

Supporting Information for manuscript

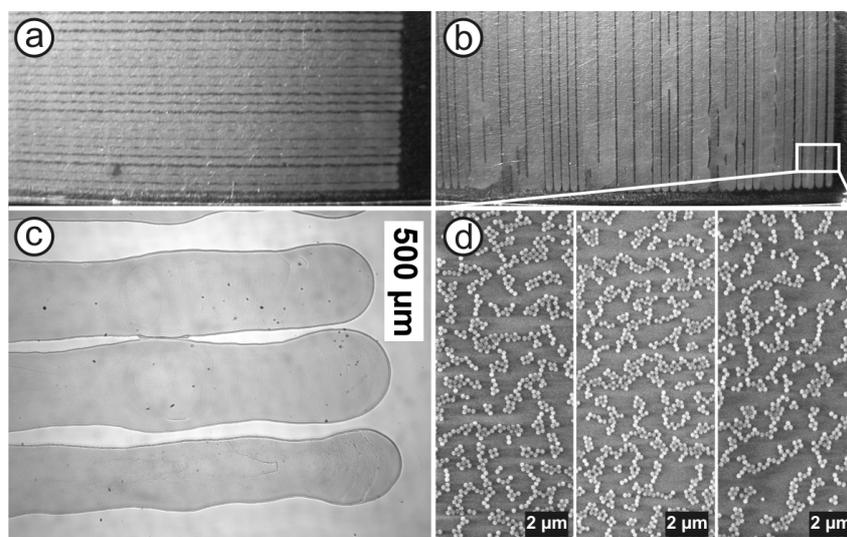
## Template-Free Structuring of Colloidal Hetero-Monolayers by Inkjet Printing and Particle Floating

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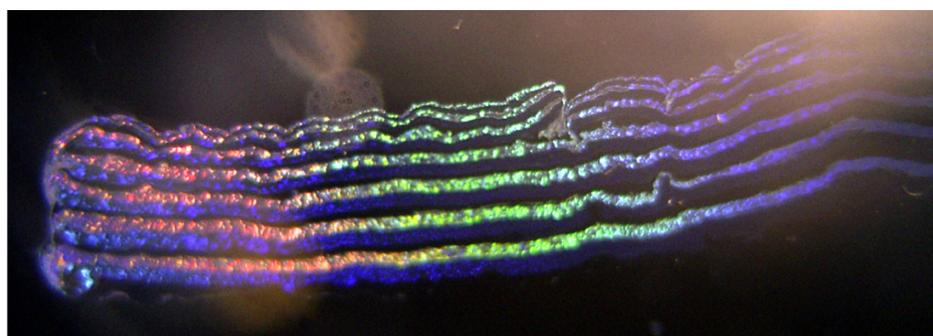
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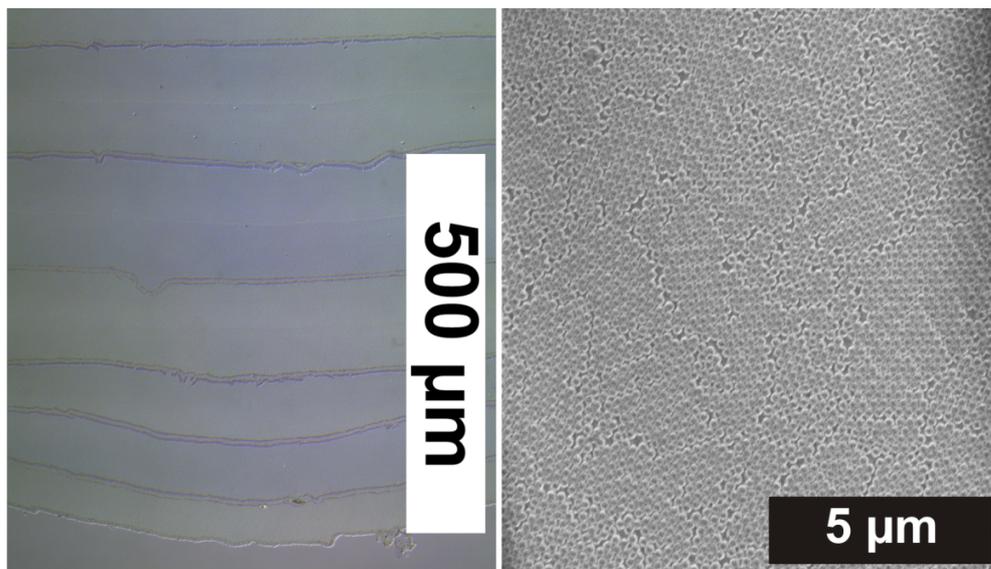
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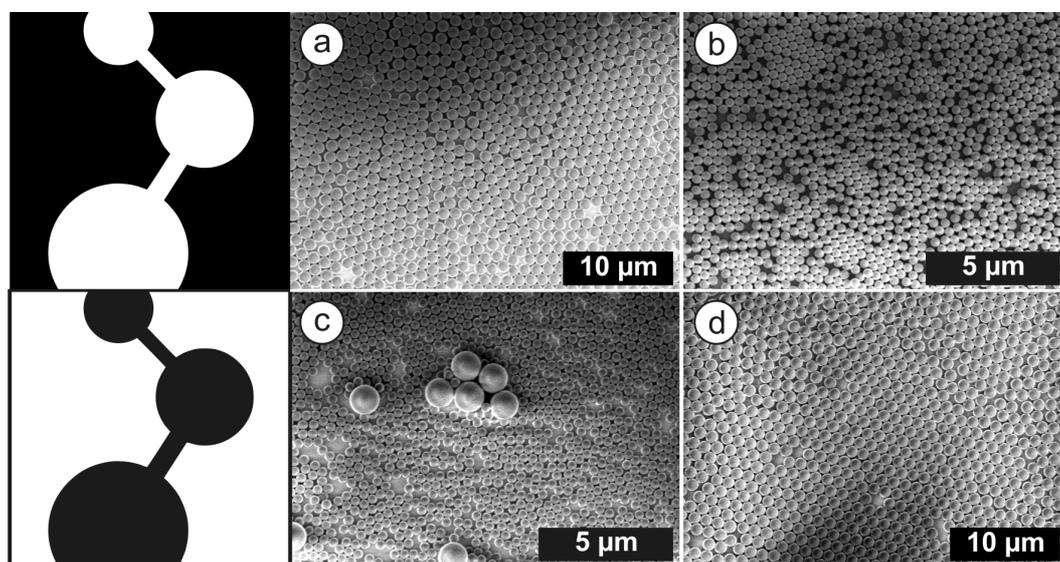
**Figure S1.** a), b) Photograph of printed sparse particles lines consisting of PMMA/nBA particles parallel and perpendicular to the three-phase-contact line. c) 5-fold magnified optical microscope image of a). An even distribution of the particles is seen with only minor coffee-stain effect. d) SEM images of the sparsely printed particles shown in b).



**Figure S2.** Photograph of a floating monolayer on the water surface. The bright colourful regions comprise 538 nm particles, the blue lines represent 356 nm regions, and the smallest 220 nm particle stripes appear black.



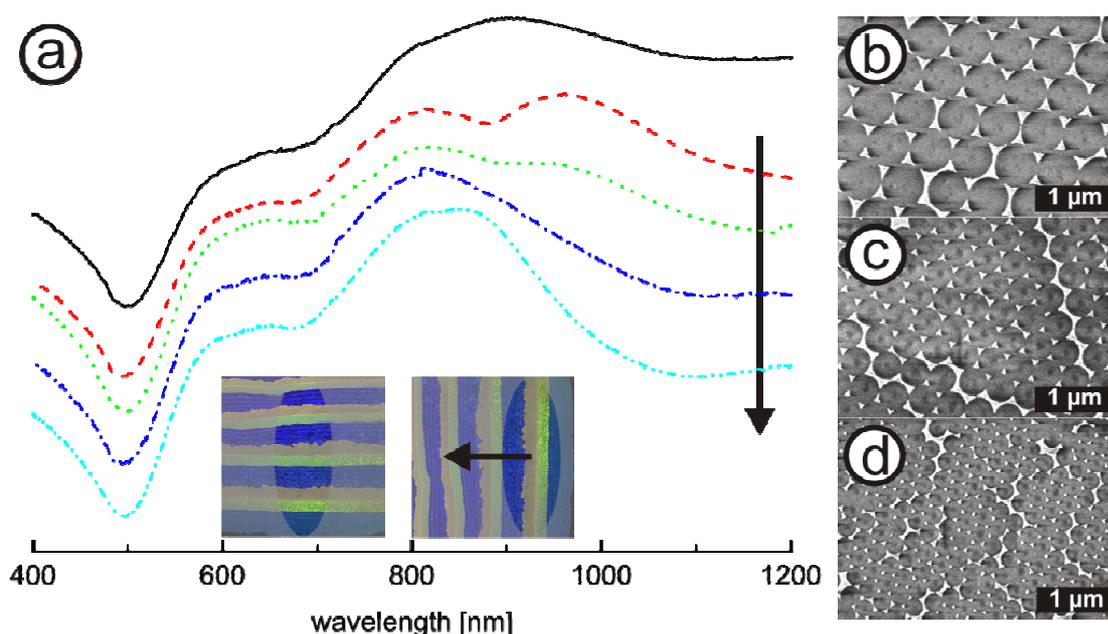
**Figure S3.** Left: 10x optical microscope (differential interference contrast) image of a heteromonolayer comprising of PMMA/nBA particles of almost identical sizes ( $\sim 200$  nm). Single and double stripes are shown. Right: SEM image of ordered PMMA/nBA particles after floating and transfer to a glass substrate.



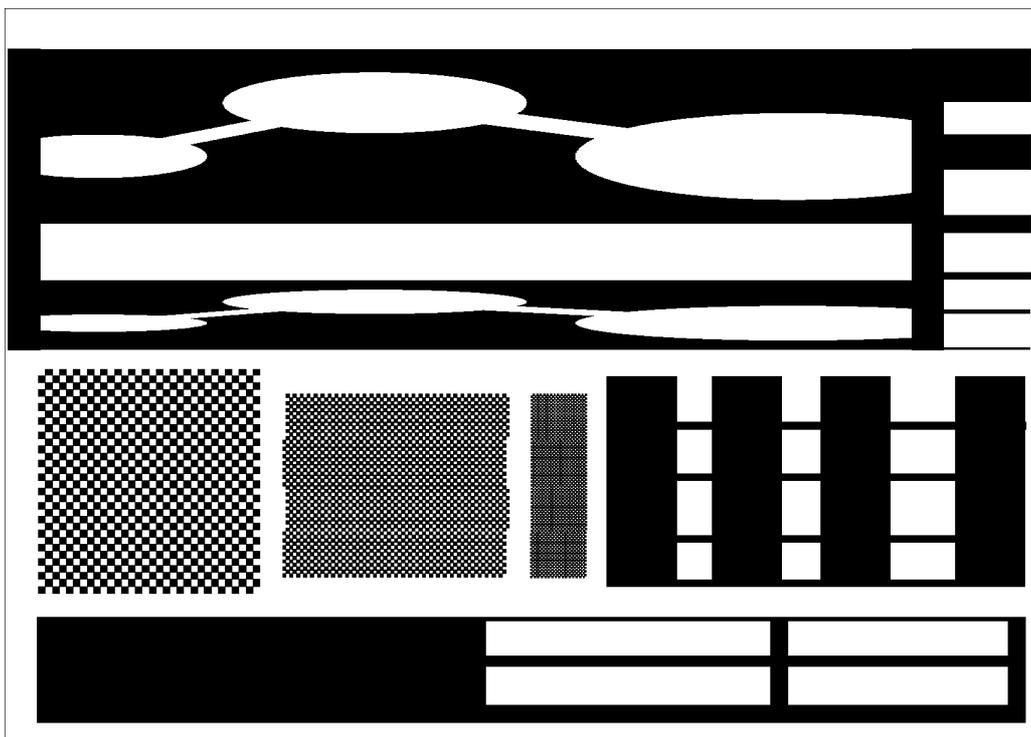
**Figure S4.** SEM images of the inner (a, c) and outer (b, d) part of the MPIP logo. The lower degree of ordering, especially in case of the 360 nm particles, must be attributed to the necessity of multiple printing in order to achieve a sufficiently high surface coverage. Furthermore, the boundaries between the two species are less well defined, due to some displacement between the individual printing steps.

### Details of using an HP 970CXI inkjet printer for the fabrication of hetero-monolayers.

Some technical shortcomings of the HP system used here are briefly discussed, as they are believed to be avoided when using a state-of-the-art piezo printer. The cartridges of HP 970CXI work thermally, which means that the ink is rapidly heated in order to evaporate explosively. This shoots the ink through a perforated membrane with pores of 20  $\mu\text{m}$  diameter. When using a latex dispersion this heating leads to a gradual and irreversible accumulation of polymer around the heating unit, eventually clogging the cartridges of the thermoprinter, and making it difficult to reproducibly deposit a defined amount of material on the substrate. Another problem is that only the black cartridge, which does not feature a sponge to store the ink, can be used. Thus, in order to pattern two types of particles, the same substrate had to be printed at least twice for changing the cartridges between the printing runs. Slight differences in the feeder reflected directly in an intersection of the printed patterns. However, these problems do not limit the general applicability of the described method. By comparison with the Nano-Plotter system, which pipettes piezoelectrically, clogging of the nozzle was not found to be a problem in any case. Thus, usage of a piezo-inkjet printer with several cartridges (black and multi-color) in parallel will immediately circumvent the registration issue mentioned above, as all particle types can be printed in a single run.



**Figure S5.** a) Vis/NIR spectrum of Au nanotriangles of 133 nm, 82 nm, and 43 nm. The black solid line shows the measurement perpendicular to the printed structure (left inset). The dotted lines resemble the measurements parallel stripes. Upon moving the spectral beam from the largest particles to the smaller ones, the relative intensities shift accordingly. However, the peak stemming from the smallest structures was not resolved. b - d) SEM images of the corresponding nano-triangles.



**Figure S6.** Test pattern, which was used to print arbitrary patterns on a HP 970cxi inkjet printer. The pattern was printed on an entire DIN A4 page. The inverse pattern was used to fill the free space with a second type of particle.



**Figure S7.** The left side shows a side view with an aluminium foil in place. The right side shows a top view with a floating monolayer (reddish and greenish patches). The black background facilitates visualizing the floating monolayer.