

## REVIEW ARTICLE

# Contact printing of colloidal nanocrystal thin films for hybrid organic/quantum dot optoelectronic devices

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## Abstract

Novel thin film optoelectronic devices containing both inorganic colloidal semiconductor quantum dots (QDs) and organic semiconductor thin films have been widely investigated in recent years for a variety of applications. Here, we review one of the most versatile and successful methods developed to integrate these two dissimilar material classes into a functional multilayered device: contact printing of colloidal QD films. Experimental details regarding the contact printing process are outlined, and the key advantages of this QD deposition method over other commonly encountered techniques are discussed. The use of tapping mode atomic force microscopy (AFM) to effectively characterize QD film morphology both on an elastomeric stamp (before contact printing) and as-transferred to the organic semiconductor receiving film (after contact printing) is also described. Finally, we offer suggestions for future efforts directed toward the goal of rapid, continuous QD deposition over larger substrates for the advancement of hybrid optoelectronic thin film devices.

Keywords: *QD; monolayer; stamp; deposition; LED; organic semiconductor*

Colloidal semiconductor nanocrystals, or quantum dots (QDs), are currently being investigated for possible application in a variety of thin film optoelectronic devices, including solar cells (1–3), photodetectors (4–7), and light-emitting devices (LEDs) (8–31). These novel devices typically feature a stratified architecture, containing a combination of organic or inorganic semiconductor thin films in addition to one or more mono- or multilayers of QDs between two conductive electrodes. Hybrid organic/QD devices containing



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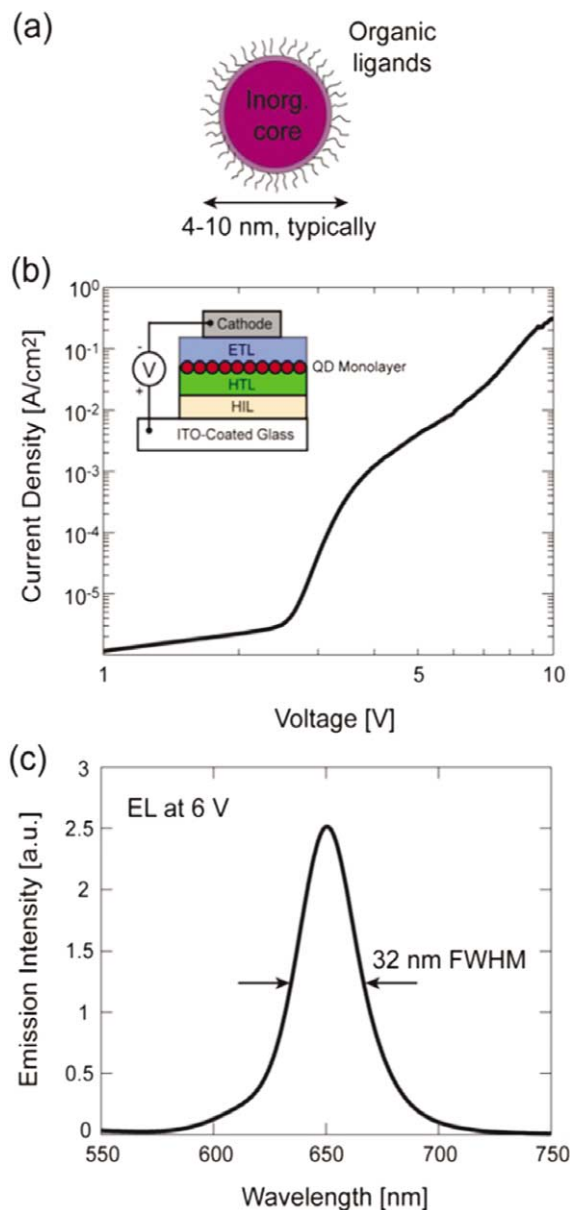


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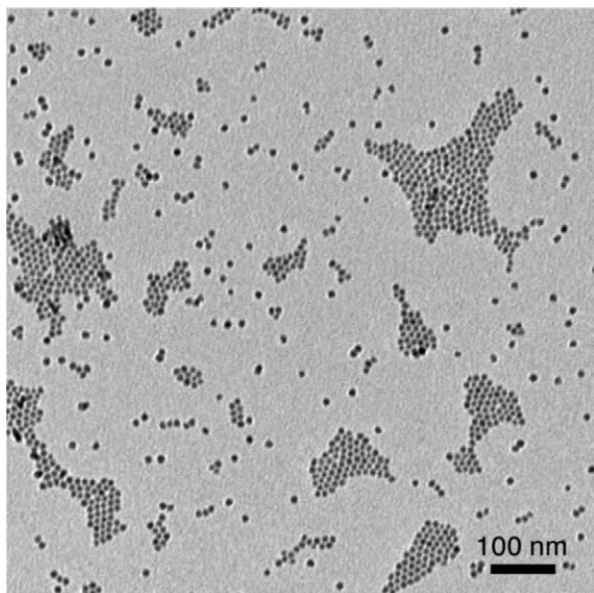
blended active layers have also been explored (32–35). QDs themselves are precisely tailored hybrid nanostructures, comprising inorganic semiconductor nanocrystals (approximately 2 nm to 10 nm in diameter) surrounded by organic surfactant molecules, as seen in Fig. 1a. The organic surfactants (ligands) serve to stabilize QD growth during their solution phase synthesis from organometallic precursors, and they also prevent the flocculation of QD colloidal suspensions in common solvents under ambient conditions. A highly monodisperse population of colloidal nanocrystals can be obtained, as shown in Fig. 2.

Favorable optoelectronic properties of QDs stem directly from their small size through quantum confinement effects. These include strong optical absorption, narrow-band optical emission, and color-tunability across the visible and near-infrared regions of the electromagnetic spectrum. A wide band gap inorganic shell is often grown surrounding the QD core to further enhance exciton confinement and chemically stabilize the QDs by passivating dangling bond states on the QD core surface. Recently, a comprehensive review of QD properties, synthetic approaches, and application in optoelectronic devices was provided by Talapin et al. (36). To date, the primary strength of QDs has been found in their optical properties. Colloidal QD suspensions can display greater than 90% photoluminescence quantum yield with negligible photobleaching (36), and electrically driven QD-LEDs have demonstrated both saturated colors (9–11, 17, 18, 25, 28, 30, 31) as well as white light emission (8, 24, 26, 29) from films of highly monodisperse QDs. Figures 1b, c show the current-voltage and electroluminescence spectral data measured simultaneously for a red-emitting (peak wavelength,  $\lambda_{\text{max}} = 650$  nm) hybrid QD-LED structure comprised of organic hole transport (HTL) and electron transport layers (ETL) surrounding a QD monolayer. The operating mechanisms behind this type of device structure are shown to include a combination of direct charge carrier injection and Förster energy transfer (9, 20).

Notably, since the ligands surrounding each QD are electronically insulating, a QD emissive layer that is more than two monolayers thick can present significant electrical resistance to charge carrier transport in the vertical direction (i.e. between the two electrodes shown in the inset of Fig. 1(b)). Conversely, sub-monolayer QD films can result in additional blue-shifted (and broadband) emission peaks due to an excess of excitons formed within the organic layers. Therefore, close-packed QD monolayers have become the standard for achieving low voltage, high efficiency hybrid LED structures with narrowband emission spectra attributed solely to the QD lumophores. The challenge of reducing QD-to-QD electrical resistance in thicker, multilayer films (as may be required for QD-based solar cells or photodetectors to



**Fig. 1.** (a) Cross-sectional drawing of a colloidal quantum dot (QD), showing an inorganic semiconductor core (e.g. CdSe, PbS, or CdSe/ZnS core/shell) surrounded by a coating of organic ligands (e.g. trioctylphosphine, oleic acid) that provide solubility and colloidal stability in organic solvents. (b) Typical current density-voltage characteristic for a hybrid organic/QD light-emitting device (QD-LED) structure; visible light emission is observed around 3 V for this device. Inset: cross-sectional QD-LED device architecture (not to scale); ITO = indium tin oxide, HIL = hole injection layer, HTL = hole transport layer, ETL = electron transport layer. (c) Electroluminescence (EL) spectrum for a red-emitting ZnCdSe QD-containing hybrid LED at 6V applied bias. The single narrowband emission peak (32 nm full width at half maximum, FWHM) is due to radiative recombination of QD excitons.



*Fig. 2.* Transmission electron micrograph of highly monodisperse colloidal ZnCdSe quantum dots with an average nanocrystal diameter of approximately 9 nm.

provide sufficient light absorption) is substantial, and remains the focus of intense research efforts (36).

The remainder of this review will focus on two important issues related to QD-based optoelectronic device development: (1) How can a close-packed QD monolayer be effectively incorporated between two fragile organic molecular charge transport layers (as in the QD-LED structure shown in the inset of Fig. 1b), given that the QDs originate from a solvent-based suspension?, and (2) How can both the lateral uniformity and vertical positioning of a QD monolayer within such a device structure be characterized at the nanoscale?

### Methods for integrating QD monolayers inside hybrid devices

One of the much-heralded advantages of QDs for optoelectronic devices is their ability to be processed using common organic solvents at ambient temperature and pressure. By eliminating the substantial energy requirements of maintaining a high vacuum or elevated temperature, one can imagine the possibility to rapidly and economically deposit large area films of QDs from colloidal suspension – even on top of flexible plastic substrates – much like a layer of ink or paint. Today, on the research laboratory scale (where device areas are commonly of order  $\sim 1$  cm<sup>2</sup>), there are at least five primary methods used to deposit QD layers inside organic/QD hybrid structures: spin-coating (12, 21–23, 27, 29–31), solution self-assembly (dipcoating) (11, 16), inkjet printing (17), phase separation (13–15), and contact printing (9, 10, 18, 19, 25, 26, 28). The first three methods

require the exposure of a previously-deposited organic semiconductor thin film directly to the colloidal QD suspension solvent, and therefore will be of little practical use if this solvent will chemically dissolve and/or physically wash away a portion of the underlying organic film. Dense polymer films that exhibit chemical orthogonality to the QD suspension solvent or are chemically cross-linked are a possible exception to this complication.

A major advancement in hybrid organic/QD-containing LED efficiencies was realized by the MIT group through the use of a fourth method, phase separation (13). Here, a suspension containing both a soluble organic molecular species as well as QDs is deposited onto a planar substrate either by spin-coating or other means. Chemical dissimilarity between aromatic organic semiconductor molecules (such as N,N'-bis(3-methylphenyl)-N,N'-bis(phenyl)benzidine, TPD) and typically aliphatic surfactant-capped QDs drives the spontaneous segregation of the two materials into a bilayered thin film upon evaporation of the co-solvent. A greater affinity for the underlying substrate and an ability to pack more densely on the substrate surface (due to their smaller size) are possible reasons for the observed vertical segregation, where the organic molecules form the bottom layer (next to the substrate) and the QDs rise to the top (next to the free surface). By adjusting the individual concentrations of organic semiconductor molecules and QDs in the suspension as well as the rotation speed used during spin-coating, the final layer thicknesses of each component in the deposited and dried, stratified film can be independently controlled. With an appropriate concentration of QDs in the suspension, a near perfect monolayer of QDs can be assembled by phase separation at the surface of the organic semiconductor film (15).

The most efficient QD-LEDs are fabricated via contact printing (10, 19). This method consists of inking an elastomeric stamp with a colloidal QD suspension to create a highly uniform monolayer of QDs on the stamp surface (typically by spin-coating a QD suspension onto the stamp) followed by mechanically contacting the QD-coated stamp with an organic thin film, which can result in an efficient transfer of the QD monolayer from the stamp to the LED device stack without exposing the organic film to any solvent. The two primary advantages of the contact printing method over other hybrid organic/QD device fabrication techniques are: (1) the organic films need not be exposed to solvent because the QD layer is first inked (and dried) on the stamp, and (2) appropriate conditions for inking the stamp with a uniform QD monolayer can be optimized separately from the deposition of the underlying organic film, facilitating QD monolayer deposition on any thickness film desired.

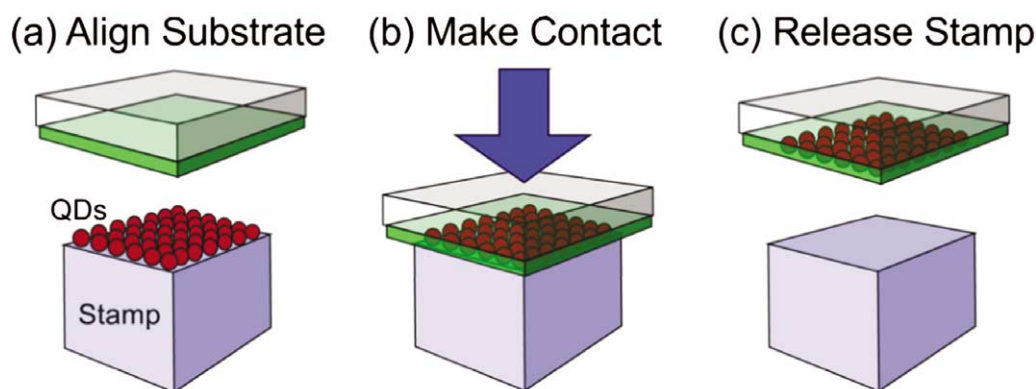
### Contact printing of colloidal QD films

Briefly, the procedure for contact printing QDs onto an organic semiconductor thin film involves: fabricating an elastomeric stamp, inking the stamp with a mono- or multilayer film of QDs (e.g. by spin-coating), transferring the dried QD layer from the stamp to a substrate coated with an organic thin film via mechanical contacting, and finally removing the stamp by peeling it apart from the substrate (Fig. 3). Each step in the process is described here briefly, although further details can be found elsewhere (18, 37, 38). The ubiquitous choice of elastomeric material for producing the stamps to date has been polydimethylsiloxane (PDMS), which can be easily produced with a commercially available two-part kit consisting of a base and curing agent (Sylgard<sup>®</sup> 184, Dow Corning). First, the base and curing agent are mixed well in a weight ratio of 10:1 (or 5:1 for firmer stamps), then the liquid mixture is degassed under vacuum for 30 min, poured into a shallow glass dish and cured either at 60 °C overnight or at room temperature for approximately one week. After the PDMS has been cured, individual stamps (approximately 1 × 1 cm) are cut out of the ~1 cm thick elastomeric film.

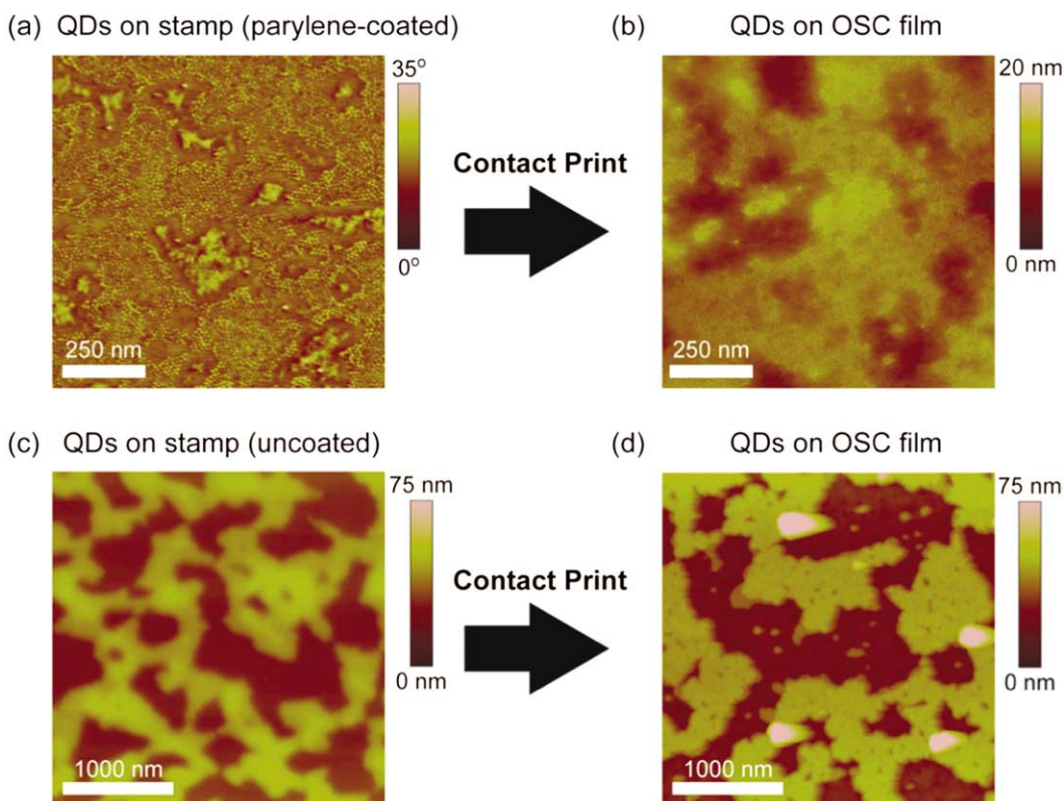
Importantly, the native PDMS surface is hydrophilic, resulting in poor wetting of ‘plain’ stamps by many organic solvents used to suspend QDs. In addition, once the solvent has dried (following spin-coating of the QD suspension on the stamp surface) QDs tend to pile up in islands rather than spread out in a uniform monolayer on bare PDMS due to their hydrophobic ligand coating. In order to promote better wetting of the stamps by both the organic solvents and aliphatic ligand-coated QDs, a thin film of parylene (poly(p-xylylene)) is deposited on the stamps via chemical vapor deposition to create an aromatic, hydrophobic surface. After the QD suspension has been spin-coated onto a stamp, a substrate carrying

the organic semiconductor (OSC) thin film (e.g. a glass substrate coated with indium tin oxide (ITO)/polystyrene sulfonate-doped poly(3,4-ethylenedioxythiophene) (PEDOT:PSS)/TPD, for building a QD-LED) is brought into physical contact with the QD-inked stamp by hand. Although a detailed study has not yet been performed, the amount of pressure used to mechanically contact the substrate with the inked stamp does not appear to significantly affect the morphology or transfer quality of the QD layer. Transfer of the QD layer to the OSC film upon separation of the stamp and substrate is presumed to proceed due to stronger energetic interactions between the QD ligands and the OSC film compared to the surface of the stamp. The (non-optimal) use of uncoated PDMS stamps can present an additional complication, as it has been demonstrated that bare PDMS can remove a portion – or the entirety – of the OSC film upon contact printing (39, 40).

Since QDs are coated in insulating organic ligands and are also typically 5–10 nm in diameter, tapping mode atomic force microscopy (AFM) is an ideal technique to investigate the morphology of QD layers (41) both as-inked (on stamps) and as-printed (on organic thin films). Differences in QD layer formation on both parylene-coated and uncoated PDMS stamps have been investigated using AFM, and are shown for the first time in Fig. 4a,c; the same QD suspension was spin-coated using identical conditions onto both stamps. The concentration of QDs in the suspension used here yielded a well-dispersed, submonolayer QD coverage on the parylene-coated stamp (see Fig. 4a) and tall, discontinuous islands of QD multilayers on the plain PDMS stamp (see Fig. 4c). Notably, the striking differences in morphology of the QD layers as-inked on the parylene-coated and uncoated PDMS stamps are mirrored in the AFM images of the very same QD layers contact printed onto thermally-evaporated organic



**Fig. 3.** Schematic cartoon (not drawn to scale) of the QD contact printing process. (a) A planar substrate coated with a receiving thin film (e.g. an organic semiconductor hole transport layer on an ITO-coated glass substrate) is inverted and aligned with an inked elastomeric stamp (shown here covered with an ordered QD monolayer). (b) The substrate is then brought into conformal mechanical contact with the inked stamp. (c) Finally, the substrate is carefully separated from the stamp; the QD layer has been transferred from the stamp to the receiving thin film on the substrate.



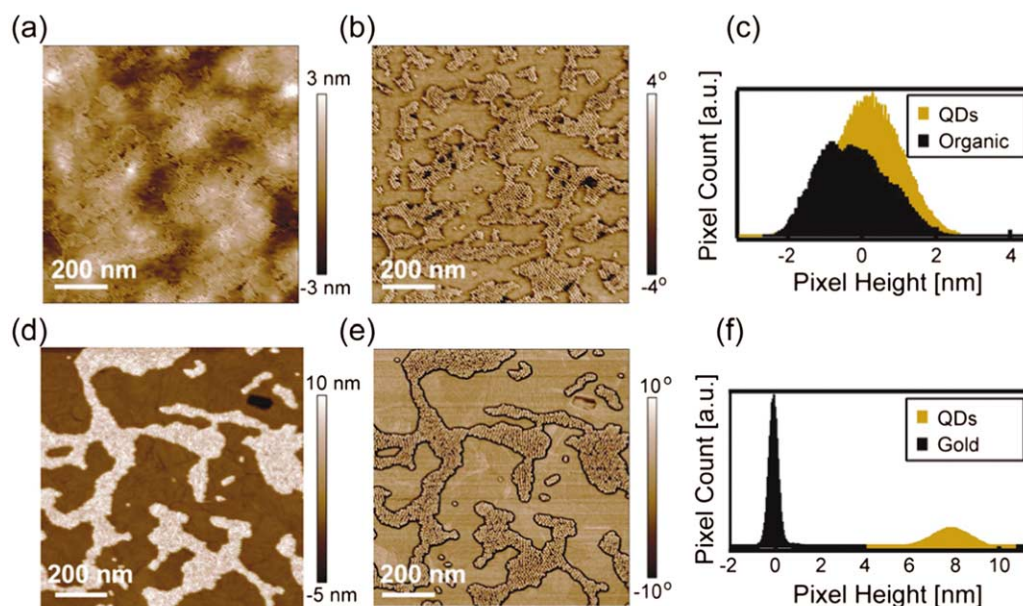
**Fig. 4.** Tapping-mode atomic force microscopy images of QD films. (a) Submonolayer QD film as-inked on a parylene-coated stamp. Phase data are shown because they provide improved clarity in displaying the ordered QDs, and are representative of the corresponding height data (see Fig. 5). Brighter areas (larger phase angle) in between ordered QD regions are ascribed to excess ligands from the ink suspension deposited on the smooth parylene-coated stamp. (b) Submonolayer QD film contact printed from a parylene-coated stamp onto an organic semiconductor (OSC) thin film (here:  $N,N'$ -bis(3-methylphenyl)- $N,N'$ -bis(phenyl)-9,9-spirobifluorene). (c) Multilayered QD islands as-inked on an uncoated (bare PDMS) stamp. This stamp was inked using the same QD suspension and identical spin-coating conditions as used for the stamp shown in panel (a); note the larger image area and data height scale, revealing multiple layers of QDs in some locations. (d) Disordered QD multilayer film contact printed from an uncoated stamp onto an OSC thin film (here:  $N,N'$ -bis(naphthalen-1-yl)- $N,N'$ -bis(phenyl)-2,2-dimethylbenzidine).

semiconductor thin films (Fig. 4b,d). This observation highlights the importance of the surface modification of bare PDMS with parylene to obtain better wetting and QD monolayer formation on the stamp, since it appears that the QD layer morphology obtained upon inking the stamp is directly preserved following transfer to the OSC film by contact printing.

#### Using AFM to characterize the QD/organic film interface

As described in a recent study (42), atomic force microscopy of QD submonolayers contact-printed on organic semiconductor thin films can be used to quantify the QD penetration depth into these films. This characterization is important because the vertical placement of a QD monolayer within a hybrid QD-LED structure is known to significantly impact device electroluminescence efficiency (9). Figure 5 highlights the ability of the AFM image analysis procedure to quantify the

vertical placement of a QD submonolayer film, both significantly embedded within an OSC film (Fig. 5a–c) as well as sitting on top of a smooth, template-stripped gold film (Fig. 5d–f). Briefly, the procedure generates a resolved pair of histograms that represent the height of each pixel in an AFM image (one corresponding to QDs, the other to the surrounding film) to determine the average height the QDs protrude from the underlying film (a quantity denoted as  $\Delta h$ ). Figures 5a, b show the AFM height and phase images, respectively, of a QD submonolayer film contact printed onto a 40 nm thick film of the organic semiconductor 2,2',2''-(1,3,5-benzenetriyl)-tris(1-phenyl-1-H-benzimidazole). The images have been flattened, but no other processing has been performed. Contact printing onto an organic film complicates the process of determining  $\Delta h$ . As seen in Fig. 5a, greater variation exists in the overall height of the surface of the organic film than the amount by which the QDs protrude from that film. Thus, a simple histogram of all

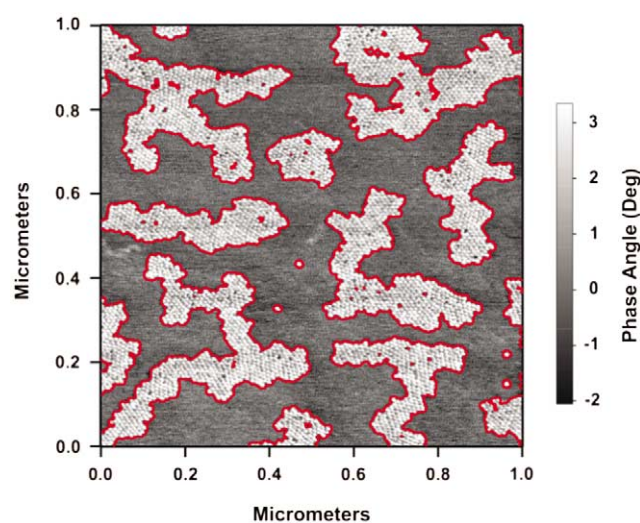


**Fig. 5.** (a) AFM image height and (b) phase data for a QD submonolayer deposited on a thermally evaporated organic semiconductor (2,2',2''-(1,3,5-benzenetriyl)-tris(1-phenyl-1-H-benzimidazole)) thin film by contact printing (from a parylene-coated stamp). (c) Pixel height histogram for the data shown in panel (a), revealing an average QD height above the surrounding organic film of  $(0.48 \pm 0.20)$  nm. (d) AFM image height and (e) phase data for a QD submonolayer deposited on a smooth, template-stripped gold surface. (f) Pixel height histogram for the data shown in panel (d), revealing an average QD height above the surrounding gold film of  $(7.94 \pm 0.20)$  nm. This is approximately equal to an individual QD diameter as measured independently by transmission electron microscopy (data not shown), verifying that contact printing does not significantly embed QDs in the metal film surface (in contrast to printing onto an organic semiconductor thin film).

pixel heights in the image consists of one broad peak. Figure 5b shows the corresponding phase image, which clearly reveals the location of the QDs on a uniformly colored background, due to substantially different interactions between the QDs and the organic film with the AFM tip (43). The phase image can therefore be used to define a mask that delineates regions of either QDs or organic film in the height image. However, while the human eye easily picks out the location of the QDs, it is necessary to run an edge detector filter on the phase image, causing the rapid phase changes at the edges of the quantum dots to 'light up' while the background organic film remains flat (see Fig. 6). A standard threshold mask will pick out the areas occupied by QDs (with the threshold set by eye), dilating the mask to encompass the desired area. After masking the regions of quantum dots from those of organic film, separate histograms are formed out of the height data as shown in Fig. 5c. Finally, a Gaussian function is fit to each of these data sets and the difference between the means defines  $\Delta h$ .

Quantifying  $\Delta h$  for QDs contact printed onto a template-stripped gold film is simpler; the height and phase data for a representative sample are shown in Fig. 5d,e. Figure 5f shows the histogram of the height data for this image; there are two clear, distinct peaks. These are interpreted as representing the gold background and the QDs sitting on top of the gold. The difference in peak

means yields a  $\Delta h$  value that is approximately equal to the diameter of an individual QD, indicating that QDs do not significantly penetrate the gold layer by contact printing (as expected). This result also validates the AFM height data analysis procedure.



**Fig. 6.** AFM phase image of QDs contact printed onto an organic semiconductor film. The red lines show the threshold mask used to distinguish areas containing QDs from the organic background.

## Summary and future work

While significant advancements have been made in recent years toward effectively incorporating highly ordered colloidal quantum dot layers within hybrid organic/QD optoelectronic devices, further challenges remain. One of the most successful fabrication techniques to emerge has been contact printing, which enables the deposition of a QD film onto an organic semiconductor layer without directly exposing the organic component to any solvent. Critical to the creation of highly ordered QD monolayers has been the chemical surface modification of hydrophilic PDMS with the hydrophobic polymer parylene to promote wetting of stamp by the QD suspension and the QDs themselves. Further improvements in QD/stamp surface wetting may be realized by exchanging native QD ligands for alternative ligands with different chemical end group functionalities (22, 44), as well as by a systematic investigation of a variety of PDMS surface-modifying agents or treatments. Another challenge lies in the scale-up of contact printing to larger stamps and eventually to continuous stamping rollers for the rapid deposition of QD layers onto flexible substrates via roll-to-roll processing. While spin-coating works well for small stamps on the laboratory scale, a less wasteful method of inking stamps for larger area substrates and continuous processing must be explored, as well. Fundamental studies regarding the fluid mechanics and colloidal science of continuous QD contact printing are expected to provide thin film QD optoelectronic devices with a bright future in the years to come.

## Conflict of interest and funding

There is no conflict of interest in the present study for any of the authors.

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