Electronic Supplementary Information

Fabrication and responsive behaviour of Quantum Dot/PNIPAM micropatterns obtained by template copolymerization in water

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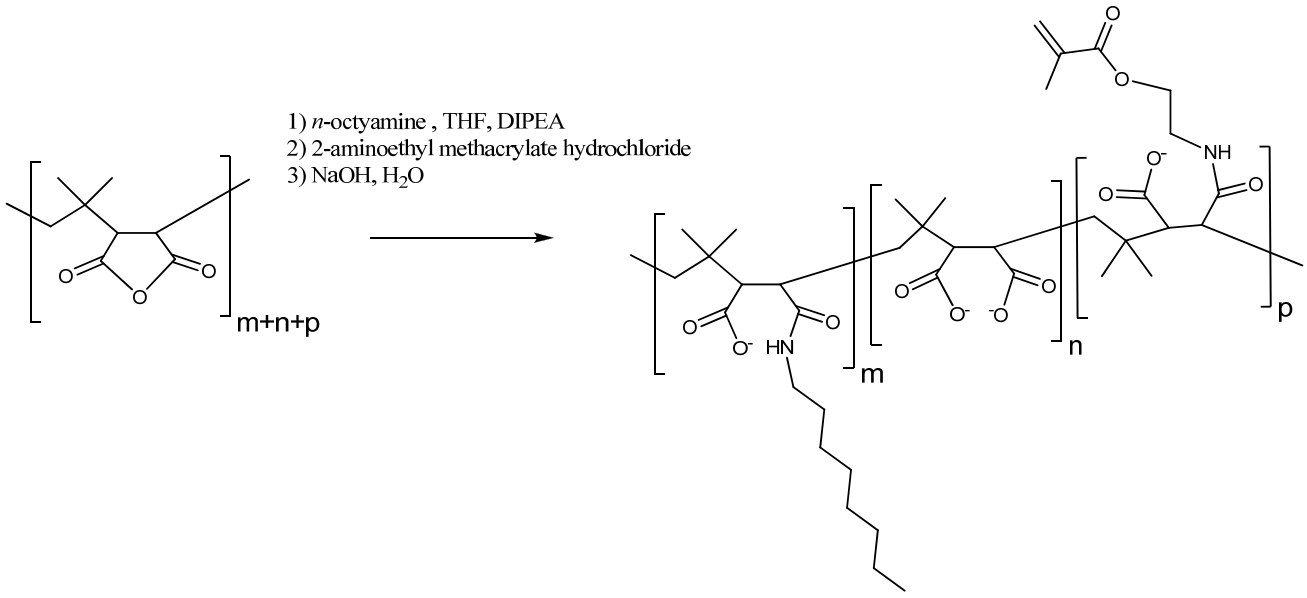
Experimental Procedures

All reagents were purchased from commercially available sources and were used without further purification except NIPAM, which was recrystallized from a toluene/hexane mixture. An Olympus BX60 microscope was used to image the silicon master and the PDMS patterns. A Veeco Bioscope II Atomic Force Microscope (AFM) with a NanoScope IIIa controller was used to investigate the topography of the patterns. AFM was performed in tapping mode using standard silicon tips with a nominal spring constant of 40 N/m. Fluorescence imaging was carried out using a confocal microscope (MicroTime 200, Pico Quant, Germany) equipped with suitable dichroic, excitation and emission filters. The samples were excited by a picosecond pulsed laser emitting at 467 nm (PicoQuant, Germany). pH response experiments were done with a Wide-Field Microscope (WFM) based on a Nikon ECLIPSE Ti-U inverted microscope frame. Light from a CW multi-line Ar laser was fiber-coupled to Nikon TIRF attachment and focused on the back aperture of a high NA objective (Nikon TIRF Apo, 100 x, NA=1.49, oil immersion). The luminescence light was collected by the same objective and after passing through the dichroic and emission filter it was directed to a iXonEM+897 EMCCD camera connected to the side port of the microscope. The camera was connected to a computer furbished with a camera-dedicated software to control the imaging parameters, and for data acquisition. Immersion oil was added between the high NA objective and the cover slip for index matching. A Scanning Electron Microscope JEOL JSM6700F instrument was used to record SEM images. 1H NMR spectra were obtained on a Bruker spectrometer (DRX 400 MHz). GPC-Size Exclusion Chromatography was performed using Watters GPC separation module with RI and Wyatt Laser Scattering detector.

Amphipilic polymer synthesis.

To the solution of 2.01 g of poly(isobutylene-*alt*-maleic anhydride) (M_w = 6000 g/mol) in 500 mL of dry THF, *n*-octylamine (0.80 mL, 4.8 mmol), and DIPEA (2.5 mL) were added and the mixture was

stirred for 0.5 h at 50 °C. After cooling down to room temperature, 2-aminoethyl methacrylate hydrochloride (0.8 g, 4.8 mmol) was added and mixture was left overnight with stirring. Subsequently THF was evaporated and the material was re-suspended in water with small excess of NaOH with respect to the carboxylic groups on the polymer backbone. Evaporation of water and DIPEA resulted in a residue, which was dissolved in water and dialyzed against diluted water solution of NaOH and pure water for a few days to obtain the polymer in a sodium salt form (1.61 g). NMR: ^{1}H(400 MHz; D_2O): 7.21 (9 H, br), 6.10 (10 H, s), 5.66 (10 H, s), 4.18 (20 H, br), 3.62 – 1.60 (247 H, m), 1.46 (44 H, br), 1.21 (181 H, br), 1.14 – 0.65 (267 H, m). An M_n value of 10 000 g/mol was obtained using 1H NMR with M_n of anhydride backbone as reference. Composition: methacrylic groups 13 %, *n*-octylamide groups 17 %, carboxylic groups 70 %. (m = 13, n = 15, p = 10). GPC measurement carried out in DMF using laser light scattering detection provides absolute molecular mass of aggregates of M_w = 40 x 10^6 g/mol.



Scheme 1. Synthesis of amphiphilic polymer – reaction scheme.

PDMS stamp preparation.

A cleaned silicon master (20 mm x 20 mm) with 2 μm x 2 μm x 2 μm grating pattern was oxidized by plasma treatment and placed in a desiccator together with 0.50 mL of trichloro (1H, 1H, 2H, 2H) perfluorooctylsilane. Vapor deposition was carried out for 16 hours under 0.1 bar. The pattern was replicated in PDMS using a standard procedure. 10.0 mL of Sylgard® 184 Silicone Elastomer base and 1.0 mL of curing agent were mixed and casted onto the master. After removing the air bubbles from the mixture under reduced pressure, the mixture was left to cure overnight at 60 °C. Detachment and cutting of the excess of PDMS produced a stamp with a grating pattern 2 μm wide, 2 μm high and with a 2 μm edge to edge distance between the stripes.

Glass substrate preparation.

Microscope glass cover slides (22 mm x 22 mm) were placed in an oven heated to 350 °C and left at this temperature for 5 hours. The slides were then cooled down slowly overnight. After the cleaning procedure, the substrates were coated with methacrylic functional groups by placing them in a desiccator together with 0.50 mL 3-(trichlorosilyl) propylmethacrylate (methacrylic silane). Vapour deposition was carried out for 16 hours under 0.1 bar.

Preparation of QD/NIPAM solution.

CdSe/ZnS core-shell nanocrystals coated with trioctylphosphine oxide / *n*-hexadecylamine ligands were synthesized and transferred into water using an amphiphilic polymer following previously described procedures.[1] 2 mg of amphiphilic polymer for 1 mg of QDs were used resulting with 20 mg/mL of QDs solution. A typical stamp ink composed of 3 mg of NIPAM dissolved in aqueous solution of QDs

[1] D. Jańczewski, N. Tomczak, M. Y. Han and G. J. Vancso, *Euro. Polym. J.*, 2009, **45**, 1912-1917.

(50 µL) contains 20 mg/mL of QDs, 40 mg/mL of amphiphilic polymer, and 60 mg/mL of NIPAM. Concentration of NIPAM in the ink solution can be varied to some extent.

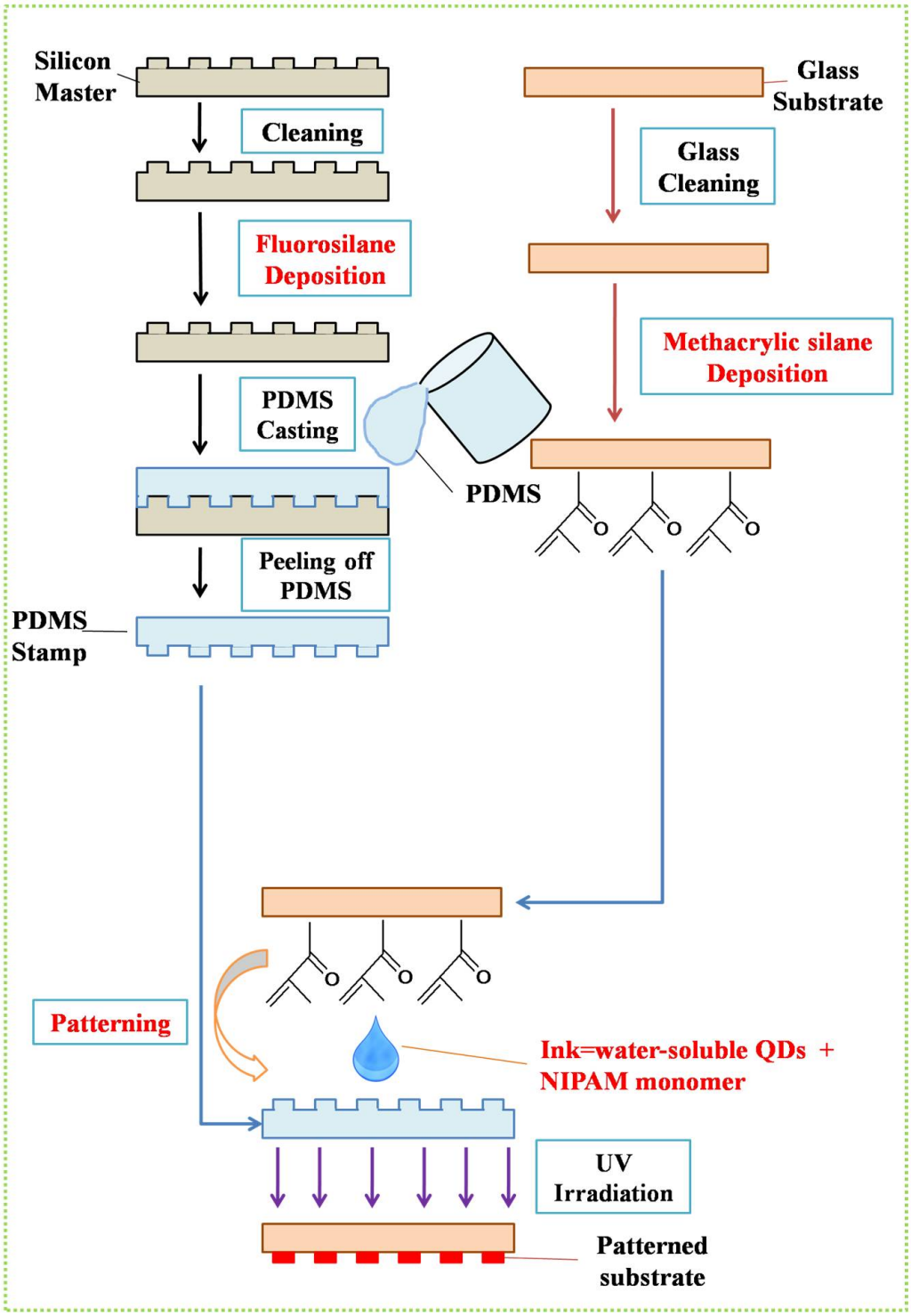
Micro-patterning.

1.0 µL of QD/NIPAM aqueous solution was dropped on the modified PDMS stamp and the acrylic functionalized glass substrate was placed on top of the stamp surface (for the preparation of PDMS stamp and glass substrates please see supporting information) The sample was placed in a SpectroLinker TM XL-1500 UV crosslinker equipped with six 15 W UV (254 nm) lamps and exposed to UV radiation for 3 hour. The temperature was not controlled during the polymerization and was allowed to rise to 40 °C. After polymerization, the substrate was detached from the stamp by gentle peeling off along the groves of the pattern. For pH response experiments, patterns were additionally exposed to UV curing for 1h after detachment of the PDMS mould.

Pattern characterization.

For characterization of thermoresponsive behaviour, patterned glass slides were placed into a sealed sample holder and immersed into hot water. The measurements were first performed at high temperature. The samples were cooled down prior to performing the measurements at RT.

For characterization of the pH-responsive behaviour, patterned glass slides were exposed to commercial phosphate buffer of pH 3 and pH 8 by alternating deposition of solution on the top of the slide. Samples were rinsed with pure water before changing the pH of the solution.



Scheme 2. Complete procedure for micro-patterning and copolymerization.

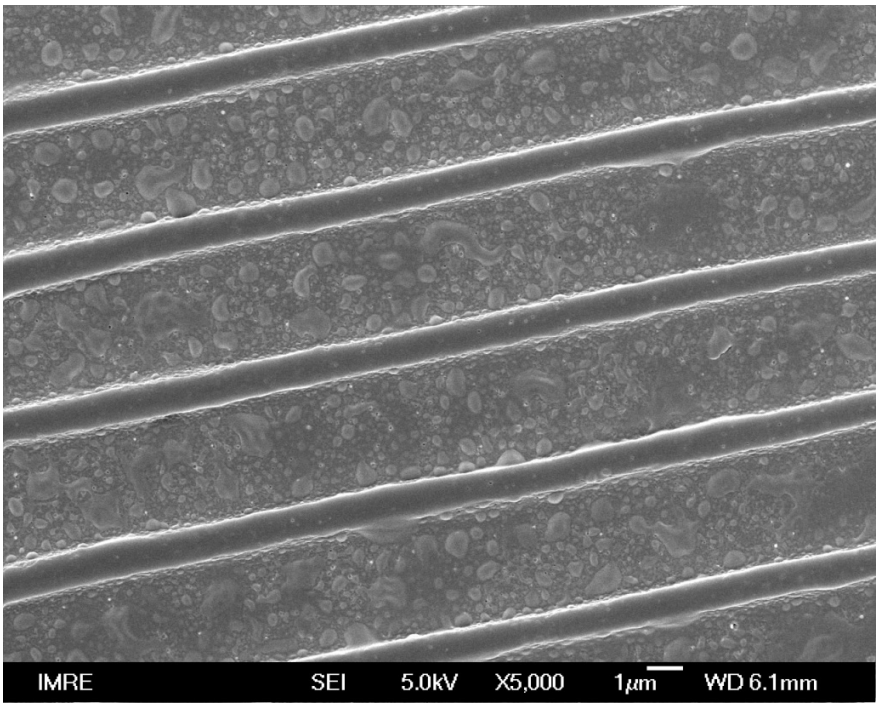


Fig. 1. SEM image of a representative polymeric pattern coated with gold layer.

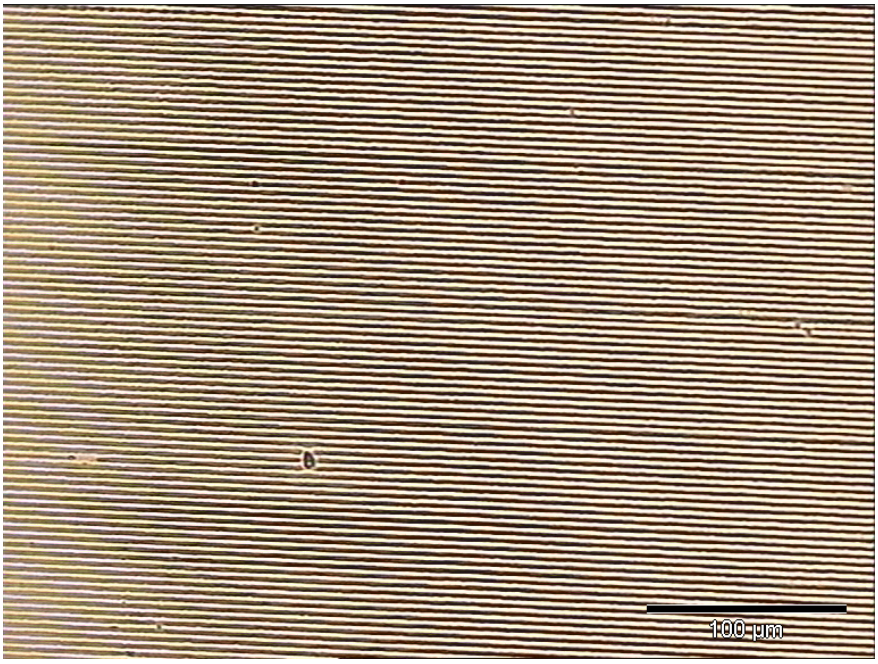


Fig. 2. Optical micrograph of a large patterned area.

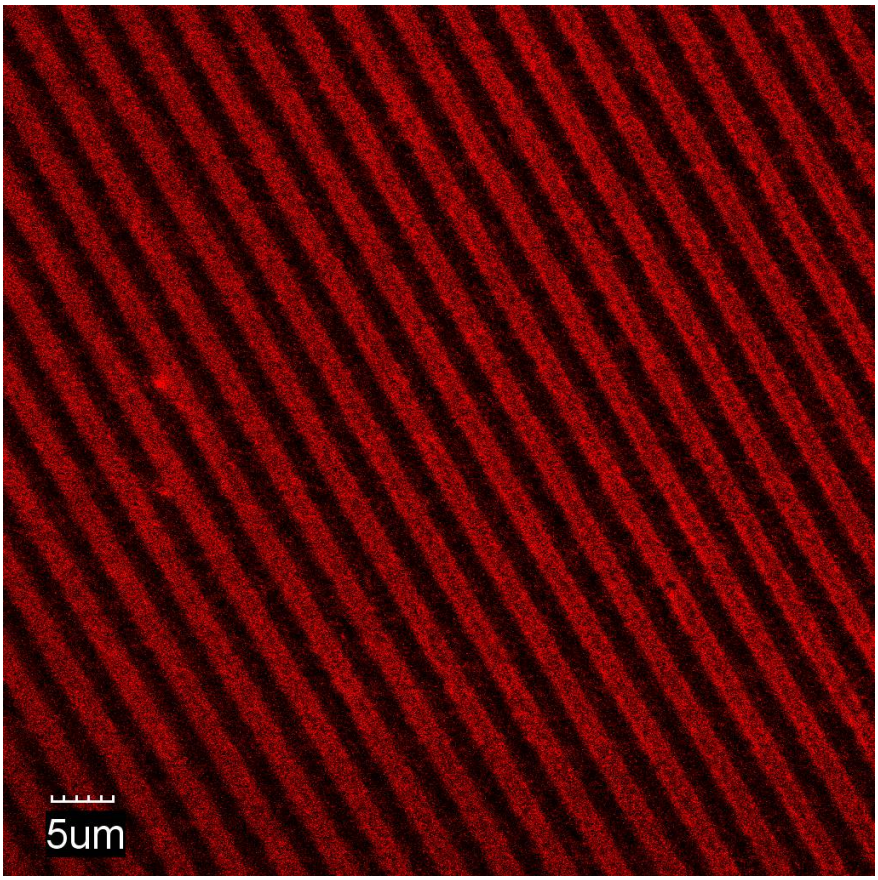


Fig. 3. Fluorescence image of QD/PNIPAM patterns obtained in air.

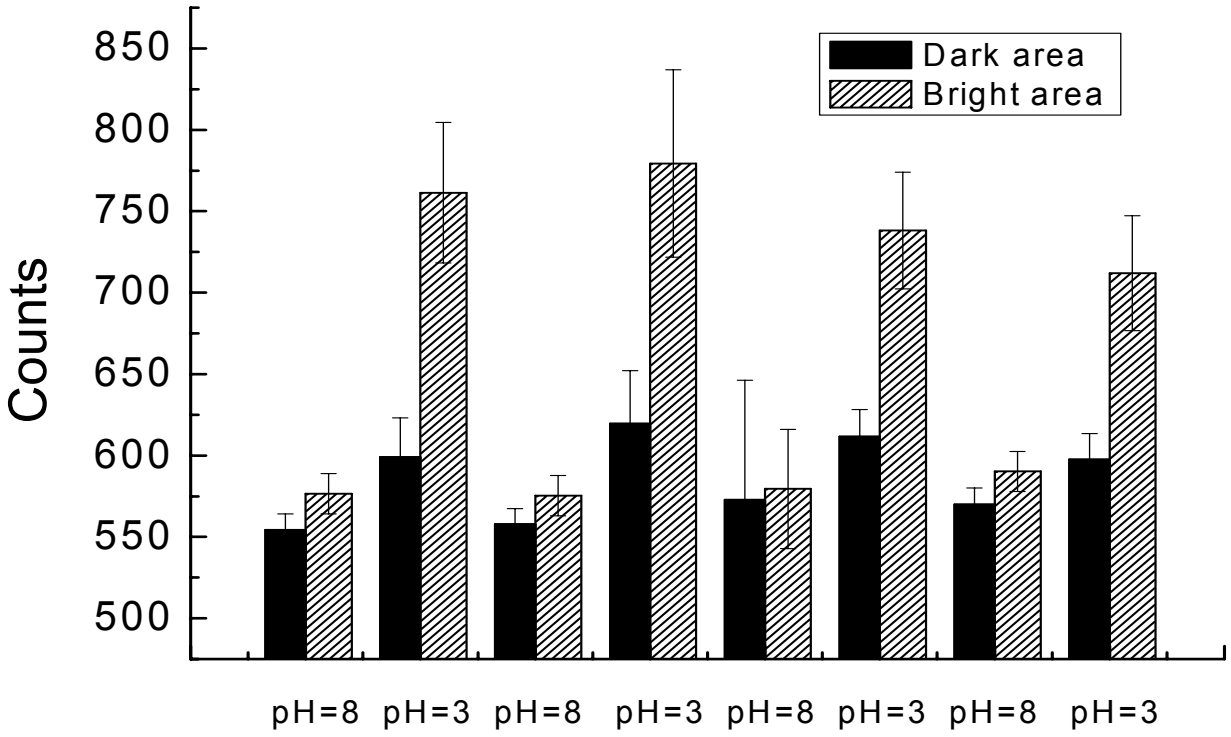


Fig. 4. Absolute fluorescence changes of patterned stripes and grooves upon changes of pH of the solution. Contrast is strongly increasing at low pH.