Electronic supplementary information for: Reactive films fabricated by click sulfur(VI)-fluoride exchange reactions-enabled layer-by-layer assembly

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Experimental section

1. Materials

Methacryloyl chloride (97%) and 3-sulfopropyl methacrylate potassium salt (95%) were purchased from Aladdin Chemistry Co. (China). Polyvinyl alcohol (M_w 89000–98000, hydrolysis 99%), 2,2'-azoisobutyronitrile (AIBN), *N*-vinyl-2-pyrrolidone (NVP), thionyl chloride (97%) and aminoethanol were purchased from Sigma-Aldrich. Potassium hydrogen difluoride (KFHF), *tert*-butyldimethylchlorosilane, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and 6-bromo-1-hexanol were purchased from TCI. Imidazole and 1-methylimidazole were purchased from J&K Chemical (China). Dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), acetonitrile and all other solvents were purchased from Sinopharm Chemical Reagent Co., Ltd. (China) and were used without further purification. NVP was purified by vacuum distillation to remove the inhibitors prior to use. 3-(Fluorosulfonyl)propyl methacrylate (FPM) was synthesized as reported previously[1]. The preparation of *tert*-butyldimethylsilyl (TBDMS)-protected poly(ethylene glycol) methyl ether and 1-(6-((tert-butyldimethylsilyl)oxy)hexyl)-3-methyl-1H-imidazol-3-ium bromide (referred to as TBDMS-PEG and TBDMS-IL, respectively) was performed as previously described[2]. 1,3-Dioxo-1,3-dihydrobenzo[*de*]isochromene-6-sulfonyl azide was synthesized and purified according to published procedures[3]. Silicon wafers (p-doped, Guangzhou Institute of Semiconductor Materials, China) were cut into square samples of 2.0 cm × 2.0 cm and ultrasonically cleaned with acetone to remove possible organic contamination. Gram-negative *Escherichia coli* (*E. coli* MG1655 and *E. coli* DH5α with red fluorescence) was supplied by the China General Microbiological Culture Collection Center (Beijing, China).

2. Instruments and measurements

Spin coating was conducted on a WS-650 Mz-23NPPB spinner (LAURELL, Inc., USA). ^{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). Fluorescence images of attached bacteria on the surfaces were observed by a fluorescence microscope (BX51, Olympus, Japan). Optical micrographs of the surfaces were obtained by an optical microscope (OLYMPUS BX53). The thickness measurements of (PVA-TBDMS/PVP-*co*-PFPM)$_n$ films and energy dispersive

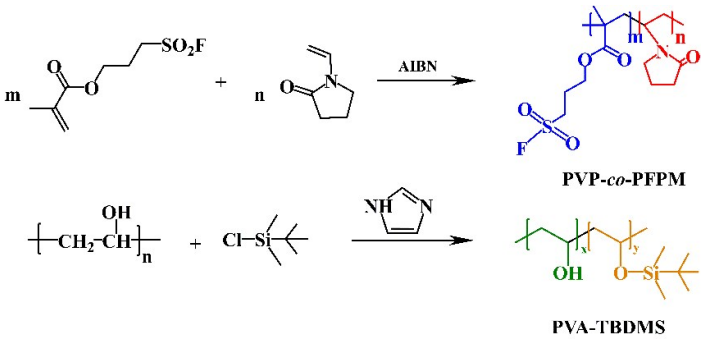
spectrometry (EDS) images were characterized using a Hitachi SU8010 scanning electron microscope (SEM, Hitachi, Japan). Gel permeation chromatography (GPC) was performed using a PL-GPC50 (Agilent Technologies, USA) with DMF as the solvent (flow rate 1.0 mL/min) at 30°C.

3. Synthesis of PVP-*co*-PFPM

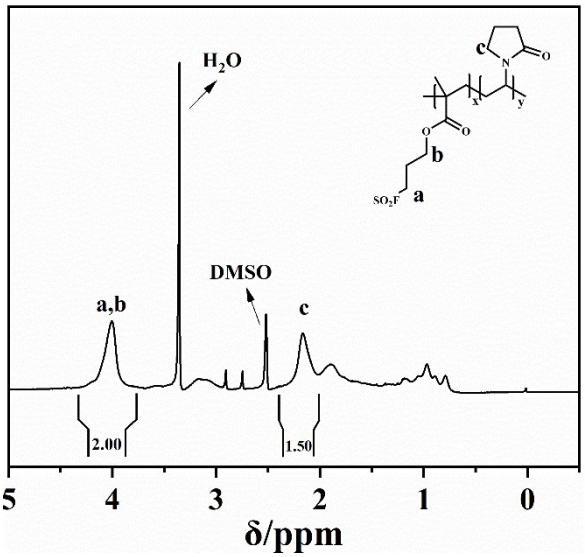
The sulfonyl fluoride-rich copolymer, PVP-co-PFPM, was prepared by free radical copolymerization using AIBN as the initiator. In brief, FPM (1.0 g, 4.8 mmol), NVP (0.539 g, 4.8 mmol) and AIBN (7.8 mg, 0.048 mmol) were dissolved in 6 mL DMF. The mixture was then bubbled under a N_2 atmosphere for half an hour and reacted at 70°C overnight. Afterwards, the reaction solution was dialyzed using seamless cellophane dialysis tubing (MWCO 20000) in distilled water for 2 days followed by lyophilization. The final product PVP-*co*-PFPM was obtained as a white powdery solid.

4. Synthesis of PVA-TBDMS

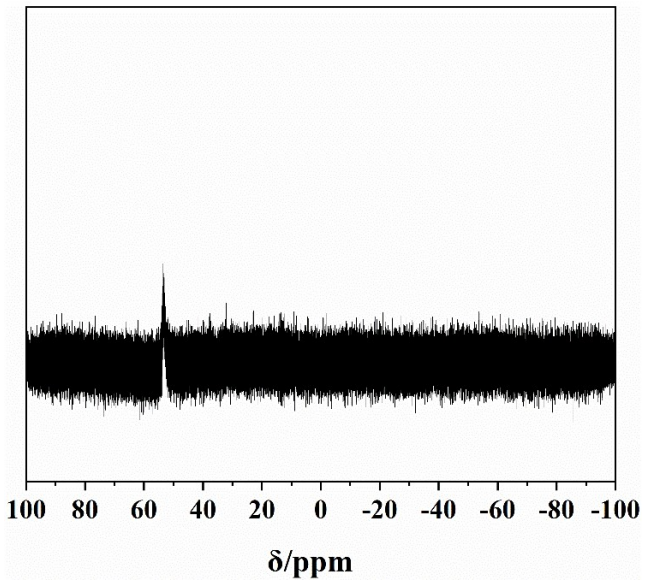
The silyl ether-rich polymer, PVA-TBDMS, can be obtained according to the following procedure. Briefly, 0.88 g (20.0 mmol) of PVA and 1.6 g (24.0 mmol) of imidazole were dissolved in 20 mL of DMSO by stirring at 80°C. After the mixture was cooled to room temperature, a *tert*-butyldimethylchlorosilane (3.0 g, 20.0 mmol) THF solution was slowly added in an ice bath. After stirring overnight at 60°C, the reaction mixture was filtered off and dialyzed using seamless cellophane dialysis tubing (MWCO 8000-14000) in distilled water for 2 days followed by lyophilization. The final product PVA-TBDMS was obtained as a white powdery solid. The degree of substitution (DS) of silyl ether groups in the OH groups of PVA can be calculated from the ^{1}H NMR integration analysis results of PVA-TBDMS using the following formula: $DS = \frac{B/6}{B/6 + A/4}$, where A is the integrated area of the signal of the –CH_2 protons in the main chains at 1.48 ppm, and B is the integrated area of the signal of the –CH_3 protons adjacent to silicon at 0.06 ppm.



Scheme S1. Synthesis of PVP-*co*-PFPM and PVA-TBDMS.



Figures S1. ^{1}H NMR spectrum of PVP-*co*-PFPM in DMSO-*d6*.



Figures S2. ^{19}F NMR spectrum of PVP-*co*-PFPM in DMSO-*d6*.

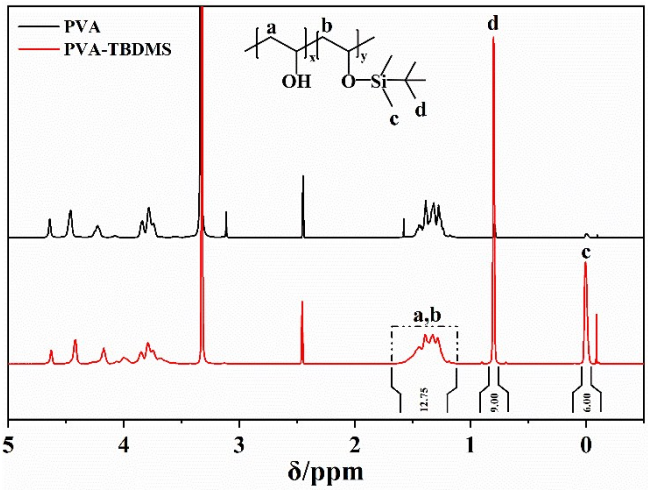


Figure S3. ^{1}H NMR spectrum of PVA and PVA-TBDMS in DMSO-*d6*.

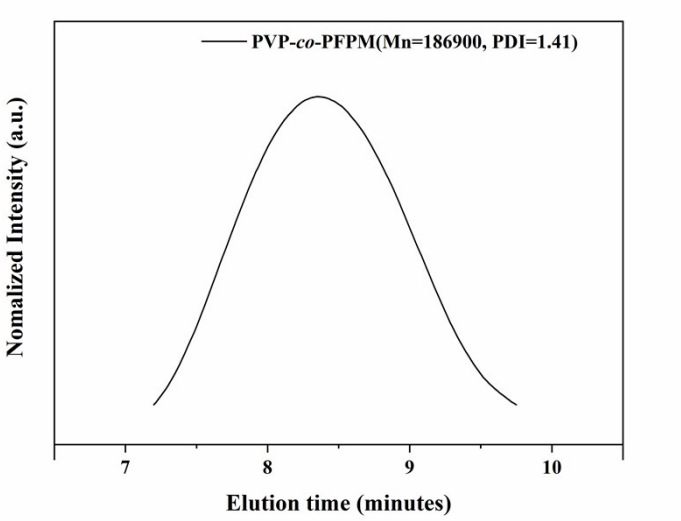


Figure S4. GPC curves of PVP-*co*-PFPM.

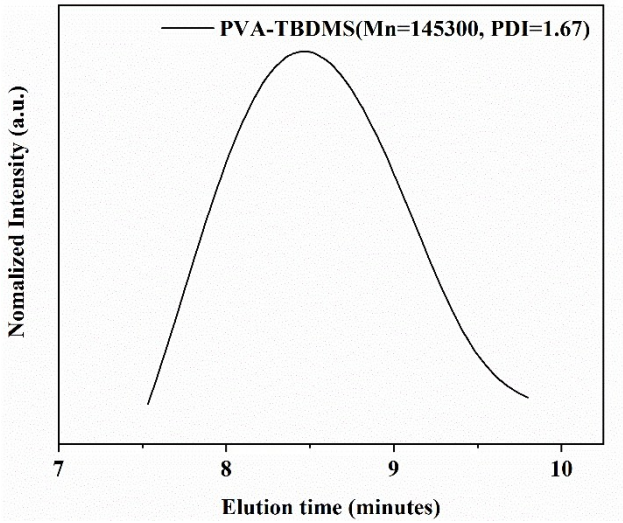


Figure S5. GPC curves PVA-TBDMS.

Table S1. The synthesis and composition of PVP-*co*-PFPM and PVA-TBDMS

Polymer	$M_{n,GPC}$ (g·mol^{-1}) [a]	PDI[a]	DS (mol %)[b]	Practical Ratio (mol:mol)[b]
PVP-*co*-PFPM	186900	1.41	---	60: 40
PVA-TBDMS	145300	1.67	24	---

[a] Determined by GPC. [b] Determined by ^{1}H NMR.

5. Fabrication and peeling of multilayered films

For the fabrication of multilayered films, a PVP-*co*-PFPM solution was prepared by dissolving 0.1 g of PVP-*co*-PFPM and TBD (0.02 g, 0.13 mmol) into 5 mL acetone. PVA-TBDMS was dissolved in

DMSO at 5% w/w. Covalent LbL assembly mediated by the click SuFEx reaction was performed by sequentially spin-coating PVA-TBDMS and PVP-*co*-PFPM solutions on a clean silicon substrate at 3000 rpm for 120 s. This cycle was repeated until the desired bilayer number of PVA-TBDMS/PVP-*co*-PFPM layers was reached (the term "bilayer" refers to a single PVA-TBDMS/PVP-*co*-PFPM layer pair). PVA-TBDMS was chosen as the initial layer in contact with the silicon substrate in this work. Afterwards, the films were dried under a stream of nitrogen and stored in a vacuum desiccator for three days. The obtained multilayered polymer films were denoted as (PVA-TBDMS/PVP-*co*-PFPM)$_n$, where n is the bilayer number.

For the fabrication of free-standing films, the multilayered film-coated silicon substrates were immersed in deionized water. After 2 minutes of immersion, the free-standing (PVA-TBDMS/PVP-*co*-PFPM)$_n$ films could be readily obtained by peeling the multilayered film from the silicon substrate using forceps.

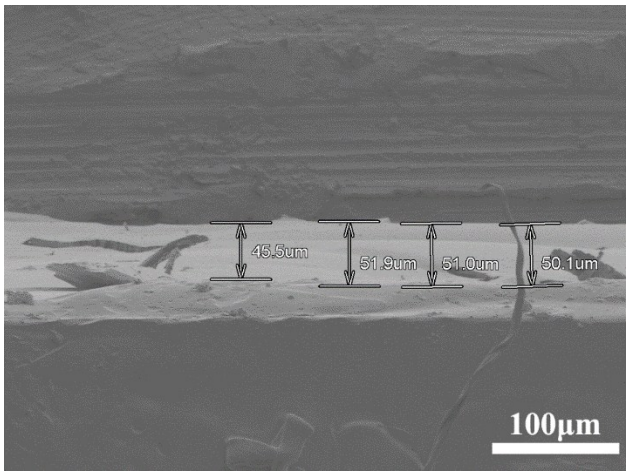


Figure S6. SEM image of the cross-sectional profile of the (PVA-TBDMS/PVP-*co*-PFPM)$_5$ film-coated silicon substrates.

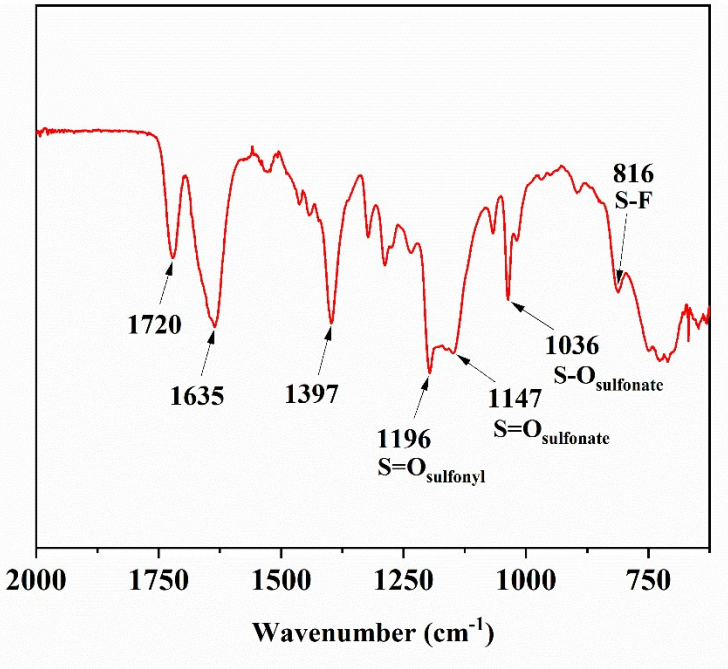


Figure S7. Reflectance FT-IR spectra of (PVA-TBDMS/PVP-*co*-PFPM)$_2$ surface.

6. Stability of the (PVA-TBDMS/PVP-*co*-PFPM)$_n$ films

To investigate the stability of the (PVA-TBDMS/PVP-*co*-PFPM)$_n$ films, the multilayered film-coated silicon substrates were first immersed in 0.1 M HCl, 1 M phosphate buffered saline (PBS), or 1 M NaCl aqueous solution for 4 h. Afterwards, the samples were observed and imaged using an optical microscope.

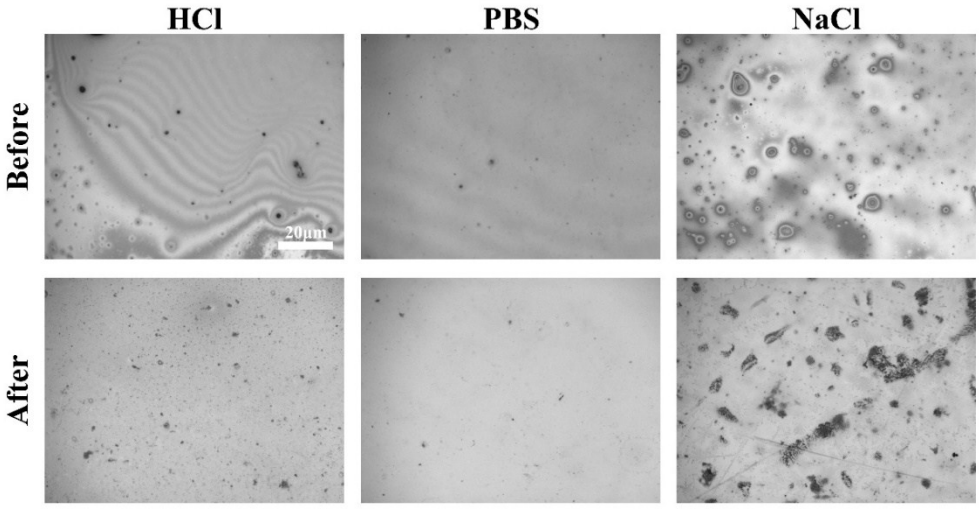
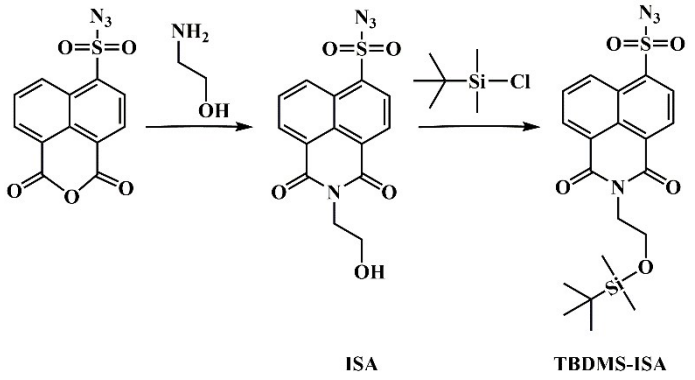


Figure S8. Optical micrographs of the (PVA-TBDMS/PVP-*co*-PFPM)$_5$ films before (a) and after soaking in 0.1 M HCl, 1 M PBS and 1 M NaCl aqueous solutions, respectively.

7. Synthesis of 2-(2-((tert-butyldimethylsilyl)oxy)ethyl)-1,3-dioxo-2,3-dihydro-1H-benzo[de] isoquinoline-6-sulfonyl azide (TBDMS-ISA)

TBDMS-ISA was synthesized using a two-step procedure. The intermediate compound, 2-(2-hydroxyethyl)-1,3-dioxo-2,3-dihydro-1H-benzo[de]isoquinoline-6-sulfonyl azide (ISA), was synthesized via an amidation reaction between 1,3-dioxo-1,3-dihydrobenzo[de]isochromene-6-sulfonyl azide and aminoethanol. Briefly, 1,3-dioxo-1,3-dihydrobenzo[de]isochromene-6-sulfonyl azide (0.506 g, 1.37 mmol) and aminoethanol (0.18 mL, 3.0 mmol) were dissolved in 40 mL of dry ethanol. Then, the mixture was refluxed in the dark for 12 h. After it was cooled to 0°C, the crude product was precipitated from the solution. The product was purified using recrystallization with ethanol and vacuum drying to give 0.446 g (94% yield) of a light yellow solid. ^{1}H NMR ($CDCl_3$), δ ppm: 8.62 (d, 1H, Ar**H**), 8.56 (d, 1H, Ar**H)**, 8.43 (d, 1H, Ar**H)**, 7.73 (t, 1H, Ar**H)**, 7.45 (d, 1H, Ar**H)**, 4.44 (t, 2H, N-C**H**$_2$), 3.98 (s, 2H, C**H**$_2$-OH) (Figure S8).

Afterwards, TBDMS-ISA was prepared from ISA and *tert*-butyldimethylchlorosilane via an etherification reaction. Briefly, ISA (0.42 g, 1.2 mmol) and imidazole (0.31 g, 4.6 mmol) were dissolved in 15 mL of dry tetrahydrofuran, and a *tert*-butyldimethylchlorosilane (0.30 g, 2.0 mmol) tetrahydrofuran solution was slowly added to the mixture. After the resulting mixture was stirred overnight at room temperature, the crude product was obtained by filtering the insoluble salt and removing the solvent under reduced pressure. Finally, the product was purified by silica gel column chromatography (dichloromethane/methanol 20: 1, v/v) and dried under vacuum to obtain a yellow-brown powder (0.513 g, 93% yield). ^{1}H NMR (DMSO-*d6*), δ ppm: 8.41 (d, 1H, Aryl-**H**a), 8.33 (d, 1H, Aryl -**He)**, 8.26 (d, 1H, Aryl -**Hc)**, 7.77 (t, 1H, Aryl -**H**d**)**, 7.61 (d, 1H, Aryl -**H**b**)**, 4.16 (t, 2H, N-C**H**$_2$), 3.83 (t, 2H, C**H**$_2$-O-Si), 0.82 (s, 9H, (C**H**$_3$)$_3$-C), 0.0 (s, 6H, (C**H**$_3$)$_2$-Si) (Figure S9); ^{13}C NMR (DMSO-*d6*), δ ppm: 163.07 (N-**C**11=O), 162.58 (N-**C**12=O), 142.65 (Aryl-**C**7), 131.43 (Aryl-**C**1), 131.32(Aryl-**C**3), 128.18(Aryl-**C**9), 127.98(Aryl-**C**6), 127.11(Aryl-**C**2), 123.26(Aryl-**C**10), 121.80(Aryl-**C**8), 117.83(Aryl-**C**4), 115.74, (Aryl-**C**5), 59.22 (Si-O-**C**14), 41.18 (N-**C**13), 25.62 (Si-**C**17), 17.77 (Si-C-**C**16), -5.50 (Si-**C**15) (Figure S10); MS: calculated for $M^+ + Na^+$: m/z: 483.1129; found: m/z 483.2864 ($M^+ + 23$, $M^+ + Na^+$) (Figure S11).



Scheme S2. Synthesis of TBDMS-ISA.

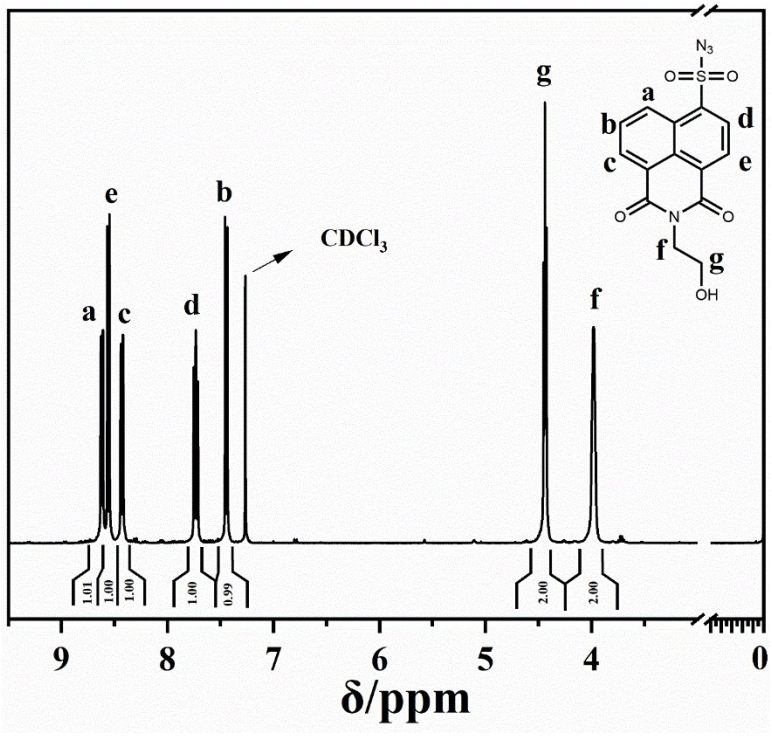


Figure S9. ^{1}H NMR spectrum of ISA in $CDCl_3$.

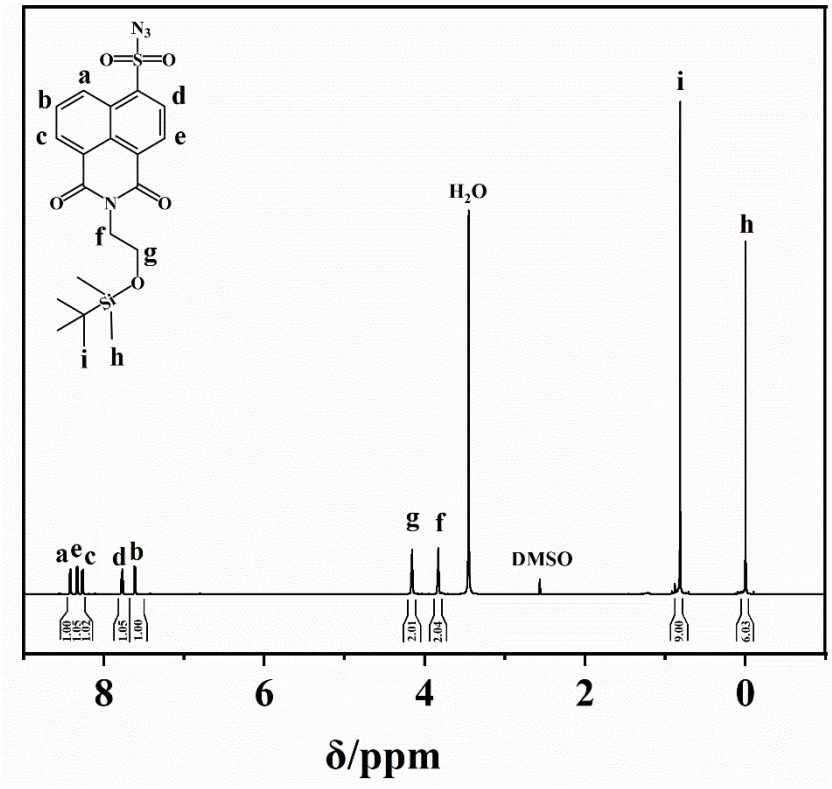


Figure S10. ^{1}H NMR spectrum of TBDMS-ISA in DMSO-*d6*.

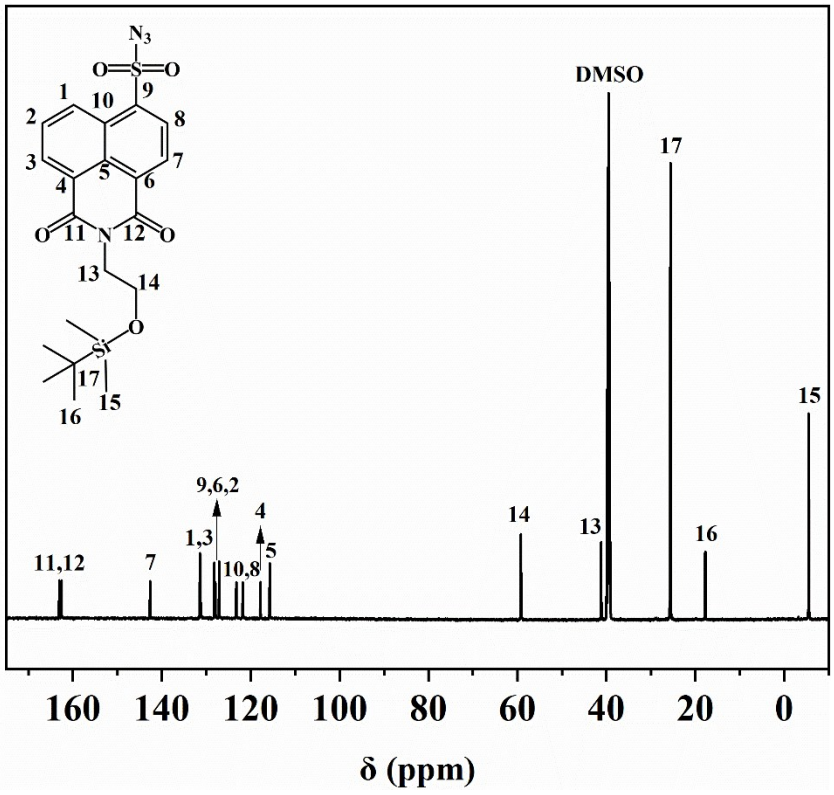


Figure S11. ^{13}C NMR spectrum of TBDMS-ISA in DMSO-*d6*.

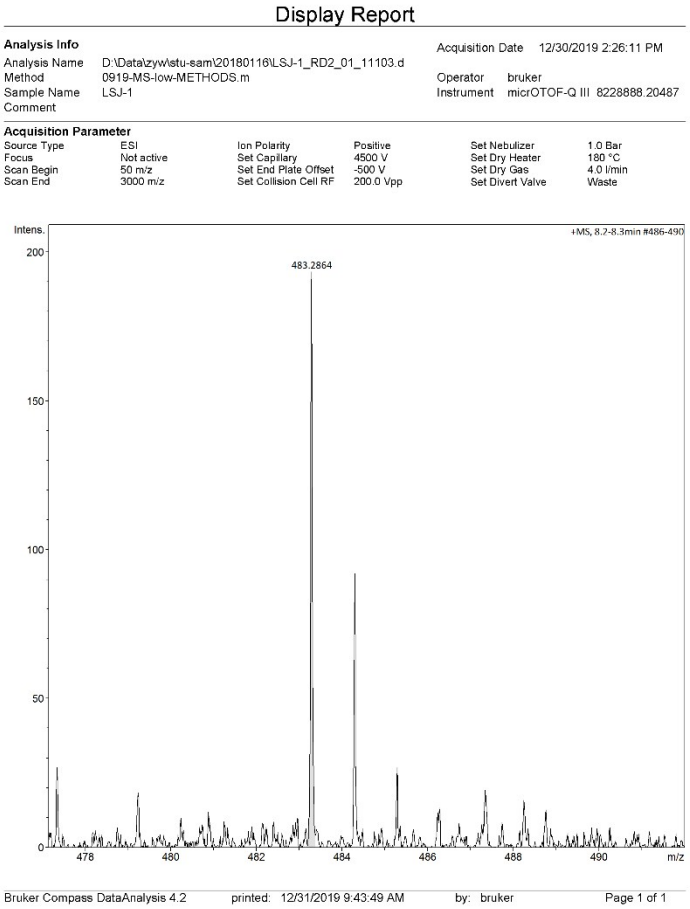


Figure S12. Mass spectrum of TBDMS-ISA.

8. Postfunctionalization of (PVA-TBDMS/PVP-*co*-PFPM)$_n$ films

The procedures for postfunctionalization of different silyl ether-containing molecules, including TBDMS-ISA, TBDMS-PEG and TBDMS-IL, onto the (PVA-TBDMS/PVP-*co*-PFPM)$_n$ films were similar. The preparation of ISA-functionalized films is used to illustrate the detailed procedure. TBDMS-ISA (32.0 mg, 0.07 mmol) and a catalytic amount of TBD (15.0 mg, 0.10 mmol) were first dissolved in 3 mL of acetone, and the prepared (PVA-TBDMS/PVP-*co*-PFPM)$_n$ films were then immersed in the above solution for 5 minutes. Finally, the films were removed and rinsed with acetone. The details of the preparation of PEG-functionalized films and IL-functionalized films were similar to those of ISA-functionalized films.

9. Fluorescent sensitivity of the ISA-functionalized films to H_2S

The ISA-functionalized films were first immersed in a 40 μM Na_2S aqueous solution for 5 minutes. Afterwards, the films were cleaned with deionized water, dried under a stream of nitrogen and imaged using a fluorescence microscope.

10. Bacterial adhesion on the PEG-functionalized films

The PEG-functionalized films were first incubated in 1 mL of an *E. coli* DH5α suspension (1 ×10^6 cells·mL^{-1}) at 37°C for 3 h to attach the bacteria. Then, the films were washed with sterile water to remove loosely bound bacteria. Finally, the attached bacteria on the surfaces were imaged using a fluorescence microscope.

11. Bactericidal activity of the IL-functionalized films

After sterilization with 75% alcohol and washing twice with phosphate-buffered saline (PBS, pH = 7.4), the IL-functionalized films were incubated in 1 mL of an *E. coli* MG1655 suspension (1 ×10^6 cells·mL^{-1}) at 37°C for 3 h to attach the bacteria. The samples were then centrifuged at 8.0 × 10^3 rpm in PBS for 5 minutes to release the attached bacteria. Afterwards, the released cells were placed on gelatinous Luria agar plates and incubated at 37°C for 18 h. Finally, the number of viable bacteria was determined in colony-forming units.

References

1. Y. Dong, X. Lu, P. Wang, W. Liu, S. Zhang, Z. Wu and H. Chen, *Journal of Materials Chemistry B*, 2018, **6**, 4579-4582.
2. W. Liu, Y. Dong, S. Zhang, Z. Wu and H. Chen, *Chem. Commun.*, 2019, **55**, 858-861.
3. K. Sun, X. L. Liu, Y. Y. Wang and Z. Q. Wu, *RSC Adv.*, 2013, **3**, 14543-14548.