Electronic supplementary information for: Tri-functional platform for the facile construction of dual-functional surfaces via a one-pot strategy

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Experimental section

1. Materials

Triazabicyclodecene (TBD), 4-(fluorosulfonyl)benzoic acid, benzoylbenzoic acid, dimanganese decacarbonyl ($Mn_2(CO)_{10}$), triethylamine (TEA, 98%), *N,N'*-dicyclohexylcarbodiimide (DCC, 98%) and 4-dimethylaminopyridine (DMAP, 99%) were purchased from J&K Chemical (Beijing, China). 2-Hydroxyethyl methacrylate (HEMA) was purchased from Aladdin Chemistry Co. (Shanghai, China) and used after removing the inhibitor with an inhibitor remover (Sigma-Aldrich). *N*-Isopropylacrylamide (NIPAAm) was purchased from Acros Organics (Beijing, China) and recrystallized from a toluene/hexane solution (50% v/v) prior to use. Fluorescein isothiocyanate-labeled concanavalin A (FITC-ConA) was purchased from Sigma-Aldrich. Rhodamine-labeled bovine serum albumin (Rh-BSA) was purchased from Solarbio Co., Ltd. (Beijing, China). Tetrahydrofuran (THF), acetonitrile, methanol and all other solvents were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and were used without further purification. 3-Benzoylbenzoyl chloride (BBCL) and butyltrimethoxysilane-modified silicon surfaces (Si-BTMS) were prepared as reported previously[1]. *Tert*-butyldimethylsilyl (TBDMS)-protected 1*H*,1*H*,2*H*,2*H*-heptadecafluoro-1-decanol, poly(ethylene glycol) methyl ether and 1-(6-((tert-butyldimethylsilyl)oxy)hexyl)-3-methyl-1H-imidazol-3-ium bromide (referred to as TBDMS- HDFD, TBDMS-PEG and TBDMS-IL, respectively) were prepared as previously described[2,3]. 2-(Methacrylamido) glucopyranose (MAG) and 2-(2-bromoisobutyrylamido) propane-1,3-diol (BPDL) were synthesized and purified according to published procedures[4,5]. Films of polyvinylchloride (PVC) were prepared as previously described[6]. LIVE/DEAD BacLight Bacterial Viability Kits were purchased from Invitrogen (Thermo Fisher Scientific, USA). Gram-negative *Escherichia coli* (*E. coli* MG1655) was provided by the China General Microbiological Culture Collection Center (Beijing, China).

2. Instruments and measurements

^{1}H, ^{13}C and ^{19}F nuclear magnetic resonance (NMR) spectra were acquired on a Varian Mercury-400 spectrometer (Varian, USA). Fourier transform-infrared (FT-IR) spectra were recorded on a Nicolet 6700 FT-IR spectrometer (Thermo Fisher Scientific, USA). Mass spectrometry (MS) data were obtained using a MICROTOF-Q III instrument (Bruker, Germany). The surface chemical compositions were measured on an ESCALAB MK II X-ray photoelectron spectrometer (VG

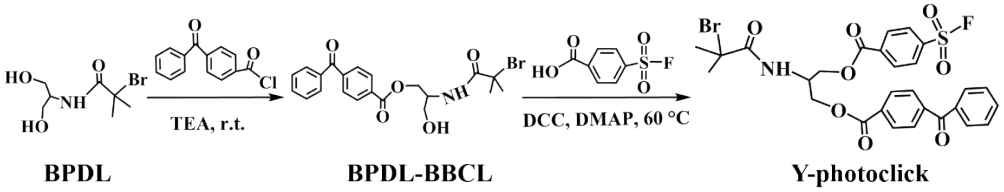
Scientific Ltd., England). Fluorescence images of the bacteria attached to the surfaces were obtained with a fluorescence microscope (BX51, Olympus, Japan). Sessile drop water contact angle measurements were acquired on a SL200C optical contact angle meter (USA Kino Industry Co., Ltd, USA). The thicknesses of the sample surfaces were measured using an α-SE spectroscopic ellipsometer (J.A. Woollam Co. Inc., USA). Protein binding on the surfaces was investigated by an SP511 laser scanning confocal microscope (LSCM, Leica Microsystems, Germany). Ultraviolet light at 365 nm (I_{365nm} = 70.0 mW/cm^2) was obtained with a GY250 device (Beijing Tianmaihenghui Electric Appliance Co., Ltd, China). Ultraviolet light at 420 nm (I_{420nm} = 0.2 mW/cm^2) was generated by filtering the shorter wavelength UV light of a 500 W mercury lamp using JB400 filters (China).

3. Synthesis of Y-photoclick

The tri-functional platform Y-photoclick was synthesized in two steps (Scheme 1): first, esterification of 2-(2-bromoisobutyrylamido)propane-1,3-diol (BPDL) with 4-benzoylbenzoyl chloride (BBCL); second, ester condensation of commercial 4-(fluorosulfonyl)benzoic acid with the product BPDL-BBCL of step 1 afforded the desired trifunctional platform Y-photoclick. Briefly, BPDL (2.45 g, 10.2 mmol) and 1.56 mL of triethylamine (1.14 g, 11.2 mmol) were first dissolved in 35 mL of dry THF, and the mixture was cooled in an ice bath. A solution of 3-benzoylbenzoyl chloride (BBCL) (2.21 g, 10.2 mmol) in THF was then added dropwise to the mixture. After stirring at room temperature for 24 h, the reaction mixture was filtered, and the solvent was removed under reduced pressure. The crude product was purified using silica gel column chromatography with ethyl acetate and hexane (1:1, v/v) as the eluent. The resulting product BPDL-BBCL was obtained as a white liquid (1.68 g, 37% yield). ^{1}H NMR ($CDCl_3$), δ ppm: 7.13-8.25 (m, 10H, -NH and Aryl-H), 4.62-4.84 (d, 2H, O-CH_2), 4.22-4.41 (s, 1H, -CH), 3.72-3.92 (m, 2H, HO-CH_2), 1.89-2.10 (d, 6H, (-CH_3)$_2$) (Figure S1).

Afterwards, BPDL-BBCL (0.35 g, 0.78 mmol), DCC (0.22 g, 1.06 mmol), and DMAP (0.022 g, 0.18 mmol) were dissolved in 30 mL of dry THF. A solution of 4-(fluorosulfonyl)benzoic acid (0.196 g, 0.96 mmol) in THF was then slowly added to the mixture. After stirring at 60 °C for 12 h, the reaction mixture was filtered, concentrated under reduced pressure and diluted using ethyl acetate. The organic layer was washed sequentially with 0.5 mol/L hydrochloric acid and brine and dried with anhydrous magnesium sulfate. The Y-photoclick product was obtained by silica gel column chromatography (ethyl acetate/hexane, 1:3, v/v) as a white solid (0.28 g, 57% yield). ^{1}H

NMR ($CDCl_3$), δ ppm: 8.24-8.36 (m, 2H, Aryl–H7, H8), 8.07-8.09 (m, 4H, Aryl–H14, H15, H16, H17), 7.76-7.91 (m, 4H, Aryl–H5, H10, H11, H12), 7.59-7.68 (m, 1H, Aryl–H6), 7.48-7.57 (m, 2H, Aryl–H9, H13), 7.17-7.20 (m, 1H, -NH), 4.54-4.80 (m, 5H, CH_2-CH-CH_2), 1.80-2.09 (d, 6H, $(-CH_3)_2$) (Figure S2). ^{13}C NMR ($CDCl_3$), δ ppm: 195.82 (C=O), 172.40 (NH-C=O), 164.34-165.69 (O-C=O), 141.91 (Aryl–C22, C16), 135.60-137.05 (Aryl–C13, C25), 132.46 (Aryl–C10, C12, C19), 127.52-131.01 (Aryl–C11, C14, C17, C18, C20, C21, C23, C24, C26, C27) (Figure S3). ^{19}F NMR ($CDCl_3$), δ ppm: 66.01 (s, 1F) (Figure S4). FT-IR (cm^{-1}): 1720 (s, ν(Ph-C=O)), 1650 (s, ν(Ph-C(O)-Ph)), 1650 (s, ν(NH-C=O)), 1520 (s, δ(NH)), 1270 (s, ν(C-(O)-O)) (Figure S5). ESI-MS: calculated for M^+: m/z 634.47; found: m/z 636.0493 (M^+ + 1, M^+ + H) (Figure S6).



Scheme S1. Synthesis of Y-photoclick.

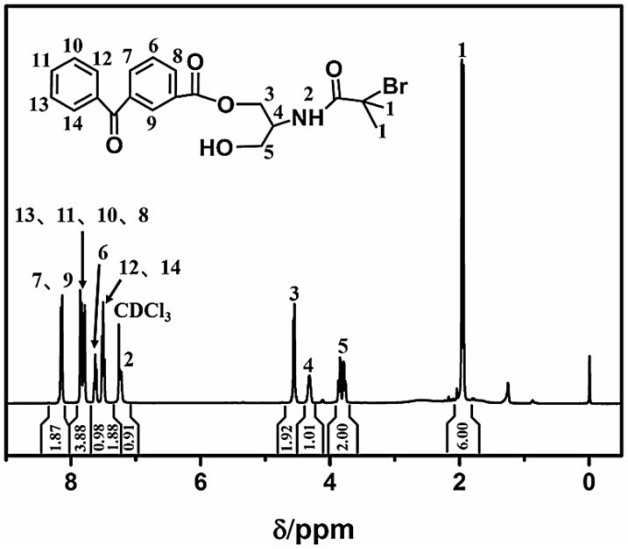


Figure S1. ^1H NMR spectrum of BPDL-BBCL in $CDCl_3$.

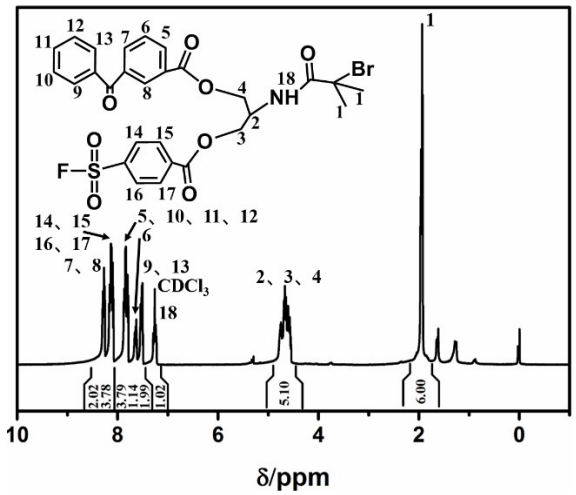


Figure S2. ^{1}H NMR spectrum of Y-photoclick in $CDCl_3$.

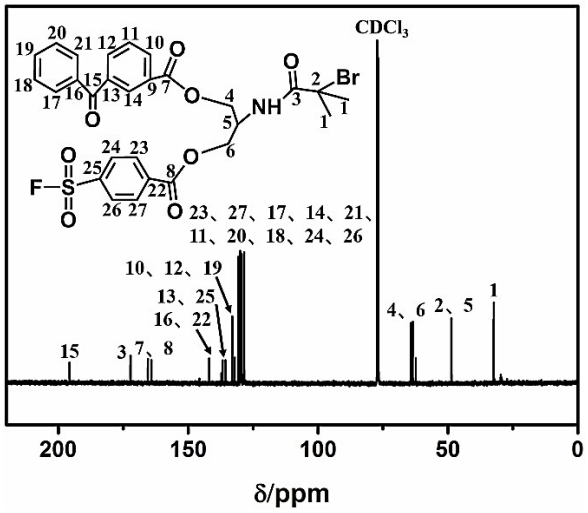


Figure S3. ^{13}C NMR spectrum of Y-photoclick in $CDCl_3$.

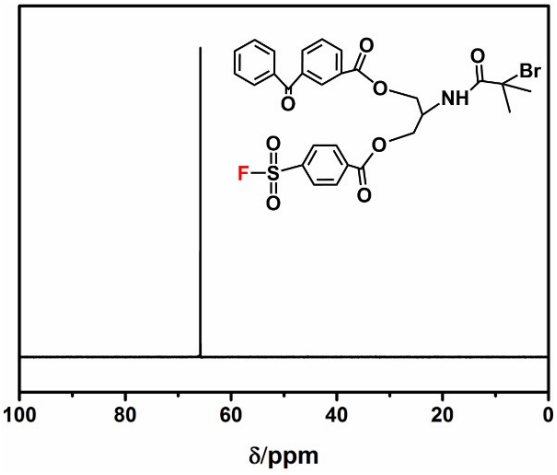


Figure S4. ^{19}F NMR spectrum of Y-photoclick in $CDCl_3$.

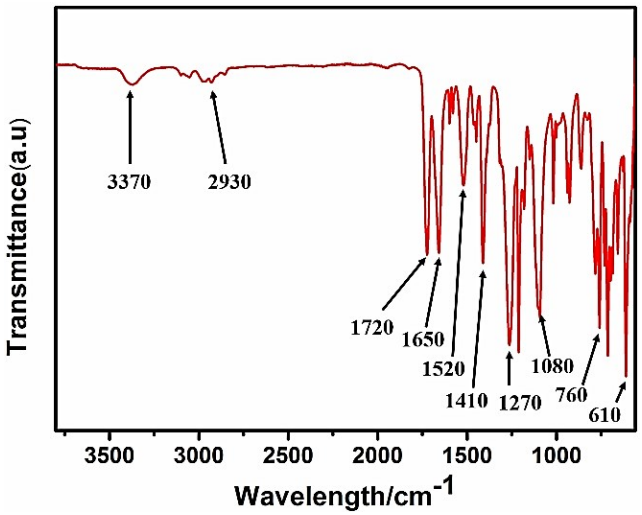


Figure S5. FT-IR spectrum of Y-photoclick.

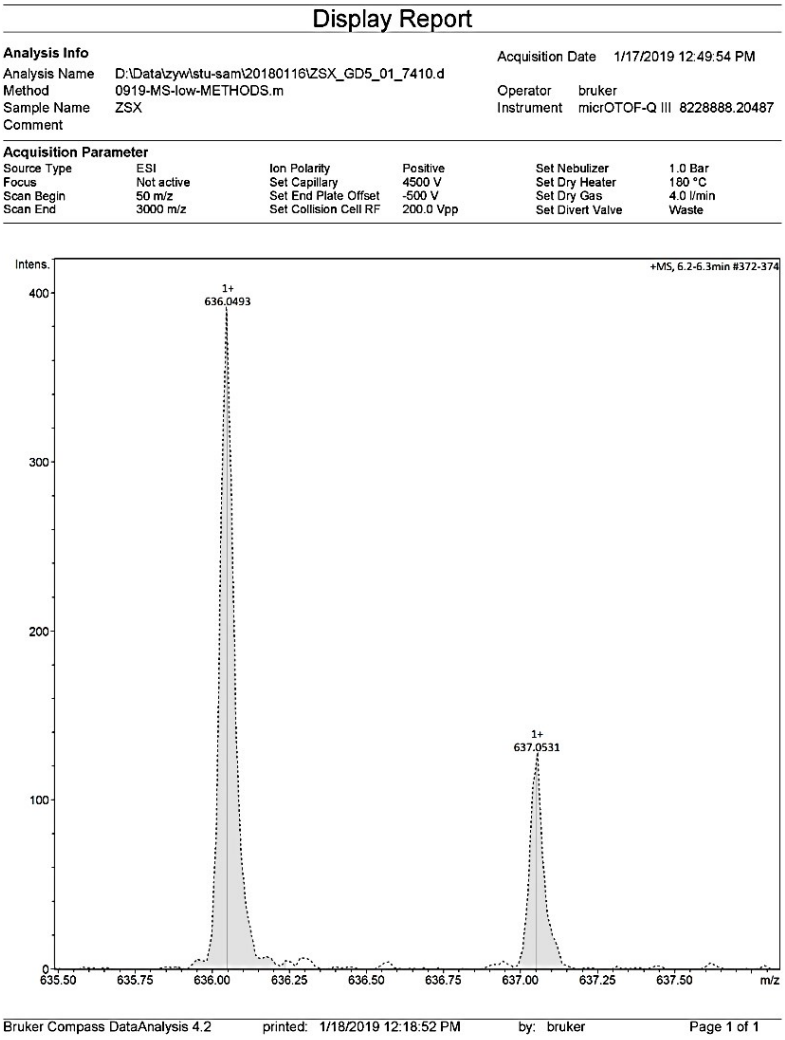


Figure S6. Mass spectrum of Y-photoclick.

4. Synthesis of Y-*g*-PNIPAAm-HDFD

The polymer Y-*g*-PNIPAAm-HDFD was obtained using the following procedure. Briefly, Y-photoclick (0.1 g, 0.16 mmol), NIPAAm (3.62 g, 32.0 mmol), $Mn_2(CO)_{10}$ (4.0 mg, 0.01 mmol), TBDMS-HDFD (0.64 g, 1.1 mmol), TBD (15.4 mg, 0.11 mmol), and 11.0 mL of acetonitrile were placed in a 25 mL round bottomed flask, and the mixture was deoxygenated by bubbling with argon gas for 30 min. After 10 min irradiation with 420 nm UV light, the reaction mixture was dialyzed using seamless cellophane dialysis tubing (MWCO 3500) in distilled water for 3 days followed by lyophilization. The final product, Y-*g*-PNIPAAm-HDFD, was obtained as a white powdery solid. ^{1}H NMR (CD_3OD), δ ppm: 1.06-1.27 (m, H4), 1.48-1.73 (m, H1), 1.81-2.23 (m, H2), 3.85-4.04 (m, H3) (Figure S7). ^{19}F NMR (CD_3OD), δ ppm: -86.27 (s, 3F, F8), -118.31 (s, 2F, F1), -126.61 - -126.96 (t, 6F, F2-F4), -127.75 (s, 2F, F5), -128.62 (s, 2F, F6), -131.25 (s, 2F, F7) (Figure S8).

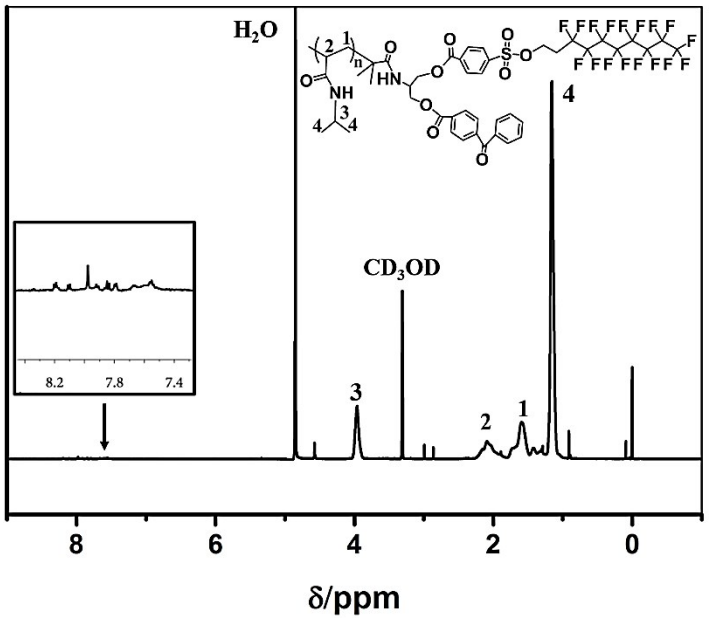


Figure S7. ^{1}H NMR spectrum of Y-*g*-PNIPAAm-HDFD in CD_3OD.

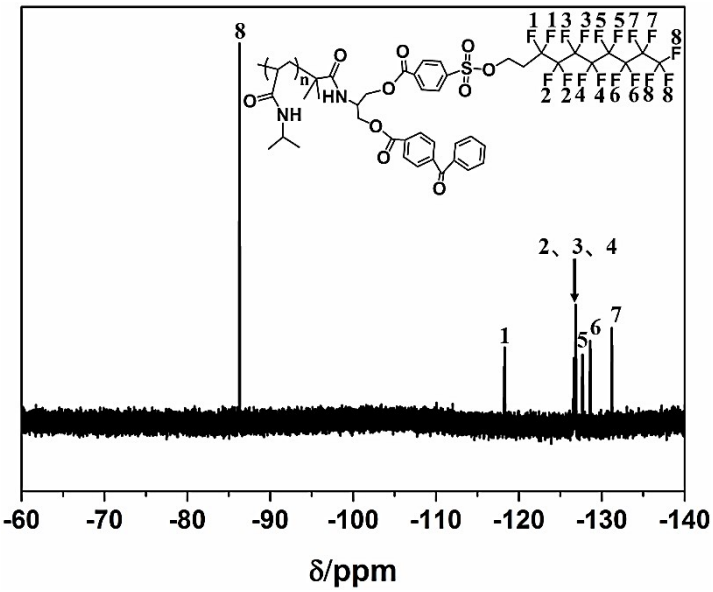


Figure S8. ^{19}F NMR spectrum of Y-*g*-PNIPAAm-HDFD in CD_3OD.

5. One-step preparation of dual-functional surfaces with antimicrobial and antifouling activities

Y-photoclick (12.7 mg, 0.02 mmol), HEMA (0.26 g, 2 mmol), TBDMS-IL (0.053 g, 0.14 mmol), $Mn_2(CO)_{10}$ (4.0 mg, 0.01 mmol), and TBD (2.0 mg, 0.014 mmol) were first dissolved in 6.0 mL of acetonitrile/methanol (1:2, v/v) and then placed in a 25 mL flask with several pieces of Si-BTMS film. Afterwards, the flask was deoxygenated by bubbling argon gas for 30 min and then irradiated with 365 nm UV light at room temperature for 15 min. Finally, the obtained substrates (Si-*g*-PHEMA-IL) were cleaned with acetonitrile and methanol and dried under a flow of nitrogen. In addition, replacement of the above mixture with a mixture of Y-photoclick (12.7 mg, 0.02 mmol), TBDMS-IL (0.053 g, 0.14 mmol) and TBD (2.0 mg, 0.014 mmol) or a mixture of Y-photoclick (12.7 mg, 0.02 mmol), HEMA (0.26 g, 2.0 mmol) and $Mn_2(CO)_{10}$ (4.0 mg, 0.01 mmol), only the SuFEx reaction-mediated IL grafted substrates (Si-*g*-IL) or only the UV-photoinitiated poly(HEMA) brush grafted (Si-*g*-PHEMA) substrates were obtained.

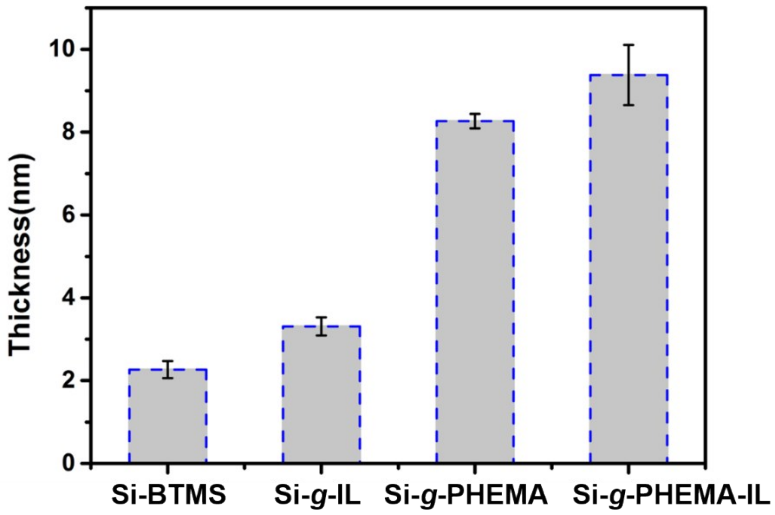


Figure S9. Ellipsometry thickness of dry layer on the modified silicon substrates. The data are presented as the standard deviation (n = 6).

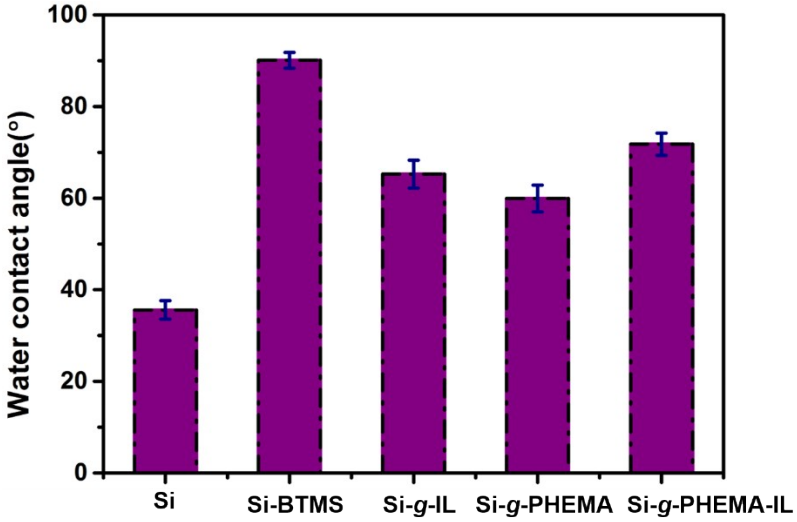


Figure S10. Sessile water drop contact angles of the unmodified and modified silicon substrates. The data are presented as the standard deviation (n = 6).

6. One-step preparation of dual-functional surfaces with protein resistance and specific protein binding properties

Y-photoclick (12.7 mg, 0.02 mmol), MAG (0.247 g, 0.1 mmol), HEMA (0.065 g, 0.5 mmol), TBDMS-PEG (0.66 g, 0.12 mmol), TBD (4.9 mg, 0.035 mmol) and $Mn_2(CO)_{10}$ (4.0 mg, 0.01 mmol) were first dissolved in 11.0 mL of acetonitrile/methanol (1:2, v/v) and then placed in a 25 mL flask with several pieces of Si-BTMS film. Afterwards, the flask was deoxygenated by bubbling argon gas for 30 min and then irradiated with 365 nm UV light at room temperature for 15 min. Finally, the

obtained substrates (Si-*g*-(PHEMA-*co*-PMAG)-PEG) were cleaned with acetonitrile and methanol and dried under a flow of nitrogen. Moreover, replacement of the above mixture with a mixture of Y-photoclick (12.7 mg, 0.02 mmol), TBDMS-PEG (0.66 g, 0.12 mmol) and TBD (4.9 mg, 0.035 mmol) afforded only SuFEx reaction-mediated PEG grafted substrates (Si-*g*-PEG).

7. One-step immobilization of both poly(NIPAAm) brushes and HDFD fragments onto PVC surfaces

Y-photoclick (12.7 mg, 0.02 mmol), NIPAAm (0.452 g, 4.0 mmol), TBDMS-HDFD (0.082 g, 0.14 mmol), $Mn_2(CO)_{10}$ (4.0 mg, 0.01 mmol) and TBD (2.0 mg, 0.014 mmol) were first dissolved in 5.0 mL of acetonitrile and then placed in a 10 mL round bottomed flask with several pieces of PVC film. Afterwards, the flask was deoxygenated by bubbling argon gas for 30 min and then irradiated with 365 nm UV light at room temperature for 10 min. Finally, the obtained substrates (PVC-*g*-PNIPAAm-HDFD) were cleaned with acetonitrile and methanol and dried under a flow of nitrogen.

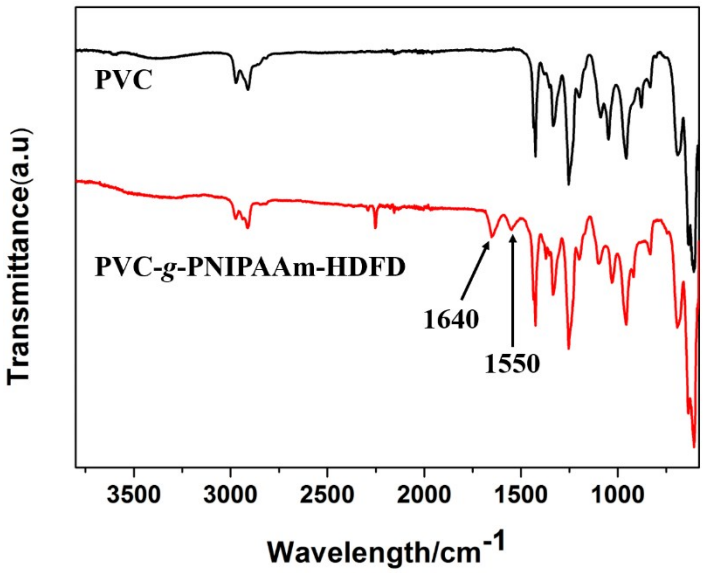


Figure S11. Reflectance FT-IR spectra of PVC and PVC-*g*-PNIPAAm-HDFD surfaces.

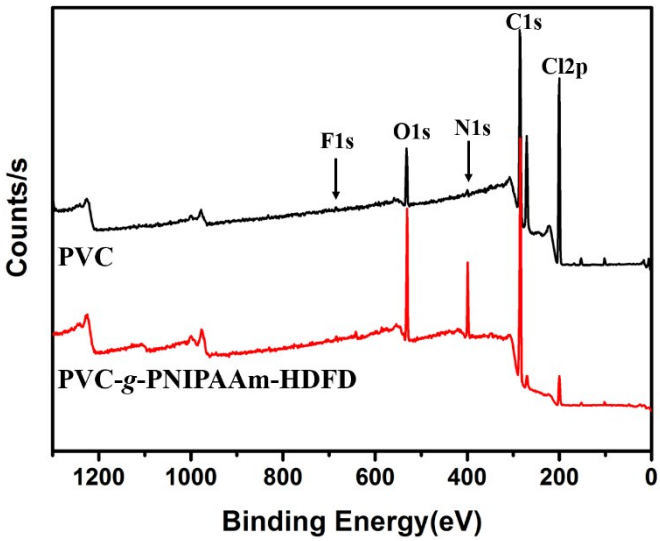


Figure S12. XPS survey spectra of PVC and PVC-*g*-PNIPAAm-HDFD surfaces.

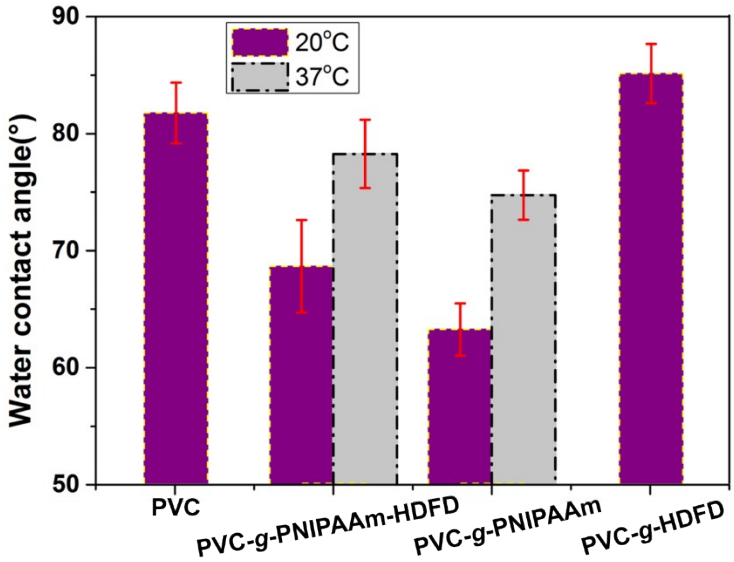


Figure S13. Sessile water drop contact angles of the unmodified and modified PVC substrates.

The data are presented as the standard deviation (n = 6).

Table S1. XPS analysis results of PVC and PVC-*g*-PNIPAAm-HDFD surfaces

Sample	XPS atom concentration (%)				
	[C]	[Cl]	[O]	[N]	[F]
PVC	72.57	17.6	9.83	0	0
PVC-*g*-PNIPAAm-HDFD	71.9	2.99	12.84	11.21	1.07

8. Antimicrobial assay of the Si-*g*-PHEMA-IL surfaces

The antimicrobial activity of the Si-*g*-PHEMA-IL surfaces was evaluated by the live/dead staining assay[1]. In brief, the sample surfaces were first sterilized with 75% alcohol and washed twice with phosphate-buffered saline (PBS). Then, the sample surfaces were incubated in 250 μL of *E. coli* MG1655 suspension (1×10^7 CFU/mL) at 37 °C for 2 h to attach the bacteria. Subsequently, these surfaces were washed with sterile water to remove any loosely bound bacteria. Afterwards, 20 μL of a staining solution (1:1 mixture of 3.34×10^{-3} M SYTO 9 and 2.0×10^{-2} M propidium iodide) was dropped onto the surfaces and incubated in the bacterial culture for 15 min. Thereafter, the surfaces were gently rinsed with sterile water and dried under a nitrogen stream. Finally, the attached bacteria on the surfaces were imaged using a fluorescence microscope, and the bacterial densities on surfaces were determined with Image-Pro Plus analysis software.

9. Specific protein adsorption assay of Si-*g*-(PHEMA-*co*-PMAG)-PEG surfaces

Protein adsorption on the Si-*g*-(PHEMA-*co*-PMAG)-PEG surfaces was studied following a reported protocol[4]. Briefly, FITC-ConA or Rh-BSA (0.1 mg/mL in PBS) was first added onto the dry sample surfaces. Then, the sample surfaces were incubated at room temperature for 3 h. Afterwards, these surfaces were washed with PBS three times. Finally, the surfaces were imaged using LSCM, and the fluorescence intensity was analyzed with ImageJ software.

References

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