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Patterning of Quantum Dots by Dip-Pen and Polymer Pen Nanolithography

Abstract: We present a direct way of patterning CdSe/ZnS quantum dots by dip-pen nanolithography and polymer pen lithography. Mixtures of cholesterol and phospholipid 1,2-dioleoyl-sn-glycero-3 phosphocholine serve as biocompatible carrier inks to facilitate the transfer of quantum dots from the tips to the surface during lithography. While dip-pen nanolithography of quantum dots can be used to achieve higher resolution and smaller pattern features (approximately 1 µm), polymer pen lithography is able to address intermediate pattern scales in the low micrometre range. This allows us to combine the advantages of micro contact printing in large area and massive parallel patterning, with the added flexibility in pattern design inherent in the DPN technique.

Keywords: Microarrays, Phospholipids, cholesterol, Nanoparticles, Fluorescence microscopy, Atomic force microscopy

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1 Introduction

Patterning techniques like inkjet printing [1], microcontact printing (µCP) [2], dip-pen nanolithography (DPN) [3] and polymer pen lithography (PPL) [4] allow the direct deposition of liquid materials on surfaces under ambient conditions. Unlike indirect methods, e.g., e-beam lithography and photolithography, these direct techniques do not rely on resist layers and multi-step processing, but allow the precise deposition of ink mixtures. Spot sizes in commercially widespread inkjet printing and other related spotting techniques are usually in the range of 50 to 500 µm [5–7], while high resolution approaches (µCP, DPN and PPL) reach sub-µm features.

Microcontact printing utilises a predesigned poly(dimethylsiloxane) (PDMS) stamp that is first coated with ink and subsequently pressed onto the surface manually. A total area up to cm^2 can be patterned retaining a lateral resolution of approximately 100 nm [8]. Dip-pen nanolithography (Figure 1a) employs an atomic force microscopy tip (AFM) as a quill pen. Dipping the pens and then precisely navigating them on a substrate generates flexible patterns down to few tens of nm lateral resolution [9]. The ink molecules are attracted to the surface by capillary forces, either resulting from a water meniscus for diffusive inks or by bulk fluid flow for liquid inks [10]. The size of ink spots can be controlled by relative humidity and / or dwell time, depending on the ink [11]. Functionalising tips with different inks (either with different materials or ink concentrations) will lead to multiplexed arrays, emphasising the flexibility of DPN. Polymer pen lithography (Figure 1b) combines both µCP and DPN [12]. Instead of utilising exclusive predesigned stamps, the idea of PPL is based on a general stamp layout that carries some 10,000 pyramidal PDMS tips. By mounting the stamp in a DPN/AFM system, PPL takes advantage of precise piezo-based motorisation. Unique patterns are then produced in parallel over cm^2. A throughput of approximately 150,000 features per second is easily achievable [13].

Ink behaviour plays an important role in direct lithography [10, 14]. Electrochemical properties of inks and substrates (hydrophobicity) are crucial factors controlling transfer rate and feature stability [9,15]. Most techniques that were established with the well-studied alkanethiol-gold system now have a huge ink library ranging from chemical inks (polymers, azides, fluorophores) [7,16-20], biological inks (phospholipids, proteins) [12,21,22], solid materials (nanoparticles) [23-26] and even whole bacterial cells [27].

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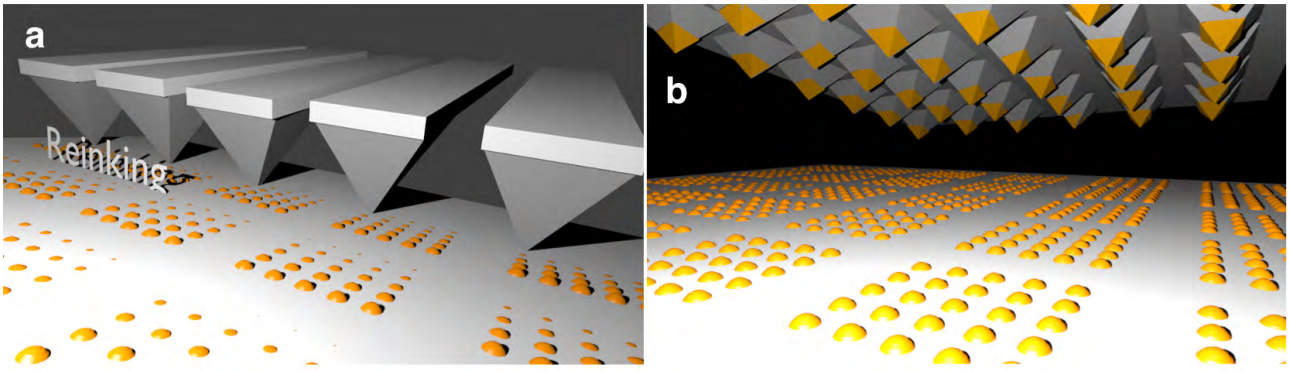

Figure 1: Schematics of quantum dot (QD) deposition by DPN and PPL. **(a)** Tips of a one-dimensional DPN array are coated with a mixture of CdSe/ZnS, cholesterol and DOPC. When the tips are brought in contact with the surface, the mixture begins to flow due to capillary forces of the carrier inks. The ink transfer decays during lithography that leads to smaller feature sizes. Re-inking of the tips after a certain time interval is necessary to continue writing. The label within the graphics indicates this fact. **(b)** This illustration shows a PPL stamp coated with ink. In contrast to µCP, a PPL stamp with its approximately 10^4 PDMS pyramids (pens) is attached to a DPN system to enable nano- and micrometre movements in all dimensions. Individual approaches of the stamp to the surface cause a transfer of quantum dots embedded in the carrier matrix by direct contact.

Matrix-assisted approaches based on polymers-mixtures generalize the material deposition in DPN and PPL [28, 29].

Quantum dots (QDs) are colloidal nanoparticles made of semiconducting materials famous for their optical properties [30]. They show specific light emission that is characterised only by size and material. This opens a new field in fluorescence microscopy as an unlimited number of emission wavelengths can be achieved. In contrast to organic fluorophores, different QDs can be excited by a broader range of wavelengths and are more stable with regards to bleaching. QDs are used in many disciplines [31]. Antigen coated QDs can be printed on biochips to serve as microarrays or sensor devices respectively [32]. Agglomerations of functionalized QDs have shown their capability to transfect cells; with potential applications in nanomedicine [33]. Light emitting diodes (LEDs) can be fabricated by printing QDs with different optical properties [34–36].

For various applications in photonics and in biotechnology, a structured pattern of QDs is necessary or desirable. Therefore, structuring methods are required to address this issue. In addition, we have utilized a cost-effective and easy (without using E-Beam lithography or a complicated multi-step process) method (DPN and PPL printing). As an example, Collins et al. have shown the ability to deliver different materials such as, Calcein AM, Calcein Red AM and quantum dots to single or few cells within hundreds of microns of each other on the same substrate by patterning the substrate using DPN [37]. Panzer, et al., have shown that one of the successful methods developed to integrate colloidal semiconductor QDs and organic semiconductor thin films into a functional multilayered device is contact printing of colloidal QD films [38]. It has also been shown by Anikeeva et al., that close-packed monolayers of different QD types inside an identical QD-LED structure can be fabricated on the same substrate by microcontact printing [39]. Kim et al., have also demonstrated that a large-area, full-colour printed quantum dot films exhibit excellent morphology, well-ordered quantum dot structure and clearly defined interfaces [40].

Here, we demonstrate the fabrication of CdSe/ZnS QD arrays by DPN and PPL. By studying the behaviour of various carrier inks, we have investigated best conditions for admixing cholesterol and 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC) as biocompatible matrix, which guides QDs from the tip to the surface. Fluorescence microscopy and spectral analysis show that the QDs retain their optical properties after lithography. AFM investigations point out a separation of the ink matrix on the surface, leaving QDs highly localized in the centre, surrounded by DOPC and a spread layer of cholesterol.

2 Methods

2.1 Lithography

DPN and PPL were carried out using a DPN 5000 or NLP 2000 system, respectively (NanoInk Inc., USA). Both devices have an environmental chamber for the precise control of humidity. Si_3N_4 cantilever arrays (type M, triangular cantilevers, NanoInk, USA) were used for writing the structures in case of DPN. Custom-made PPL

stamps were glued to microscopy glass slides, which were subsequently mounted to a custom-made holder of the NLP system. The humidity was set to 50% and the dwell time 10 s (if not stated otherwise).

2.2 Ink Preparation

CdSe/ZnS quantum dots (Sigma Aldrich) were diluted in toluene to a concentration of 5 mg/ml. Two different sizes of QDs (4 nm with emission wavelength of 590 nm and 5.2 nm with emission wavelength 610 nm) were used in this study. The QDs were core-shelled structures with a ZnS layer on the surface. The solution containing the nanoparticles was used as received. The QDs were mixed with cholesterol of 5 mg/ml and DOPC (both were purchased from Avanti Polar Lipids, USA) of 10 mg/ml in chloroform with different ratios, depending on the experiment.

2.3 Substrate Preparation (cleaning steps)

The dot patterns were written on glass cover slips (Menzel Gläser, Germany). Surface cleaning was performed using oxygen plasma (10 sccm O_2, 100 mTorr, 100 W, 30 s) and then sonicated in isopropanol and deionised water (5 min each). The substrates were dried using N_2.

2.4 PPL Stamp Preparation

PPL stamps were fabricated following the protocol described elsewhere [12].

2.5 PPL Process

Inking of the PPL stamps was performed using the stamp pad method as described elsewhere [12]. Cleaned pieces of silicon wafer were coated with the respective ink mixture by depositing 10-15 µL of ink onto the bare surface by a pipette and allowing the droplet to spread. The polymer pens were then approached onto this coated silicon wafer (either by making 10X10 dot patterns with dwell time 1s or by making arbitrary lines) for inking at RH 70%. Figure 2 in supporting Information shows the optical micrographs of the polymer pens coated with ink.

2.6 Fluorescence Imaging and Spectroscopy

The CdSe/ZnS structures were characterised by luminescence microscopy and spectroscopy using a Nikon upright Eclipse 80i microscope. Fluorescence spectra were recorded with an Avaspec-2048 Spectrometer (Avantes).

2.7 AFM Imaging:

AFM images were obtained using a Dimension Icon AFM (Bruker, Germany) in tapping mode equipped with a Tap300AL-G cantilever (BudgetSensors, Bulgaria).

3 Results and Discussion

Finding a feasible ink composition, which first coats the tips after inking, and second releases from the tips while in contact with a substrate is crucial for the patterning process. We tried different admixtures of cholesterol and DOPC to create a well-flowing carrier ink that leads to reproducible QD features on glass cover slides. DOPC has been shown to be a suitable carrier matrix for the added functional components e.g., in the form of fluorophore conjugated or biotinylated lipids and haptenated lipid components [41,42]. Especially the excellent biocompatibility of lipid inks offers their utilization for micro patterns used for experiments in cell culture [22,43,44]. Cholesterol alters the ink flow as can be seen from the previous works on DPN [8, 11]. We, therefore, tried to check the influence of cholesterol on the ink flow in case of PPL. In this work, DOPC (and admixtures of cholesterol to tune writing properties) was investigated as feasible carrier for QDs.

Table 1 lists the tested ink compositions. From the fluorescence microscopy images (shown in SI Figure 1), we observed that all ink mixtures did not demonstrate reliable and homogeneous transfer of QDs. Most homogeneous and reliable pattern qualities, in this regard, were obtained for a composition of QD solution and cholesterol at a volume ratio of 15: 2 and QD: cholesterol: DOPC at 10: 2: 1.

Table 1: Different ink mixtures used for QD deposition by DPN. Symbols ++/+/- correspond to well suited for writing / suitable for writing / not suitable for writing. Evaluation of pattern quality was carried out by fluorescence microscopy (SI Figure 1). See experimental section for precise information on concentrations.

Mixture (Volume ratios in µl)	Writing Behaviour (++ / + / -)
QD (4 nm): cholesterol 45: 4	-
QD (4 nm): cholesterol 15: 2	++
QD (4 nm): cholesterol: DOPC 10: 2: 1	+
QD (4 nm): cholesterol: DOPC 15: 2: 1	-
QD (5.2 nm): cholesterol: DOPC 20: 2: 1	+

A representative outcome for one of the mixtures is shown in Figure 2. The pattern was written starting from the bottom left, in alternating directions left to right and then right to left in each line. Subsequently the deposited dot features decrease in size, indicating that the tip is depleting in ink. Two or three grids consisting of 6x6 dots could be printed by DPN (depending on the ink composition) after one inking step. After that re-inking of the tips was needed for further writing. The variation in dot size is from 3 µm in diameter to 500 nm. A prior "bleeding pattern" was required before printing to obtain a more homogeneous ink transfer. Phospholipid ink, by itself however, shows a long-lasting writing behaviour and basically does not deplete. Interestingly, our investigations have shown that the adjustment of relative humidity and dwell time do not interfere with the QD feature size. However, atomic force micrographs show a separation of the three mixed materials on the surface after lithography that explains this finding (Figures 2c, d). While the centre of the observed feature has a diameter of less than 500 nm, the middle layer is about 1x3 μm^2 and the outer layer is almost 5 µm in diameter. Supported by the respective fluorescence micrographs, we assume that the QDs remain in the middle of each feature, surrounded by DOPC and a sparse spread layer of cholesterol. Some smaller scattered QDs can be found within the DOPC

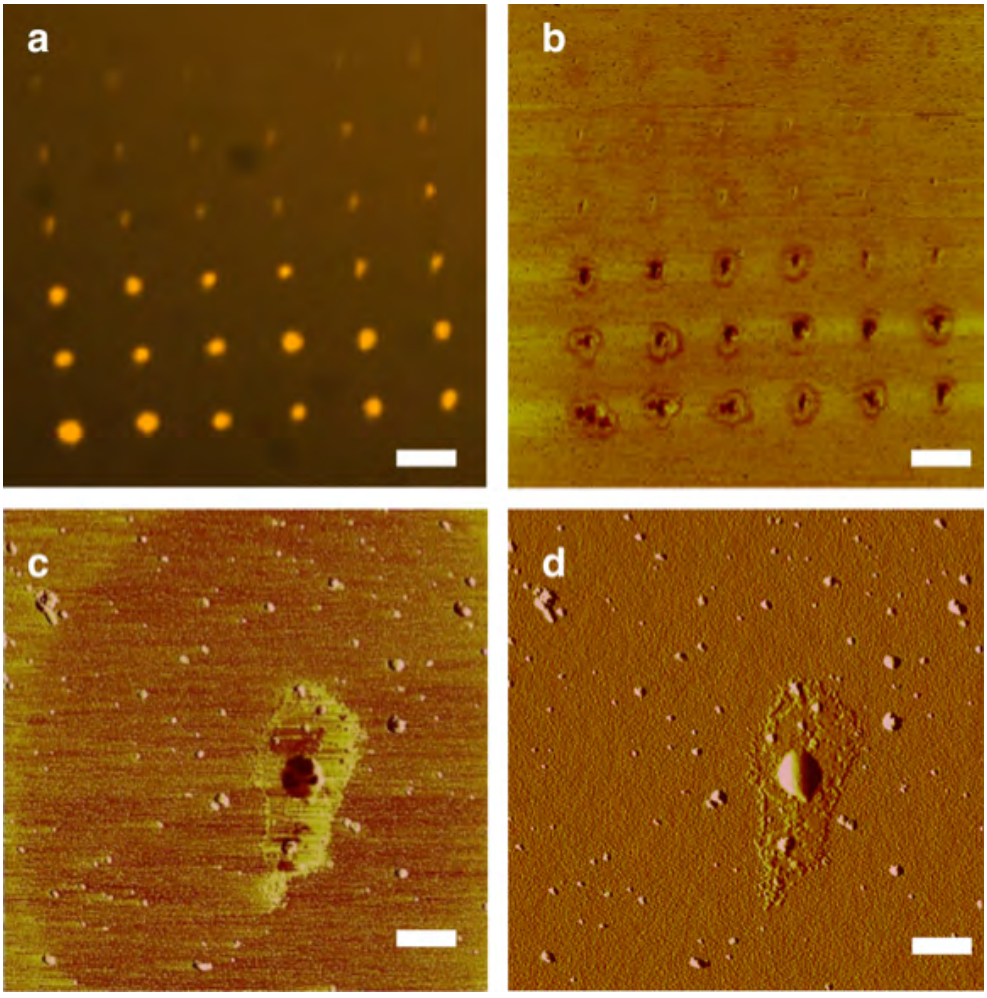

Figure 2: QD pattern by DPN. As ink, a mixture of QD (4 nm), cholesterol and DOPC was used (10: 2: 1, volume ratio in µL). Lithography was performed at RH = 50% with a dwell time of 10 s. This is the second printed grid. **(a)** The fluorescence microscopy image shows a depleting quantum dot pattern. The spot size decreases from 3 µm in diameter to about 500 nm. Scale bar equals 10 µm. **(b)** The corresponding AFM phase image shows a halo-effect that indicates a separation of the inks. The scale bar is equal to 10 µm. **(c)** The inks separate in three regions on the surface. The magnified image illustrates an agglomeration of QDs visible as darker phase contrast in the middle. DOPC is located directly around the main QD cluster; cholesterol is spread circularly (see edge on the left), which is only visible in the phase image. The scale bar equals 500 nm. **(d)** The amplitude channel of the AFM investigation shows a flat layer around the main QD agglomeration that corresponds to DOPC. Edges of lipid bilayers can be seen in this area, too. Smaller QD clusters have scattered almost over the whole image. The outer cholesterol layer, which is visible in the phase contrast, does not appear in the amplitude image.

and outer cholesterol layer. In our investigations, the agglomerated QD features are located in the centre, which is independent of dwell time and humidity. This can be explained by the least mobility of these clusters. Only the smaller QD agglomerations flow to the outer regions, with support of the matrix spreading. Nevertheless, the carrier inks diffuse on the surface yielding a dwell-time and humidity dependence of feature size.

Photoemission spectra of the QD features were taken by a micro spectrometer in order to investigate the optical properties of the QDs after lithography and the influence of the admixtures (Figure 3). QD patterns with different carrier ink compositions were generated and then excited by a fluorescence microscope. Emitted light from the corresponding QD mixture was then collected by the microscope setup and further analysed by the spectrometer. The spectra of the patterned QDs in carrier matrix do not significantly differ from the ones obtained from pure QD stock solution spotted into bulk droplets by pipetting.

Commercially available QDs used in these experiments were stabilized with a mixture of hexadecylamine (HDA) and trioctylphosphine (TOPO) ligands (in case of red emitting QDs, λ_{em}= 610 nm) and with a hexadecylamine (HDA) ligand coating (in case of orange emitting QDs, λ_{em}= 590 nm). These surface treatments protect the QDs from agglomeration in the toluene solution. While using QDs as ink for writing using DPN/PPL, they were mixed with cholesterol and DOPC dissolved in chloroform. The solvents were evaporated in vacuum after preparation of the final ink. QD agglomeration, as found in the AFM investigation (Figure 2), may occur due to the loss of the

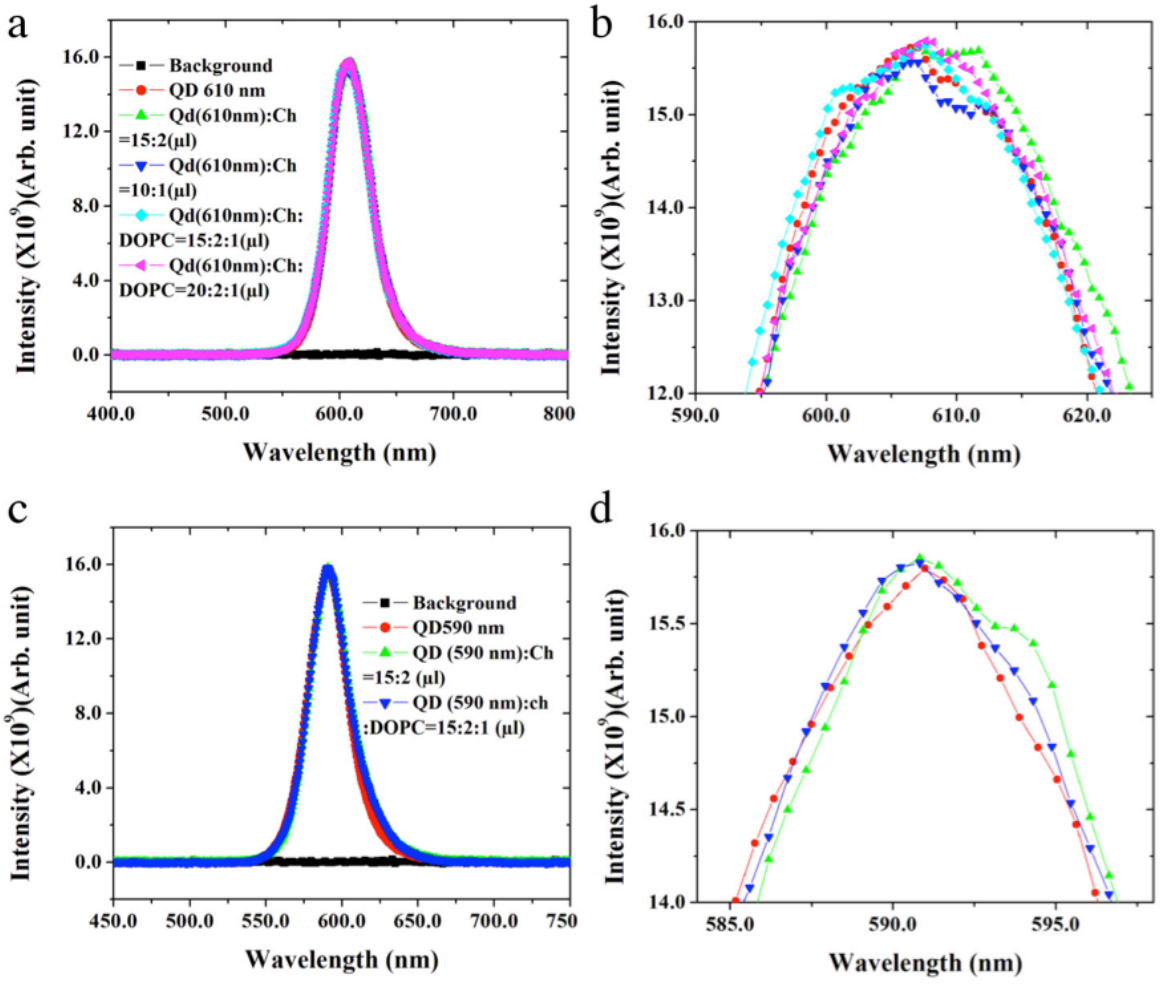

Figure 3: Photoemission spectra of CdSe/ZnS features. **(a)** Spectra of CdSe/ZnS (4.0 nm) features emitting at 610 nm. Different colours indicate the different ink compositions used. **(b)** Zoom-in of the data shown in (a). **(c)** Spectra of CdSe/ZnS (5.2 nm) patterns mixed with carrier inks emitting at 590 nm and **(d)** close-up of the peak area.

stabilizing solvents in combination with an interaction with the biomaterials DOPC and cholesterol. Other studies have also reported on QD clustering effects when interacting with biomaterials [33]. While carefully observing the fluorescence spectra of the ink compositions shown in figures 3(b) and (d), it can be noticed that apart from the main peak at 610 nm (4 nm QDs) and 590 nm (5.2 nm QDs), another small peak appears at higher wavelength (at around 615 nm in figure 3(b) and around 594 nm in figure 3(d)) in case of ink mixtures – QD: cholesterol and QD: cholesterol: DOPC. We think that this second peak may appear as a result of the interaction of QDs with cholesterol and DOPC in the ink mixture.

When performing parallel patterning by DPN, usually one-dimensional arrays are used (typical parameters e.g., 26 tips with 35 µm spacing, in our case we used cantilever with 12 tips), though 2D arrays with cm^2 size and 55,000 cantilevers for massive parallel patterning are available [45]. Even though, re-inking has to be performed frequently, especially when ink reservoirs on the tips run out fast; the use of the 2D arrays is still comparatively expensive. PPL stamps, however, already bring a large number of tips (approximately 10^4 to 10^5) on a 1x1 cm^2 stamp made of inexpensive polymer. After levelling, i.e. aligning the stamp parallel to the substrate, and coating the tips via the stamp pad method [12], one approach on the desired surface already covers a 100 times larger area with QDs compared to a 1D-DPN array. Due to the different modes of material deposition in PPL, e.g., by bulk fluid flow, ink transfer through a meniscus (like DPN) or by direct contact stamping (like µCP) [12], QD can be transferred to the surface in a more reproducible way (Figure 4). Compared to the ink compositions in DPN, it is possible to use a higher concentration of QDs in PPL. After studying all inks mentioned in Table 1, we found that a QD: cholesterol mixture of 10: 1 (volume ratio in µL) works best for PPL. These dense mixtures are not appropriate for DPN due to the weak ink flow, but they are fine for the contact transfer based printing in PPL. However, features consisting of a higher number of scattered QD agglomerations are obtained (see Figure 4 of SI). As more material is transferred from tip to substrate using a high stamping force, the dot densities deplete rapidly in PPL without re-inking. The array in Figure 4a was generated by a PPL stamp with 40-µm spacing between pens. Each pen created four QD-features subsequently. The stamp was loaded freshly before each approach to ensure a proper material-deposition. Different ink thicknesses on the stamp pad of the viscous ink explain the feature deviation of 33%. QDs are physisorbed on the surface however, the patterns are quite stable. It is verified by placing the patterned surface for cell culture and even after that the patterns are clearly visible as can be seen in Figure 5 of SI.

4 Conclusion

We demonstrated and compared the direct writing of QDs in different cholesterol/ phospholipid carrier inks by DPN and PPL. QDs can be transferred with these mixtures by DPN, but tip ink depletion limits this approach to either a small number of deposited features, or a frequent re-inking of the tips is required. PPL can overcome this limitation due to its sheer amount of tip parallelization. Large arrays in the cm^2 range can be printed with homogeneous quality. In spite of agglomeration effects that were observed by AFM, photoemission spectra confirmed the photonic properties of the QD within the matrix.

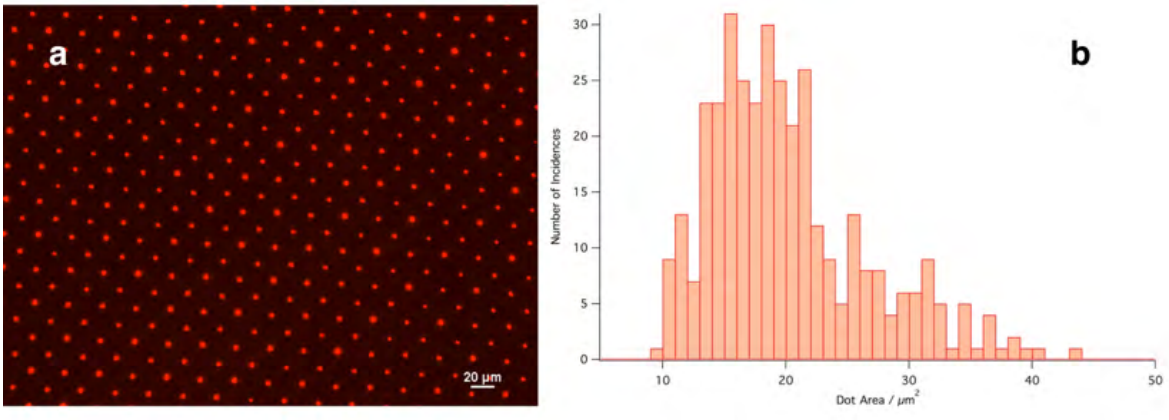

Figure 4: QD array by PPL. An ink composition of QD (4 nm): cholesterol 10:1 was used. **(a)** The fluorescence micrograph shows a part of a 1x1 cm^2 QD pattern. The spacing between the pens is 40 µm. Each pen generated four spots. The stamp was automatically re-inked with a stamp pad after each approach. **(b)** shows the histogram of the dot area distribution of the dot pattern in (a). The average dot area was found to be (20.1±6.5) $µm^2$.

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