Electronic Supplementary Information to:

Z. Wang, H. Zuilhof - Self-Healing Fluoropolymer Brushes as Highly Polymer-Repellent Coatings

Experimental section

Materials: 10-Undecyn-1-ol; 97% were purchased from ABCR and used as received. Polystyrene (PS, M_n = 5000 g/mol, PDI = 1.06) and poly(N–isopropyl acrylamide) (PNIPAM, M_n = 5000 g/mol) were got from Sigma-Aldrich. Poly(acrylic acid) (PAA, M_n = 5000 g/mol, PDI = 1.2); poly(4–chloro styrene) (P4CS, M_n = 5000 g/mol, PDI = 1.3); Poly(2-vinyl pyridine) (P2VP, M_n = 5000 g/mol, PDI = 1.06); poly(adipic anhydride) (PAAD, M_n = 5000 g/mol) and poly(hydroxyl propyl methacrylate) (PHPMA, M_n = 5000 g/mol, PDI = 2.20) were provided by Polymer Source Inc. α,α,α-Trifluorotoluene (anhydrous), toluene (general purpose grade), dichloromethane (laboratory reagent grade), methanol (laboratory reagent grade); acetone (laboratory reagent grade), ethyl acetate (HPLC, 99.8%); dimethylformamide (laboratory reagent grade) and trifluoroethanol (laboratory reagent grade) acetone (semiconductor grade VLSI PURANAL), 4,4′-dinonyl-2,2′-bipyridine (dNbpy), α-bromoisobutyryl bromide, copper(I) bromide (Cu(I)Br) and Fluorinert® FC-40 were received from Sigma-Aldrich and used without further purification. 2-Perfluorooctylethyl methacrylate (MAF17) was purchased from Sigma-Aldrich and passed through basic alumina column before using. Silicon wafers, with a 0.2° miscut angle along the ⟨112⟩ plane, were (111)-oriented, n-type, phosphorus-doped and with a specific resistance of 1−10 Ω cm^{-1}, as purchased from Siltronix (France). Ammonium fluoride (Riedel-de Haën, 40%, semiconductor grade VLSI PURANAL Honeywell 17600) and acetone (Aldrich, semiconductor grade VLSI PURANAL Honeywell 17617) were obtained from Sigma-Aldrich and used without further purification.

Surface functionalization: The surface functionalization and initiator immobilization were performed as the procedure reported previously. Briefly, a three-necked flask was charged with 2 mL 10-Undecyn-1-ol and purged with argon under reduced pressure for 30 min, while being heated to 80 °C. Si(111) wafers were cut into 1 × 1 cm^2 pieces. The surfaces were sonicated for 5 min in pure acetone and subsequently cleaned using air plasma (Harrick Scientific Products, Inc. Pleasantville, NY) for 5 min and quickly transferred to freshly prepared, argon-saturated 40% aqueous ammonium fluoride solution for 15 min. The surfaces were again rinsed with water and dried with a stream of argon. These samples were then immediately transferred into the flask, which was immediately depressurized again. The reaction mixture was kept at 80 °C for 16 h. The sample was then removed from the flask and immediately extensively rinsed with CH_2Cl_2, sonicated for 5 min in CH_2Cl_2 to remove physisorbed molecules, and blown dry with a stream of dry argon. The surfaces were directly used for surface characterization or stored in the glovebox until fouling experiment.

Initiator immobilization: A 25 mL vial containing 1 mL of dichloromethane and a clean hydroxyl-terminated surface was flushed using a stream of dry argon for 5 min. Initiator α-bromoisobutyryl bromide (2 mL) and triethylamine (5 drops) were added into the vial. The inert atmosphere was maintained by a continuous flow of argon for 5 min and followed by shaking at 80 rpm at 25 °C for 2 h. The resulting initiator functionalized surface was washed using dichloromethane several times, sonicated for 5 min in CH_2Cl_2 and dried with a stream of argon.

Preparation of the PMAF17 brush: A single-neck 15 mL flask was filled with initiator immobilized Si(111) surface, 1 mL MAF17, 1 mL TFT and 25 mg dNbpy. The mixture was put into liquid nitrogen, after the mixture was completely frozen, 5 mg CuBr was added. The flask was connected with vacuum line and depressurized immediately to 1 mbar, and then the frozen mixture was melt and diluted with argon, frozen and go to vacuum again. Repeated the freezing-melting procedure for three times, and at last the flask was put into 110 °C oil bath at vacuum for reacting set time to obtain optimized thicknesses of the resulting polymer brushes. The polymerization was stopped after a fixed time by exposing the reaction mixture to air. The mixture were diluted with 5 mL TFT and kept in 110 °C for half an hour, then take it out and dried by argon, followed by sonication by FC-40 and TFT for 30 and 10 min to remove any physisorbed reaction components, and dried under a stream of argon. In the end, the surface was put in the vacuum overnight to eliminated any left solvent.

Polymer adsorption behavior onto the fluoropolymer brush: Clean and well-characterized PMAF17 brushes were used for fouling studies. For all experiments the concentration of fouling polymer was 10 mg/mL in toluene for PS and 10 mg/mL in DMF for P2VP. The well-cleaned surface was immersed into the polymer solution for 12 h, and then taken out, washed with the same solvent for 2 min in an autoshaker (at 50 rpm), taken out, rinsed, and this washing step was performed in total three times. Next, the sample was dried with argon stream and put into vacuum for 2 h. Unfouled polymer brushes are not affected in any observed manner by this sonication and drying treatment. The extent of absorption (fouling) and the morphology of the adhered polymer on these monolayers were characterized by XPS and AFM measurements. Unmodified silicon, **F1** and **F17** monolayers was used as reference in this polymer absorption survey. For each surface, the fouling experiments were conducted on three different samples, and on each sample the ellipsometry and AFM were carried out at five different places.

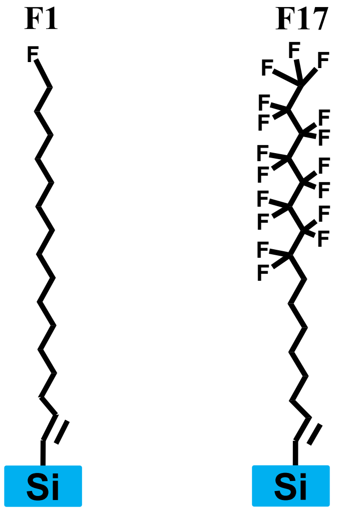
Static contact angle measurements: The static contact angle measurements were conducted using a Krüss DSA 100 contact angle goniometer having an automated drop dispenser and an image/video capture system. The static contact angles were measured at three different places on a modified surface by dispensing three small droplets (3.0 μL volume of deionized water or toluene) with the help of an automated drop dispenser. The tangent 1 fitting model was implemented for contact angle measurements with an accuracy of ± 2°.

X-ray photoelectron spectroscopy (XPS): X-ray photoelectron spectra at ambient temperature were obtained using a JPS-9200 photoelectron spectrometer (JEOL, Japan) for all 1 × 1 cm^2 samples used in the study of the anti-fouling experiment. A monochromatic Al Kα X-ray source (h_v = 1486.7 eV, 12 kV and 20 mA) with an analyzer pass energy of 10 eV was used. A base pressure of 3×10^{-7} Torr was maintained in the XPS chamber during measurements and the spectra were collected at room temperature. The X-ray incidence angle and the electron acceptance angle was 10° to the surface normal. The takeoff angle φ (angle between sample and detector) of 80° is defined to a precision of 1°. The intensity of the XPS core-level electron was measured as the peak area after standard background subtraction according to the linear procedure. All XPS spectra were evaluated using the Casa XPS software (version 2.3.15). The symmetrical GL(30) line shape was employed, which consists of a Gaussian (70%) and a Lorentzian (30%) component. The full width at half maximum of each component was constrained to 1.0 – 1.1 eV.

The relative areas of each component peak were fixed by the stoichiometry of the main hydrocarbon peak, which was assigned to aliphatic carbon (CH_2) with a binding energy of 285.0 eV.

Ellipsometry: The ellipsometric thickness of the modified surfaces was measured using a rotating Sentech Instruments (Type SE-400) ellipsometer, operating at 632.8 nm (He−Ne laser), and an angle of incidence of 70°. The optical constants of a freshly etched H-terminated Si(111) surface were taken as n = 3.850 and k = 0.057. The thicknesses of the polymer brushes were determined with a planar three layer (ambient, polymer brush, substrate) isotropic model, with assumed refractive index of 1.36 for all of the polymer brushes. The reported values are the average of at least 5 measurements.

AFM characterization: AFM images (256 × 256 pixels) were obtained with an MFP3D AFM (Asylum Research, Santa Barbara, CA). The imaging was performed in tapping mode in air using OMCL-AC240 silicon cantilevers (Olympus Corporation, Japan) with a stiffness of 1.54 N/m. Images were flattened with a first-order flattening procedure using the MFP3D software. The root-mean-square (RMS) roughness was calculated from the fluctuations of the surface height around the average height in the image. In this way the RMS value describes the topography of the surface. To quantitatively determine the polymer surface coverage at low surface coverages, the measured surface height at a given pixel was compared to a predetermined threshold value. If the measured height exceeded the threshold, a polymer was considered to be adsorbed at that position. Analysis of the entire surface allowed the determination of the fraction of polymer surface coverage (i.e. the fraction of surface with a height above the threshold value).



Scheme S1. Schematic illustration of the **F1** and **F17** monolayer structures.

Table S1. Ellipsometry thickness and static contact angle of Si(111)-YNE-C11-OH and Si(111)-YNE-C11-Br.

	Si(111)-YNE-C11-OH	Si(111)-YNE-C11-Br
Ellipsometric thickness (nm)	1.60 ± 0.10	1.80 ± 0.10
Static contact angle (°)	50 ± 1	70 ± 2

Table S1 shows the ellipsometric thickness and static contact angle of Si(111)-YNE-C11-OH and Si(111)-YNE-C11-Br. The static contact angle and thickness of the silicon surface modified with the hydroxyl terminated alkyne are 50° and 1.60 nm, which demonstrates the successful surface modification. After the hydroxyl group was converted to a bromo moiety, the static contact angle and thickness increases to 70° and 1.80 nm, confirming the successful immobilization of ATRP initiator. The surface functionalization and initiator immobilization process was also confirmed by XPS measurements, please refer to figure S1.

Table S2. Thickness changes of the **PMAF17** brush after 12 damage-repair cycle.

Thickness (nm)	Spot 1	Spot 2	Spot 3	Spot 4	Spot 5	Average
Original	72.13	75.13	74.76	76.31	74.69	74.60
After 12 damage-repair cycles	40.48	45.10	43.23	41.10	44.48	42.94

This table shows the ellipsometric thickness of the freshly prepared **PMAF17** brush and the thickness decrease after 12 damage-repair cycles. The thicknesses of the polymer brushes were determined with a planar three layer (ambient, polymer brush, substrate) isotropic model, with assumed refractive index of 1.36 for the perfluoropolymer brushes. The reported values are the average of 5 measurements. From this table we can see that the freshly-prepared brush has an average thickness of 74.60 nm which decreases to 42.94 nm after 12 damage-repair cycles.

Table S3. Static contact angle of the freshly-prepared, damaged at pH 3 for 24 h and repaired by heating at 120 °C for 2 h **PMAF17** brush.

Freshly prepared PMAF17 brush	Damaged at pH 3 for 24 h	Repaired by heating at 120 °C for 2 h
121°	116°	121°

This table shows static contact angle of the freshly-prepared, damaged at pH 3 for 24 h and repaired by heating at 120 °C for 2 h **PMAF17** brush. The freshly-prepared **PMAF17** brush has a static contact angle of 121° which decrease to 116° after damage at pH 3 for 24 h. The static contact angle recovers to 121° after heating at 120 °C for 2 h, which illustrates that the hydrophobicity is repaired.

Table S4. Static contact angle of the freshly-prepared, damaged by UV with 254 nm for 1 h and repaired by heating at 120 °C for 2 h **PMAF17** brush.

Freshly prepared PMAF17 brush	Damaged by UV 254 nm for 1 h	Repaired by heating at 120 °C for 2 h
121°	119°	121°

Table S4 shows static contact angle of the freshly-prepared, damaged by UV 254 nm for 1 h and repaired by heating at 120 °C for 2 h PMAF17 brush. The freshly-prepared PMAF17 brush has a static contact angle of 121° which decrease to 119° after damage by UV 254 nm for 1 h. The static contact angle recovers to 121° after heating at 120 °C for 2 h, which illustrates that the UV damaged hydrophobicity can also be repaired by heating.

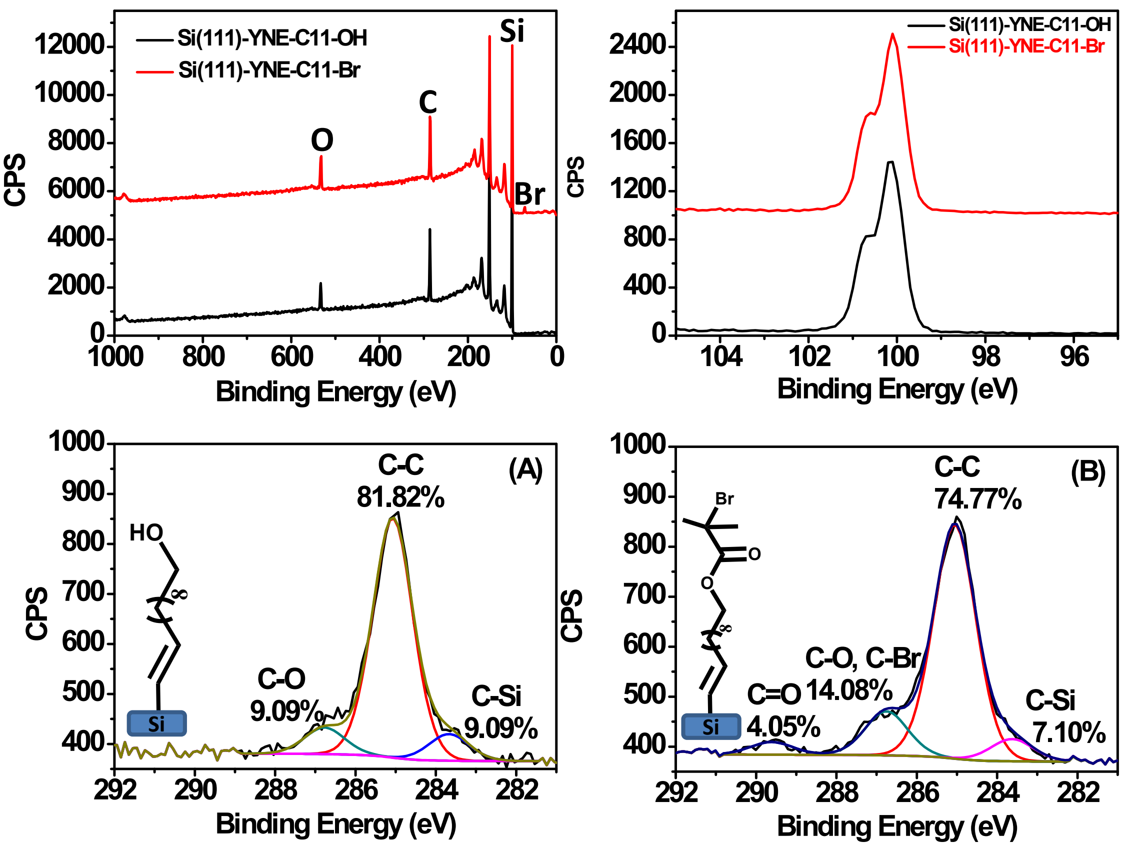


Fig. S1. XPS wide, carbon and silicon narrow scan of Si(111)-YNE-C11-OH and Si(111)-YNE-C11-Br.

Figure S1 shows XPS wide, carbon and silicon narrow scan of Si(111)-YNE-C11-OH and Si(111)-YNE-C11-Br. After converting the hydroxyl group to the bromo, we can clearly see the bromine peak at the XPS wide scan, confirming the successful initiator immobilization. The peaks appeared on the deconvoluted XPS C 1s spectrum of Si(111)-YNE-C11-OH and Si(111)-YNE-C11-Br correspond to the different carbons in this two molecules, further confirming the successful surface functionalization and initiator immobilization. The Si2p high-resolution spectrum shows binding energies of the Si2p1/2 and Si2p3/2 doublet at 100.1 and 99.5 eV, respectively. Importantly, no contribution related to oxide or suboxide species in the energy range of 101−104 eV was observed, indicating the oxide-free nature of the silicon substrate underneath this initiator immobilized substrate.

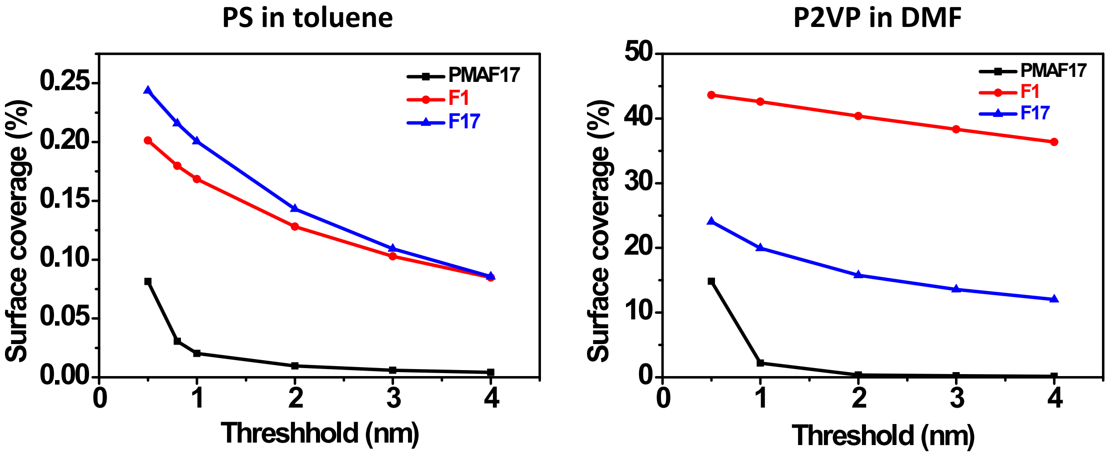


Fig. S2. Surface coverage of the **PMAF17** brush **F1**, and **F17** monolayer after fouling study in PS in toluene and P2VP in DMF solution as a function of threshold. As can be seen, irrespectively of the exact value of this threshold, the relative degree of fouling between the monolayers and the perfluoropolymer brush can be directly evaluated.

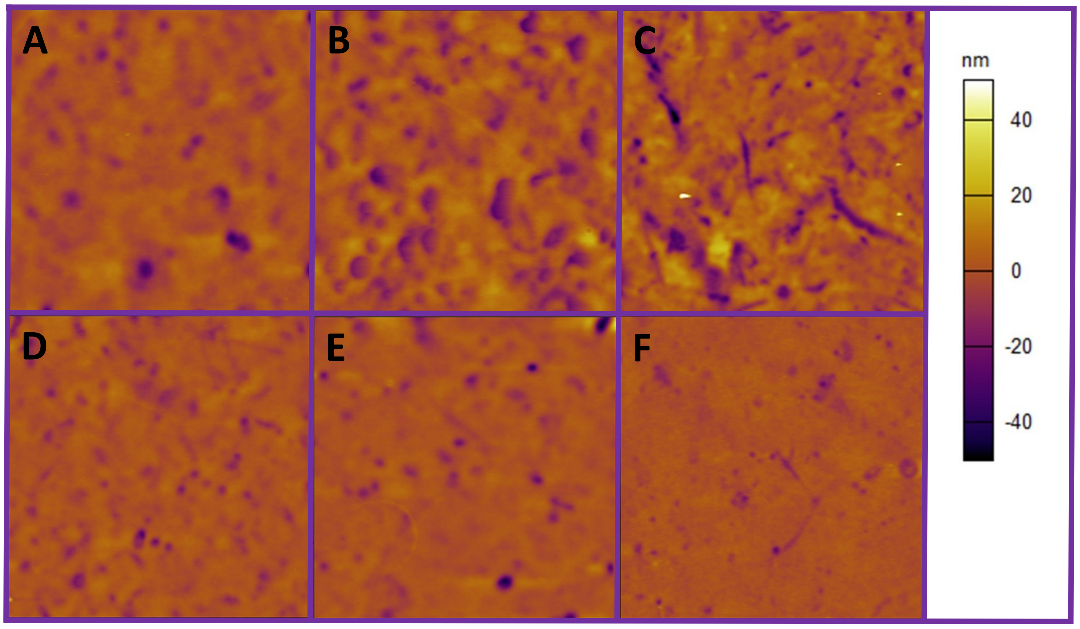


Fig. S3. Tapping mode AFM images (20 × 20 µm^2) in air of the **PMAF17** brush after dipping into some polymer solution for 12 hrs. A - PAA in methanol; B - PHPMA in acetone; C - P4CS in ethyl acetate; D - PS in dichloromethane; E - PAADA in DMF; F - PNIPAM in trifluoroethanol. As can be seen in this figure, no polymers were found for all these tested polymers in different solvents. These observations illustrate that the PMAF17 brush possess excellent anti-fouling property against many polymers in different environments.