Supporting Information

A Smart AIEgen-Functionalized Surface with Reversible Modulation of Fluorescence and Wettability

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Experimental Procedures

Materials and instrumentation

Chemicals were purchased from Energy-Chemical, Sigma-Aldrich, J&K and used without further purification. Solvents and other common reagents were obtained from Sigma-Aldrich. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker ARX 400 MHz spectrometer. High-resolution mass spectra (HRMS) were recorded on a GCT Premier CAB 048 mass spectrometer operating in MALDI-TOF mode. Photoluminescence (PL) spectra were measured on Fluorolog®-3 spectrofluorometer and FLSP920 fluorescence spectrophotometer. TPI-OH was synthesized according to the literature.[1]

Fabrication of TPI-Si functionalized surface

The fabrication processes of TPI-Si functionalized substrate are schematically shown in Figure. A 525μm thick silicon wafer was used in the experiment. First, the silicon wafer was initially cleaned to remove the metals and organic residues by immerse the wafer in a mixture of H_2SO_4 : H_2O_2 (10:1) under 120 ℃ for 10 minutes. Then dipped the wafer in the mixture of H_2O : HF (50:1) for 1minute to remove the native oxide layer. The TPI-Si modified substrate was fabricated by self-assembly approach. TPI-Si was first dispersed in THF to form a 0.5 mg/mL solution. The resulting solution was spin-coated on the silicon wafer followed by heating in oven under 140 ℃ for 1 hour. The coated wafer was then washed by THF to remove the extra TPI-Si which did not self-assembled onto the substrate. Afterward, the coated wafer was dried with an air gun.

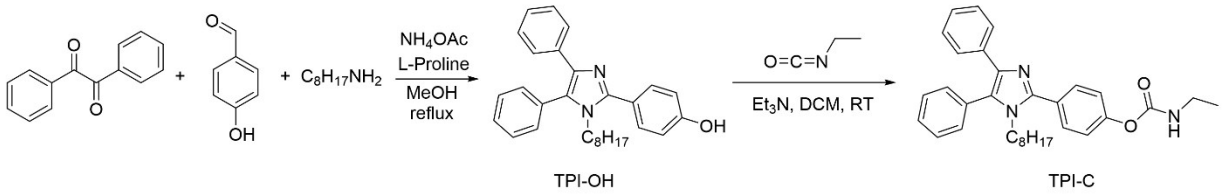
Bacterial Adhesion

All the *E. coli*. bacteria were from ATCC. E. coli were cultured in the (Luria-Bertani (LB) broth) LB medium overnight at 37 °C with a shaking speed of 200 rpm. Bacteria were harvested by centrifuged at 8000 rpm for 3 minutes, and washed twice by PBS. The optical density of the bacteria suspension was measured on a microplate reader (Tecan, infinite M200, Switzerland) at 600 nm. All samples were individually placed in a 24 well-plate. A volume of 300 μL (10^6 CFU/mL) of bacterial culture was added in each well, and the plate was then statically incubated at 37 °C for 3 hours. The samples washed with normal saline twice and stained with 2.5 μL of SYTO®9 (S34854, Invitrogen.) dye solution (3 μM) for 15 minutes. After a washing step with normal saline twice, the samples were imaged using a confocal microscopy (Zeiss LSM 710 laser scanning confocal microscope). The amount of attached bacterial cells was expressed as the mean of bacteria standard deviation of six images. Statistical analysis was done using Software ImageJ.

Synthesis of TPI-C

To a solution of TPI-OH (212 mg, 0.5 mmol) in dry dichloromethane (5 mL) was added one drop of Et_3N and ethyl isocyanate (43 mg, 0.6 mmol). The reaction mixture was stirred at room temperature for 4 h. The solvent was removed under vacuum. Then the residue was washed and recrystallized with acetonitrile. TPI-OH was obtained as white solid (480 mg, 97%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (d, J = 8.5 Hz, 2H), 7.55 – 7.44 (m, 5H), 7.43 – 7.41 (m, 2H), 7.27 (d, J = 8.5 Hz, 2H), 7.23 – 7.17 (m, 2H), 7.16 – 7.10 (m, 1H), 5.08 (t, J = 5.2 Hz, 1H), 3.87 (t, J = 7.7 Hz, 2H), 3.38 – 3.31 (m, 2H), 1.38 – 1.31 (m, 2H), 1.27 – 1.18 (m, 5H), 1.15 – 1.02 (m, 4H), 1.01 – 0.92 (m, 4H), 0.84 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.48, 150.90, 146.35, 137.07, 133.95, 130.92, 130.38, 129.52, 129.03, 128.37, 127.97, 127.75, 127.38, 126.17, 125.55, 121.04, 44.19, 35.53, 30.96, 29.79, 28.19, 27.97, 25.55, 21.92, 14.50, 13.42. HRMS (MALDI-TOF): m/z: $[M+H]^+$ calcd for $C_{32}H_{38}N_3O_2$: 496.2964; found: 496.2988.

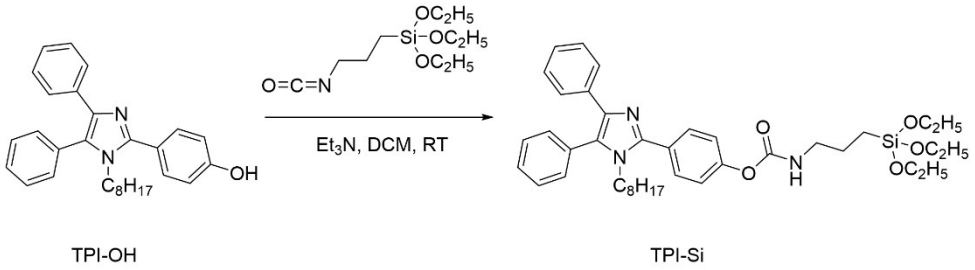
Scheme S1. Synthetic route of TPI-C



Synthesis of TPI-Si

To a solution of TPI-OH (212 mg, 0.5 mmol) in dry dichloromethane (5 mL) was added one drop of Et_3N and 3-isocyanatopropyltriethoxysilane (124 mg, 0.5 mmol). The reaction mixture was stirred at room temperature for 8 h. The solvent was removed under vacuum. TPI-CT was obtained as colorless oil liquid. HRMS (MALDI-TOF): m/z: $[M+H]^+$ calcd for $C_{39}H_{54}N_3O_5Si$: 672.3833; found: 672.3809.

Scheme S2. Synthetic route of TPI-Si



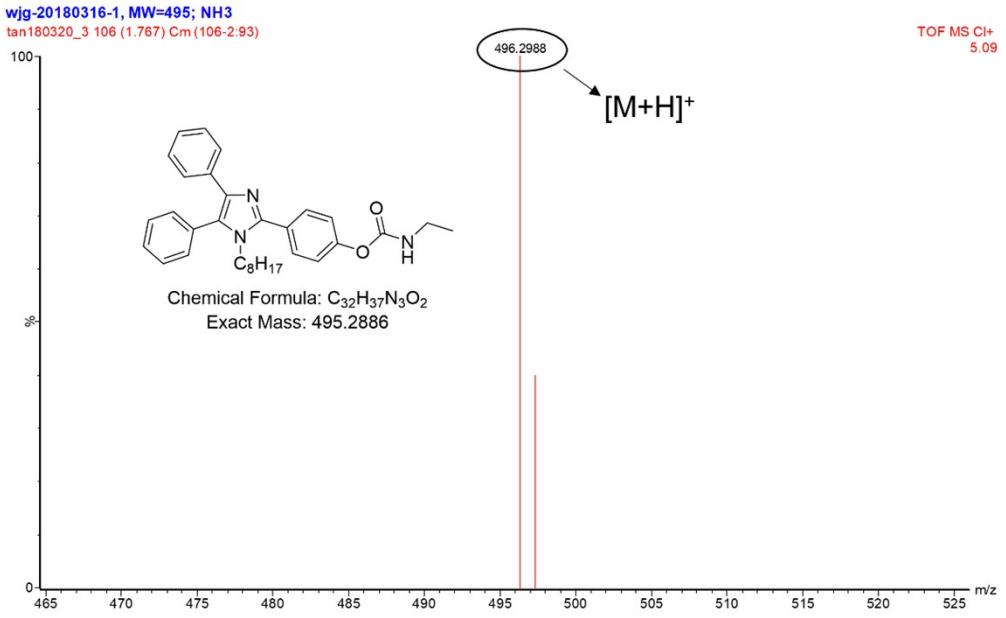


Fig. S1 HRMS of TPI-C.

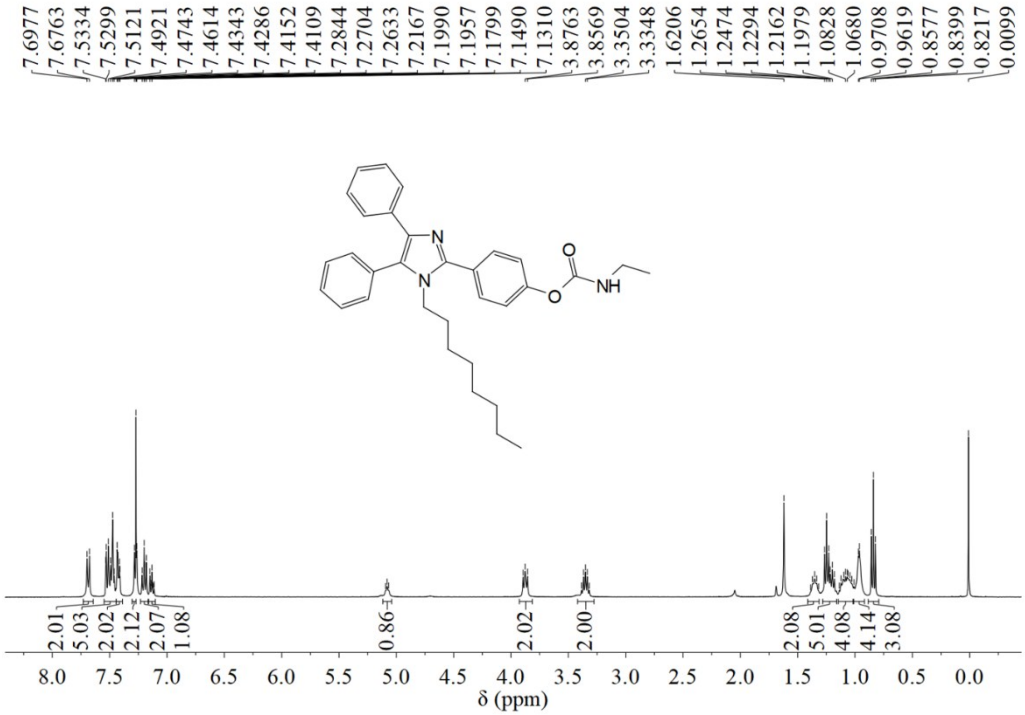


Fig. S2 ^{1}H NMR of TPI-C in $CDCl_3$.

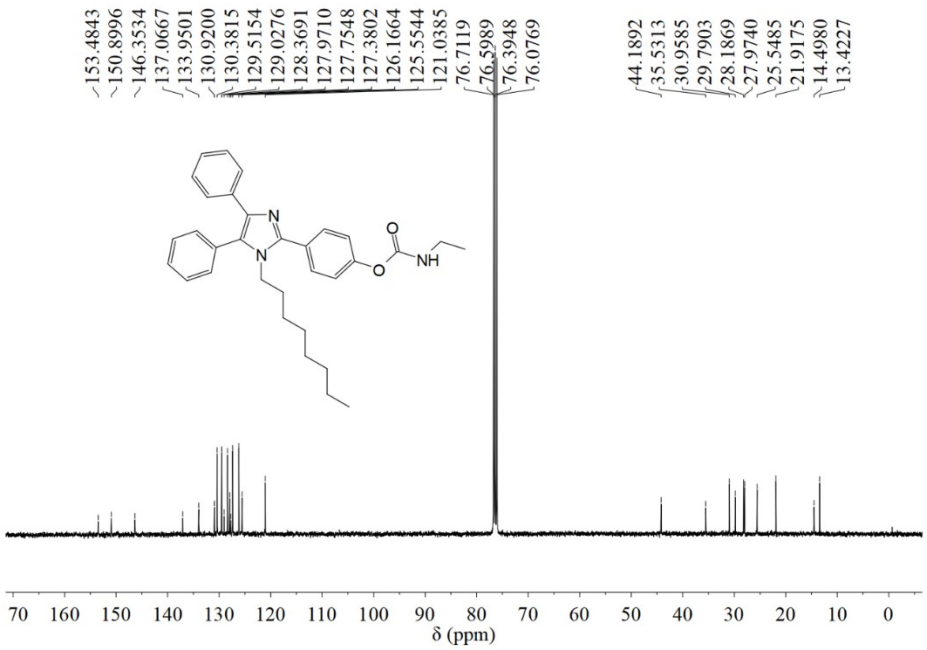


Fig. S3 ^{13}C NMR of TPI-C in $CDCl_3$.

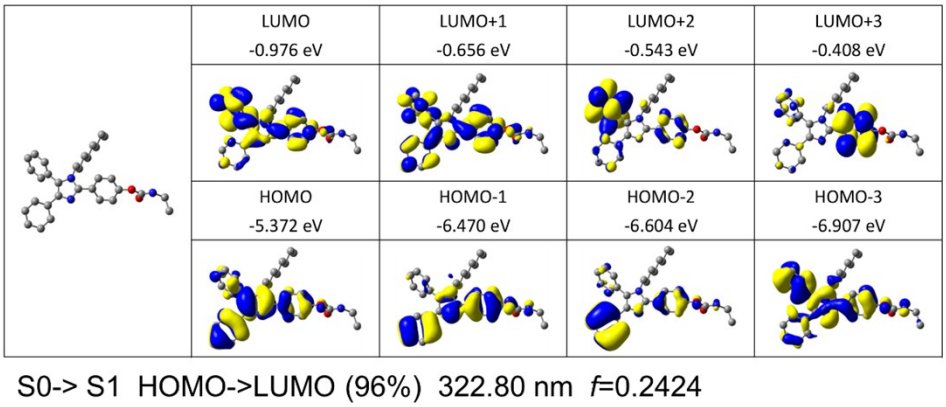


Fig. S4 Structure, energy levels and electron cloud distribution of TPI-C calculated at the B3LYP/ 6-31G(d) level.

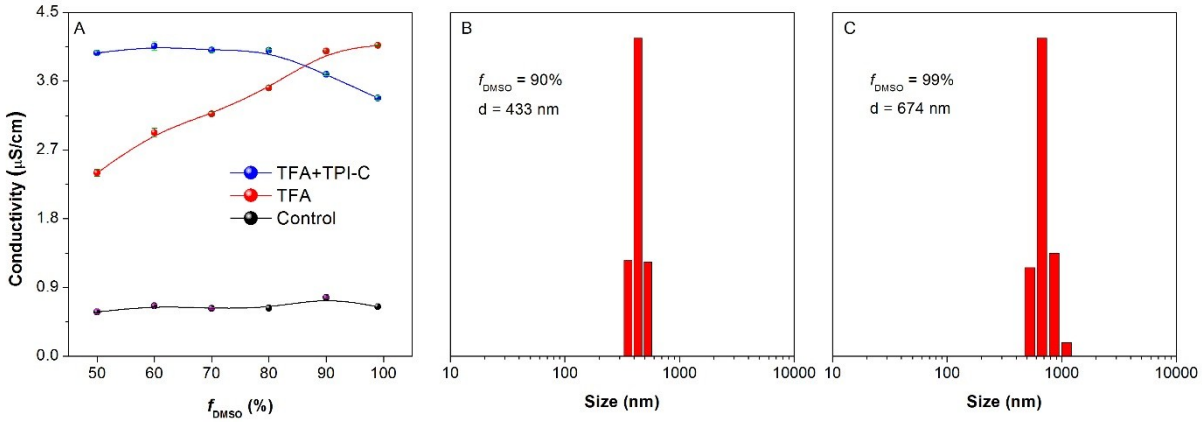


Fig. S5 (A) Conductivities of TFA and TFA+TPI-C in THF/DMSO mixtures with different DMSO fractions (f_{DMSO}). DLS data of TPI-C in THF/DMSO mixtures with f_{DMSO} of (B) 90% and (C) 99%.

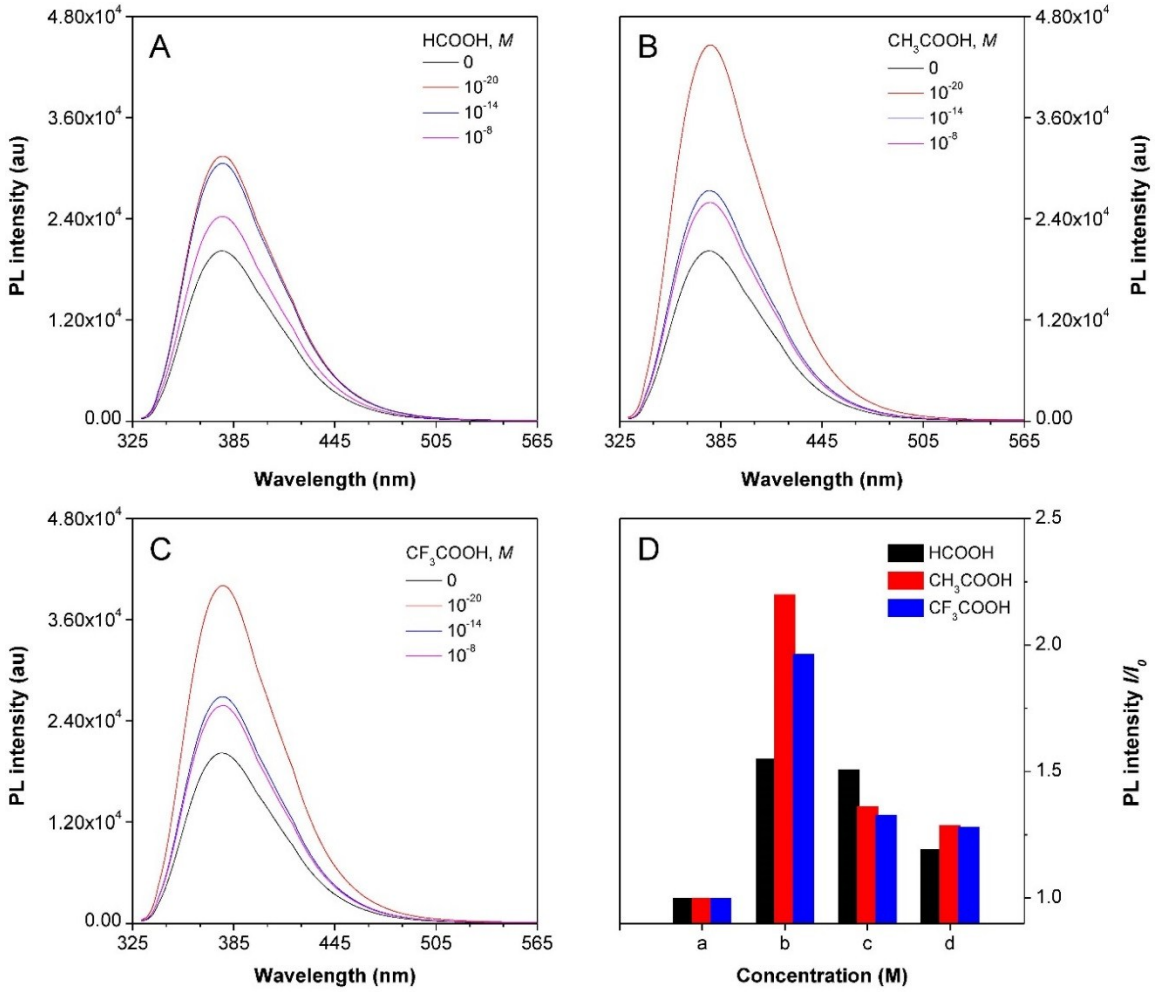


Fig. S6 PL spectra of TPI-C (10 μM in THF/hexane mixtures with f_H=99%) with adding (A) HCOOH, (B) CH_3COOH and (C) CF_3COOH at different concentrations. (D) Plot of relative PL intensity (I/I_0) at different acid concentrations. In x-axis concentration represents for acid concentration at (a) 0 M, (b) 10^{-20} M, (c) 10^{-14} M and (d) 10^{-8} M, respectively.

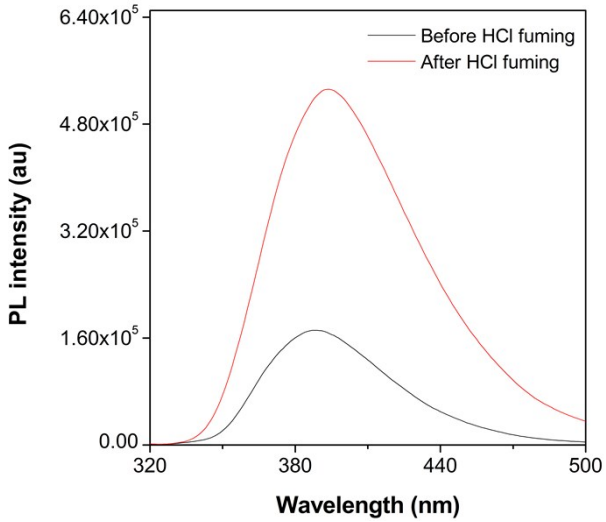


Fig. S7 PL spectra of TPI-C films before and after 3 min HCl fuming.

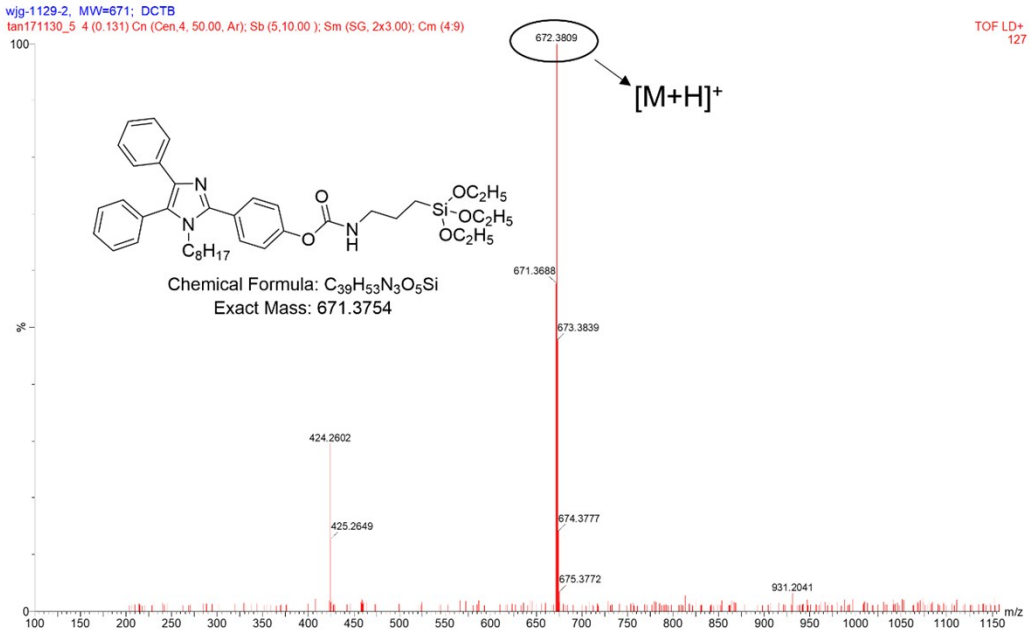


Fig. S8 HRMS of TPI-Si.

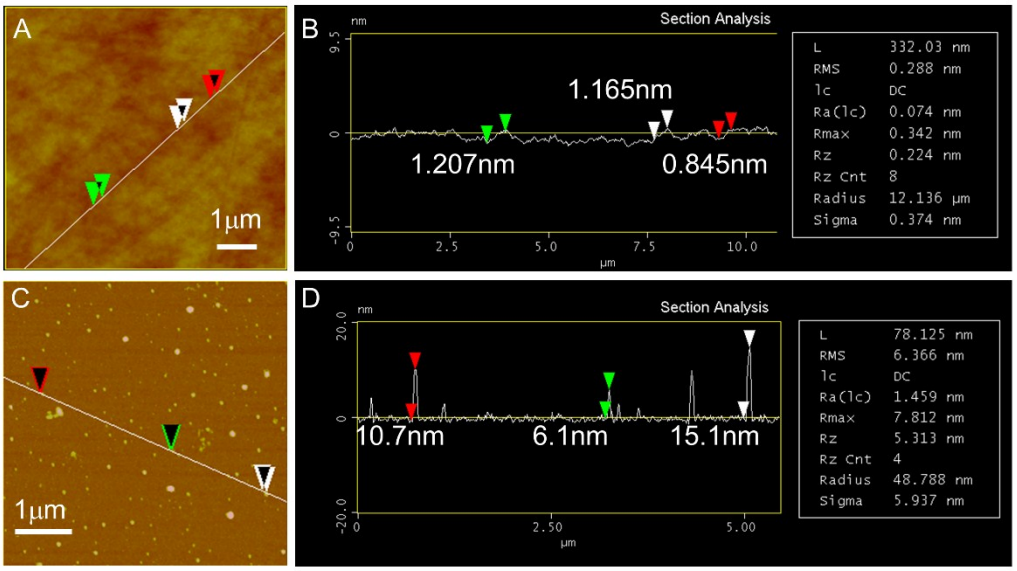


Fig. S9 (A) AFM images and (B) section analysis of the silicon substrate. (C) AFM images and (D) section analysis of TPI-Si-functionalized surface (TFS).

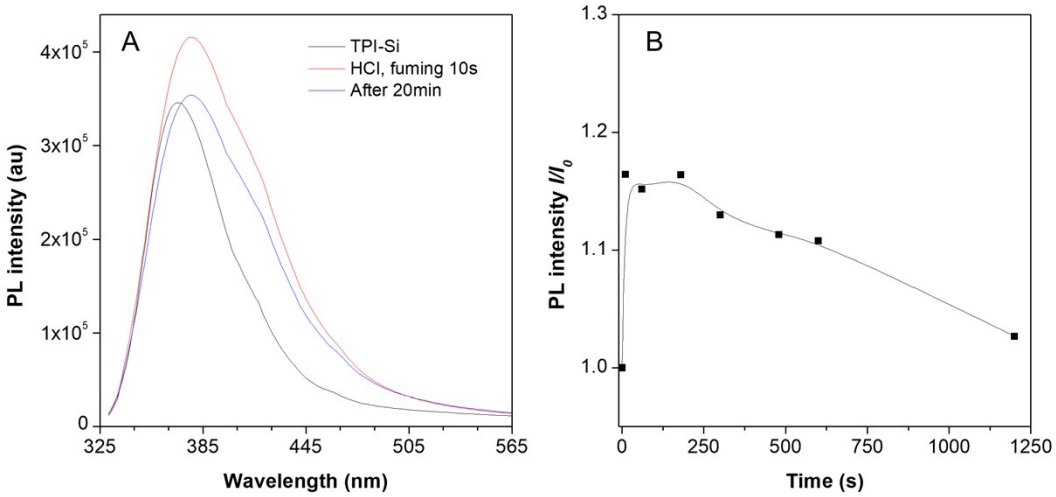


Fig. S10 (A) PL spectra of TFS before and after 10 s HCl fuming. Black line: TFS without fuming; Red line: the substrate after 10 s HCl fuming; Blue line: 20 min after HCl fuming. (B) Plot of relative PL intensity (I/I_0) of TFS before and after 10 seconds HCl fuming under different time steps.

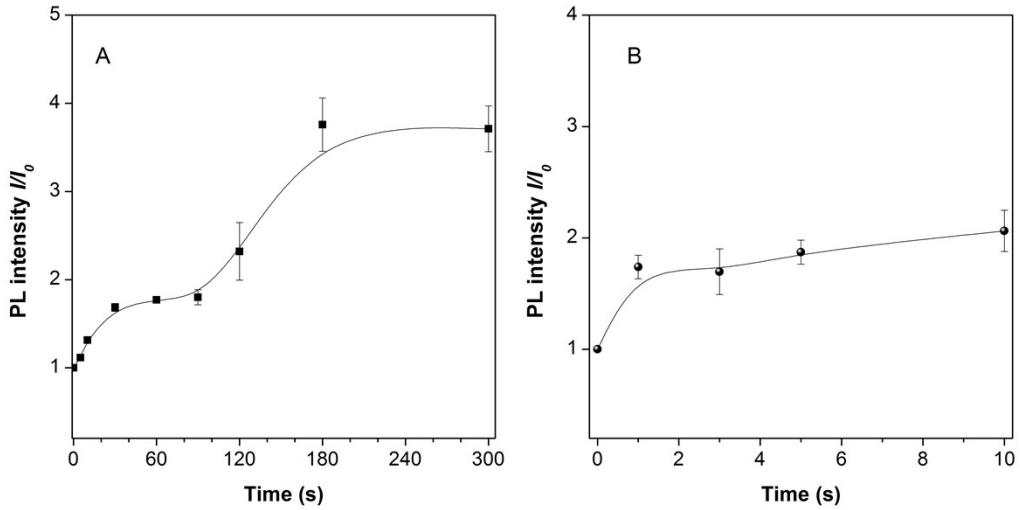


Fig. S11 Relative PL intensity (I/I_0) of TFS upon different (A) HCl vapor and (B) TFA vapor fuming times.

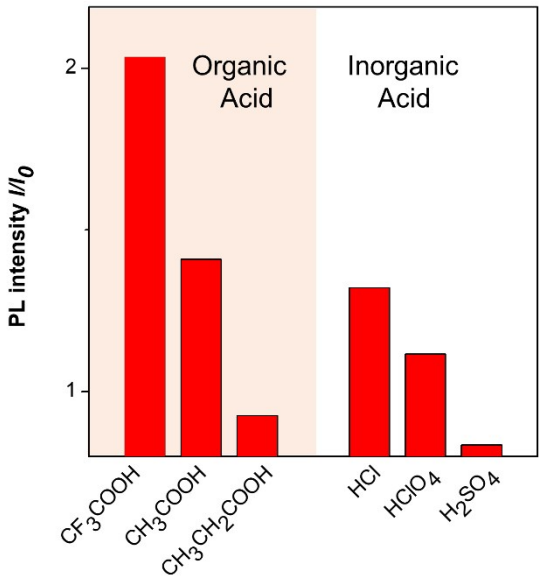


Fig. S12 The fluorescent intensity of TFS under different acid gas stimulus. For each acid, the surface was fumed for 10 s.

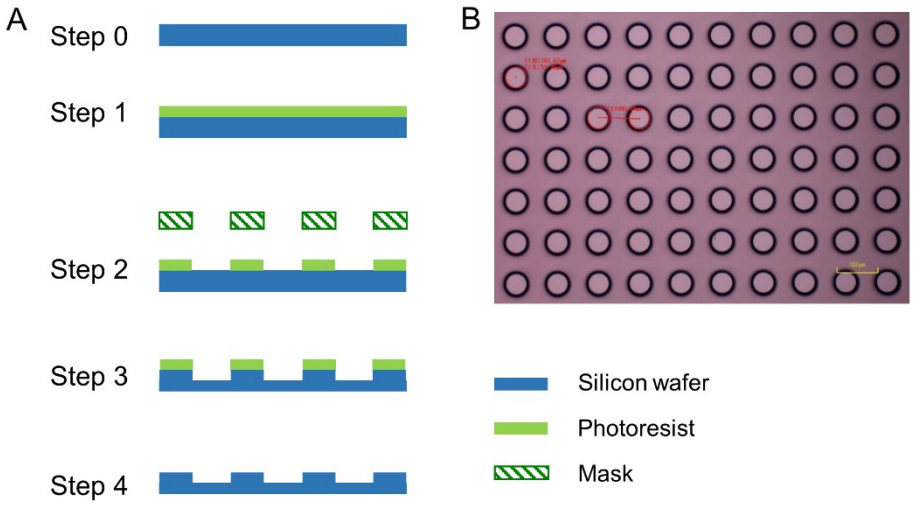


Fig. S13 (A) Fabrication process of the micro-pillar structure on silicon substrate. (B) Silicon micro-pillar under microscope, the micro-pillar structure we prepared are circle pillars on a flat silicon wafer, and are 50 μm in diameter, 50 μm high and with spacing of 50 μm between the silicon pillars.

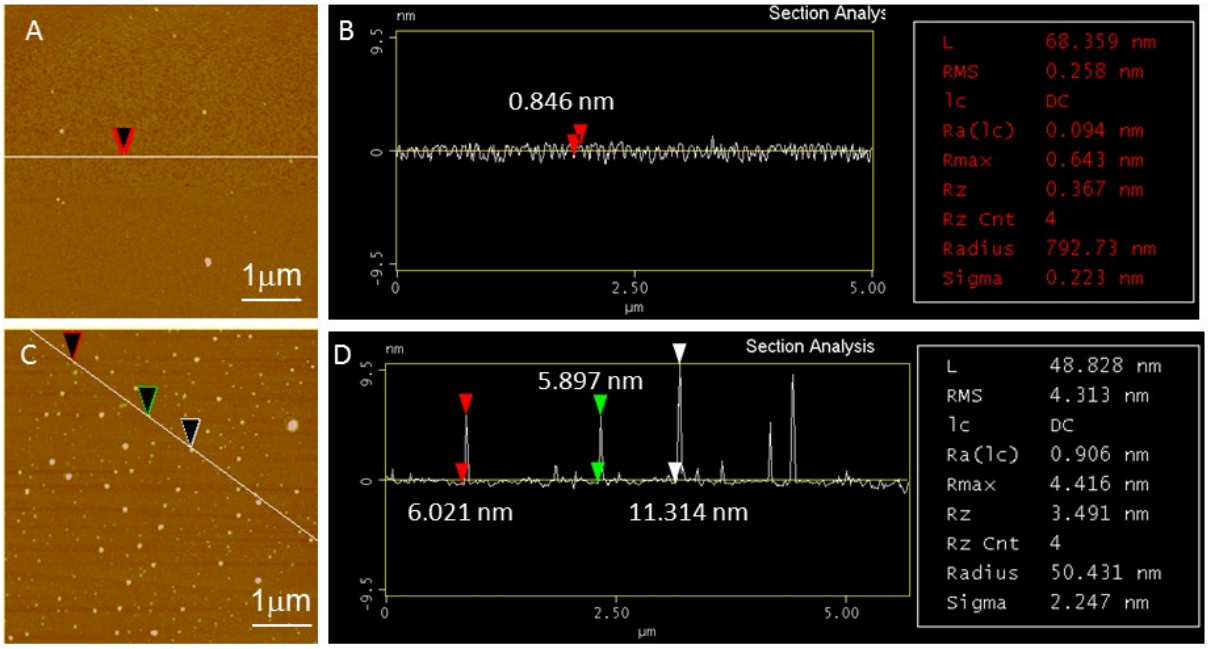


Fig. S14 (A) AFM images and (B) section analysis of the top of silicon micro-pillar. (C) AFM images and (D) section analysis of the top of micro-pillar functionalized by TPI-Si.

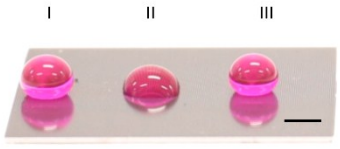


Fig. S15 Area I, II and III are fumed by HCl for 0 s, 60 s and 0 s respectively. Different wetting status can be obtained from left to right. Scale bars represent 2 mm.

Supplementary References

[1] S. Samai, G. C. Nandi, P. Singh, M.S. Singh, *Tetrahedron.* **2009**, *65*, 10155-10161.