates. Conventional photolithography employs a photopatternable polymer layer, i.e., a photoresist (PR), that serves as a masking layer in forming QD patterns underneath\(^16\)–\(^19\). However, the solution-processing for PR deposition and development could damage the underlying QD layers\(^16\),\(^17\). Moreover, already-patterned QD layers can readily dissolve while processing the subsequent QD layer, as the patterning process must be carried out at least three times to get the true tone of RGB images. Without ensuring the structural robustness of QD patterns already in place,
conventional PR-based photolithography cannot yield high-resolution full-color QD-LEDs. Direct photolithography, a method in which light exposure directly induces solubility change in QD layers, is considered as an effective solution to mitigate the aforementioned issues\textsuperscript{11,20–23}. Several approaches have been proposed, such as the detachment or decomposition of ligands upon UV irradiation\textsuperscript{20–23}. Yet, corrosive chemicals (e.g., acid) are produced as by-products from these reactions, deteriorating the luminescence efficiency of QDs\textsuperscript{20,22}. Alternatively, azide group-containing photoactive crosslinkable additives can form relatively benign direct chemical bonds to the aliphatic ligands of neighboring QDs\textsuperscript{11}. However, the addition of electrically insulating crosslinker molecules can impair the transport properties of QD films and hence lower their electroluminescence performance.

Herein, we offer a simple and versatile approach for the non-destructive direct patterning of QDs within standard microfabrication systems. Specifically, we design and synthesize QDs passivated with dual-ligands consisting of photocrosslinkable ligands (referred to as PXLs throughout the rest of this manuscript) and dispersing ligands (referred to as DLs). PXLs are structurally engineered molecular scaffolds that construct covalent bonds with neighboring ligands in response to UV-A irradiation, enabling high throughput QD patterning without compromising their optical properties. The freedom to modify DLs confers solvent versatility, allowing the present approach to be compatible with nearly any solution processing techniques including spin-coating and inkjet printing. Using dual-ligands QDs, we demonstrate fine QD patterns (up to 15,000 pixels per inch (ppi)), which can be applied to the light-emissive layers of down-conversion and electroluminescent devices, and assess the feasibility of the present approach for use in state-of-the-art photonic devices.

The technological advances in QD-based display devices depend on the precision and reliability with which multicolor QD pixels are patterned on a substrate over a large area. Inarguably, the most important and challenging requirement is that the patterning process should not compromise the optical or electrical properties of QDs. Current QD patterning methods include transfer printing\textsuperscript{12,13,24–26}, inkjet printing\textsuperscript{18,27–32} and photolithographic patterning\textsuperscript{11,16–22}. Transfer printing can only cover small area patterns (typically, less than 1 cm\textsuperscript{2}), and standard instruments for its use have yet to be developed. Inkjet printing is effective only for low resolution patterns (500 ppi at most with an assist of bank) due to feature size limitations (at least 25–30 µm in diameter) of ejected drops. Photolithography is a promising approach to realize QD patterns in high-definition over a large area, as the process can take advantage of equipment currently used in microelectronics fabrication facilities. However, conventional photolithography makes use of photoresists and photoinitiators, which can deteriorate the optical and electrical properties of QDs.

Here we devise QD materials that can be processed via photolithographic processes without the presence of photoresists and photoinitiators. Specifically, the surface of QDs is functionalized with the photocrosslinkable ligands (PXLs) and the dispersing ligands (DLs) (Fig. 1). PXLs are linear organic compounds that hold a thiol anchor group (-SH) at one end and a benzophenone derivative at the other end (Fig. 1a,b and \textbf{Supplementary Fig. 1,2}). The thiolate end group of PXLs has a greater binding affinity
to the QD surface than that of oleate ligands\textsuperscript{33,34}. Therefore, PXLs can readily displace the native ligands of as-synthesized QDs at room temperature following the typical ligand exchange protocol (see Methods Section). The benzophenone derivatives on the other end of PXLs are well-known photo-responsive moieties that are extensively used for photo-initiators, photophysical probes, or photo-crosslinkers\textsuperscript{35–39}. Upon UV irradiation, the carbonyl group of benzophenone moiety transforms into ketyl radical by abstracting a hydrogen atom from a hydrocarbon group nearby (hydrogen abstraction) and creates a covalent bond between the ligands of neighboring QDs (Fig. 1c). The chemically crosslinked QD films are no longer dispersible when solvent is applied. Hence, we can achieve QD patterns by selective UV irradiation on QD films followed by development with good solvents (Fig. 1d,e). We note that only a fraction of PXL displacement, less than 10 mol\% of the entire bound ligands, is necessary for fully crosslinking in the QD film (Supplementary Fig. 3). Thus, we can control the solubility of QDs in different solvents by engineering the rest of the majority ligands (> 90 mol\%) (Fig. 1b).

Benzophenone has a relatively low absorbance in the UV-A (320–400 nm) region. Thus, there are significant limitations on its use with industrial standard light sources for optical lithography (i-line, peak wavelength = 365 nm). In order to boost the photosensitivity of PXLs to UV-A, we use reverse engineering to design the chemical structure of a benzophenone moiety via density functional theory (DFT) calculations (Fig. 2a,b, Supplementary Note 3 and Supplementary Fig. 1,2). Specifically, we substitute electron-donating groups (i.e., pyrrolidinyl (-N(CH\textsubscript{2})\textsubscript{4}), oxy (-O-), and thio (-S-)) to the para positions of benzophenone to increase the oscillator strength in the UV-A region. The electron-donating groups in place of hydrogen enhance the oscillator strength in the UV-A region of each PXL. The enhancement appears more pronounced with a stronger electron-donating substituent, and the effect is even more evident when two substituents are in place. For example, the extinction coefficient of PXL increases from 60 to 106 and 588 M\textsuperscript{-1}.cm\textsuperscript{-1} (at 365 nm) by substituting the -O- and -S- groups to the para position of benzophenone in replacement of a proton, respectively, and soars to $2.02 \times 10^4$ M\textsuperscript{-1}.cm\textsuperscript{-1} (at 365 nm) with -N(CH\textsubscript{2})\textsubscript{4} and -S- substituents at both para positions of benzophenone (Fig. 2b). PXLs with different substituents to benzophenone are denoted as O-BP, S-BP and NS-BP.

Because of the greater binding affinity of thiolates to the QD surface, PXLs could readily displace native oleate ligands with a graft yield (the ratio of the grafted versus added PXLs) above 80\% (Supplementary Fig. 4). The extent of grafted PXLs could be altered by varying the added content of PXLs. UV-Vis, FT-IR and \textsuperscript{1}H-NMR spectra of dual-ligand passivated QDs show the characteristic peaks of benzophenone moieties even after repeated purifications (Supplementary Fig. 5–8), indicating that PXLs are strongly bound on the surface of QDs. The small fraction PXL displacement under the mild reaction condition allows QDs to retain their photophysical characteristics throughout the ligand displacement procedure (Supplementary Fig. 9). Dual-ligand QDs with 7 mol\% PXLs are used for the subsequent experiments in the manuscript unless otherwise noted.

QD deposition followed by exposure to UV source results in chemically crosslinked QDs films. The degree of crosslinking is assessed by monitoring the changes made in absorbance of QD films after soaking the
films into the mother solvent used for QD deposition. Figure 2c summarizes the relative variations in the film absorbance for InP ($r = 1.2$ nm)/ZnSe$_x$S$_{1-x}$ ($h = 2.3$ nm) QD films crosslinked under different conditions, which we refer to as the film retention ratio. Due to their enhanced extinction coefficient, QD films bearing NS-BP could be completely crosslinked even under an exposure dose of $35$ mJ/cm$^2$, which corresponds to an exposure time of $1.4$ s under commercially available i-line light source (radiation power of $25$ mW/cm$^2$). Figure 2d contrasts the photochemical response of PXLs upon exposure to i-line light source. Even after dipping into the mother solvent for few minutes, NS-BP-decorated QD films barely dissolve, whereas other QD films are partially washed off upon brief contact with toluene.

The photophysical properties of QDs are preserved throughout the entire process of ligand exchange, photocrosslinking and development (Fig. 2e and Supplementary Fig. 10). The mild ligand displacement condition prevents the degradation of photoluminescence (PL) characteristics while grafting PXLs onto the surface of QDs. The quick photocrosslinking reaction with the lower energy photon source is benign enough to retain the photophysical properties of QDs. Specifically, a crosslinked NS-BP-decorated QD film with a film retention ratio greater than 0.95 could be readily obtained without compromising the photoluminescence quantum yield (PL QY), whereas substantial PL QY drops (24–26%) appear during photo-crosslinking processes in the cases of S-BP and O-BP (Fig. 2e). Control experiments under an inert atmosphere show that the reactive oxygen species generated under UV-A irradiation, rather than ketyl radicals, are responsible for the PL QY loss of QDs (Supplementary Fig. 11), implying that the UV irradiation time for photocrosslinking is critical to the optical quality of the QD patterns. By exploiting NS-BP-decorated RGB QDs with the minimal exposure to UV-A irradiation, the resulting crosslinked RGB QD films retain their morphology (Supplementary Fig. 12) as well as their photophysical properties (PL spectra and PL QY) throughout the entire photo-crosslinking and the rinsing steps under ambient conditions (Fig. 2e). We note that InP (radius, $r = 1.9$ nm)/ZnSe$_x$S$_{1-x}$ (shell thickness, $h = 3.2$ nm) QDs, InP ($r = 1.2$ nm)/ZnSe$_x$S$_{1-x}$ ($h = 2.3$ nm) QDs, and Cd$_x$Zn$_{1-x}$S ($r = 2.7$ nm)/ZnS ($h = 3.6$ nm) QDs are red (R), green (G) and blue (B) emitters used in this study, respectively (Supplementary Fig. 13 and Supplementary Table. 1).

We prepared QD photo-patterns in three steps: (i) QD deposition onto a substrate, (ii) selective UV irradiation (365 nm, 35 mJ/cm$^2$) through a patterned photomask, and (iii) removal of the uncrosslinked QDs using a proper solvent. The present approach using a conventional photolithography equipment (e.g., stepper or contact aligner) renders well-defined QD patterns of varying shapes and dimensions with high fidelity (Fig. 3a-e). Repeating the processes with red, green and blue QDs renders various color QD patterns. For example, the lateral deposition yields RGB QD patterns with a resolution greater than 7,000 ppi (Fig. 3b and Supplementary Fig. 14), which meets the requirement for near-eye hyper-realistic displays. The vertical stacks of QD patterns enable RGB primary color combinations that can express multiple colors, including yellow, cyan, and magenta and ultimately full-color images after the delicate pixel design (Fig. 3c-e and Supplementary Fig. 15).
The present approach demands PXLs with less than 10 mol% of surface ligands, and thus the solubility of QDs is still dictated by the remaining ligands. This implies that structural engineering of the rest of DLs into ones containing polar (i.e., mono-2-(methacryloyloxy)ethyl succinate (MMES)) or fluorinated tails (i.e., 4-(trifluoromethyl)benzenethiolate (TFMBT)) permits dual-ligand QDs to be processed with solvents of different polarities across polar organic solvents (e.g., propylene glycol methyl ether acetate (PGMEA) or diethylene glycol monoethyl ether acetate (DGMEA)) and fluorinated solvents (e.g., trifluorotoluene (TFT)), as exemplified in Fig. 3f and Supplementary Fig. 16,17. The present approach renders hetero-ligand QDs into a desired solvent that even PXL itself can barely dissolve in (i.e., hexane, PGMEA, DGMEA, and TFT). This clearly contrasts to the previous approaches recruiting crosslinkable polymeric ligands or additives, wherein the solubility of QD dispersions for crosslinking is restricted to the solubility of the crosslinkable agents.

Importantly, the versatility in controlling the solvent media offers extensive compatibility of our ligand engineered QDs with nearly any solution processing methods. For instance, the dual-ligand passivated QDs can readily integrate with inkjet printing, which is a low-cost, large-area, and non-vacuum process capable of depositing micrometer-scale patterns without needless waste of materials. The fluidic characteristics of inks (i.e., viscosity, surface tension, density, and inertia force) should meet the criteria for inkjet printing in regard to the minimal volume of ink droplets and the uniformity of the deposited films. We accomplish well-defined QD ink droplets by means of the ligand engineering and solvent optimization (MMES for the dispersion ligand and PGMEA/DGMEA co-solvent (PGMEA : DGMEA = 40 : 60 vol. %) that produce clear QD patterns via inkjet printing (Fig. 3g). A short period of UV irradiation onto the printed patterns confers structural robustness to the pre-deposited QD patterns against exposure to subsequent solution processes, enabling the assembly of multiple functional materials with well-defined interfaces. The process orthogonality eliminates the color blurring effect at the crossings of patterns, and each pattern is clearly represented by its own color (Fig. 3h and Supplementary Fig. 18).

The present approach avoids changes in the transport characteristics of charge carriers as it does not involve additional photocrosslinkable agents, which are typically electrical insulators, nor does it expand the effective ligand length. We compare electron and hole transport from neighboring charge transport layers into pristine versus photocrosslinked CdSe \( (r = 2.5 \text{ nm})/\text{Cd}_{x}\text{Zn}_{1-x}\text{Se}/\text{ZnSe}_{y}\text{S}_{1-y} \) \( (h = 8.0 \text{ nm}) \), CdSe \( (r = 2.0 \text{ nm})/\text{Cd}_{x}\text{Zn}_{1-x}\text{Se}/\text{ZnSe}_{y}\text{S}_{1-y} \) \( (h = 7.7 \text{ nm}) \) and InP \( (r = 1.9 \text{ nm})/\text{ZnSe}_{x}\text{S}_{1-x} \) \( (h = 3.2 \text{ nm}) \) QD films in the electron-only device and the hole-only device, respectively (Fig. 4a and Supplementary Fig. 19).

Notable differences are not observed in the current density–voltage characteristics for both devices, indicating that photocrosslinking with PXLs does not impair the transport characteristics of the devices implementing them. The optical properties of QD films and electrical characteristics of devices are well-preserved throughout the implantation of PXLs and the photocrosslinking steps, allowing us to fully exploit the performance of optoelectronic devices employing QDs. Figure 4b,c demonstrate the optoelectronic characteristics of light-emitting diodes implementing the QD film as the emissive layer. Nearly identical electrical and optoelectronic performances are observed for QD-LEDs with pristine QD
films or photocrosslinked QD films (Fig. 4c and Supplementary Fig. 20). As device performance is determined by electron versus hole injection balance in QDs and the charge to photon conversion efficiency, these results confirm that the photochemical reaction of PXLs does not leave electrical or optical defects either at QDs or at neighboring charge transport layers. These results demonstrate the effectiveness of the present approach in nearly all photonic applications employing QDs. Finally, we use our approach to create passive matrix driven RGB QD-LED arrays by positioning photopatterned RGB QD films between common charge transport layers and patterned electrodes (Fig. 4d-h, Supplementary Video 1 and Supplementary Fig. 21).

The use of dual-ligand QDs is not limited to PR-free, direct QD patterning, but can also be used in conventional photopatterning methods. For instance, state-of-the-art displays employ submicron to micron thick, photo-emissive red and green QD patterns directly on blue-emitting organic light-emitting devices (OLEDs), which demands a rather stringent QD patterning process capable of being conducted at low temperature (below 100 °C) in order to prevent OLEDs from thermal damage. NS-BP-decorated QDs blended with transparent polymeric resins can be photocrosslinked by a low energy UV light source (i-line) with a higher penetration depth, which are suited for attaining micrometer-thick fine QD patterns for full color QD-OLED displays (Supplementary Note 4 and Supplementary Fig. 22).

In summary, a non-destructive, adaptive approach for direct pattering of luminescent QDs has been demonstrated. We have devised dual-ligand QDs consisting of photocrosslinkable ligands and dispersing ligands. We demonstrate that we can perform structural engineering on both ligands to integrate seamlessly into the industrial standard microfabrication processes. Structural engineering on a photoreactive benzophenone moiety boosts the photochemical responsivity of PXLs to low energy UV light sources, while the polarity control of dispersing ligands confers solvent versatility. We successfully create well-defined multicolored QD patterns with commercialized photolithography or inkjet printing systems at no cost to the optical or electrical properties of QDs. In addition, we test these photocrosslinked QDs in state-of-the-art displays. Our approach offers a versatile way of creating various structures of luminescent QDs in a cost-effective and non-destructive manner, and thus fosters the practicable use of QDs in a range of photonic applications.

Methods

Synthesis of quantum dots. InP/ZnSe$_x$S$_{1-x}$ QDs were synthesized as detailed previously$^{46,47}$ with minor modifications. For green-emitting InP/ZnSe$_x$S$_{1-x}$ QDs, a round bottom (RB) flask containing 5 mmol of zinc oleate (Zn(OA)$_2$) and 10 ml of tri-n-octylamine were degassed at 110 °C for 1 hour, back-filled with argon and heated to 180 °C. 100 mg of InP cores with radius of 1.2 nm was added into the flask, followed by adding 1.5 ml of 2M Se precursor dissolved in tri-n-octylphosphine. The temperature was elevated to 320 °C and kept for 2 hours to proceed ZnSe inner shell growth. 15 mmol of Zn(OA)$_2$ precursor and 8.5 mmol of 2M S precursor dissolved in tri-n-octylphosphine were injected to the flask, and reacted for 3 hours to grow ZnS outer shell. Synthesized QDs were purified repeatedly via precipitation
(ethanol)/redispersion (toluene) method before use. Larger InP cores (r = 1.9 nm) produced with a synthetic procedure yielded red-emitting InP/ZnSe\textsubscript{x}S\textsubscript{1-x} QDs. Chemicals, synthetic procedures, and structural and photophysical characteristics for all QDs of the present study are detailed in the Supplementary Information.

**Synthesis of photocrosslinkable ligands (NS-BP).** 4,4'-difluorobenzophenone (20 g), 2-pyrrolidone (6.52 g), and 200 ml of anhydrous DMSO were loaded in a flame dried RB flask and heated to 60 °C for 8 hours under an argon atmosphere. The mixture was cooled to room temperature and quenched with deionized water. The resulting precipitate was collected by filtration and recrystallized with a mixture of acetone and ethanol to acquire the intermediate product. 15 g of the intermediate product was added to an RB flask containing 1,10-decanedithiol (19.2 g), K\textsubscript{2}CO\textsubscript{3} (15.4 g) and 70 ml of anhydrous DMF. The reaction flask was heated to 60 °C and kept overnight. The precipitate was collected after precipitation with deionized water. The solid was dissolved into ethyl acetate, and the impurity was removed through filtration. The filtrate was concentrated under reduced pressure and the residue was purified by recrystallization to give NS-BP as an off-white solid. Chemicals, synthetic procedures and characteristics for O-BP and S-BP are detailed in the Supplementary Information.

\[ ^1H \text{NMR (δ ppm; CDCl}_3, 500 MHz): 7.76 (d, 2H), 7.63 (d, 2H), 7.30 (d, 2H), 6.52 (d, 2H), 3.36 (t, 4H), 2.96 (t, 2H), 2.49 (q, 2H), 2.03 (t, 4H), 1.69 ~ 1.24 (m, 17H). \]

**Graft of photocrosslinkable ligands onto QDs.** To decorate PXLs onto the surface of oleic acid (OA)-capped QDs, an adequate amount of PXL solution dissolved in chloroform was added dropwise into 100 mg of OA-capped QD dispersion (50 mg/ml, chloroform) under rigorous stirring. After an hour of ligand exchange reaction, the resulting dual-ligand QDs were purified repeatedly via the precipitation (ethanol)/redispersion (toluene) method. The dual-ligand QDs were finally redispersed in desired non-polar organic solvents. To obtain dual-ligand QDs dispersed in polar organic solvents (i.e., PGMEA or DGMEA) or fluorinated solvent (i.e., TFT), native oleate ligands were displaced to MMES or TFMBT prior to PXL decoration. Typically, 100 mg of QD powder and an excess amount of DLs (MMES or TFMBT) were stirred in PGMEA (or DGMEA) or TFT until it turned to a clear solution. The final products were purified via the precipitation/redispersion method before use.

**Photolithography.** Photolithography was performed using a mask aligner (MA6, Karl Suss) or an i-line stepper (Nikon NSR2205i11D). First, substrates were cleaned with acetone and isopropyl alcohol in an ultrasonic bath for 15 min each. Then, 20 mg/ml of dual-ligand QD dispersions (toluene) were spin-coated at 4000 rpm for 30 sec. The resulting films were irradiated with a UV-light source built in the mask aligner (UV-A, 20 mW/cm\textsuperscript{2}) through a patterned photomask or the stepper set-up (365 nm, 500 mW/cm\textsuperscript{2}) through a reticle to crosslink the irradiated region of QD layer. After the irradiation process, the films were developed by removing the un-crosslinked layer of the films with proper solvents (i.e., toluene). Photolithographic processes were repeated with red-, green- and blue-emitting QD dispersions to realize full color images.
**Inkjet printing.** 80 mg/ml of NS-BP-decorated QD dispersion was prepared in a mixed solution of PGMEA and DGMEA (2:3 in volume). The inkjet printing was performed using a piezoelectric inkjet printer (OmniJet300, Unijet Corp.). Cartridge-type multi-nozzles with a diameter of 10 µm (Dimatix Corp.) were used to eject the QD inks. The dual-ligand QD inks were printed with a drop velocity of 3 m/s, a drop frequency of 3 kHz, and a drop spacing of 30 µm by maintaining the substrate temperature at room temperature in ambient.

**Device fabrication.** All solution process were taken under an inert N$_2$-filled glovebox. For QD-LED fabrication, glass substrates pre-patterned with indium tin oxide (ITO, 150 nm) electrodes (sheet resistance under 15 Ω/square) were first cleaned with isopropyl alcohol, acetone, and deionized water in an ultrasonic bath for 15 min each. These substrates were spun-cast (2000 rpm for 30 sec) by Zn$_{0.95}$Mg$_{0.05}$O (20 mg/ml in ethanol) followed by thermal annealing at 75°C for 30 min. QD films (30 nm) were deposited on the ZnMgO/ITO films by spin-casting QD dispersion (20 mg/ml in toluene) at 4000 rpm for 30 sec followed by thermal annealing at 80°C for 30 min. Later, QD/ZnMgO/ITO films were loaded into a high-vacuum deposition chamber (pressure of ~ $10^{-7}$ torr). Lastly, CBP (60 nm), MoO$_x$ (10 nm), and Al (130 nm) were thermally evaporated on top of QD/ZnMgO/ITO films at deposition rate of 1.0, 0.1–0.2, and 2.0–3.0 Å/s, respectively. For 10 × 10 RGB pixel array, RGB QD solution (10 mg/ml in toluene) were spun-cast (4000 rpm for 30 sec) and photo-patterned side by side to be placed between 30 vertical lines of sputtered ITO with sub-pixel pitch of 0.3 mm and 10 horizontal line patterns of thermally deposited Al.

**Characterization.** Absorption and photoluminescence spectra of QD solutions were obtained with Shimadzu UV-1800 and Horiba FluoroMax-4, respectively. Absolute PL QY of QD samples was measured with the Otsuka QE-2000. The measurements to characterize the PL decay dynamics were conducted with time-correlated single-photon counting (TCSPC) system from Picoquant (HydraHarp 400) and detected with single-photon avalanche photodiodes (PDM Series, Micro Photon Devices) having a 200 ps time resolution. The QD samples were excited at 2.6 eV to prevent an excitation laser from absorbed by PXLs. The laser repetition rate of 1 MHz is selected to be slower than the PL decay rate of the samples to allow for complete relaxation of QDs between sequential laser pulses. $^1$H-NMR was measured by a Varian UNITY INOVA 500 spectrometer (Agilent Technologies, Inc.) with deuterated chloroform (CDCl$_3$) as solvent. FT-IR spectra were collected in an attenuated total reflection (ATR) mode under ambient conditions using an IRTracer-100 (Shimadzu Corporation). Transmission Electron Microscope (TEM) images were measured by JEM-2100 (JEOL Ltd) installed at the National Center for Inter-university Research Facilities (NCIRF) at Seoul National University. Scanning Electron Microscope (SEM) images were measured by S-4800 (Hitachi). AFM images were taken with a XE150 (Park Systems) under ambient conditions in non-contact mode installed at the Korea Advanced Nano Fab Center (KANC). Fluorescent images of patterned QD films were measured by a fluorescence microscope (Nikon eclipse Ti2) equipped with a multi-sensor CCD camera (01-MP3.3-RTV-R-CLR-10-C, Q-Imaging) and CMOS camera (C2CMOS05100KPB, AMDSP). Low magnification images were measured by a long-working-distance microscope (AM7915MZTL, Dino-Lite).
Declarations

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Authors contributions
D.H., J.L., H.K., C.K., M.S.K. and W.K.B. conceived the original idea and designed the experiments. D.H., J.L., J.H.C., Y.S.P. and D.C.L. conducted synthesis and characterization of QD and analyzed the spectroscopic data. D.H., J.M., H.K., J.-W.S., J.Y., C.H.L. and C.K. prepared dual-ligand QDs and carried out the patterning experiment and thin film characterization. S.H. and S.C. conducted inkjet printing and characterization. B.C. and E.H. carried out the computational calculation. J.-W.S., S.R. and C.K. fabricated all devices and analyzed the data. All authors contributed to the preparation of the paper.

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Competing financial interests
The authors declare no competing interests.

Data availability. The authors declare that all data supporting this work are contained in graphics displayed in the main text or in Supplementary Information. Correspondence and requests for materials should be addressed to corresponding authors.

Supplementary information
Supplementary Information
Supplementary Notes 1-4, Figs. 1-22, Table 1, Caption for Supplementary Video 1 and References.

**Supplementary Video 1**

**Electroluminescence of 10 × 10 RGB QD-LED arrays implementing photocrosslinked QD patterns.** Real time movie of light emission from each primary color 10 × 10 QD-LED arrays and RGB QD-LED arrays.

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Figures
Figure 1

Concept of direct patterning with dual-ligand QDs. (a) Chemical structure of photocrosslinkable ligands (PXLs). Pyrrolidinyl (-N(CH$_2$)$_4$), oxy (-O-), and thio (-S-) groups are at the para positions of benzophenone to modulate its photochemical properties. (b) Schematic illustration of dual-ligand QDs. Addition of 1-10 mol% PXLs turns QD films crosslinkable upon UV irradiation. The dispersing ligands (DLs) (> 90 mol%) determine the solubility of QDs. (c) Schematics illustrating the photocrosslinking between dual-ligand QDs. (d) Fluorescent images (top) and a schematic description of laterally pixelated and stacked RGB QD patterns (bottom) that are fabricated using dual-ligand RGB QDs. Scale bars indicate 200 μm. (e) A photograph of RGB QD patterns on a 6-inch silicon wafer attained by consecutive photolithographic QD patterning processes using an i-line stepper.
Figure 2

Structurally engineered PXLs for non-destructive QD photocrosslink. (a) Chemical structures of benzophenone and PXLs with different chemical substitutions to the para positions of benzophenone (NS-BP, S-BP, and O-BP). Prefixes (O-, S- and NS-) indicate chemical elements substituted to benzophenone. (b) Molar extinction spectra for PXLs and the unsubstituted benzophenone. Inset: semi-log plots of molar extinction spectra for PXLs and the unsubstituted benzophenone between 300-450 nm. (c) Exposure dose-dependent film retention ratios and (d) fluorescent images of QD films having different PXLs (all films are exposed to UV with an exposure dose of 630 mJ/cm$^2$ and rinsed with toluene). Scale bars indicate 50 μm. (e) Normalized PL QYs of QD films (film retention ratio > 0.9) employing different PXLs after the photo-crosslinking and the rinsing steps under ambient condition. Exposure dose-dependent changes of PL QY of QD films exposed to different wavelengths of UV sources (i.e., 365 nm (blue) and 254 nm (purple)) are overlaid for comparison. (f) PL spectra of photocrosslinked RGB QD films with NS-BP InP (core radius ($r$) = 1.9 nm)/ZnSe$_x$S$_{1-x}$ (shell thickness ($h$) = 3.2 nm) QDs, InP ($r$ = 1.2 nm)/ZnSe$_x$S$_{1-x}$ ($h$ = 2.3 nm) QDs, and Cd$_x$Zn$_{1-x}$S ($r$ = 2.7 nm)/ZnS ($h$ = 3.6 nm) QDs are adopted for red, green and blue emitters, respectively. The fixed amount of PXLs (7 mol%) is grafted to each colored QDs. All QD films are exposed to UV-A (365 nm, exposure dose = 35 mJ/cm$^2$). PXL synthesis and photocrosslink test are detailed in Methods Section and Supplementary Information.
Figure 3

Multi-colored patterns made of dual-ligand QDs. (a) Fluorescent image (left, top), SEM image (left, bottom), and AFM image (right, top) and its height profile (right, bottom) of QD line patterns (width = 3.6 μm, spacing = 6.6 μm) obtained from a single photolithographic process using an i-line stepper. Line-edge roughness (LER) and linewidth roughness (LWR) are estimated to be 74 nm and 99 nm, respectively. Scale bars indicate 10 μm. (b) Fluorescent images of RGB QD patterns obtained after consecutive photolithographic processes of primary colored QDs using an i-line stepper. Scale bars indicate 10 μm.
The dimensions of sub-pixels are $3.8 \times 3.8 \, \mu m^2$ (left), $1.8 \times 1.8 \, \mu m^2$ (right, top) and $0.8 \times 0.8 \, \mu m^2$ (right, bottom), which correspond to a resolution of 3,342 ppi (left), 7,056 ppi (right, top) and 15,875 ppi (right, bottom), respectively. (c-e) Fluorescent images composed of laterally positioned and vertically stacked RGB QD patterns obtained with a contact aligner$^{40}$. Fig. 3d is a magnified view of the marked square in Fig. 3c. Scale bars indicate 1 mm for Fig. 3c and the left side of Fig. 3e, and 200 µm for Fig. 3d and the right side of Fig. 3e. (f) A photograph of dual-ligand RGB QD dispersions in TFT, PGMEA and hexane. OA, MMES, and TFMBT are DLs to render QDs dispersed in TFT, PGMEA and hexane, respectively. (g) A series of images showing an ejected droplet including dual-ligand QDs with a time interval of 14 µs. (h) Fluorescent images of inkjet-printed RGB cross-line patterns attained with photocrosslinked QDs (top, left) versus pristine QDs (top, right). The PL intensity profiles across the noted green lines are shown (bottom). Scale bars indicate 1 mm. Materials and experimental procedures are detailed in Methods Section and Supplementary Information.
Optoelectronic devices implementing photocrosslinked QD patterns. (a) Current density–voltage characteristics of an electron-only device (left) and a hole-only device (right) implementing photocrosslinked QD films. (b) Schematic illustrations of device architecture (top) and energy band diagram (bottom) and (c) current density dependent external quantum efficiencies (EQEs) of QD-LED implementing photocrosslinked QD films. Device characteristics with pristine QDs (oleic acids only) are shown for comparison. Inset: a photograph of operating QD-LED. (d) Schematics illustrating passive matrix driven 10 × 10 RGB QD-LED arrays. (e) A cross-sectional scheme and (f) associated electric circuit of RGB pixels. Electroluminescent images of (g) 10 × 10 RGB QD-LED arrays and (h) each primary color QD-LED arrays. Scale bars indicate 2 mm. Device fabrication and characterization methods are detailed in the Methods Section.

**Supplementary Files**

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