Electronic supplementary information for:

A Rapid One-Step Surface Functionalization of Polyvinyl Chloride by Combining Click Sulfur(VI)-Fluoride Exchange with Benzophenone Photochemistry

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Experimental section

1. Materials

4-Aminobenzophenone, 1H,1H,2H,2H-heptadecafluoro-1-decanol, 2-bromo-2-methylpropionic acid, 2-mercaptoethanol, 4-(fluorosulfonyl) benzoyl chloride, *N*-isopropylacrylamide (NIPAAm), N,N,N′,N′,N″-pentamethyldiethylenetriamine (PMDETA), N-(5-fluoresceinyl) maleimide and rhodamine 110-azide were purchased from Sigma-Aldrich. Triazabicyclodecene (TBD), *tert*-butyldimethylchlorosilane and 2,2'-azoisobutyronitrile (AIBN) were purchased from TCI. Imidazole and methylimidazole were purchased from J&K Chemical. Dimethyl formamide (DMF), carbon disulfide, acetonitrile, methanol and all other solvents were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Tert-butyldimethylsilyl (TBDMS)-protected poly(ethylene glycol) methyl ether (TBDMS-PEG), 1-(6-((tert-butyldimethylsilyl)oxy)hexyl)-3-methyl-1H-imidazol-3-ium bromide (TBDMS-IL), 2-((tert-butyldimethylsilyl)oxy)ethane-1-thiol (TBDMS-Thio) and (but-3-yn-1-yloxy)(tert-butyl)dimethyl silane (TBDMS-Yne) were synthesized according to previous studies.[1] Gram-negative Escherichia coli (E. coli) was supplied by the China General Microbiological Culture Collection Center (Beijing, China). Films of polyvinylchloride (PVC) and polyurethane (PU) were prepared as previously described.[2] Cellulose acetate (CA) films were cast from a solution of acetone/DMF (2 : 1, v/v). Poly(ethylene terephthalate) (PET) films with a thickness of approximately 188 μm were obtained from Feixia Factory (Shanghai, China). The PVC, PU, CA and PET films were all punched into discs that were approximately 6 mm in diameter.

2. Instruments and measurements

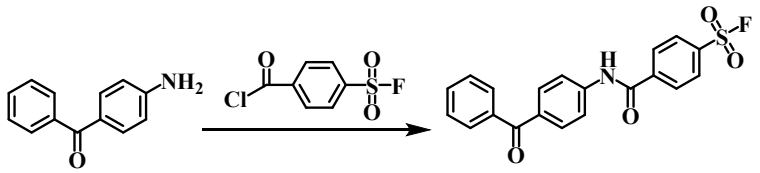
^{1}H, ^{13}C and ^{19}F nuclear magnetic resonance (NMR) spectra were acquired on a Varian Mercury-400 spectrometer (Varian, USA). Fourier transform-infrared (FT-IR) spectra were acquired using a Nicolet 6700 FT-IR spectrometer (Thermo Fisher Scientific, USA). Mass spectra (MS) were obtained using a micrOTOF-Q III instrument (Bruker, Germany). An ESCALAB MK II X-ray photoelectron spectrometer (VG Scientific Ltd, England) was used to measure the chemical compositions of the

surfaces. An SL200C optical contact angle meter (USA Kino Industry Co., Ltd.) was used to measure the static water contact angles via the sessile drop method. A fluorescence microscope (BX51, Olympus, Japan) was used to observe the dyed surfaces. GY250 devices with 365 nm-centered ultraviolet (UV) light were provided by Beijing Tianmaihenghui Electric Appliance Co., Ltd. (China).

3. Synthesis

3.1 Synthesis of 4-((3-benzoylphenyl)carbamoyl)benzenesulfonyl fluoride (BPSF)

BPSF was synthesized via a one-step amidation reaction of 4-aminobenzophenone and 4-(fluorosulfonyl) benzoyl chloride (Scheme S1). Briefly, 4-aminobenzophenone (0.89 g, 4.5 mmol) and triethylamine (0.61 g, 6.0 mmol) were dissolved in 30 mL of dichloromethane. Then, a 4-(fluorosulfonyl) benzoyl chloride (1.0 g, 4.5 mmol) dichloromethane solution was slowly added to the mixture, and the mixture was stirred at room temperature overnight. Afterwards, the solvent was removed, and the crude product was purified using silica gel column chromatography with ethyl acetate and hexane (1 : 5, v/v) as the eluent. The resulting product was obtained as a light yellow solid (1.34 g, 78% yield). ^{1}H NMR ($CDCl_3$), δ ppm: 8.19 (d, 2H, Aryl–***H***f), 8.13 (d, 2H, Aryl–***H***g), 7.89 (d, 2H, Aryl–***H***c), 7.79 (d, 4H, Aryl–***H***d,***H***e), 7.60 (t, 1H, Aryl–***H***a), 7.49 (t, 2H, Aryl–***H***b)(Figure S1). ^{13}C NMR ($CDCl_3$), δ ppm: 195.57 (***C***=O), 163.53 (-NH***C***=O), 140.99 (Aryl–***C***9,11), 137.52 (Aryl–***C***4), 134.07 (Aryl–***C***14), 132.48 (Aryl–***C***6,1), 131.66 (Aryl–***C***7), 129.89 (Aryl–***C***3), 129.04 (Aryl–***C***2), 128.39 (Aryl–***C***13,12), 119.49 (Aryl–***C***8) (Figure S2). ^{19}F NMR ($CDCl_3$), δ ppm: 66.01 (s, 1F) (Figure S3). FT-IR (cm^{-1}, KBr): 1680 (s, *v*(Ph-C=O)), 1640 (s, *v*(NH-C=O)), 1524 (s, *v*(Ph)) (Figure S4). MS: calculated for $M^+ + Na^+$: m/z 406.1099; found: m/z 406.0482 ($M^+ + 23$, $M^+ + Na^+$) (Figure S5).



Scheme S1. Synthesis of BPSF.

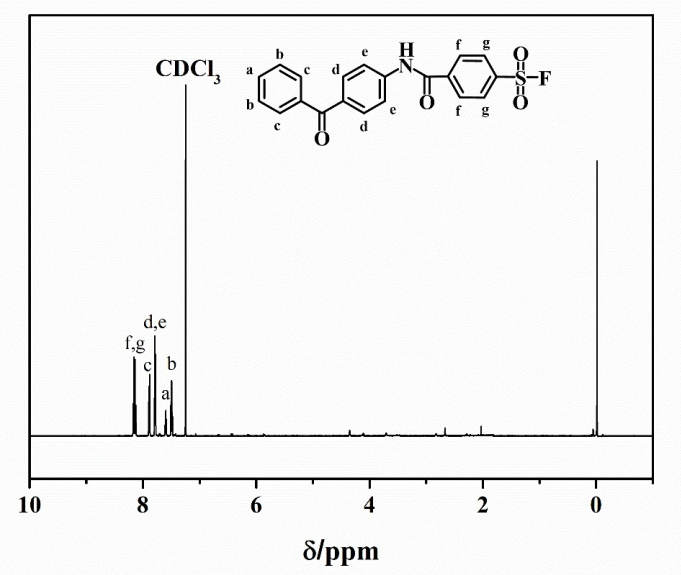


Figure S1. ^{1}H NMR spectrum of BPSF in $CDCl_3$.

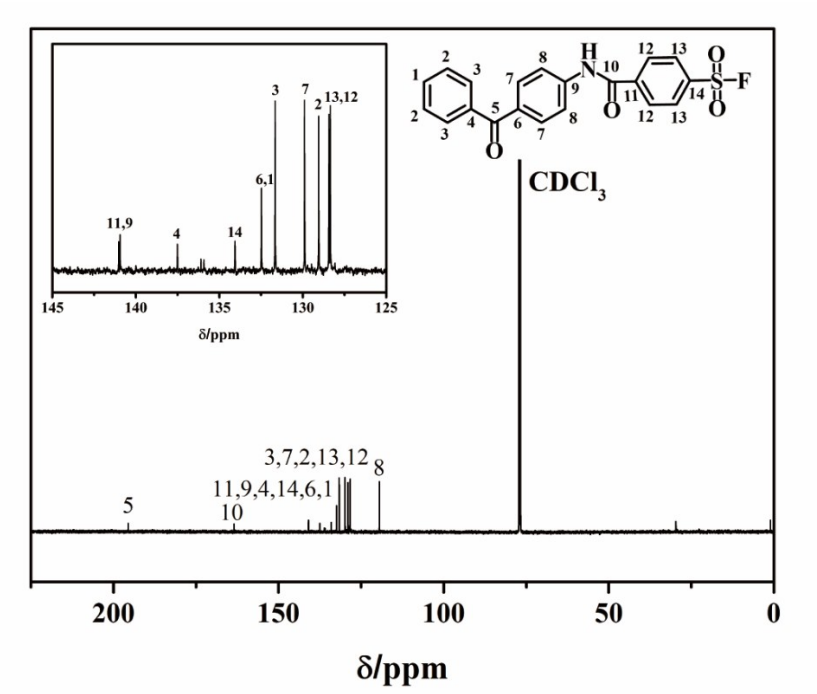


Figure S2. ^{13}C NMR spectrum of BPSF in $CDCl_3$.

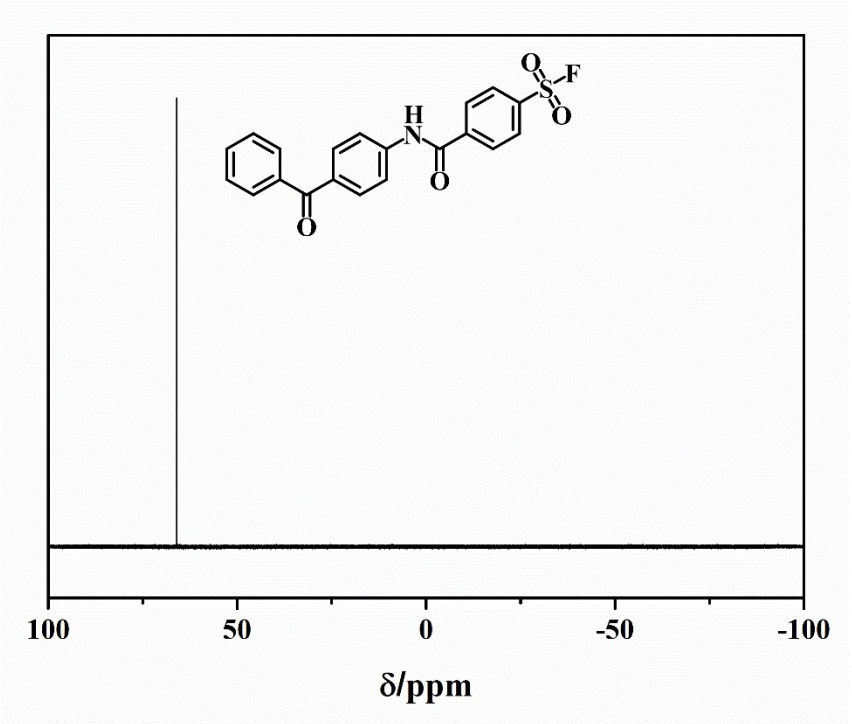


Figure S3. ^{19}F NMR spectrum of BPSF in $CDCl_3$.

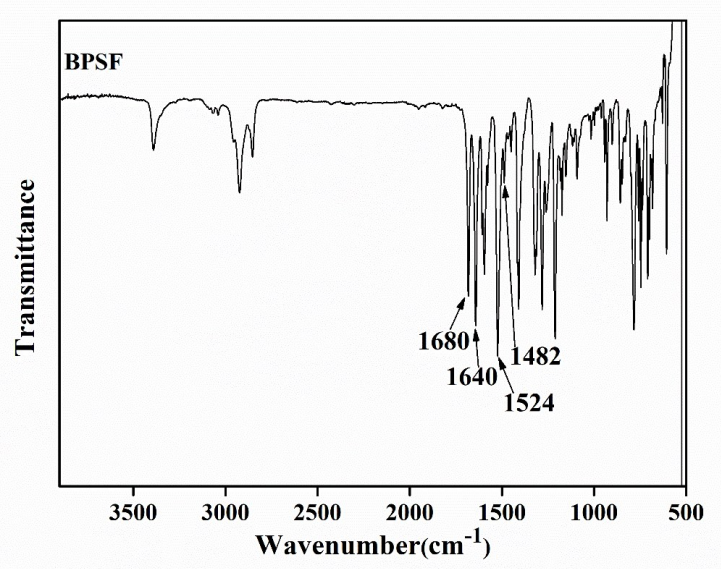


Figure S4. FT-IR spectrum of BPSF.

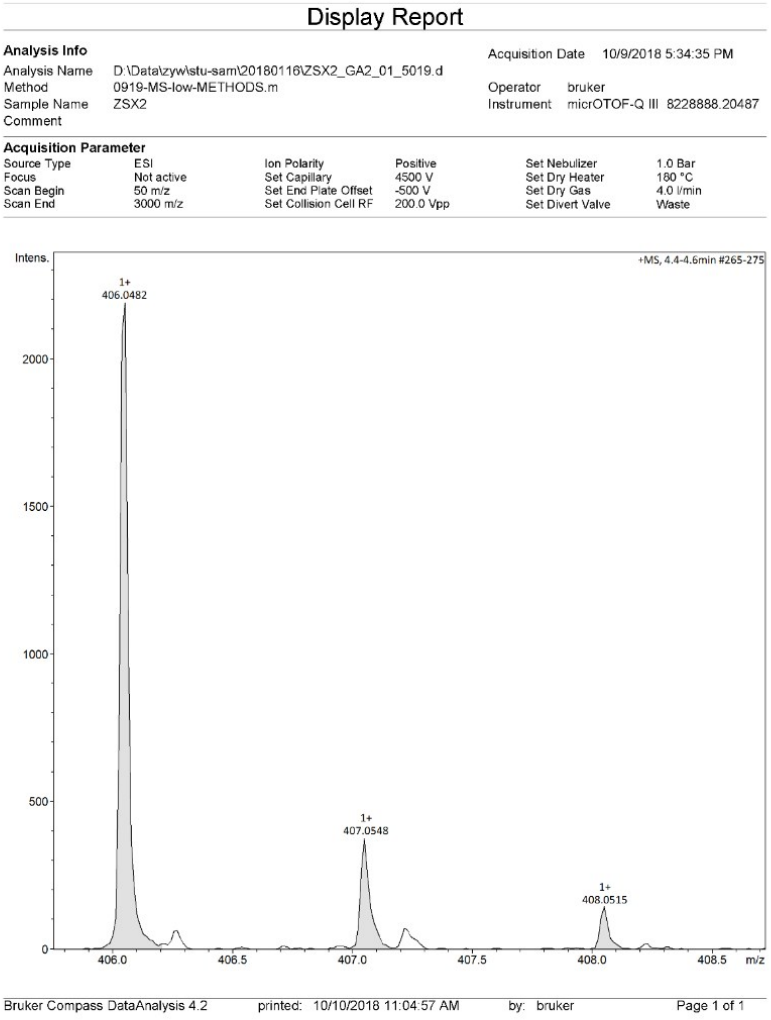
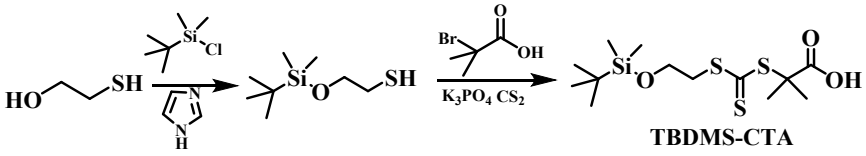


Figure S5. Mass spectrum of BPSF.

3.2 Synthesis of reversible addition-fragmentation chain transfer (RAFT) agent, TBDMS-CTA

The new TBDMS-protected RAFT agent, TBDMS-CTA, was synthesized using a two-step procedure (Scheme S2). The intermediate compound, 2-((*tert*-butyldimethylsilyl)oxy)ethane-1-thiol, was synthesized via an etherification reaction between *tert*-butyldimethylchlorosilane and 2-mercaptoethanol. Briefly, 2-mercaptoethanol (3.43 g, 43.9 mmol) and imidazole (6.5 g, 96.0 mmol) were dissolved in 50 mL of dry dichloromethane, and a *tert*-butyldimethylchlorosilane (6.03 g, 40.0 mmol) dichloromethane solution was slowly added to the mixture. Then, the mixture was stirred at room temperature overnight. After removing the solvent, the product was purified using silica gel column chromatography with ethyl acetate and hexane (1 : 1, v/v) to give 6.15 g (80% yield) of a clear liquid. ^{1}H NMR ($CDCl_3$), δ ppm: 3.72 (t, 2H, C***H***$_2$-O-), 2.62 (t, 2H, C***H***$_2$-S-), 0.89 (s, 9H, (C***H***$_3$)$_3$-C-), 0.07 (s, 6H, (C***H***$_3$)$_2$-Si-) (Figure S6). ^{13}C NMR ($CDCl_3$), δ ppm: 63.93 (***C***H$_2$-O-), 26.18 (***C***H$_2$-S-), 24.76 ((***C*****1**H$_3$)$_3$-C-), 17.28 ((CH$_3$)$_3$-***C*****2**-), -6.12 ((***C*****3**H$_3$)$_2$-Si-) (Figure S7). MS: calculated for $M^+ + Na^+$: m/z 215.0999; found: m/z 215.0890 (M^+ + 23, $M^+ + Na^+$) (Figure S8).

The RAFT agent, TBDMS-CTA, was then conveniently prepared from the intermediate compound and commercially available 2-bromo-2-methylpropionic acid. In brief, carbon disulfide (6.18 g, 81.0 mmol), 2-((*tert*-butyldimethylsilyl)oxy)ethane-1-thiol (5.2 g, 27.0 mmol), potassium phosphate (7.2 g, 27.0 mmol) and 2-bromo-2-methylpropionic acid (4.51 g, 27.0 mmol) were dissolved in 50 mL of acetone. The resulting mixture was allowed to stir overnight at room temperature; then, it was acidized to a pH of < 2 with concentrated hydrochloric acid and extracted with dichloromethane three times. The organic phase was dried over anhydrous magnesium sulfate. After filtering, the dichloromethane solvent was evaporated, leaving a crude product, which was then purified by silica gel column chromatography (ethyl acetate/hexane 1 : 1, v/v). The product was obtained as a light yellow solid (7.18 g, 75% yield). ^{1}H NMR ($CDCl_3$), δ ppm: 3.84 (t, 2H, C***H***$_2$-O-), 3.47 (t, 2H, C***H***$_2$-S-), 1.72 (s, 6H, -C***H***$_3$), 0.88 (s, 9H, (C***H***$_3$)$_3$-C-), 0.08 (s, 6H, (C***H***$_3$)$_2$-Si-) (Figure S9). ^{13}C NMR ($CDCl_3$), δ ppm: 177.87 (***C***=O), 60.71 (***C***H$_2$-O-), 55.67 ((CH$_3$)$_2$-***C*****6**-), 39.33 (C***H***$_2$-S-), 25.86 ((***C*****1**H$_3$)$_3$-C-), 25.64 ((***C*****7**H$_3$)$_2$-C-), 18.29 ((CH$_3$)$_3$-***C*****2**-), -5.31 ((***C*****3**H$_3$)$_2$-Si-) (Figure S10). MS: calculated for $M^+ + Na^+$: m/z 377.0808; found: m/z 377.0689 (M^+ + 23, $M^+ + Na^+$) (Figure S11).



Scheme S2. Synthesis of TBDMS-CTA.

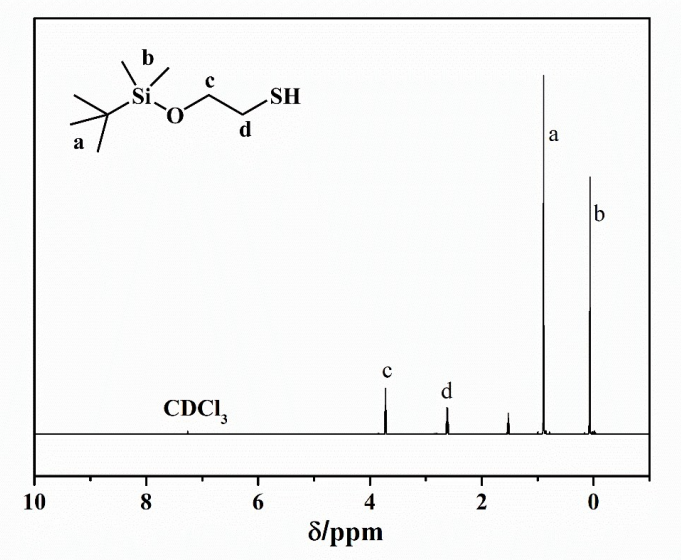


Figure S6. ^{1}H NMR spectrum of 2-((tert-butyldimethylsilyl)oxy)ethane-1-thiol in $CDCl_3$.

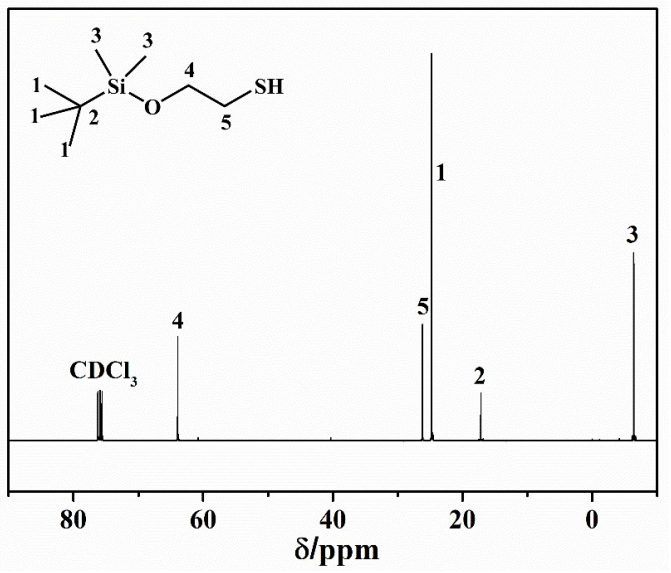


Figure S7. ^{13}C NMR spectrum of 2-((tert-butyldimethylsilyl)oxy)ethane-1-thiol in $CDCl_3$.

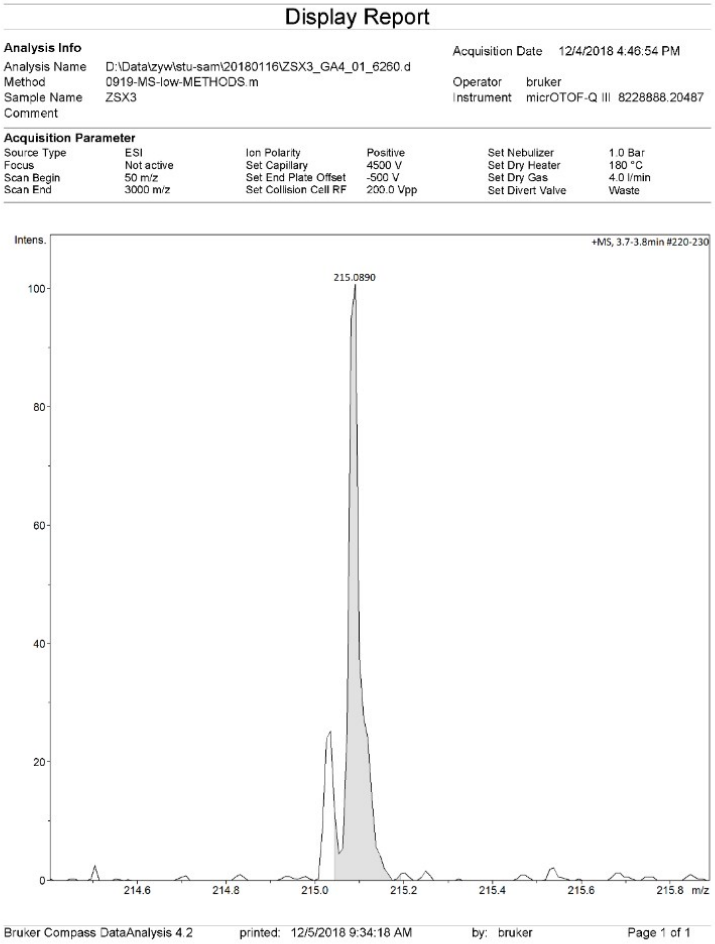


Figure S8. Mass spectrum of 2-((tert-butyldimethylsilyl)oxy)ethane-1-thiol.

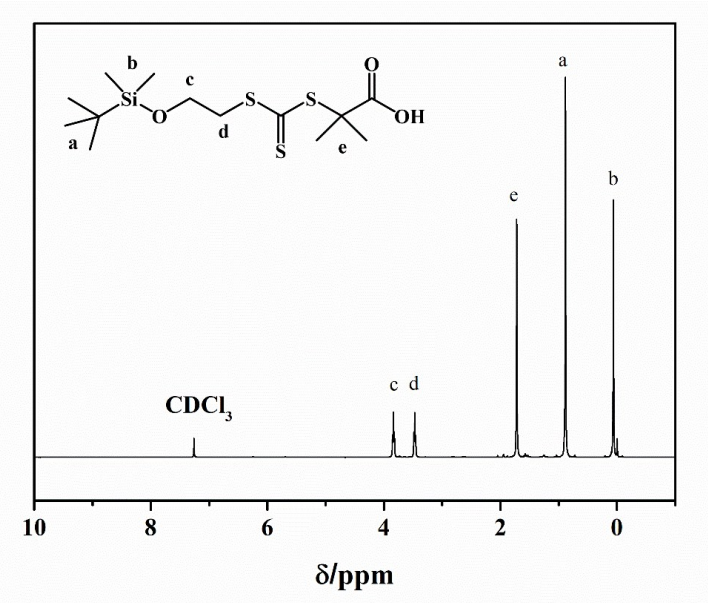


Figure S9. ^{1}H NMR spectrum of TBDMS-CTA in $CDCl_3$.

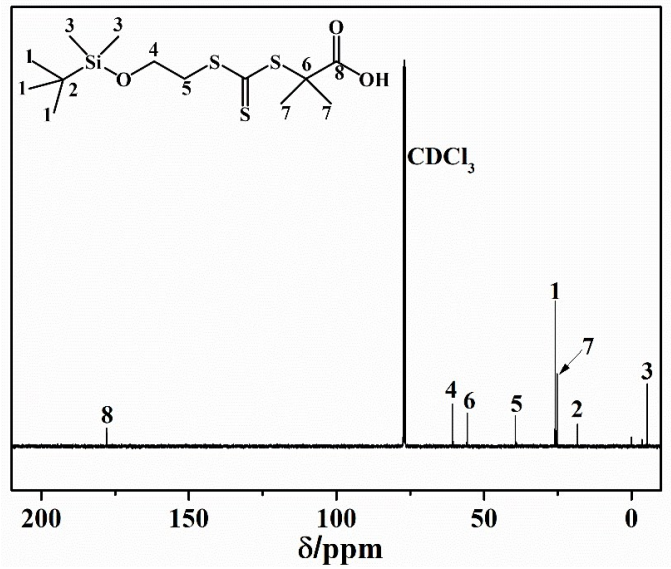


Figure S10. ^{13}C NMR spectrum of TBDMS-CTA in $CDCl_3$.

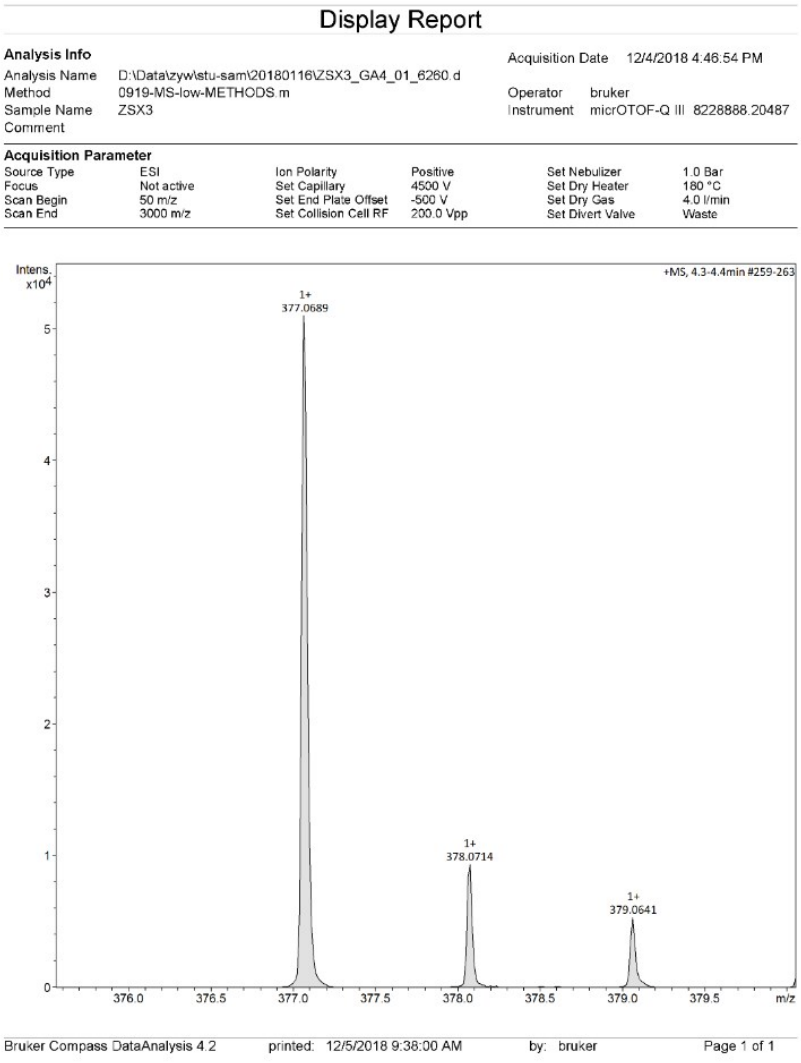
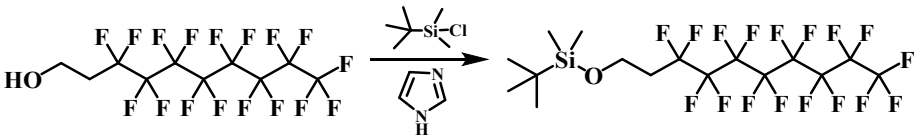


Figure S11. Mass spectrum of TBDMS-CAT.

3.3 Synthesis of *tert*-butyldimethyl(3,3,4,4,4-pentafluorobutoxy)silane (TBDMS-HDFD)

TBDMS-HDFD was synthesized via an etherification reaction between 1H,1H,2H,2H-heptadecafluoro-1-decanol and tert-butyldimethylchlorosilane (Scheme S3). Briefly, 10.18 g (21.93 mmol) of 1H,1H,2H,2H-heptadecafluoro-1-decanol and 3.27 g (48.0 mmol) of imidazole were dissolved in 50 mL of dry dichloromethane, and a tert-butyldimethylchlorosilane (3.01 g, 20.0 mmol) dichloromethane solution was slowly added to the mixture. Then, the mixture was stirred overnight at room temperature. Afterwards, the reaction solution was washed with water, and the solvent was removed via evaporation under reduced pressure to yield a clear oil (8.21 g, 71%yield). ^{1}H NMR ($CDCl_3$), δ ppm: 3.92 (m, 2H, C***H***$_2$-O-), 2.33 (t, 2H, C***H***$_2$-), 0.88 (s, 9H, (C***H***$_3$)$_3$-C-), 0.07 (s, 6H, (C***H***$_3$)$_2$-Si-) (Figure S12). ^{19}F NMR ($CDCl_3$), δ ppm: -80.79 (s, 3F, ***F*8**) , -113.52 (s, 2F, ***F*1**), -121.78-121.92 (t， 6F, ***F*2**-***F*4**), -122.53 (s, 2F, ***F*5**), -123.58 (s, 3F, ***F*6**), -126.79 (s, 3F, ***F*7**) (Figure S13). MS: calculated for $M^+ + Na^+$: m/z 601.0928; found: m/z 601.0851 (M^+ + 23, $M^+ + Na^+$) (Figure S14).



Scheme S3. Synthesis of TBDMS-HDFD.

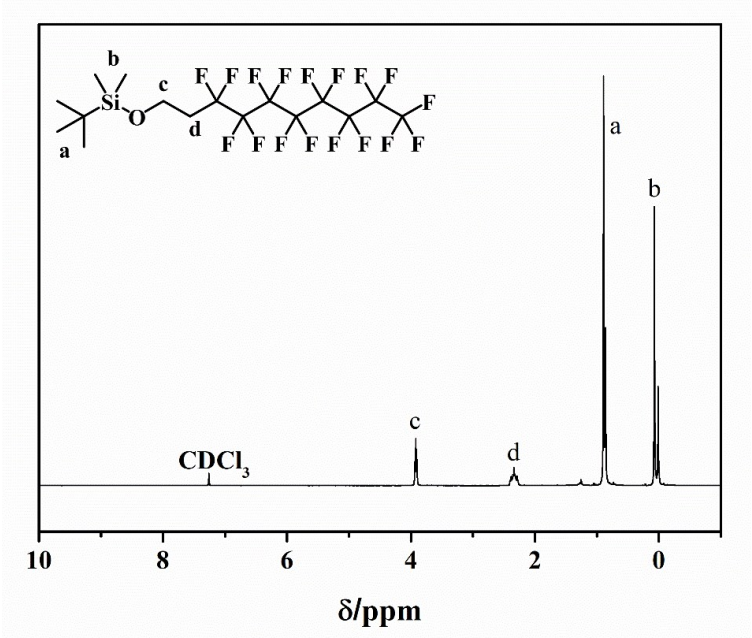


Figure S12. ^{1}H NMR spectrum of TBDMS-HDFD in $CDCl_3$.

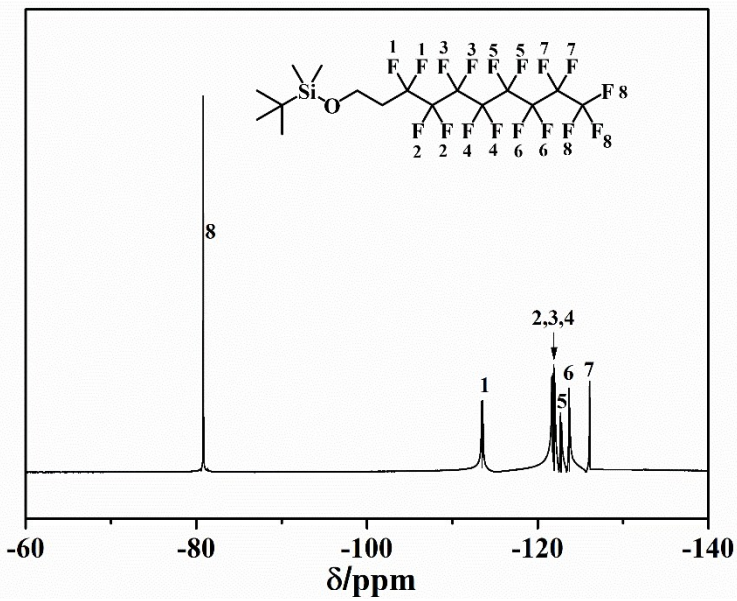


Figure S13. ^{19}F NMR spectrum of TBDMS-HDFD in $CDCl_3$.

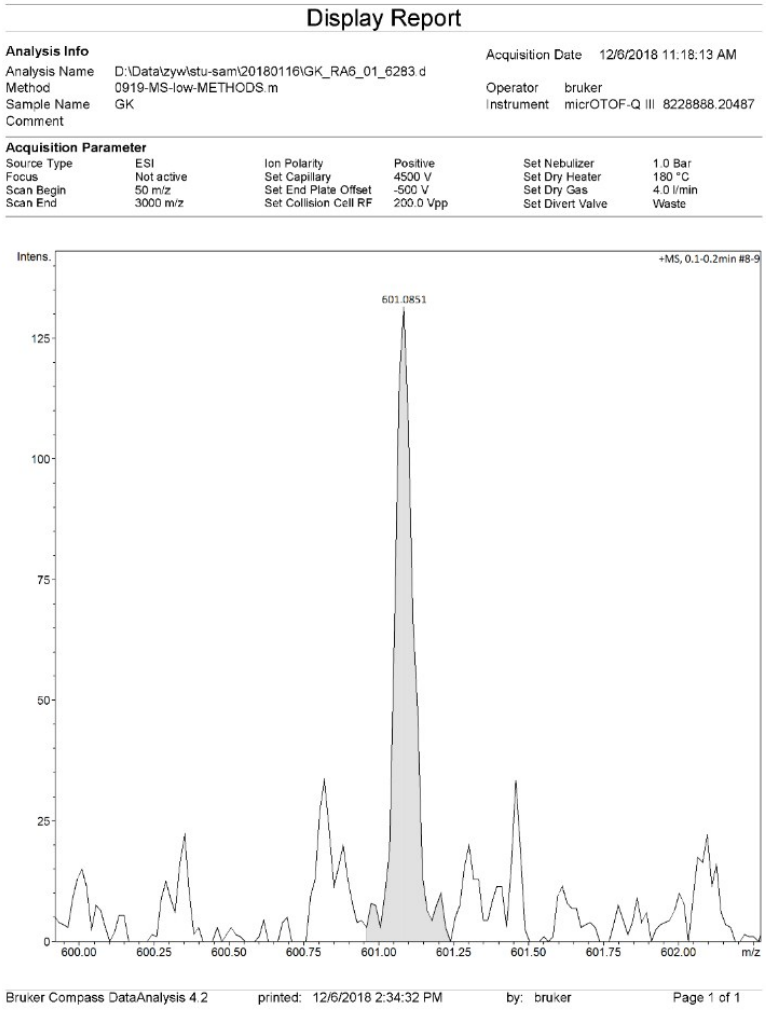


Figure S14. Mass spectrum of TBDMS-HDFD.

4. One-step photoimmobilization of different molecules onto the PVC surfaces

The procedures for the one-pot photoimmobilization of different silyl ether-containing molecules including TBDMS-CTA, TBDMS-IL, TBDMS-PEG, TBDMS-HDFD, TBDMS-Thio and TBDMS-Yne onto the PVC surfaces were similar. The preparation of PVC-CTA is used to illustrate the detailed immobilization procedure. BPSF (50.0 mg, 0.13 mmol), a catalytic amount of TBD (7.0 mg, 0.05 mmol) and TBDMS-CTA (88.6 mg, 0.25 mmol) were dissolved in 5 mL of acetonitrile and then placed in a 10 mL flask with several pieces of PVC film, respectively. UV light irradiation source is Hg-lamp and the irradiation intensity is 70 mW/cm^2, which is 5 cm away from the samples. After 5 min of UV light irradiation, the samples were subsequently cleaned with acetonitrile and methanol and dried under a flow of nitrogen.

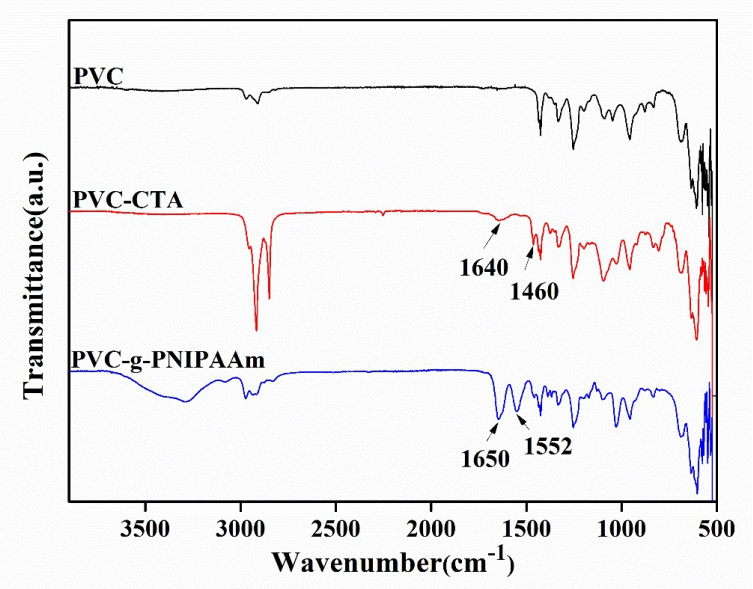


Figure S15. Reflectance FT-IR spectra of PVC, PVC-CTA and PVC-*g*-PNIPAAm surfaces.

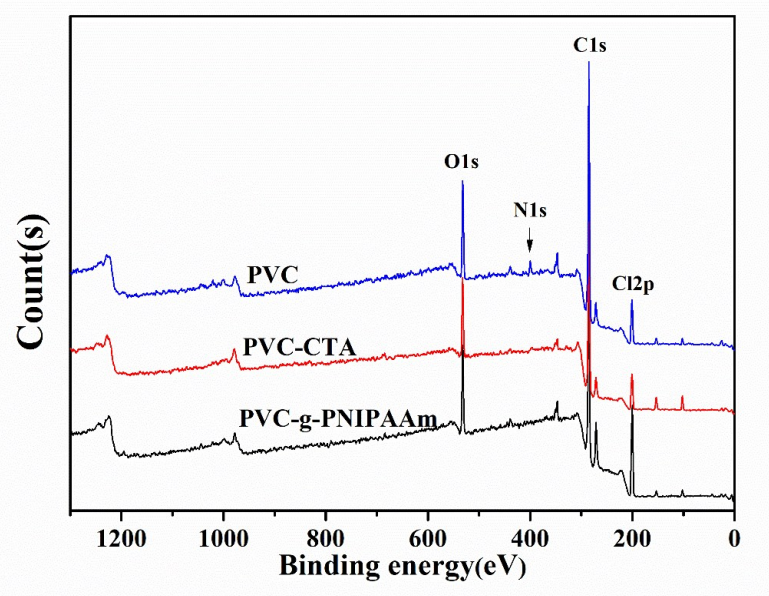


Figure S16. XPS survey spectra of PVC, PVC-CTA and PVC-*g*-PNIPAAm surfaces.

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

Sample	XPS atom concentration (%)				
	[C]	[Cl]	[O]	[N]	[S]
PVA	74.51	16.04	9.45	0	0
PVA-CTA	86.53	4.86	8.32	0.09	0.2
PVC-*g*-PNIPAAm	79.66	4.63	11.9	3.65	0.16

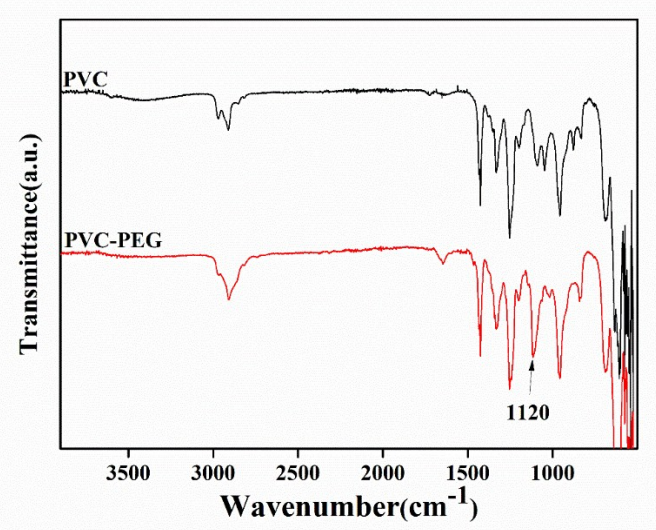


Figure S17. Reflectance FT-IR spectra of PVC and PVC-PEG surfaces.

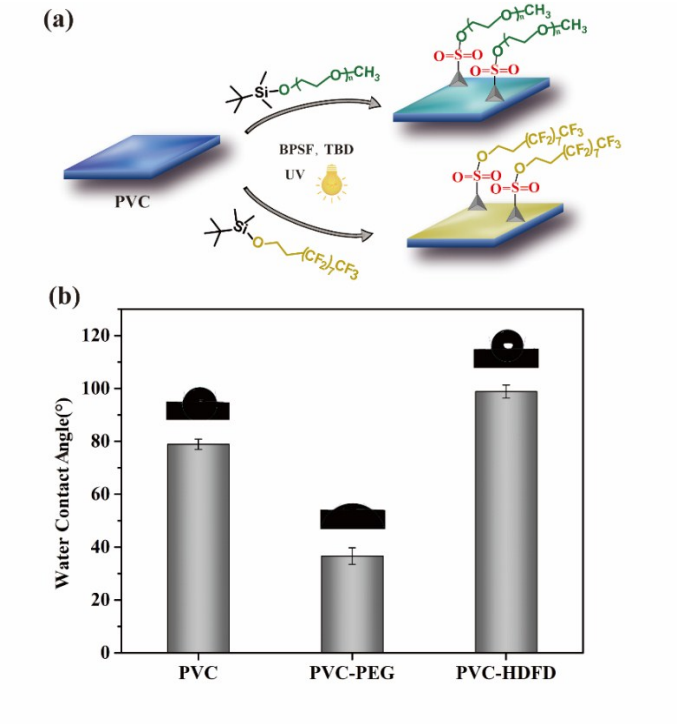


Figure S18. (a) One-step photoimmobilization of PEG or HDFD on PVC surfaces. (b) Sessile water drop contact angles of the unmodified PVC, PVC-PEG and PVC-HDFD substrates. The data are presented as the standard deviation (n = 6).

5. Surface-initiated RAFT (SI-RAFT) polymerization on the RAFT agent-immobilized substrates

RAFT agent-immobilized substrates, including PVC, PU, CA and PET, were prepared as described in part 4. The preparation of poly(NIPAAm)-grafted PVC substrates (PVC-*g*-PNIPAAm) is used to illustrate the detailed grafting polymerization procedure. A mixture of NIPAAm (2.26 g, 20.00 mmol) and AIBN (3.28 mg, 0.02 mmol) in 7 mL of methanol was added into a 10 mL round bottom flask; then, the RAFT agent-coated PVC substrate (PVC-CTA) was immersed in the mixture. The flask was deoxygenated using bubbling argon gas for 30 min and then allowed to react for 5 h at 70 °C. The PVC-*g*-PNIPAAm surfaces were rinsed with methanol and dried under a stream of nitrogen.

6. Bactericidal activity of the ionic liquid-immobilized PVC surfaces (PVC-IL)

The unmodified PVC and PVC-IL substrates sterilized with ethanol were first incubated in 500 μL of an *E. coli* suspension (1×10^7 cells·mL^{-1}) at 37°C for 2 h to attach the bacteria; then, the substrates were centrifuged at 8.0×10^3 rpm in phosphate-buffered saline (PBS, pH = 7.4) for 5 min to release the attached cells. Afterwards, the released cells were placed on gelatinous Luria agar plates and incubated at 37°C for 18 h. Finally, the number of viable cells was investigated in colony-forming units (CFU).

7. Thio-Michael addition reaction on the thiol-immobilized PVC surfaces (PVC-SH)

The PVC-SH substrates were immersed in a N-(5-fluoresceinyl) maleimide methanol solution and reacted overnight at room temperature. Afterwards, the resulting substrates were cleaned with methanol and dried under a stream of nitrogen. Finally, the films were imaged using a fluorescence microscope with a 100 × objective. In this study, the effect of irradiation time on the grafting density of thiol functional groups on the PVC substrates was investigated. As shown in Figure S19, at first, surface fluorescence intensity rapidly increased as the irradiation time increased. However, after 5 min the surface fluorescence intensity no longer increased. In addition, the effect of the reaction solution concentration on the grafting density of thiol functional groups on the PVC substrates when the irradiation time was also held constant at 5 min. As shown in Figure S20, the surface fluorescence intensity increased as the reaction solution concentration increased. After a reaction solution concentration of 0.025 mmol/mL, the surface fluorescence intensity increased slowly. These results indicated the potential for controlling grafting density of functional groups on the PVC substrates by adjusting the irradiation time and the reaction solution concentration.

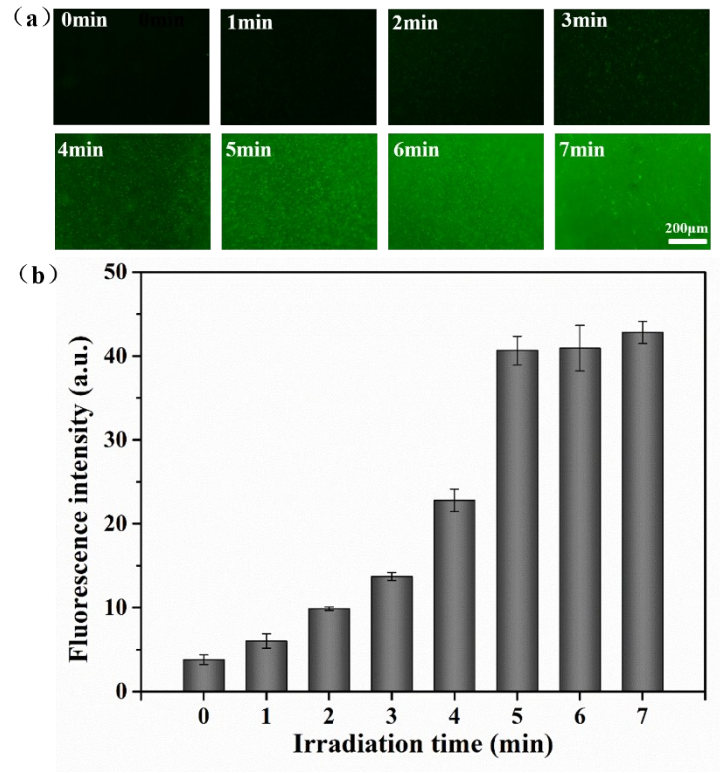


Figure S19. (a) Fluorescence microscopy images of the PVC-SH surfaces treated with N-(5-fluoresceinyl) maleimide in different irradiation time. (b) The fluorescence intensity of PVC-SH surfaces treated with N-(5-fluoresceinyl) maleimide in different irradiation time (n = 6).

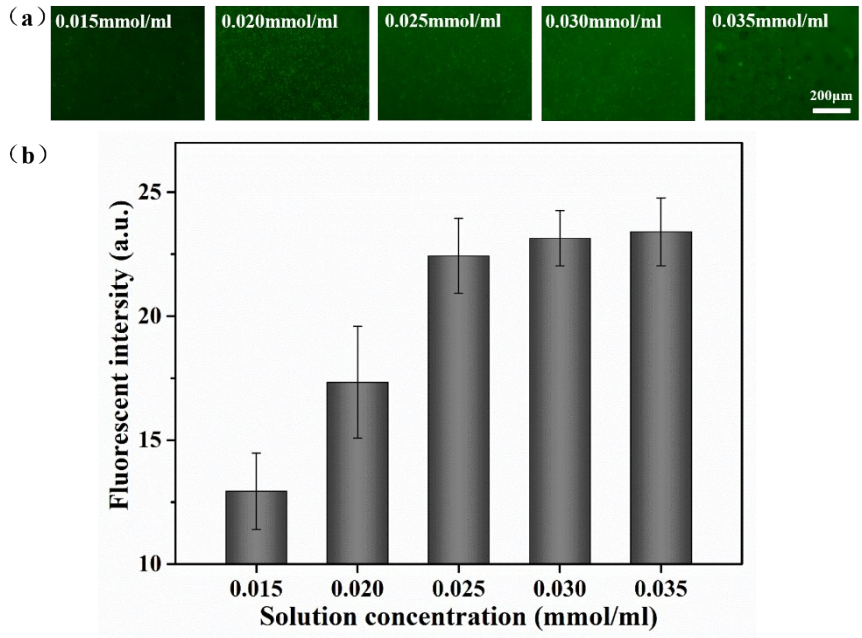


Figure S20. (a) Fluorescence microscopy images of the PVC-SH surfaces treated with N-(5-fluoresceinyl) maleimide in different solution concentration. (b) The fluorescence intensity of PVC-SH surfaces treated with N-(5-fluoresceinyl) maleimide in different solution concentration (n = 6).

8. Copper(I)-catalyzed azide–alkyne cycloaddition (CuAAC) on the alkynyl-immobilized PVC surfaces (PVC-Yne)

After the PVC-Yne substrates were immersed in the rhodamine 110-azide methanol solution for 30 min, PMDETA (55.0 mg, 0.32 mmol) and CuBr (23.0 mg, 0.16 mmol) were added. The mixture was then deoxygenated by bubbling argon gas for 30 min and allowed to react for 6 h at room temperature. Finally, the resulting substrates were cleaned with methanol, dried under a stream of nitrogen, and imaged using a fluorescence microscope with a 100 × objective.

9. PVC-SH surface patterning and sequential Thio-Michael addition reaction

To prepare the patterned PVC-SH surfaces, BPSF (50.0 mg, 0.13 mmol), TBD (7.0 mg, 0.05 mmol) and TBDMS-Thiol (48.1 mg, 0.25 mmol) were first dissolved in 5 mL of acetonitrile. Afterwards, 50 μL of the resulting mixture was added to and spread evenly over the surface of the PVC film. The pretreated PVC film was then loaded using a 300-mesh transmission electron microscopy (TEM) grid as a mask and exposed to UV light for 5 min. Finally, the films were subsequently cleaned with acetonitrile and methanol and dried under a flow of nitrogen.

To conduct the sequential Thio-Michael addition reaction, the patterned PVC-SH films were immersed in a N-(5-fluoresceinyl) maleimide methanol solution and reacted overnight at room temperature. Afterwards, the resulting films were cleaned with large amounts of methanol and dried in a vacuum oven. Finally, the films were imaged using a fluorescence microscope with a 100 × objective and a 200 × objective.

References

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