Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information

From 2D to 3D patches on multifunctional particles: How Microcontact Printing creates a new Dimension of Functionality

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XPS Measurements

To investigate the PDMS oligomer transfer during our printing process, we conducted X-ray photoelectron spectroscopy (XPS) experiments of three different particle samples:

1. Unmodified silica particles
2. Patchy particles printed with 3wt% of LPEI
3. Unmodified silica particles which were dispersed in acetone in the presence of an unloaded PDMS stamp for 25 min.

All samples were washed in ethanol and drop casted onto a PTFE substrate for the measurement.

Figure S1 shows the XPS spectra of the silicon region for all three samples. A slight shift to lower binding energies and a broadening of the silicon peak occurred after the µCP process. Both observations are indications for small contaminations with PDMS oligomers (SiO_3C & SiO_2C_2) on the topmost layer of our patches.

The third experiment should show if the PDMS transfer could be a result of free PDMS oligomers diffusing into the solvent during the particles release step and therefore contaminating the whole particle surface. Due to the fact there is no shift or broadening of the silicon oxide peak for this experiment, this is not the case.

Despite these results we did not examine any conspicuous effects during the course of our investigations concerning patch printing, patch functionalization or coupling of our particles.

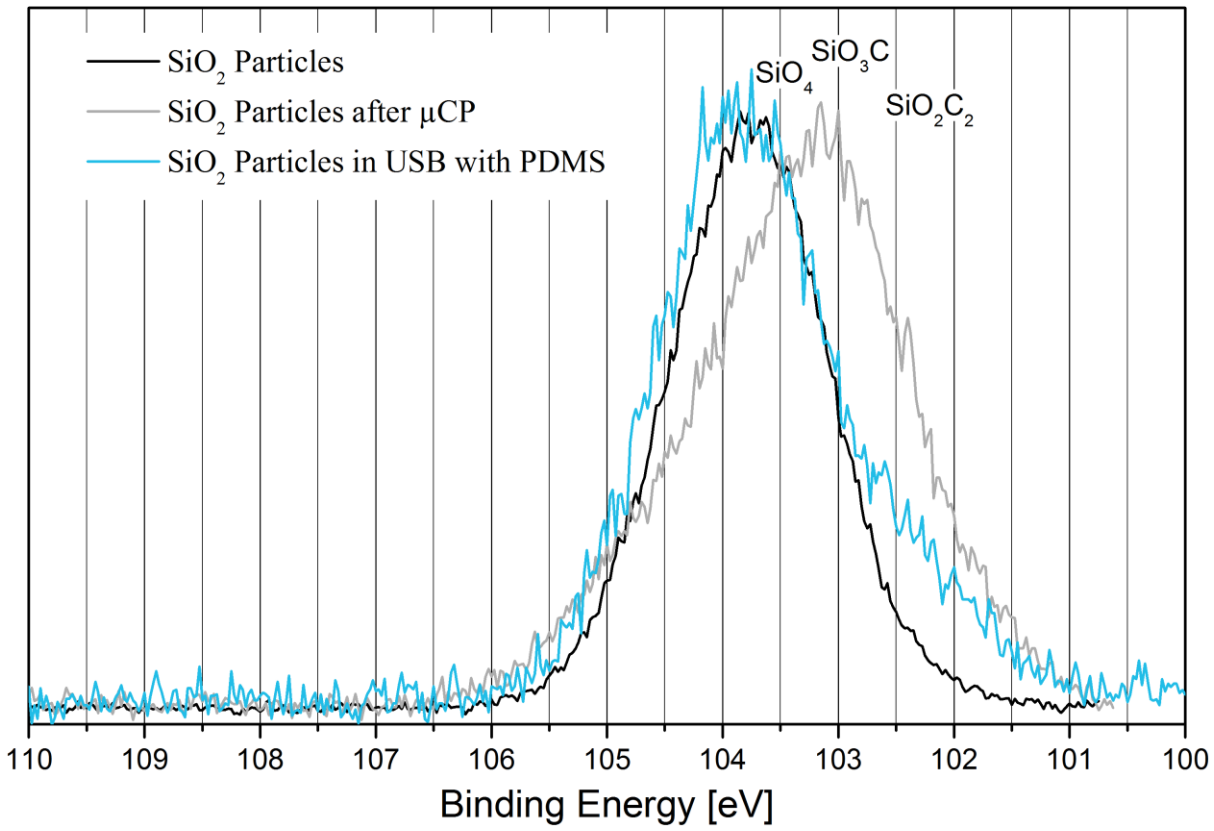

Figure S1 XPS spectra of the silicon region for three different samples: Unmodified silica particles, patchy particles printed with 3 wt% LPEI and a batch of unmodified particles which were in the presence of a PDMS stamp in the ultrasonic bath.

AFM Measurements

Figure S2 and S3 show SFM images of the dried PDMS stamps after particle release in acetone with LPEI and BPEI using different concentrations reaching from 1 to 4 wt%. The indentations, indicating the released PEI patch, were measured leading to values for patch thickness of 3D patches.

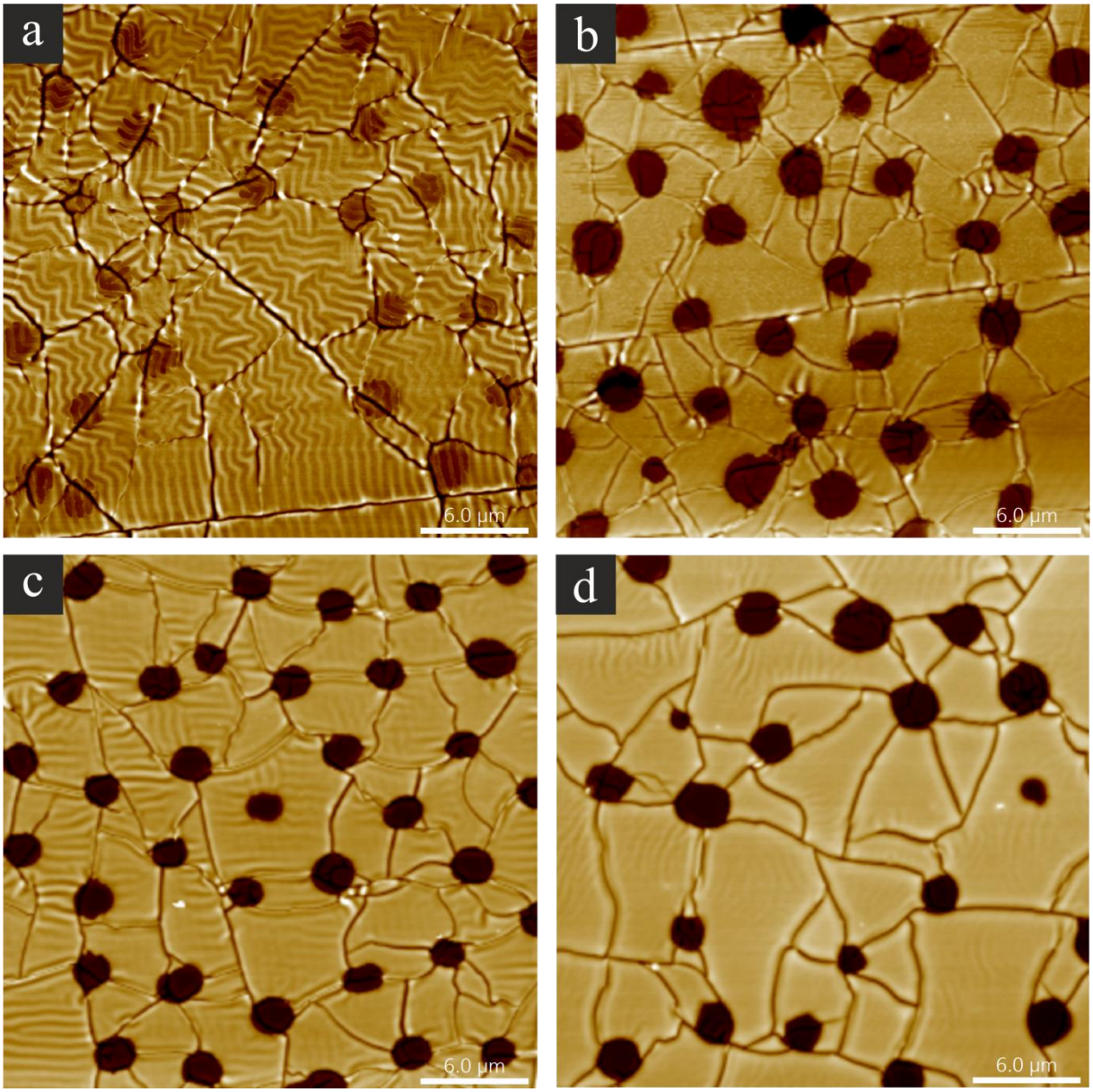

Figure S2 SFM images of PDMS stamps after particle release in acetone: (a) 1 wt% LPEI - Height Scale 80 nm (b) 2 wt% LPEI - Height Scale 130 nm (c) 3 wt% LPEI - Height Scale 170 nm (d) 4wt% LPEI - Height Scale 230 nm.

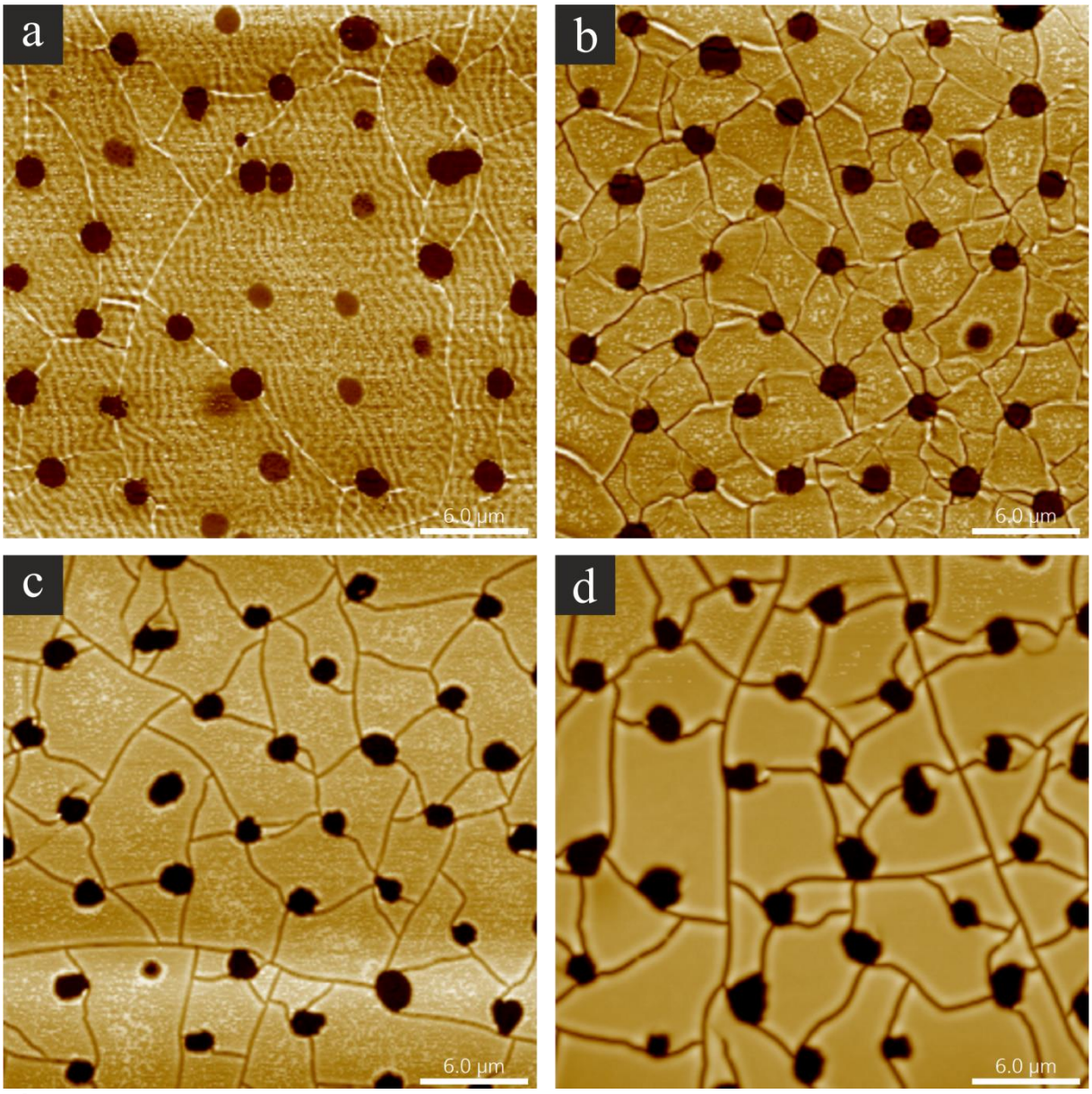

Figure S3 SFM images of PDMS stamps after particle release in acetone: (a) 1 wt% BPEI - Height Scale 40 nm (b) 2 wt% BPEI - Height Scale 80 nm (c) 3 wt% BPEI - Height Scale 120 nm (d) 4wt% BPEI - Height Scale 200 nm.

Particle Behaviour

Figure S4 shows a sequence of fluorescence microscopy images of labelled patchy particles at an air-solvent interface. This sequence was chosen to show that the particles, even in a forced situation, do not stick to each other and are still able to rotate freely around their own axis.

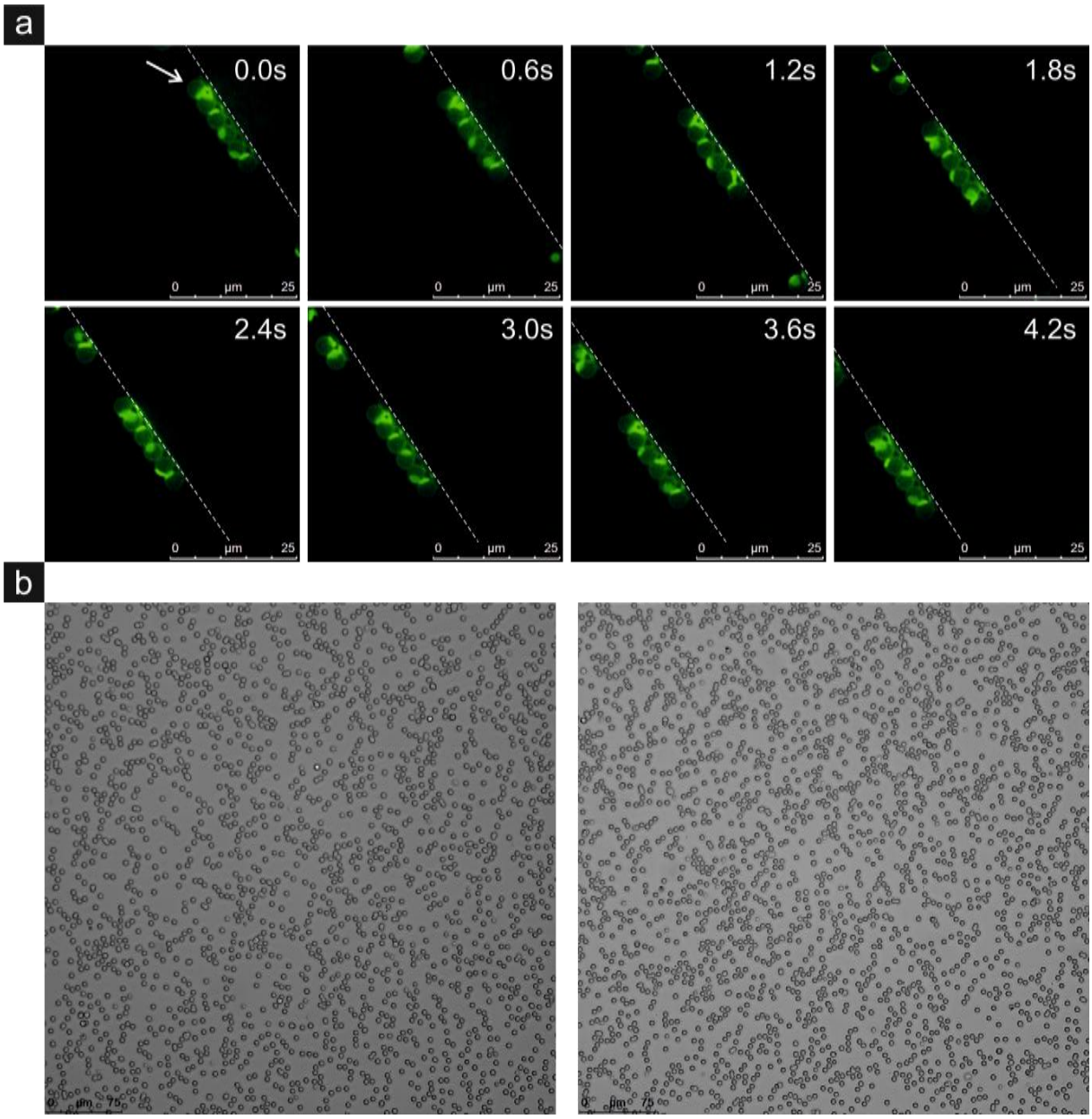

Figure S4 a) Sequence of fluorescence microscopy images of patchy particles labelled with FITC at an air-solvent interface (dashed line). Silica particles with a size of 4 µm were printed with 3 wt% LPEI and released in acetone to produce 3D patches. Arrow in the first image indicates particle with the most notable rotational movement (compare full movie in supporting information). b) 5 µm silica particles printed with 4 wt% LPEI and released in acetone. Microscope pictures were taken at high concentration in water. Even in water no agglomeration of patchy particles is visible.

Particle Coupling

Figure S5 shows fluorescence microscopy images of patchy particles functionalized with avidin. The images show no undirected agglomeration of the patchy particles following the functionalization step. Additionally, all avidin functionalized particles still show fluorescence due to the incorporation of quantum dots inside the 3D patches. Only in one picture (top right) the very rare case of two avidin functionalized patches in direct contact is shown. Due to the fact that this formation is barely observable we strongly disbelieve, that a formation of homodimers takes places during our experiments. Figure S6 shows microscopy images of patchy particles functionalized with biotin. Also for this system no crucial amount of agglomeration was observable. Because these particles did not receive any kind of fluorescent staining, no statement for directed agglomeration can be given compared to the avidin sample in Figure S5. Nevertheless, the functionalized patchy particles of both species are stable and do not shown an excessive amount of agglomerates in solution.

Figure S7 shows fluorescence microscopy images of coupled heterodimers consisting of avidin and biotin functionalized patchy particles. To calculate a binding efficiency for our system we analysed various images searching for three different kinds of particle species:

1. Correctly coupled heterodimers
2. Free or agglomerated avidin functionalized Patchy Particles
3. Free or agglomerated biotin functionalized Patchy Particles

With this information we were able to calculate the amount of possible heterodimers consisting of an avidin and a biotin functionalized patchy particle. This is important, because the ratio between the avidin and biotin species can differ between experiments. Using this procedure we calculated a binding efficiency of 57% for the pictures shown in Figure S7.

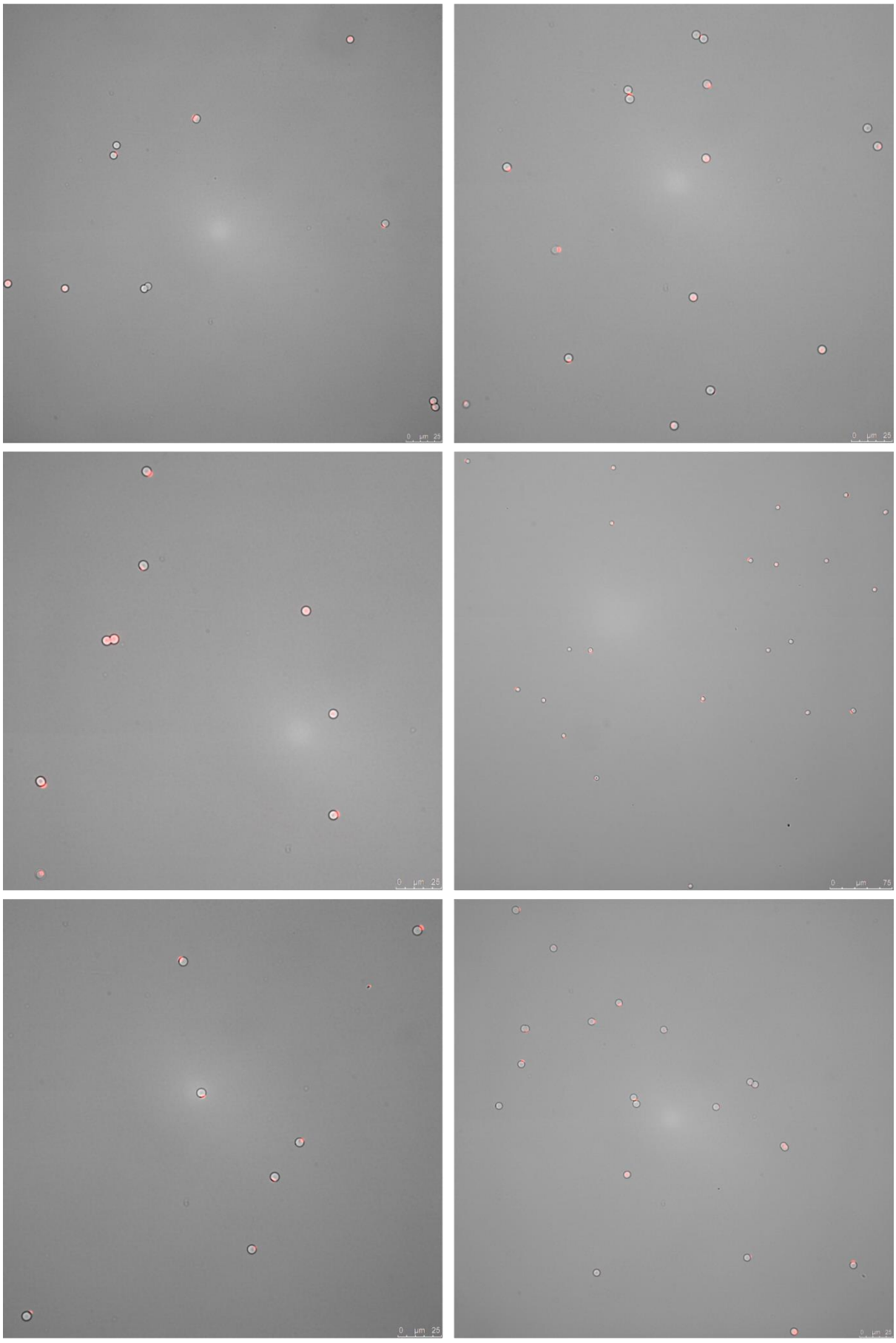

Figure S5 Fluorescence microscopy images of patchy particles functionalized with avidin dispersed in PBS-buffer.

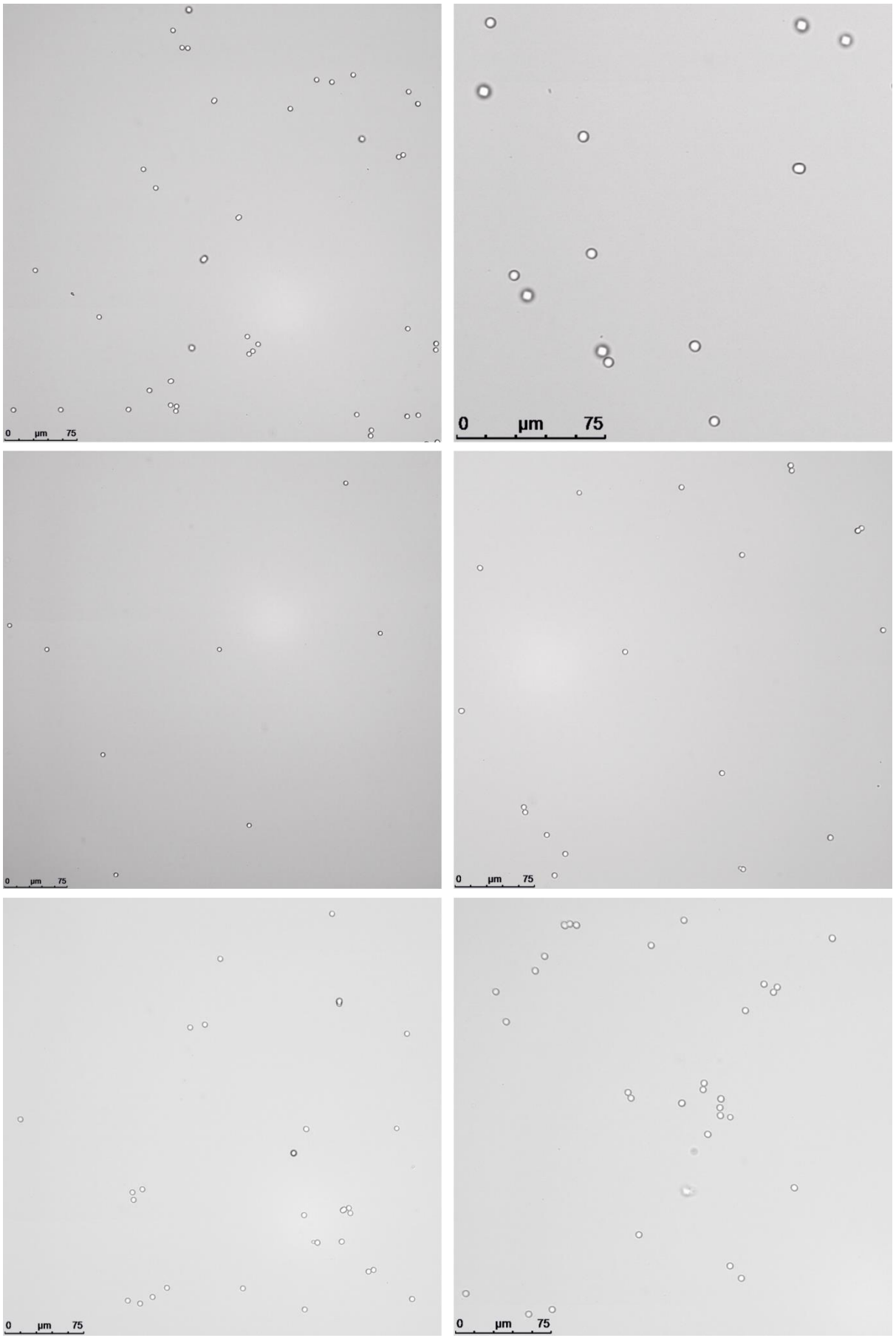

Figure S6 Fluorescence microscopy images of patchy particles functionalized with biotin dispersed in PBS-buffer.

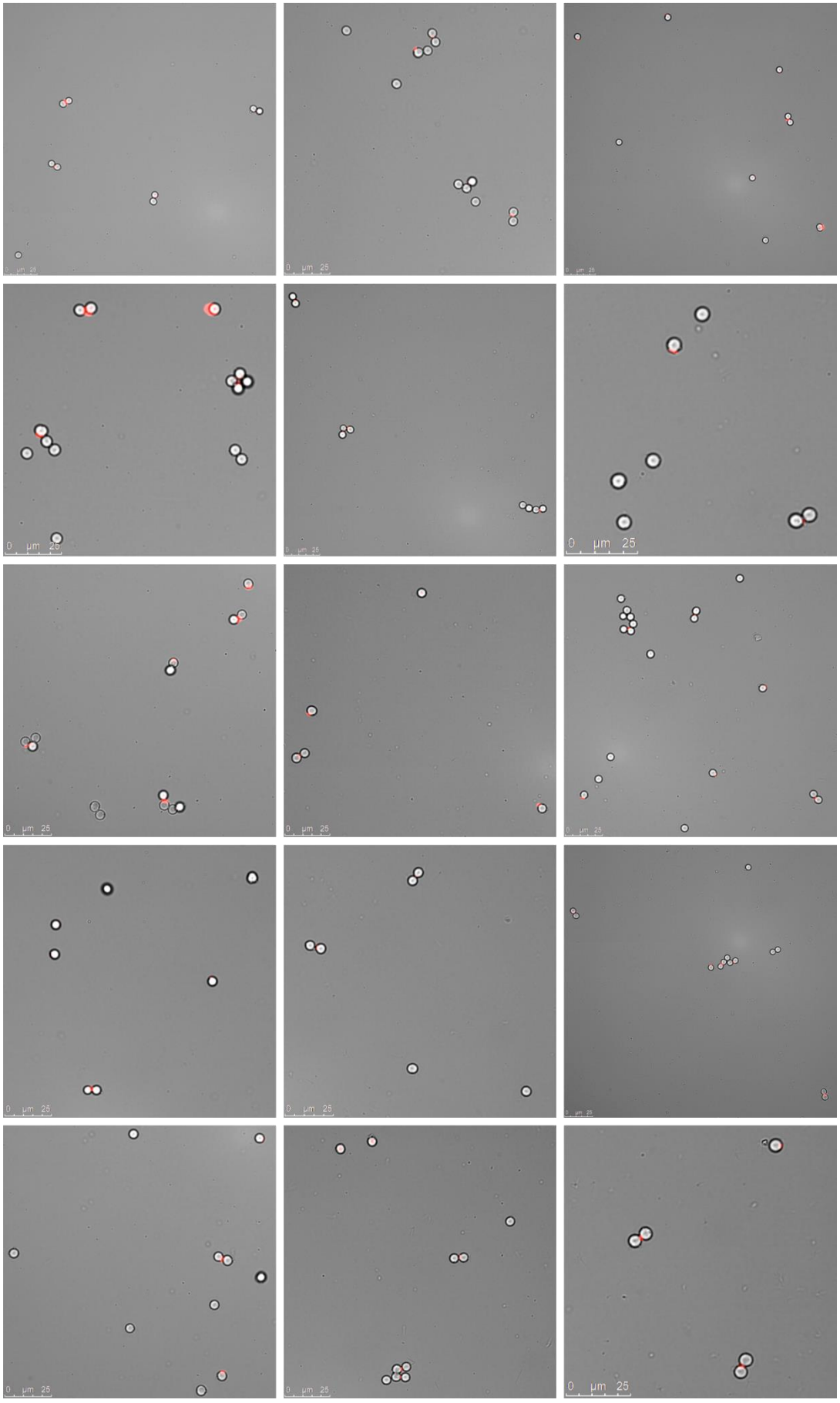

Figure S7 Fluorescence microscopy images of two species of patchy particles self-assembled into heterodimers in PBS-buffer.

Printing Pressure

Figure S8 shows the calculated printing pressures for 43 consecutive printing processes conducted by hand. The pressure was calculated for every point using the area of the PDMS stamp and the used glass substrate and the weight which was read out with a balance during the printing procedure. After this the average printing pressure along with a standard deviation was calculated.

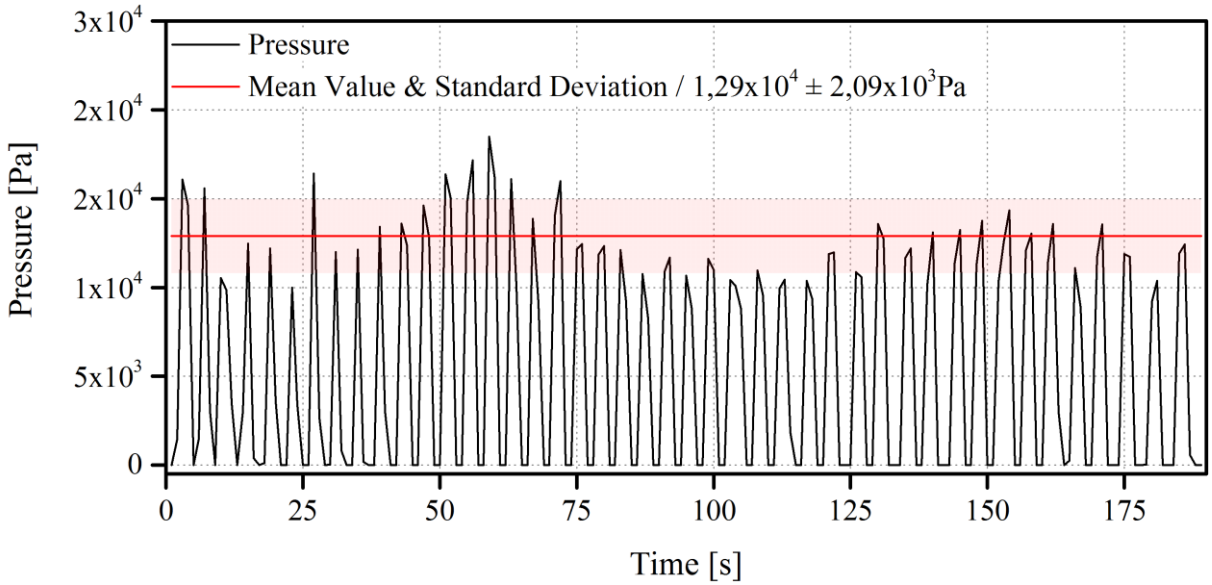

Figure S8 Diagram shows the calculated pressure of 43 printing processes over time. An average printing pressure of 1.3 x 10^4 Pa was calculated. The pressure was calculated using the achieved weight on a balance and the area of the substrates during printing process.