Supporting Information.

Ultra-Low Adhesion and Friction of Fluoro-Hydro Alkyne-Derived Self-Assembled Monolayers on H-terminated Si(111)

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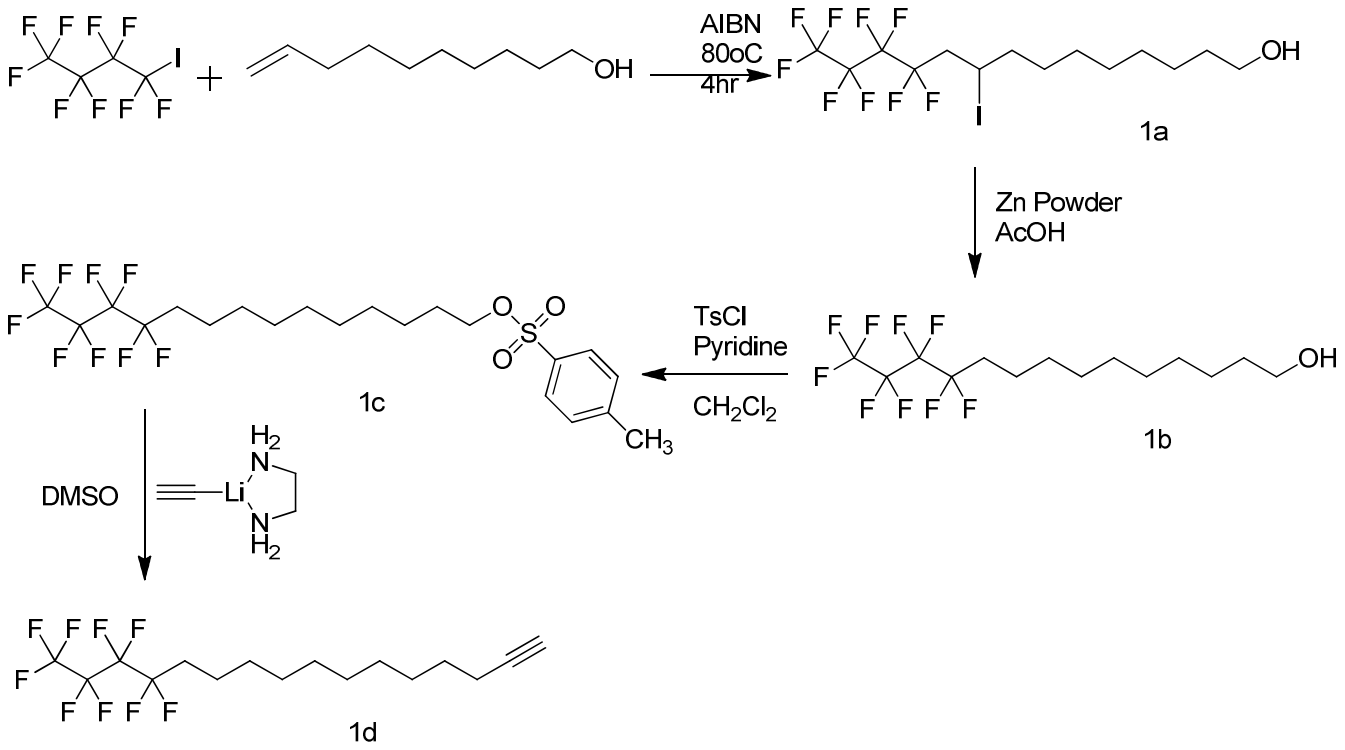
1 Synthesis and characterization.

2 General procedures.

Commercially available reagents were purchased and used as supplied. Dichloromethane was distilled from $CaCl_2$ stored away from bright light in a brown bottle with Linde type 4Å molecular sieves, in an atmosphere of dry argon. Diethyl ether, heptane, ethyl acetate, DMSO (dimethyl sulfoxide), acetic acid were degassed before use. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm silica gel foils 60 F254 plates using UV light as visualizing agent and ceric ammonium molybdate (CAM) and vanilla stain and heat as developing agents.

^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) and ^{19}F NMR (376 MHz) spectra were recorded on a Bruker 400 spectrometer and calibrated using residual undeuterated solvent ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.36 ppm) as an internal reference.[1] The following abbreviations were used to designate the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet. Elemental analysis was carried out using DART (Direct Analysis in Real Time) mass spectrometer[2-4] Samples for DART was prepared by adding a solution of the corresponding compound in toluene (1 mL, c=10 mg/mL). IR spectra (Bruker). were recorded in the range of 400-4000 cm^{-1} for the synthesized compounds in a KBr disk Heptadecafluoro-1-iodooctane (98%) was purchased from Fluka, 2,2-azobis(isobutyronitrile)(AIBN) was purchased from Acros and recrystallized in acetone, nonafluoro-1-iodobutane (98%), 5-hexen-1-ol (98%), 9-decen-1-ol (98%), and lithium acetylide ethylenediamine complex (90%), was purchased from Merck used as received.

2.1 Synthesis of 13,13,14,14,15,15,16,16,16-Nonafluoro-hexadec-1-yne (F9)



Scheme S1. Synthetic routes for 13,13,14,14,15,15,16,16,16-Nonafluoro-hexadec-1-yne (F9).

2.1.1 11,11,12,12,13,13,14,14,14-nonafluoro-9-iodotetradecan-1-ol (1a).

Nonafluoro-1-iodobutane (15.0 g, 43.4 mmol), 9-decen-1-ol (6.64 g, 42.5 mmol) and 2,2-azobis(isobutyronitrile) (2.08 g, 12.69 mmol) was added without using any solvent under a flow of argon, in a two necked 250 mL round bottom flask equipped with a condenser and heated at 65 ºC for 1 hr. The mixture was stirred overnight at 80 ºC. The progress of the reaction was monitored by thin layer chromatography. After completion of the reaction flask has cooled to room temperature. The product was purified by silica column chromatography (Rf = 0.50,

heptane/ethyl acetate 1:1.5). the product was obtained as clear oil as 96% yield 20.45 gm, 40.7 mmol, of 11,11,12,12,13,13,14,14,14-nonafluoro-9-iodotetradecan-1-ol (**1a**): 1H NMR (400 MHz, CDCl3,) δ in ppm: 4.36-4.29 (m, 1H, CHI), 3.65-3.62(t, 2H, CH2-OH), 2.99-2.70 (m, 2H, CF2-CH2), 1.88-1.68 (m, 2H, alkyl), 1.64-1.54 (m, 4H, alkyl), 1.44-1.33 (m, 9H, alkyl, OH). 13C NMR (100 MHz, CDCl3, δ ppm): 122.08-105.94 (m, 4C, CF3-CF2-CF2-CF2), 63.09 (s, 1C, CH2-OH), 41.96, 41.76, 41.55 (t, 1C, CF_2-*C*H_2), 40.48, 40.46 (d, 1C, alkyl), 32.87 (s, 1C, alkyl), 29.66 (s, 1C, alkyl), 29.44, 29.42 (d, 2C, alkyl), 28.55 (s, 1C, alkyl), 25.81 (s, 1C, alkyl), 20.83 (s, 1C, alkyl). FTIR (neat, cm^{-1}): 3345 (CH_2-*OH*), 2931 (ν_a CH_2), 2879 (ν_s CH_2), 1235 (ν_a CF_2), 1135 (ν_a CF_2). HRMS (DART-TOF) $[M - H]^-$ calcd. for $C_{14}H_{19}F_9IO$, 501.0336; found, 501.0329.

2.1.2 11,11,12,12,13,13,14,14,14-Nonafluoro-tetradecan-1-ol (1b).

The (19.77 g, 39.36 mmol) of 11,11,12,12,13,13,14,14,14-nonafluoro-9-iodotetradecan-1-ol (**1a**) was dissolved in 100 ml of glacial acetic acid (HOAc). Zinc dust (7.55 g 118.10 mmol) was added at room temperature under argon. The mixture was stirred for 16 hr. The solution was then vacuum-filtered through a Buchner funnel, and 1.0 M NaOH was added to the acidic solution until the mixture exhibited a neutral pH as indicated by pH paper. The mixture was extracted with diethyl ether (3 x 100 mL), and the solution was washed with water (2 x 100 mL), saturated aqueous $NaHCO_3$ solution (1 x 100 mL), and brine (1 x 100 mL), and then dried over $MgSO_4$. Removal of the solvent afforded the crude **1b**. The crude product was purified by column chromatography on silica gel (R_f = 0.54, heptane/ethyl acetate 1:1). Yield 12.45 g, 33.10 mmol, 84% of 11,11,12,12,13,13,14,14,14-Nonafluoro-tetradecan-1-ol (**1b**) as white solid: ^{1}H NMR

(400 MHz, $CDCl_3$, δ_{ppm}): 3.63-3.60 (t, 2H, C*H*$_2$-OH), 2.09-1.96 (m, 2H, CF_2-C*H*$_2$), 1.68 (s, 1H, -O*H*), 1.62-1.52(m, 4H, alkyl), 1.36-1.29 (m, 12H, alkyl). ^{13}C NMR (100 MHz, $CDCl_3$, δ_{ppm}): 122.23-105.77 (m, 4C, *C*F_3-*C*F_2-*C*F_2-*C*F_2), 63.10 (s, 1C, *C*H_2-OH), 32.91 (s, 1C, alkyl), 31.16, 30.93, 30.72 (t, 1C, CF_2-*C*H_2), 29.62, 29.52, 29.43, 29.33, 29.22 (m, 5C, alkyl), 25.87 (s, 1C, alkyl), 20.23, 20.20, 20.16 (t, 1C, alkyl). HRMS (DART-TOF) $[M - H]^-$ calcd for $C_{14}H_{20}F_9O$, 375.1370; found, 375.1367.

2.1.3 Toluene-4-sulfonic acid 11,11,12,12,13,13,14,14,14-nonafluoro-tetradecyl ester (1c).

To an oven-dried and argon-purged 250 mL round-bottom flask were added the 11,11,12,12,13,13,14,14,14-nonafluoro-tetradecan-1-ol (**1b**) (12.45 g, 33.10 mmol) at 0 ^oC in absolute dichloromethane (DCM) (40 mL) pyridine (5.33mL, 66.19 mmol) and the mixture was stirred at 25 °C for 10 min. The flask was cooled to 0 °C with an ice bath, and recrystallized p-toluenesulfonyl chloride (9.46 g, 49.64 mmol) was added to the reaction. The mixture was stirred at 0°C for 1 h, then kept at room temperature for 3 hr. The reaction was quenched with distilled water at 0 °C and warmed to 23 °C. The layers were separated, and the aqueous layer was extracted with ether. The combined organic layers were washed with brine and dried over MgSO4. The mixtures was sequentially washed with 2 N HCl (10 mL), saturated $NaHCO_3$ solution (2 x 25 mL) and (3 x 50 mL) water. The organic layer extract was dried ($MgSO_4$), concentrated in vacuo, and purification of the crude product by silica gel column chromatography (R_f = 0.52, Heptane/EtOAc, 2:1) afforded 13.11 g, 24.72 mmol, 75% of the Toluene-4-sulfonic acid 11,11,12,12,13,13,14,14,14-nonafluoro-tetradecyl (**1c**) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$, δ_{ppm}): 7.80-7.78 (d, 2H, Ph), 7.34-7.33 (d, 2H, Ph), 4.04-4.00 (t,

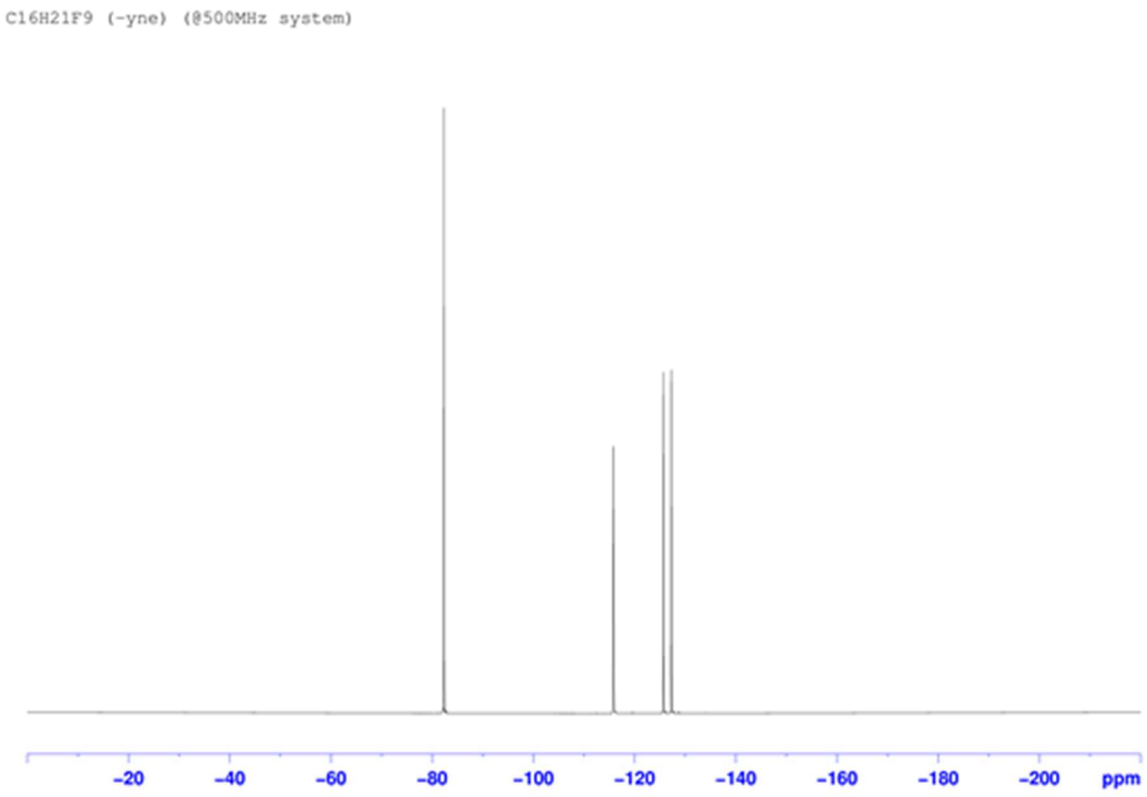
2H, C*H*$_2$-OTs), 2.45 (s, 3H, Ph-C*H*$_3$), 2.11-1.97 (m, 2H, CF_2-C*H*$_2$), 1.67-1.55 (m, 4H, Alkyl), 1.38-1.24(m, 12H, alkyl). ^{13}C NMR (100 MHz, $CDCl_3$, δ_{ppm}): 144.75 (s, 1C, Ph), 133.49 (s, 1C, Ph), 129.93 (s, 1C, Ph), 128.03 (s, 1C, Ph), 121.88-105.34 (m, 4C, *C*F_3-*C*F_2-*C*F_2-*C*F_2), 70.79 (s, 1C, *C*H_2-OTs), 31.16, 30.94, 30.71 (t, 1C, CF_2-*C*H_2), 29.40, 29.33, 29.28, 29.19, 29.02, 28.98 (m, 6C, alkyl), 25.47 (s, 1C, alkyl), 21.74 (s, 1C, Ph-*C*H_3), 20.24, 20.21, 20.17 (t, 1C, alkyl). HRMS (DART-TOF) $[M - H]^-$ calcd for $C_{21}H_{26}O_3F_9S$, 529.1459; found, 529.1465.

2.1.4 13,13,14,14,15,15,16,16,16-nonafluoro-hexadec-1-yne (1d).

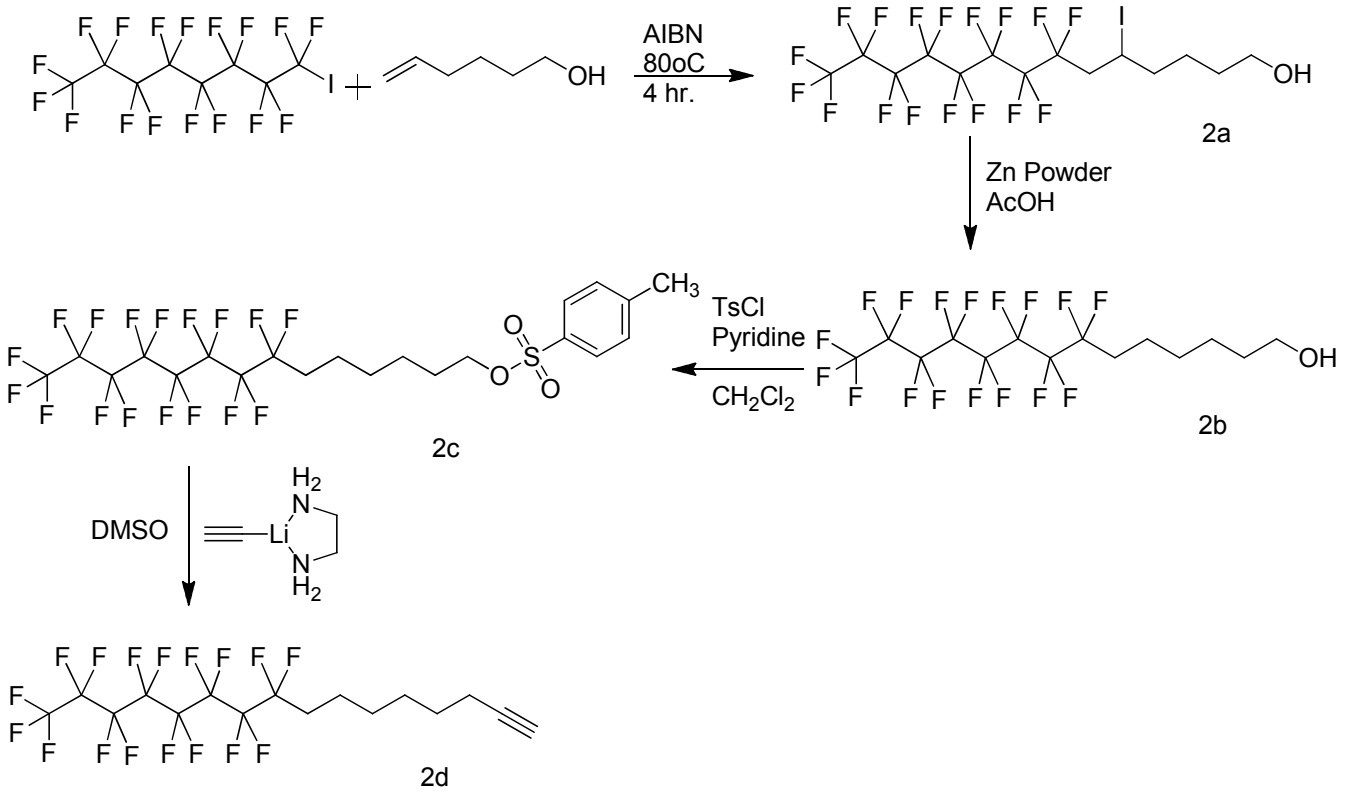
To an oven-dried, three-necked, round-bottom flask equipped with a magnetic stirring bar, argon line, pressure-equalizing dropping funnel and reflux condenser, protected from moisture by a calcium chloride-filled drying tube was flushed with argon and charged with lithium acetylide ethylenediamine (2.14 g, 23.23 mmol) dimethyl sulfoxide was then added to make the slurry ~2 M in lithium acetylide ethylenediamine (11 mL of DMSO). The solution was rapidly stirred under a dry argon atmosphere and the temperature was brought to 0 ^oC in ice bath. The toluene-4-sulfonic acid 11,11,12,12,13,13,14,14,14-nonafluoro-tetradecyl (**1c**) (9.47 g, 17.87 mmol) was dissolved in 20 mL dimethyl sulfoxide then added dropwise for 25 min with the temperature maintained 0 ^oC external cooling. When the addition was complete the reaction mixture was heated to 50 ^oC for four hours. The brown mixture was hydrolyzed with 60 mL of H_2O, and the aqueous phase was extracted with heptane (3 x 100 mL). The organic layer was washed with brine solution and dried over $MgSO_4$. The solvent was evaporated in vacuo to yield a colorless oil was obtained after by purification by silica gel column chromatography (R_f = 0.54, Heptane) afforded 5.53 g, 14.39 mmol, 80% of the 13,13,14,14,15,15,16,16,16-Nonafluoro-

hexadec-1-yne (**1d**): ^{1}H NMR (400 MHz, $CDCl_3$, δ_{ppm}): 2.21-2.17 (m, 2H, Alkyl), 2.12-1.99 (m, 2H, CF_2-C*H*$_2$), 1.95-1.93 (t, 1H, C≡C-*H*), 1.64-1.50 (m, 4H, Alkyl), 1.42-1.31(m, 12H, alkyl). ^{13}C NMR (100 MHz, $CDCl_3$, δ_{ppm}): 121.89-105.36 (m, 4C, *C*F_3-*C*F_2-*C*F_2-*C*F_2), 84.88 (s, 1C, *C*≡C-H), 68.19 (s, 1C, C≡*C*-H), 31.18, 30.96, 30.73 (t, 1C, CF_2-*C*H_2), 29.51, 29.44, 29.33, 29.24, 29.19, (m, 5C, alkyl), 28.86 (s, 1C, alkyl), 28.62 (s, 1C, alkyl), 20.25, 20.22, 20.18 (t, 1C, alkyl). 18.54 (s, 1C, alkyl); HRMS (DART-TOF) $[M + H]^+$ calcd for $C_{16}H_{22}F_9$, 385.1578; found, 385.1560.

^{19}F NMR:



2.2 9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16-heptadecafluorohexadec-1-yne (F17).



Scheme S2. Synthetic routes for 9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16-heptadecafluorohexadec-1-yne (F17).

2.2.1 7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-heptadecafluoro-5-iodotetradecan-1-ol (2a).

The procedure described for 11,11,12,12,13,13,14,14,14-nonafluoro-9-iodotetradecan-1-ol (**1a**) was used with Heptadecafluoro-1-iodooctane (41.34 g 75.71 mmol) and 5-Hexen-1-ol (7.36 g, 73.45 mmol) to give 7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-heptadecafluoro-5-iodotetradecan-1-ol (**2a**) as an off-white solid (38.73 g, 59.96 mmol, 82%): ^{1}H NMR (400 MHz,

$CDCl_3$, δ_{ppm}): 4.37-4.30 (m, 1H, C*H*I), 3.70-3.3.66(q, 2H, C*H*$_2$-OH), 3.00-2.71 (m, 2H, CF_2-C*H*$_2$), 1.92-1.77 (m, 2H, alkyl), 1.69-1.47 (m, 5H, alkyl, OH). ^{13}C NMR (100 MHz, $CDCl_3$, δ_{ppm}): 121.93-105.64 (m, 8C, *C*F_3-*C*F_2-*C*F_2-*C*F_2-*C*F_2-*C*F_2-*C*F_2-*C*F_2), 62.65 (s, 1C, *C*H_2-OH), 42.07, 41.86, 41.66 (t, 1C, CF_2-*C*H_2), 40.24, 40.22 (d, 1C, alkyl), 31.69 (s, 1C, alkyl), 26.16 (s, 1C, alkyl), 20.53 (s, 1C, alkyl). HRMS (DART-TOF) $[M - H]^-$ calcd for $C_{14}H_{11}OF_{17}I$, 644.9583; found, 644.9587.

2.2.2 7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-heptadecafluorotetradecan-1-ol (2b).

The procedure described for 11,11,12,12,13,13,14,14,14-Nonafluoro-tetradecan-1-ol (**1b**) was used with 7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-heptadecafluoro-5-iodotetradecan-1-ol (36.75 g 56.89 mmol) and zinc powder (10.91 g, 107.67 mmol) to give 7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-heptadecafluorotetradecan-1-ol (**2b**) as an off-white solid (27.87 g, 53.59 mmol, 94%): ^{1}H NMR (400 MHz, $CDCl_3$, δ_{ppm}): 3.66-3.63 (t, 2H, C*H*$_2$-OH), 2.12-1.99 (m, 2H, CF_2-C*H*$_2$), 1.68-1.52 (m, 4H, alkyl), 1.43-1.40 (m, 5H, alkyl). ^{13}C NMR (100 MHz, $CDCl_3$, δ_{ppm}): 122.17-105.29 (m, 8C, *C*F_3-*C*F_2-*C*F_2-*C*F_2-*C*F_2-*C*F_2-*C*F_2-*C*F_2), 62.90 (s, 1C, *C*H_2-OH), 32.60 (s, 1C, alkyl), 31.60, 31.00, 30.78 (t, 1C, CF_2-*C*H_2), 29.05 (m, 1C, alkyl), 25.59 (s, 1C, alkyl), 20.27 (t, 1C, alkyl). HRMS (DART-TOF) $[M - H]^-$ calcd for $C_{14}H_{12}F_{17}O$, 519.0617; found, 519.0616.

2.2.3 7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-heptadecafluorotetradecyl 4-methylbenzenesulfonate (2c).

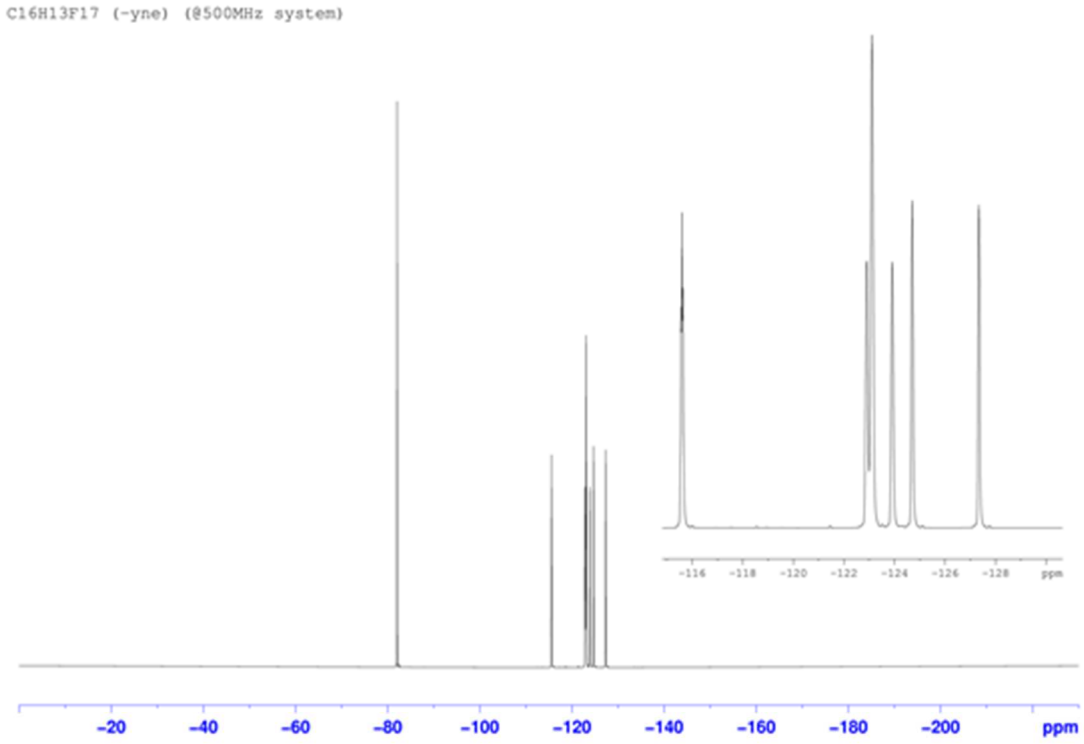
The procedure described for Toluene-4-sulfonic acid 11,11,12,12,13,13,14,14,14-nonafluoro-tetradecyl ester (**1c**) was used with 7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-heptadecafluorotetradecan-1-ol (**2b**) (10.00 g 19.23 mmol) and p-Toluenesulfonyl chloride (4.03 g, 21.15 mmol) to give 7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-heptadecafluorotetradecyl 4-methylbenzenesulfonate (**2c**) as an shine white solid (10.27gm, 15.24 mmol, 79%): ^{1}H NMR (400 MHz, $CDCl_3$, δ_{ppm}): 7.79-7.77 (d, 2H, Ph), 7.35-7.33 (d, 2H, Ph), 4.05-4.02 (t, 2H, C*H*$_2$-OTs), 2.44 (s, 3H, Ph-C*H*$_3$), 2.07-1.94 (m, 2H, CF_2-C*H*$_2$), 1.69-1.62 (m, 2H, Alkyl), 1.58-1.51 (m, 2H, Alkyl), 1.40-1.28 (m, 4H, alkyl). ^{13}C NMR (100 MHz, $CDCl_3$, δ_{ppm}): 144.91(s, 1C, Ph), 133.44(s, 1C, Ph), 129.97 (s, 1C, Ph), 128.02 (s, 1C, Ph), 121.59-105.70(m, 8C, *C*F_3-*C*F_2-*C*F_2-*C*F_2), 70.40 (s, 1C, *C*H_2-OTs), 31.10, 30.88, 30.65 (t, 1C, CF_2-*C*H_2), 28.72 (s, 1C, alkyl), 28.53 (s, 1C, alkyl), 25.23 (s, 1C, alkyl), 21.64 (s, 1C, Ph-*C*H_3), 20.15, 20.12, 20.08 (t, 1C, alkyl). FTIR (neat, cm^{-1}): 2978, 2954 (phenyl), 2926 (ν_a CH_2), 2865 (ν_s CH_2), 1216 (ν_a CF_2), 1134 (ν_a CF_2). HRMS (DART-TOF) $[M - H]^-$ calcd for $C_{21}H_{18}F_{17}O_3S$, 673.0705; found, 673.0710.

2.2.4 9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16-heptadecafluorohexadec-1-yne (2d).

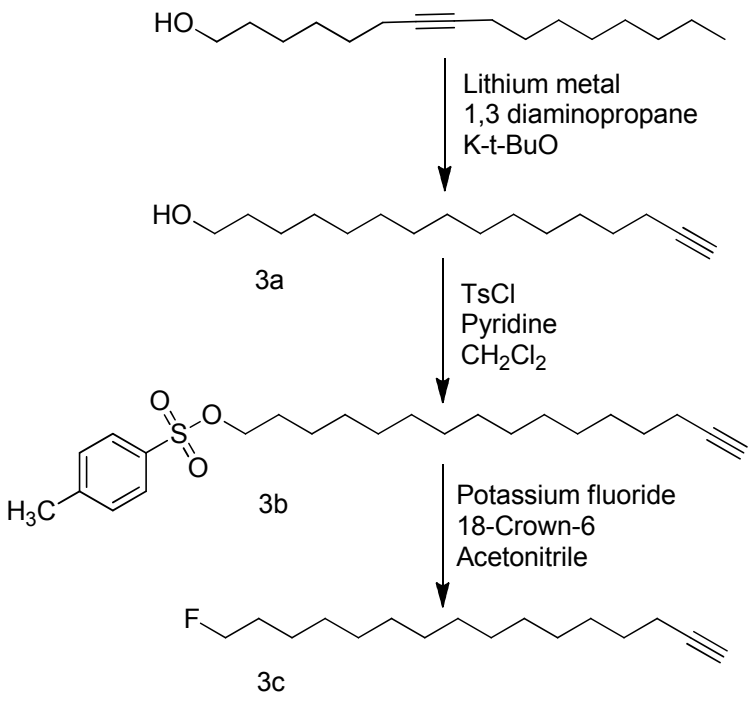
The procedure described for 13,13,14,14,15,15,16,16,16-Nonafluoro-hexadec-1-yne (**1d**) was used with 7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-heptadecafluorotetradecyl 4-methylbenzenesulfonate (**2c**) (10.29 g 15.27 mmol) and lithium acetylide ethylenediamine (2.25 g, 24.44 mmol) to give 9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16-heptadecafluorohexadec-1-yne (2d) as an shine white solid (4.84 g, 8.99 mmol, 60%): ^{1}H NMR (400 MHz, $CDCl_3$, δppm): 2.21-2.19 (m, 2H, Alkyl), 2.14-2.00 (m, 2H, CF_2-CH_2), 1.96-1.95 (t, 1H, C≡C-H), 1.66-1.52 (m, 4H, Alkyl), 1.50-1.40(m, 4H, alkyl). 13C NMR (100 MHz, $CDCl_3$,

δppm): 121.42-105.15(m, 8C, CF_3-CF_2-CF_2-CF_2-CF_3-CF_2-CF_2-CF_2), 84.26 (s, 1C, C≡C-H), 68.31 (s, 1C, C≡C-H), 31.05, 30.82, 30.60 (t, 1C, CF_2-CH_2), 28.54 (s, 1C, alkyl), 28.21, 28.09 (d, 2C, alkyl), 20.03, 19.99, 19.96 (t, 1C, alkyl). 18.26 (s, 1C, alkyl); HRMS (DART-TOF) [M + NH4] calcd for C16H13F17, 546.10895; found, 546.10720.

^{19}F NMR:



2.3 16-fluorohexadec-1-yne (F1).



Scheme S3. Synthetic routes for 16-fluorohexadec-1-yne (F1).

2.3.1 Hexadec-15-yn-1-ol (3a).

The mixture of Li (3.49 g, 503.3 mmol) in 1,3-diaminopropane (240 mL) was stirred and heated in an oil bath at 70°C until the blue color discharges (1 h), affording a white suspension of the lithium amide. After cooling to room temperature, potassium tert-butoxide (37.6 g, 335.54 mmol,) was added to the mixture. The resultant pale yellow solution is stirred for 20 min at room temperature, and then hexadec-7-yn-1-ol (20 g, 83.9. mmol) was added. Residual hexadec-7-yn-1-ol was washed into the mixture with small portion of 1,3-diaminopropane (20 mL). After stirring at room temperature for 3h, the reaction mixture was poured into plenty of ice-water and extracted with ether for three times. The organic phase was combined and washed with 5%

aqueous HCl and saturated NaCl(Brine), then dried over anhydrous Na2SO4. The solvent was evaporated under vacuum. The residue was purified by silica gel column chromatography (Heptane : Ethyl acetate = 7:1) to afford hexadec-15-yn-1-ol **3a** (13.95 g, 58.51 mmol 73%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, δ_{ppm}) 3.62-3.59 (t, 2H, C*H*$_2$-OH), 2.17-2.13 (dt 2H, CH_2-C*H*$_2$-C≡C-H), 1.91-1.90 (t, 1H, C≡C-*H*), 1.61 (s, 1H, CH_2-O*H*), 1.56-1.46 (m, 4H, Alkyl), 1.38-1.24(m, 20H, alkyl). 13C NMR (100 MHz, $CDCl_3$, δppm): 85.08(s, 1C, C≡C-H), 68.34 (s, 1C, C≡C-H), 63.29 (s, 1C, -CH_2-OH), 33.10 (s, 1C, alkyl), 29.93, 29.92, 29.90 (t, 5C, alkyl), 29.80 (s, 1C, alkyl), 29.74 (s, 1C, alkyl), 29.41 (s, 1C, alkyl), 29.06 (s, 1C, alkyl), 28.81 (s, 1C, alkyl), 26.06(s, 1C, alkyl), 18.70 (s, 1C, alkyl); HRMS (DART-TOF) $[M + H]^+$ calcd for $C_{16}H_{31}O$, 239.2375; found, 239.2367.

2.3.2 Hexadec-15-yn-1-yl 4-methylbenzenesulfonate (3b).

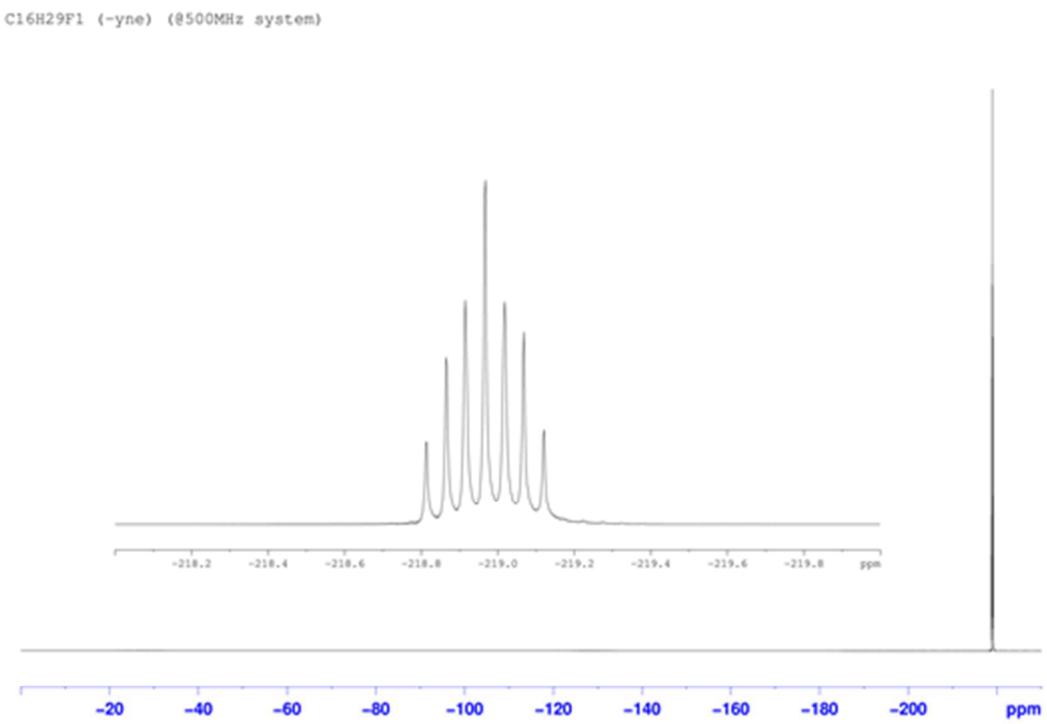
The procedure described for Toluene-4-sulfonic acid 11,11,12,12,13,13,14,14,14-nonafluoro-tetradecyl ester **(1c)** was used with hexadec-15-yn-1-ol **3a** (10.00 g 42.0 mmol) and p-Toluenesulfonyl chloride (9.60g , 50.4 mmol) to give hexadec-15-yn-1-yl 4-methylbenzenesulfonate (**3b**) as an shine white solid (13.35 g, 34.04 mmol, 81%): ^{1}H NMR (400 MHz, $CDCl_3$, δ_{ppm}): 7.79-7.77 (d, 2H, Ph), 7.34-7.32 (d, 2H, Ph), 4.03-3.99 (t, 2H, C*H*$_2$-OTs), 2.44 (s, 3H, Ph-C*H*$_3$), 2.19-2.15 (m 2H, CH_2-C*H*$_2$-C≡C-H), 1.93-1.91 (t, 1H, C≡C-*H*), 1.65-1.58 (m, 2H, alkyl), 1.54-1.48 (m, 2H, alkyl), 1.41-1.21 (m, 20H, alkyl). ^{13}C NMR (100 MHz, $CDCl_3$, δ_{ppm}): 144.90 (s, 1C, Ph), 133.67 (s, 1C, Ph), 130.10 (s, 1C, Ph), 128.19 (s, 1C, Ph), 85.09 (s, 1C, *C*≡C-H), 71.00 (s, 1C, *C*H_2-OTs), 68.35 (s, 1C, C≡*C*-H), 29.90, 29.89, 29.80, 29.79, 29.69, 29.42, 29.24, 29.15, 29.07, 28.82 (m, 13C, alkyl), 25.64 (s, 1C, alkyl), 21.92 (s, 1C,

alkyl), 18.71 (s, 1C, alkyl). HRMS (DART-TOF) [M + Na] calcd for $C_{23}H_{36}O_3NaS$, 415.2283; found, 415.2273.

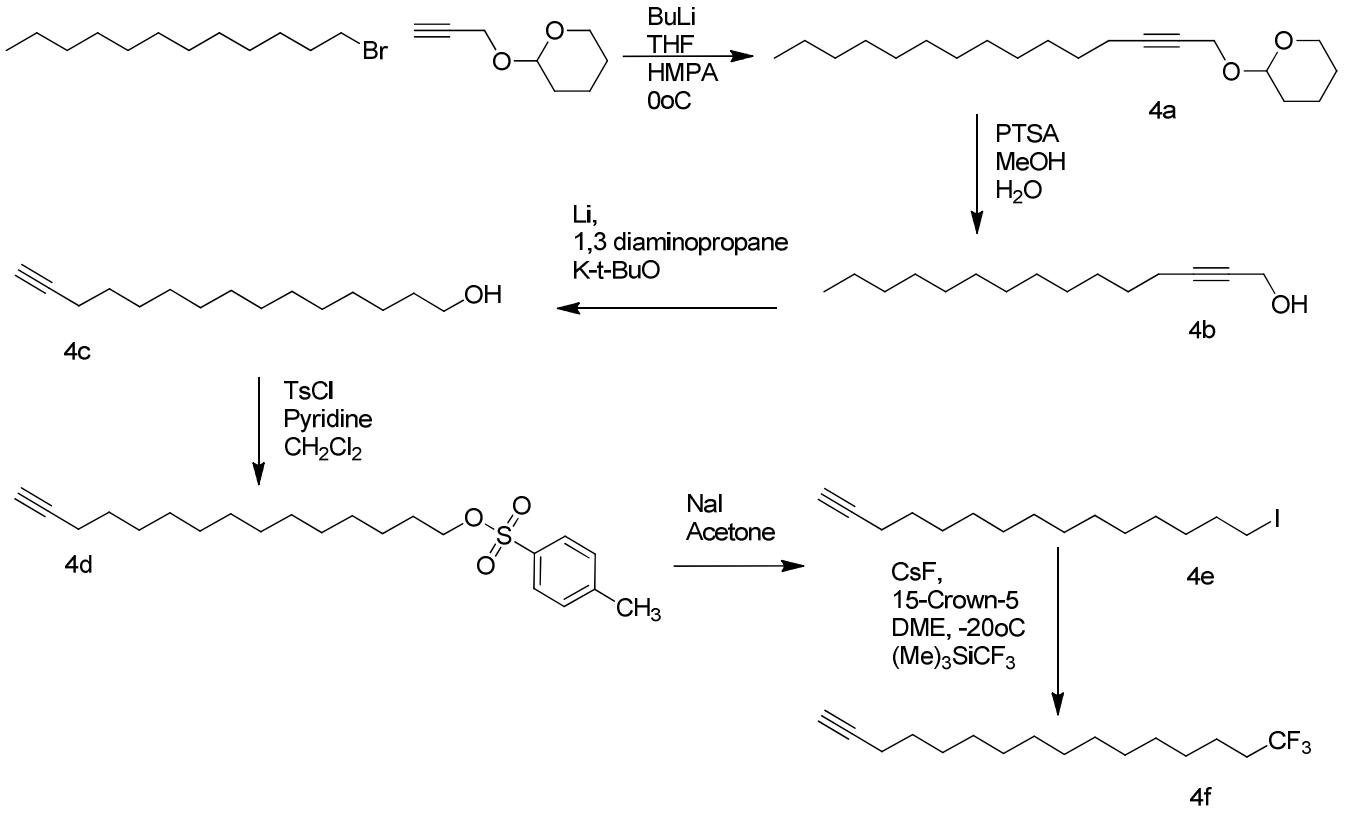
2.3.3 16-Fluorohexadec-1-yne (3c).

In a 250 mL three-neck flask, equipped with condenser and dropping funnel, KF (3.26 g, 56.09 mmol) and 18-crown-6 (14.8 g, 56.09 mmol) are dissolved in 50 mL of acetonitrile. The solution heated to 60 ºC. A solution of hexadec-15-yne-1-tosyl (11.0 g, 28.04 mmol) in 55 mL of acetonitrile is added dropwise over a period of 45 minutes. The solution refluxed 24 hr. After 24 hr, an additional equivalent of KF (1.62 g, 28.04 mmol) and 18-crown-6 (7.4 g, 28.04 mmol) are added and the reaction is continued for another 24 hr. The solvent was removed under reduced pressure, and the residue was dissolved in ether and washed with H_2O, organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by column chromatography to afford 16-fluorohexadec-1-yne (**3c**) (6.40 g, 26.64 mmol) as a clear oil: (heptane/EtOAc=2/1). ^{1}H NMR (400 MHz, $CDCl_3$, δ_{ppm}) 4.49-4.46(t, 1H, F-C*H*$_2$-CH$_2$), 4.37-4.34 (t, 1H, F-C*H*$_2$-CH$_2$), 2.19-2.15 (m 2H, CH$_2$-C*H*$_2$-C≡C-H), 1.92-1.91(t, 1H, C≡C-*H*), 1.74-1.61 (m, 2H, alkyl), 1.55-1.48 (m, 2H, alkyl), 1.40-1.26 (m, 20H, alkyl). ^{13}C NMR (100 MHz, $CDCl_3$, δ_{ppm}): 85.29(s, 1C, F-*C*H2), 85.05 (s, 1C, *C*≡C-H), 83.66 (s, 1C, F-*C*H2), 68.35(s, 1C, C≡*C*-H), 30.86 (s, 1C, alkyl), 30.67 (s, 1C, alkyl), 29.96, 29.93, 29.89, 29.85 (m, 5C, alkyl), 29.59 (s, 1C, alkyl), 29.45(s, 1C, alkyl), 29.10 (s, 1C, alkyl), 28.85 (s, 1C, alkyl), 25.52, 25.47 (d, 1C, FCH$_2$-*C*H$_2$-CH$_2$), 18.73(s, 1C, alkyl). HRMS (DART-TOF) $[M + H]^+$ calcd for $C_{16}H_{30}F$, 241.2332; found, 241.2325.

^{19}F NMR:


C16H29F1 (-yne) (@500MHz system)
-218.2
-218.4
-218.6
-218.8
-219.0
-219.2
-219.4
-219.6
-219.8
ppm
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

2.4 16,16,16-Trifluorohexadec-1-yne (F3)



Scheme S4. Synthetic routes for 16,16,16-trifluorohexadec-1-yne (F3).

2.4.1 2-(Pentadec-2-yn-1-yloxy)tetrahydro-2H-pyran (4a).

To an oven-dried and argon-purged 100 mL round-bottomed flask were added the a solution of tetrahydro-2-(2-propynyloxy)-2H-pyran (0.98 mL, 6.98 mmol) in dry THF (20 mL) was cooled to 0 °C in an ice bath and treated with 1.6 M solution of n-butyllithium in hexane (1.89 mL, 8.02 mmol). Thereafter, 1-bromoalkane (1.93 mL 8.02 mmol) in dry distilled HMPA (14 mL) was added at 0 °C and the resulting reaction mixture stirred 1.5 h at room temperature. The reaction was quenched with saturated aqueous NH_4Cl solution followed by extraction with

pentane. The combined organic extracts were washed with water and dried ($MgSO_4$). The residue was purified by column chromatography to afford 2-(pentadec-2-yn-1-yloxy)tetrahydro-2H-pyran (**4a**) (0.69 g, 2.23 mmol) as a clear oil: (hepatane/EtOAc=9:1). . ^{1}H NMR (400 MHz, $CDCl_3$, δ_{ppm}) 4.82-4.80(t, 1H, O-C*H*-O), 4.27-4.18(m, 2H, alkyl), 3.84-3.81(m, 1H, alkyl), 3.53-3.50(m, 1H, alkyl), 2.23-2.18(m, 2H, alkyl), 1.73-1.64(m, 2H, alkyl), 1.63-1.46(m, 6H, alkyl), 1.38-1.26(m, 18H, alkyl), 0.89-0.26(t, 3H, CH_2-C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, δ_{ppm}): 96.61 (s, 1C, C≡*C*-CH_2-O-), 86.73 (s, 1C, *C*≡C-CH_2-O-), 61.97 (s, 1C, alkyl), 54.63 (s, 1C, alkyl), 31.89(s, 1C, alkyl), 30.30 (s, 1C, alkyl), 29.66, 29.60, 29.51, 29.32, 29.11, 28.86, 28.60 (m, 8C, alkyl), 25.39 (s, 1C, alkyl), 22.65 (s, 1C, alkyl), 19.13(s, 1C, alkyl), 18.80 (s, 1C, alkyl), 14.07 (s, 1C, CH_2-*C*H_3). HRMS (DART-TOF) [M + NH_4] calcd for $C_{20}H_{40}O_2N$, 326.3059; found, 326.3043.

2.4.2 Pentadec-2-yn-1-ol (4b).

To a 0.61 g (1.96 mmol) solution of 2-(pentadec-2-yn-1-yloxy)tetrahydro-2H-pyran (**4a**) in 10 mL methanol was added 0.19 g (0.98 mmol) of 4-toluene sulfonic acid monohydrate at room temperature. The mixture was allowed to stir overnight at room temperature and then quenched with 10 mL of ice-cold water. The organic layer was washed with saturated NaCl and dried over anhydrous $MgSO_4$. The solvent was removed by rotary evaporation. The residue was purified by silica column chromatography (9:1, heptane/ether) to give 0.362 g (83%) of a light yellow oil: (9:1, heptane/ether). ^{1}H NMR (400 MHz, $CDCl_3$, δ_{ppm}): 4.25-4.24 (t, 2H, HO-C*H*$_2$-), 2.22-2.18 (m, 2H, C≡C-C*H*$_2$-CH_2), 1.60-1.59 (t, 1H, *HO*-CH_2-), 1.53-1.46 (m, 2H, alkyl), 1.38-1.26 (m, 18H, alkyl), 0.89-0.86 (t, 3H, CH_2-C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, δ_{ppm}): 87.02 (s, 1C, C≡*C*-

CH_2-OH), 78.62 (s, 1C, CH_2-*C*≡C-CH_2-OH), 51.77 (s, 1C, CH_2-OH), 32.26 (s, 1C, alkyl), 30.00, 29.97, 29.86, 29.69, 29.49, 29.23, 28.96 (m, 8C, alkyl), 23.02(s, 1C, alkyl), 19.08(s, 1C, alkyl), 14.44 (s, 1C, CH_2-*C*H_3). HRMS (DART-TOF) $[M + H]^+$ calcd for $C_{15}H_{29}O$, 225.2218; found, 225.2205.

2.4.3 Pentadec-14-yn-1-ol (4c).

The procedure described for hexadec-15-yn-1-ol (**3a**) was used with Pentadec-2-yn-1-ol (**4b**) (0.307 g 1.37 mmol), lithium, 0.06 g (8.01 mmol), 1,3 diaminopropane 10 mL and potassium tert-butoxide (0.61 g, 5.47 mmol) to give Pentadec-14-yn-1-ol (**4c**) as an clear oil (0.276 g, 1.23 mmol, 90%): ^{1}H NMR (400 MHz, $CDCl_3$, δ_{ppm}) 3.64-3.61 (t, 2H, C*H*$_2$-OH), 2.19-2.15 (dt 2H, CH_2-C*H*$_2$-C≡C-H), 1.93-1.92 (t, 1H, C≡C-*H*), 1.59-1.48 (m, 4H, Alkyl), 1.45-1.26 (m, 19H, alkyl). ^{13}C NMR (100 MHz, $CDCl_3$, δppm): 85.14(s, 1C, *C*≡C-H), 68.36 (s, 1C, C≡*C*-H), 63.40 (s, 1C, -*C*H_2-OH), 33.15 (s, 1C, alkyl), 29.94, 29.91, 29.82, 29.76(m, 6C, alkyl), 29.44(s, 1C, alkyl), 29.09(s, 1C, alkyl), 28.84(s, 1C, alkyl), 26.08(s, 1C, alkyl), 18.73 (s, 1C, alkyl). HRMS (DART-TOF) $[M + H]^+$ calcd for $C_{15}H_{29}O$, 225.2218; found, 225.2207.

2.4.4 Pentadec-14-yn-1-yl 4-methylbenzenesulfonate (4d).

The procedure described for Toluene-4-sulfonic acid 11,11,12,12,13,13,14,14,14-nonafluoro-tetradecyl ester (**1c**) was used with Pentadec-14-yn-1-ol **4c** (0.195 g 0.87 mmol) and p-Toluenesulfonyl chloride (0.18 g , 0.95 mmol) to give Pentadec-14-yn-1-yl 4-methylbenzenesulfonate (**4d**) as an shine white solid 0.31 g, 0.82 mmol, 93%): ^{1}H NMR (400

MHz, $CDCl_3$, δ_{ppm}): 7.80-7.78 (d, 2H, Ph), 7.35-7.33 (d, 2H, Ph), 4.04-4.00 (t, 2H, C*H*$_2$-OTs), 2.45 (s, 3H, Ph-C*H*$_3$), 2.20-2.16 (dt, 2H, CH_2-C*H*$_2$-C≡C-H), 1.94-1.92 (t, 1H, C≡C-*H*), 1.66-1.60 (m, 2H, alkyl), 1.56-1.49 (m, 2H, alkyl), 1.40-1.22(m, 18H, alkyl). ^{13}C NMR (100 MHz, $CDCl_3$, δ_{ppm}): 144.93 (s, 1C, Ph), 133.71 (s, 1C, Ph), 130.13(s, 1C, Ph), 128.24 (s, 1C, Ph), 85.15 (s, 1C, *C*≡C-H), 71.04 (s, 1C, *C*H_2-OTs), 68.38 (s, 1C, C≡*C*-H), 29.90, 29.82, 29.72 (m, 5C, alkyl), 29.45 (s, 1C, alkyl), 29.28 (s, 1C, alkyl), 29.19 (s, 1C, alkyl), 29.11 (s, 1C, alkyl), 28.85 (s, 1C, alkyl), 25.68 (s, 1C, alkyl), 21.97 (s, 1C, alkyl), 18.75 (s, 1C, alkyl). HRMS (DART-TOF) $[M + H]^+$ calcd for $C_{22}H_{35}O_3S$, 379.2307; found, 379.2294.

2.4.5 15-iodopentadec-1-yne (4e).

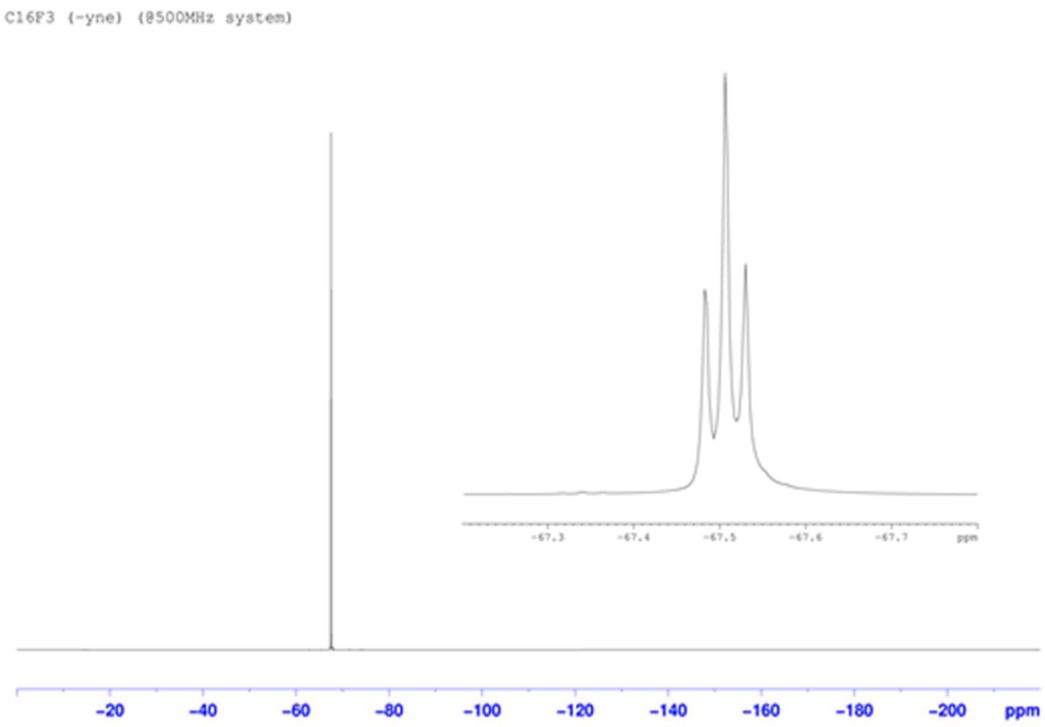
To a stirred mixture of sodium iodide (1.64 g, 10.95 mmol) in acetone (100 mL), a solution of 14-yn-1-yl 4-methylbenzenesulfonate (**4d**) (2.07 g, 5.47 mmol) in acetone (25 mL) was added and the reaction mixture was stirred and heated under reflux for 8 h under nitrogen atmosphere and then concentrated in vacuo to remove the acetone. The obtained residue was diluted with water and extracted with ethyl acetate (2 x 40 mL). The combined ethyl acetate extract was washed with water, brine and dried over Na_2SO_4. The concentration of organic layer in vacuo followed by silica gel column chromatographic purification of the resulting residue using ethyl acetate/heptane (1:5) as an eluent afforded pure product 15-iodopentadec-1-yne (**4e**) as a colorless oil (1.86 g, 5.57 mmol, 99%). ^{1}H NMR (400 MHz, $CDCl_3$, δ_{ppm}): 3.05-3.02 (t, 2H, C*H*$_2$-I), 2.08-2.01(dt, 2H, CH_2-C*H*$_2$-C≡C-H), 1.79-1.78(t, 1H, C≡C-H), 1.71-1.63 (m, 2H, alkyl), 1.41-1.33 (m, 2H, alkyl), 1.25-1.07 (m, 18H, alkyl). ^{13}C NMR (100 MHz, $CDCl_3$, δ_{ppm}): 84.61(s, 1C, *C*≡C-H), 67.82(s, 1C, C≡*C*-H), 33.40 (s, 1C, alkyl), 30.32 (s, 1C, alkyl), 29.37, 29.33, 29.28,

29.22 (m, 6C, alkyl), 28.90 (s, 1C, alkyl), 28.60 (s, 1C, alkyl), 28.35 (s, 1C, alkyl), 18.21 (s, 1C, alkyl), 7.07 (s, 1C, -*C*H_2-I). HRMS (DART-TOF) $[M + H]^+$ calcd for $C_{15}H_{28}I$, 335.1256; found, 335.1250.

2.4.6 16,16,16-trifluorohexadec-1-yne (4f).

Under an argon atmosphere, a mixture of dried CsF (1.62 g, 10.77 mmol) 15-crown-5 (2.13 mL, 10.77 mmol) and dry 1,2-dimethoxyethane (DME) 25 mL was stirred for 5 min at -20 ºC (ice:NaCl 33:66). Then a mixture of Me_3SiCF_3 (1.58 mL, 10.77 mmol) and 15-iodopentadec-1-yne (**4e**) (1.80 g, 5.39 mmol) in 25 mL DME was slowly added to the reaction flask. The reaction temperature was raised to 10 ºC in 4 hr, followed by adding H_2O (20 mL) to the reaction mixture. The organic phase was combined and washed with saturated NaCl(Brine), then dried over anhydrous Na_2SO_4. The solvent was evaporated under vacuum. The residue was purified by silica gel column chromatography (Heptane) to afford 17,17,17-trifluoroheptadec-1-yne **4f** (1.30 g, 4.76 mmol 88%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, δ_{ppm}): 2.20-2.16 (m, 2H, CH_2-*C*H_2-C≡C-H), 2.10-2.00 (m, 2H, CF_3-*C*H_2), 1.94-1.93 (t, 1H, C≡C-*H*), 1.57-1.49 (m, 4H, Alkyl), 1.40-1.25(m, 12H, alkyl). ^{13}C NMR (100 MHz, $CDCl_3$, δ_{ppm}): 141.11, 126.55, 110.78, 103.68(q, 1C, *C*F_3-CH_2-), 85.17(s, 1C, *C*≡C-H), 68.37(s, 1C, C≡*C*-H), 34.41, 34.19, 33.96, 33.73(q, 1C, CF_3-*C*H_2), 30.05, 29.92, 29.88, 29.83, 29.70, 29.53, 29.45, 29.11, 28.84 (m, 11C, alkyl), 22.21, 22.19, 22.17, 22.15(q, 1C, CF_3-CH_2-*C*H_2-). 18.75 (s, 1C, alkyl). HRMS (DART-TOF) $[M + H]^+$ calcd for $C_{16}H_{28}F_3$, 277.2143; found, 277.2152.

^{19}F NMR:


C16F3 (-yne) (8500MHz system)
-67.3
-67.4
-67.5
-67.6
-67.7
ppm
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

3 Contact angle

Table S1. Advancing (θ_a) and Static Contact Angles of Liquids on Fluoro-Hydro Alkyne Monolayers on Si(111) [a,b,c.]

Monolayers	Water	1,5 pentanol	C16	C14	C12	C10	C7	C6
F0	116 [110]	79	37	34	30	26	[a]	[a]
F1	116 [113]	81	45	42	40	37	[a]	[a]
F3	118 [115]	95	61	62	58	54	43	35
F9	123 [117]	99	78	76	74	70	62	57
F17	124 [119]	104	81	79	77	74	63	62

[a] Not measurable. [b] The number in square brackets denotes static contact angles measurement. [c] Contact angle error < ±2□.

4 XPS and DFT calculation of C1s and F1s binding energy.

4.1 DFT calculation of XPS chemical shifts of carbon and fluorine atoms

The assignment of the C_{1s} XPS spectra is supported by density functional theory B3LYP/6-311G(d,p) calculations of the core orbital energy levels by "initial state approximation". The absolute values of calculated binding energies cannot be compared directly with the experimental data because of the difference in reference energies in theory and experiment. As a point of reference the CH_2 moiety in the center of the aliphatic hydrocarbon chain was positioned at a binding energy of 285 eV. For every carbon atom, a gaussian centered at the corresponding binding energy was used with a fwhm of 1.0437 eV. The sum of all Gaussians gave the simulated XPS spectra. Electronic Core Level Calculations: All calculations were done using the GAUSSIAN09 program.[5,6] The geometries of the different systems were optimized at the

B3LYP/6-311G(d,p) level of theory. Natural bond orbital (NBO) analysis was employed to obtain the core orbital energies.

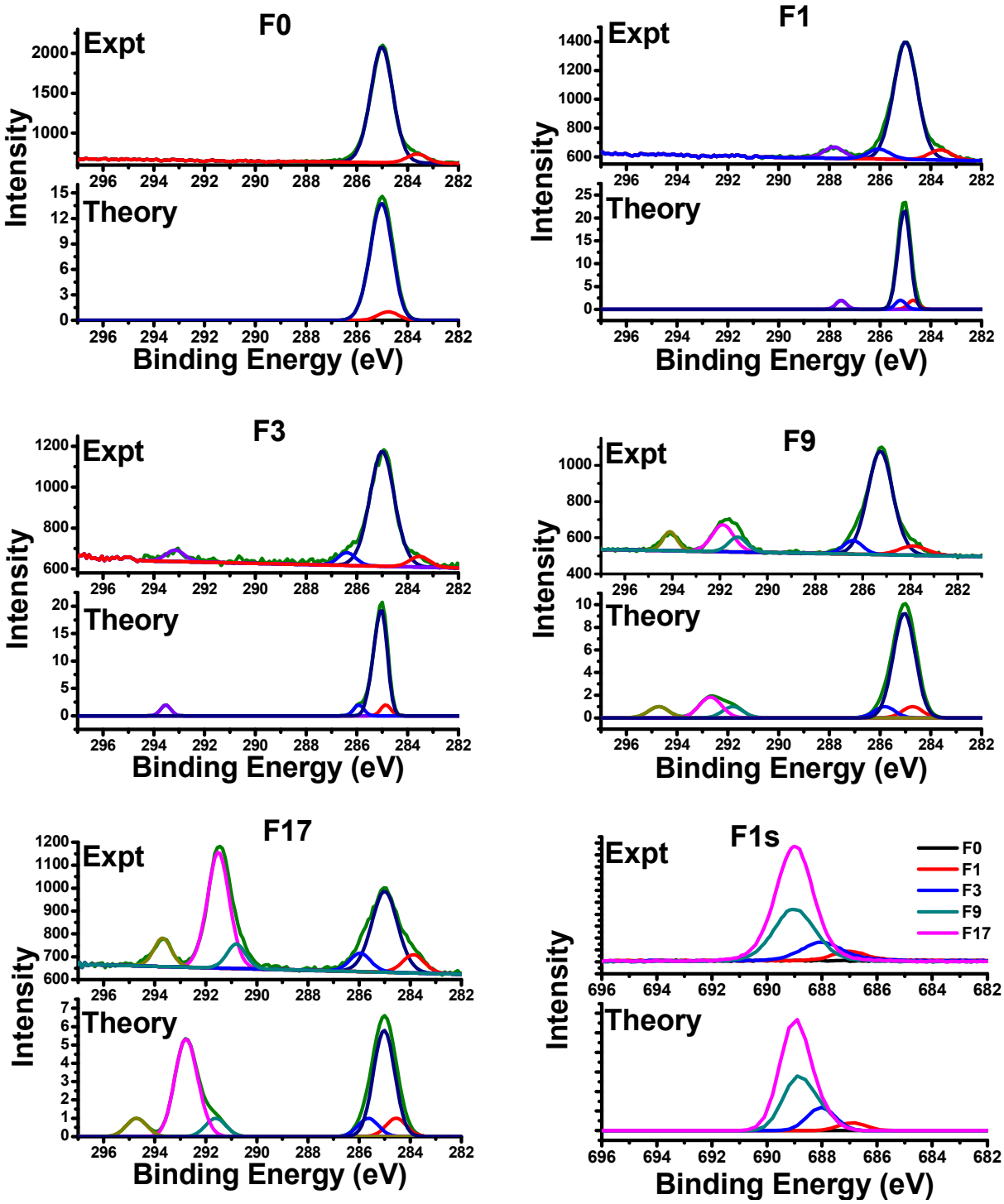


Figure S1. Experimental and calculated (DFT) core level C_{1s} XPS spectra of **F0**, **F1**, **F3**, **F9**, and **F17** alkyne monolayer on H-Si(111); the bottom right spectra are of the F_{1s}.

5 Friction image.

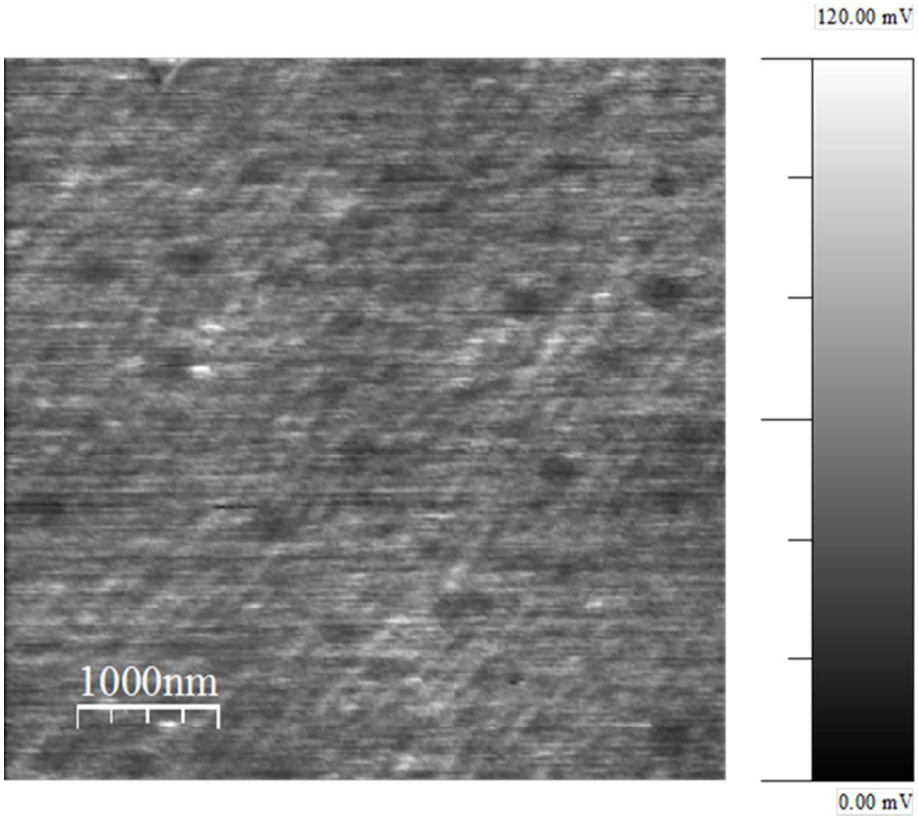


Figure S2. AFM friction images with lateral force mode on the **F9** SAMs.

6 Molecular modeling (Material studio)

The average packing energy per chain was then calculated according to [$E_{packing} = (E_{chains}/n) - E_{single}$] in which E_{chains} is the total packing energy of the layer, n is the number of chains in the layer, and E_{single} is the energy of a separately optimized chain.[7,8]

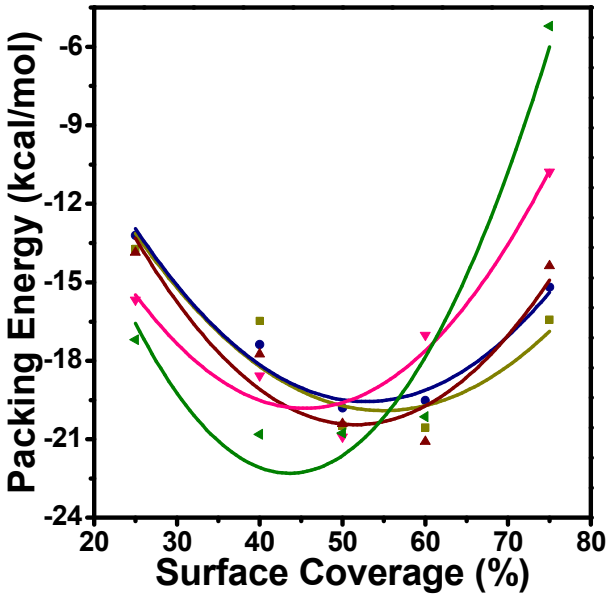


Figure S3. Average packing energies of fluoro-hydro alkyne derived (■) **F0**, (●) **F1**, (▲) **F3**, (▼) **F9**, and (◀) **F17** monolayers on Si(111); the fits are to parabolic functions.

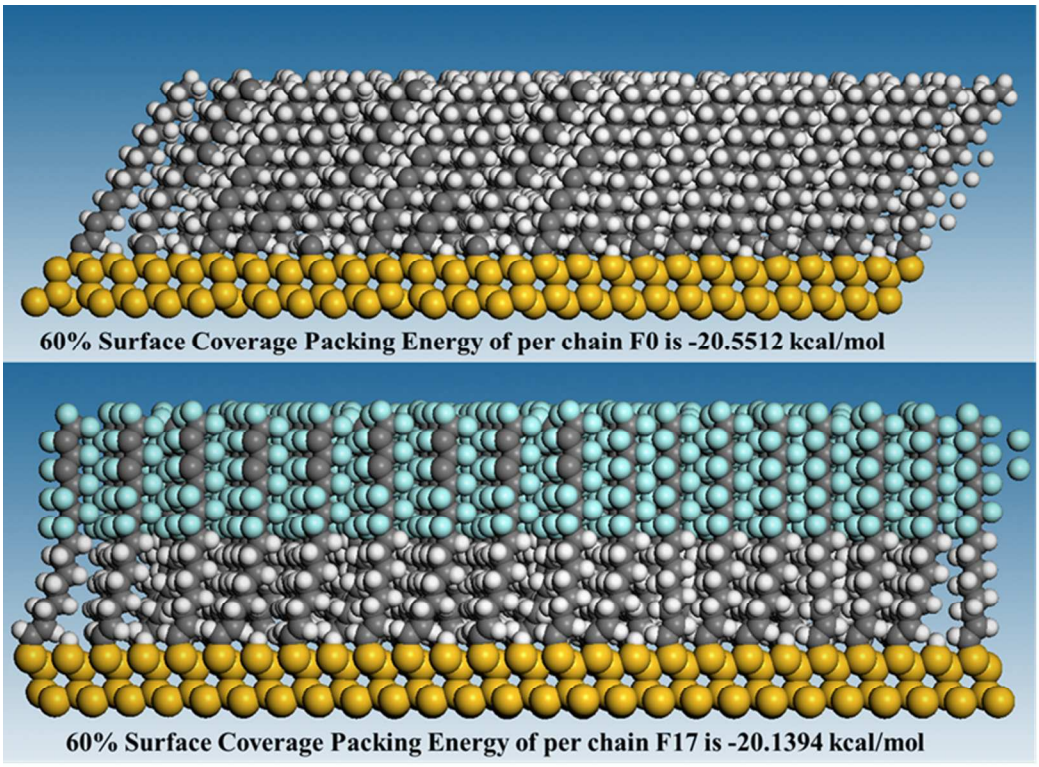


Figure S4. Side view of simulation cell 60A after optimization. The gold color represent (Silicon), gray (carbon), white (hydrogen), and aqua(fluorine). Top is **F0**and bottom **F17** optimized model on Si(111).

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Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. In Gaussian 09, Revision A.1; Gaussian, Inc., Wallingford CT.: **2009**.

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