Supplementary Information

Island brushes to control adhesion of water in oil droplets on planar surfaces

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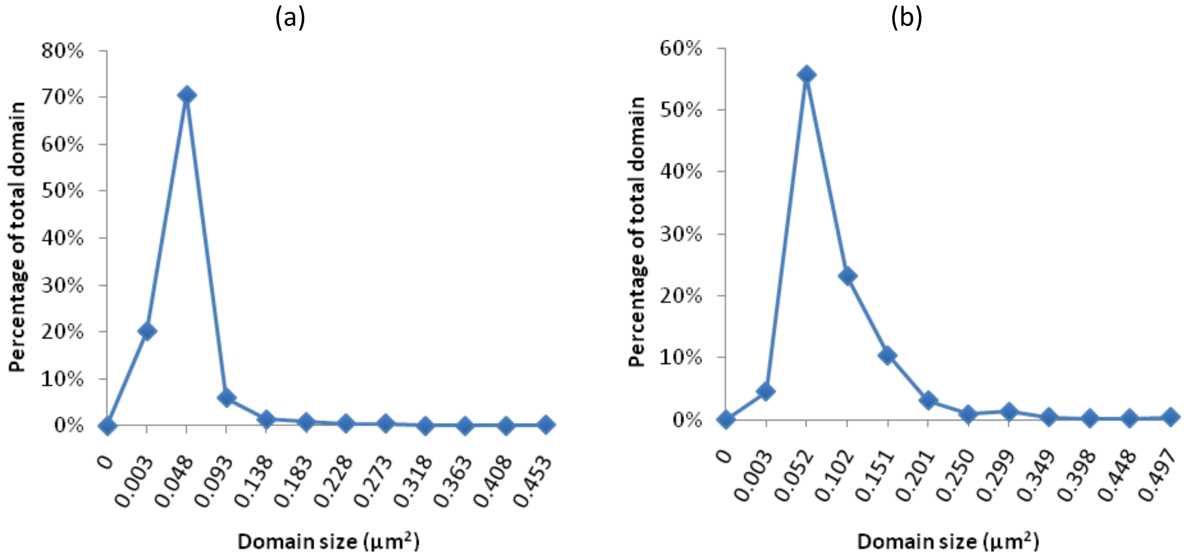

Figure S1. Domain size distribution for silicon substrates coated with (a) 40:1 and (b) 60:1 PFOTS:poly(MEO$_2$MA-*co*-OEGMA) ($h_{\mathrm{ref}} \approx$ 10-12 nm).

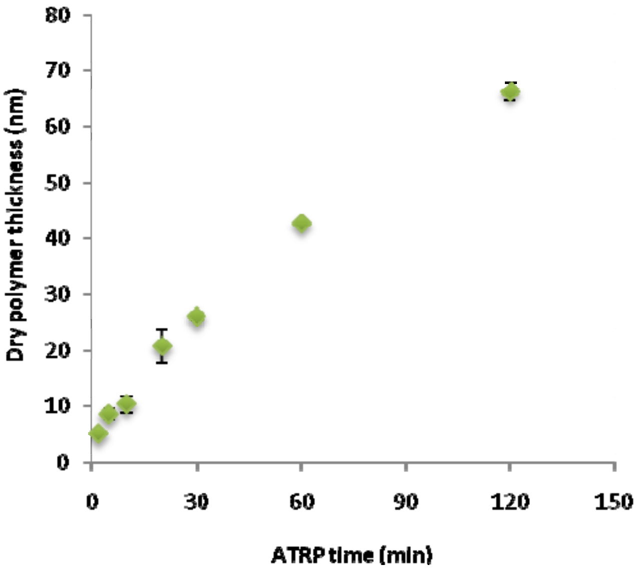

Figure S2. Dry poly(MEO$_2$MA-*co*-OEGMA) thickness as a function of the ATRP time. Polymer thickness was determined via ellipsometry.

Coating of gold substrates

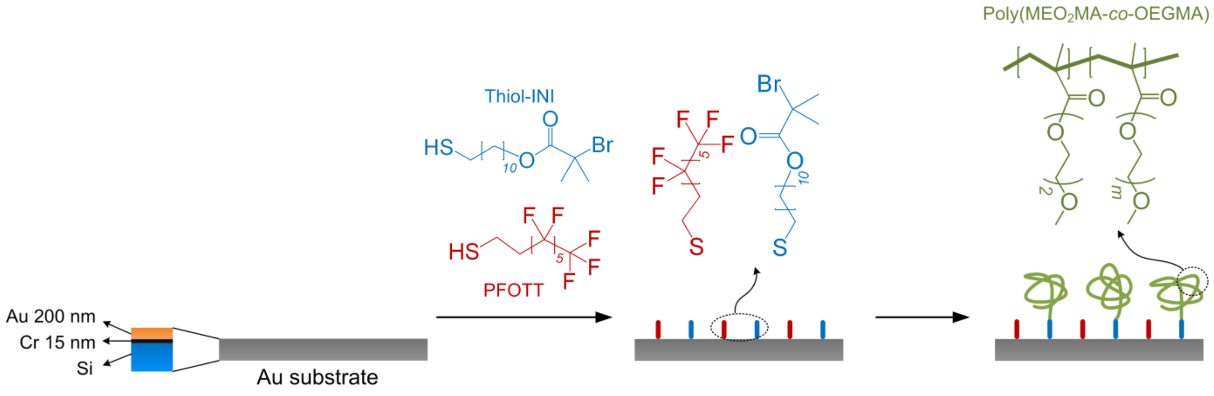

Figure S3. Schematic overview of polymer brush formation on gold substrates via self-assembly of Thiol-INI and PFOTT and subsequent surface-initiated ATRP.

Gold-coated substrates were prepared by evaporating a chromium layer (15 nm) followed by a gold layer (200 nm) on plasma-oxidised silicon wafers (Figure S3), using an Edwards Auto 500 evaporator. Surface functionalisation of gold substrates was carried out according to the procedures as for silicon substrates, with the exception that ATRP initiator ω-mercaptoundecylbromoisobutyrate (Thiol-INI) and fluorine-containing thiol molecule 1*H*,1*H*,2*H*,2*H*-Perfluoro-1-octanethiol (PFOTT) were used. Thiol-INI was synthesised following a published procedure.[1] PFOTT was obtained from Aldrich. Briefly, gold substrates (~1×1 cm^2 each) were transferred to a crystallisation dish and immersed in a solution of Thiol-INI (3 μL), PFOTT (volume depended on the desired volume ratio with respect to Thiol-INI) and absolute ethanol (50 mL). The crystallisation dish was covered and left at RT for 18 h. Subsequently, the substrates were rinsed thoroughly with absolute ethanol and dried under a stream of nitrogen. The coated gold substrates were used immediately in ATRP of MEO$_2$MA (90 mol%) and OEGMA (10 mol%) using the same materials and following the identical procedures as for silicon substrates.

Reference

1 D. M. Jones, A. A. Brown and W. T. S. Huck, *Langmuir*, 2002, **18**, 1265-1269.

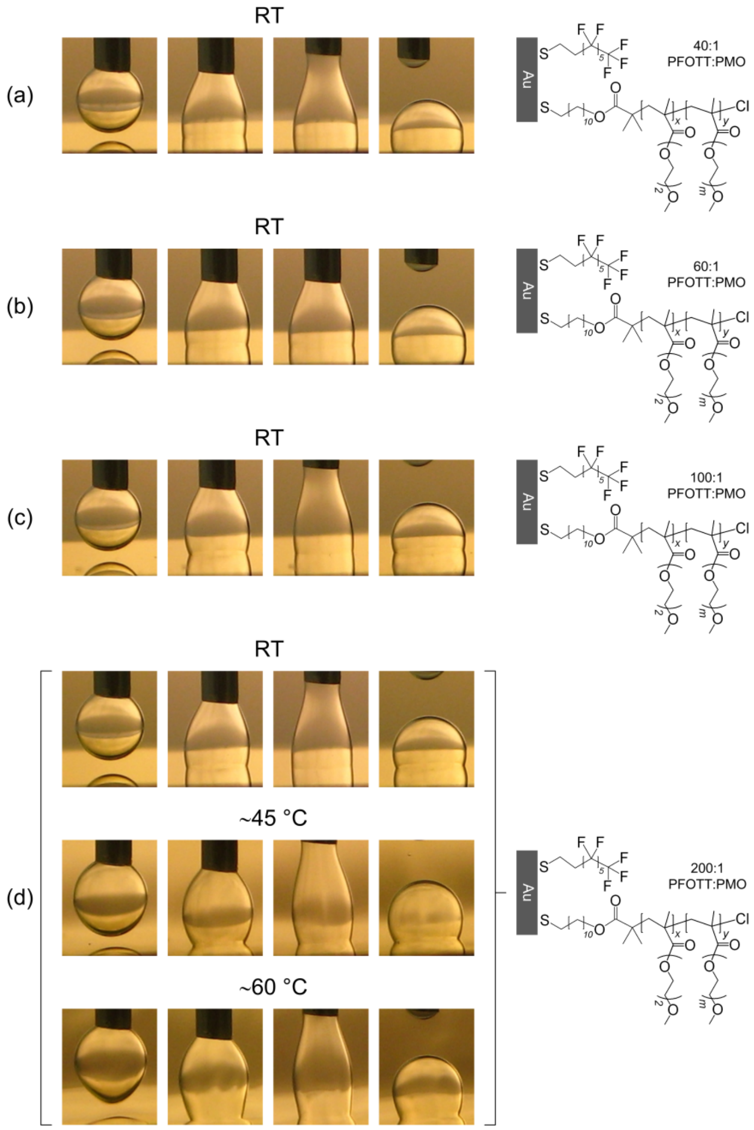

Figure S4. Adhesion of water in decane on coated gold substrates as a function of the PFOTT:poly(MEO$_2$MA-*co*-OEGMA) ratio. Substrates were coated with poly(MEO$_2$MA-*co*-OEGMA) (PMO) ($h_{\text{ref}} \approx$ 11-13 nm) at different PFOTT:PMO ratios: (a) 40:1, (b) 60:1, (c) 100:1 and (d) 200:1.

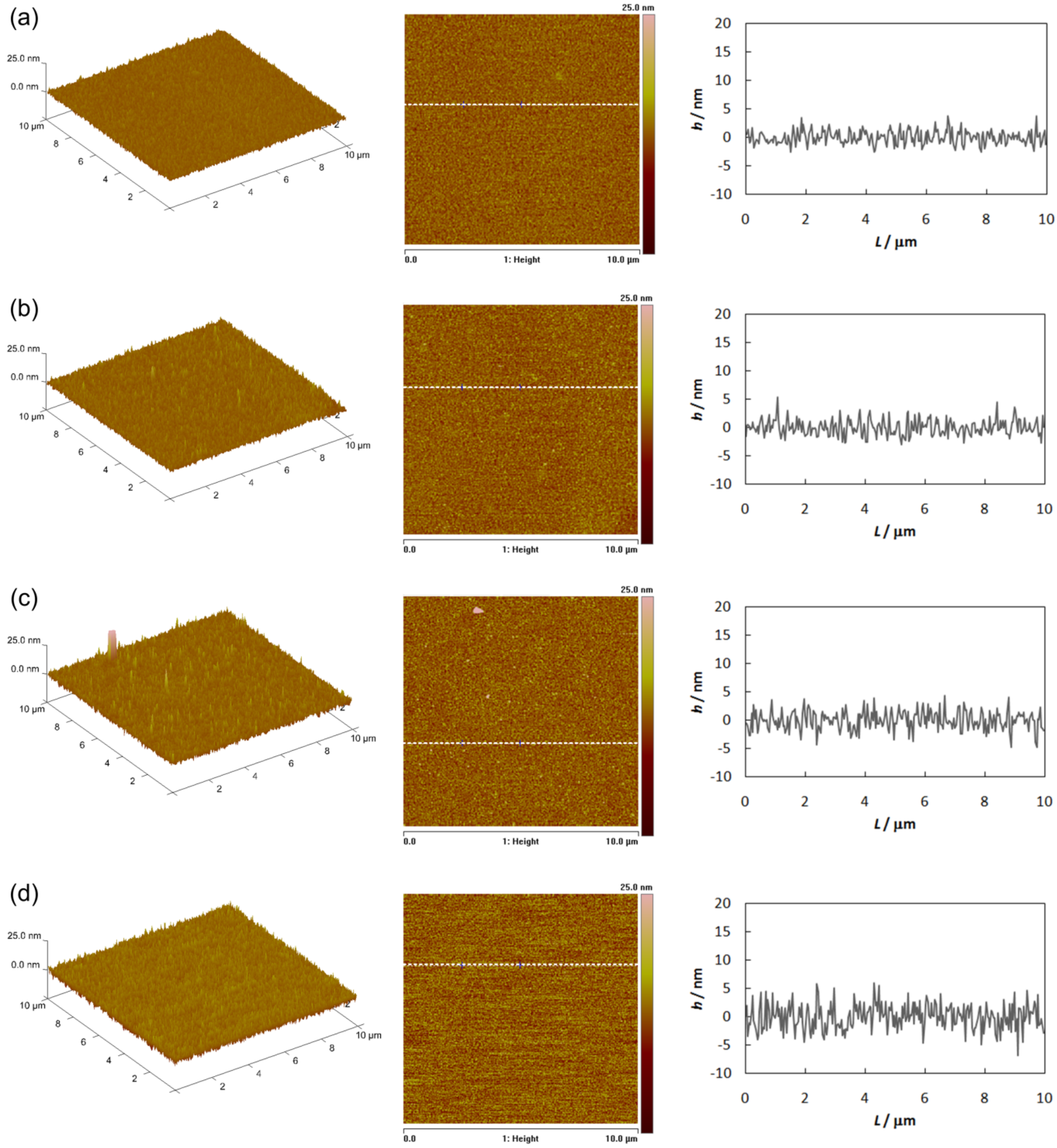

Figure S5. AFM images (3D, 2D and cross-sectional views) for gold substrates coated with various PFOTT:Thiol-INI ratios and grafted with poly(MEO$_2$MA-*co*-OEGMA) (ATRP 10 min and $T_{\mathrm{ref}} \approx$ 11-13 nm). PFOTS:poly(MEO$_2$MA-*co*-OEGMA) ratio: (a) 100% poly(MEO$_2$MA-*co*-OEGMA) brush, (b) 40:1, (c) 60:1, (d) 100:1 and (e) 200:1. Cross-sectional views were taken from 2D images as indicated by the white broken lines.

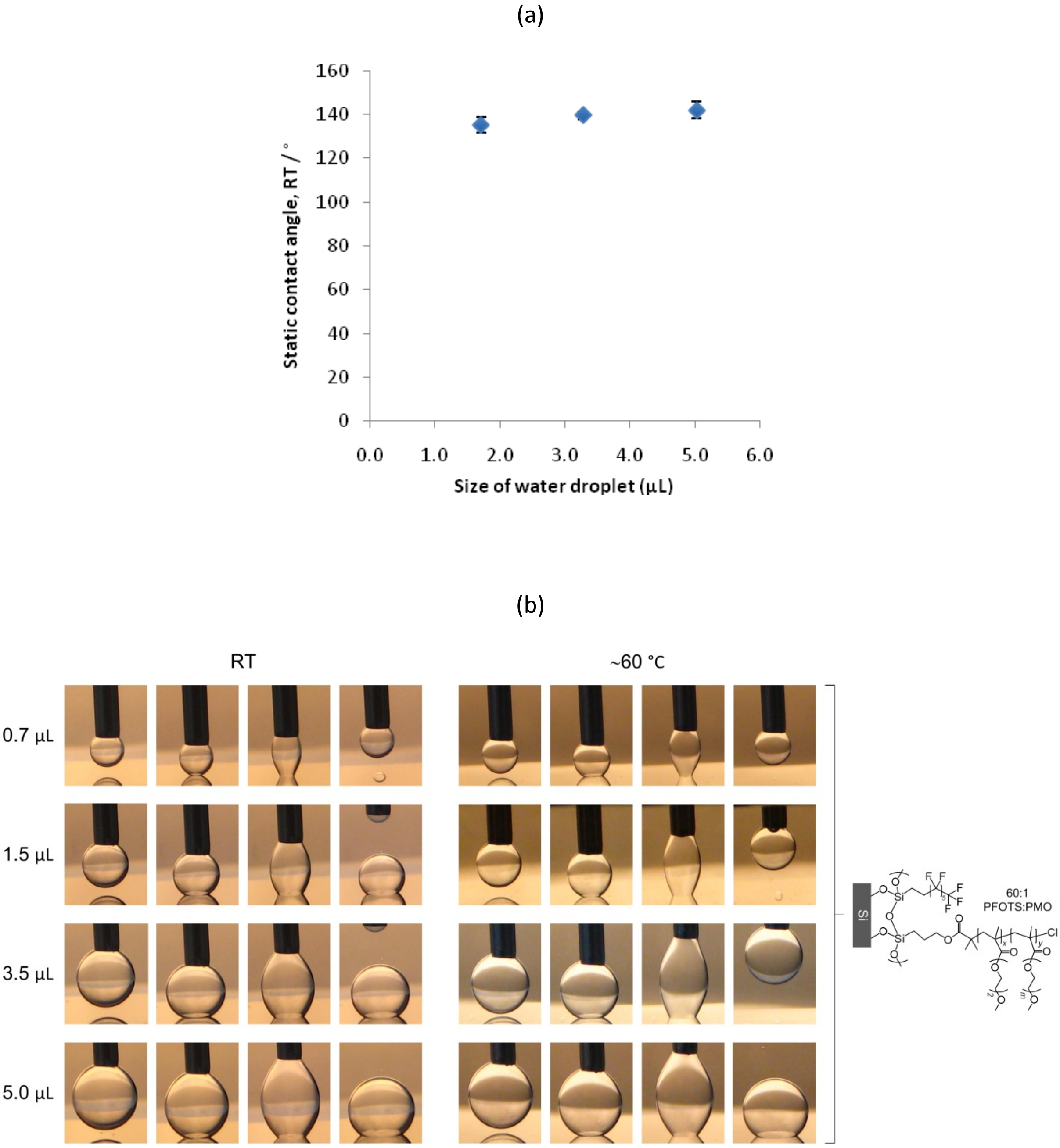

Figure S6. (a) Static contact angles and (b) adhesion of water in decane on coated silicon substrates as a function of the water droplet size. All substrates were coated with 60:1 PFOTS:poly(MEO$_2$MA-*co*-OEGMA) (PFOTS:PMO) ($h_{ref} \approx 9$ nm).