

Supporting Information.
Preparation of Compounds.

(1H,1H-nonadecafluorodecyl)propargyl ether. A suspension of NaH (60%/oil, 240 mg, 6.0 mmol) in 20 ml THF was cooled to 0°C under N₂. To this was added a solution of 1H, 1H-nonadecafluorodecanol (2.0 g, 4.0 mmol) in THF (20 ml) dropwise, and the mixture stirred for 30 minutes. Propargyl bromide (80 wt%/toluene, 1.1 ml, 10 mmol) was added, and the solution allowed to warm slowly to room temperature, and stirred at room temperature overnight. The reaction was then quenched in water and extracted with diethyl ether. The combined organic extracts were washed with saturated NaCl and dried over MgSO₄. After filtration and removal of the solvent *in vacuo*, the resulting oil was purified by flash column chromatography (silica gel, 10:1 petroleum ether:ethyl acetate) to yield a clear oil (1.70 g, 79%). ¹H NMR (400 MHz, CDCl₃): δ 4.30 (t, J = 2.8 Hz, 2H), 4.04 (t, J = 14.6 Hz), 2.52 (t, J = 2.4 Hz, 1H).

N-(2-(propargyloxy)ethyl)-benzaldimine. NaH (60%/oil, 3.30 g, 82.5 mmol) was suspended in 250 ml dry THF and cooled to 0°C (ice). To this suspension was added N-(2-hydroxyethyl)-benzaldimine (11.18 g, 75 mmol) dissolved in 50 ml THF dropwise at a rate to control the evolution of H₂. After complete addition, the resulting solution was stirred at 0°C for 1 hr, then propargyl bromide (12.5 ml, 120 mmol, 80 wt %/toluene) was added and the solution allowed to warm slowly to room temperature, and stirred overnight. The reaction was quenched by the addition of 500 ml water, the organic layer separated, and the aqueous layer extracted further with ether. The combined organic layers were washed with water and NaCl, followed by drying over MgSO₄. After filtration and removal of the solvent *in vacuo*, the remaining oil was distilled (58-60°C, 50 mTorr) to yield a clear oil (12.82 g, 94%). ¹H NMR (400 MHz, CDCl₃): δ 8.29 (s, 1H), 7.72 (m, 2H), 7.39 (m, 3H), 4.17 (t, J = 2.4 Hz, 2H), 3.82 (m, 4H), 2.43 (t, J = 2.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 162.9, 136.1, 130.8, 128.6, 128.3, 79.8, 74.6, 69.5, 61.0, 58.4.

N-(2-(propargyloxy)ethyl)ammonium tosylate. N-benzylidene-2-(prop-2-ynyloxy)ethanamine (445 mg, 2.38 mmol) and *p*-toluenesulphonic acid hydrate (456 mg, 2.40 mmol) were dissolved in dichloromethane at room temperature. Methanol was added (1.0 ml) and the reaction monitored by thin-layer chromatography until no starting material remained or stirred overnight. The solvents were removed *in vacuo* and the resulting crystalline solid washed multiple times with petroleum ether and diethyl ether to yield a white crystalline solid (592 mg, 92%). ¹H NMR (400 MHz, CDCl₃): δ 7.75 (d, J = 8.0 Hz, 2H), 7.69 (br s, 3H), 7.14 (d, J = 8.0 Hz, 2H), 3.97 (t, J = 2.4 Hz, 2H), 3.59 (t, J = 5.0 Hz, 2H), 3.04 (m, 2H), 2.37 (s, 1H), 2.34 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 141.5, 140.8, 129.2, 126.1, 79.2, 75.3, 65.4, 58.2, 39.7, 21.5.

N,N-bis(methylpropionate)-N'(2-(propargyloxy)ethyl)amine.

2-(prop-2-ynyloxy)ethanaminium chloride (271 mg, 1.0 mmol) was dissolved in methanol (1.0 ml) and potassium carbonate (138 mg, 1.0 mmol) was added followed by methyl acrylate (1.8 ml, 20 mmol). The resulting mixture was stirred at 35°C for 24 hours. The solution was cooled and filtered through a pad of Celite with EtOAc. After removal of the solvent *in vacuo*, the paste-like solid was partitioned into ethyl acetate, insoluble solids filtered, and the solvent removed from the clear filtrate *in vacuo* to yield a pale yellow oil (251 mg, 93%). ¹H NMR (400 MHz, CDCl₃): δ 4.12 (t, J = 2.4 Hz, 1H), 3.64 (s, 6H), 3.56 (t, J = 6.0 Hz, 2H), 2.81 (t, J = 7.2 Hz, 4H), 2.67 (t, J = 6.0 Hz, 2H), 2.44 (t, J = 7.2 Hz, 4H), 2.41 (t, J = 2.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 173.1, 79.9, 74.6, 68.3, 58.4, 53.3, 51.7, 49.9, 32.7.

G1.0 dendron. G0.5 dendron (2.78 g, 10 mmol) was dissolved in methanol (10 ml) and ethylenediamine (67 ml) was added. The solution was purged with N₂ and stirred at room temperature for 96 hours. After cooling, solvent and excess ethylenediamine were removed *in vacuo* to yield a dark orange oil (3.35g, 100%).

G1.5 dendron. G1.0 dendron (982 mg, 3.0 mmol) was dissolved in 5 ml methanol and methyl acrylate (15 ml) was added. The solution was purged with N₂ and heated to 35°C for 48 hours. After cooling, solvent and excess methyl acrylate were removed *in vacuo* to yield a orange oil, which was purified by passing through a short plug of silica gel with a solution of 10% methanol in ethyl acetate (1.67 g, 83%). ¹H NMR (400 MHz, CDCl₃): δ4.08 (d, J = 2.4 Hz, 2H), 3.61 (s, 12H), 3.54 (t, J = 5.7 Hz, 2H), 3.21 (q, J = 5.8 Hz, 4H), 2.77 (t, J = 6.8 Hz, 4H), 2.68 (m, 10H), 2.48 (t, J = 6.0 Hz, 4H), 2.43 (t, J = 1.3 Hz, 1H), 2.37 (t, J = 6.8 Hz, 8H), 2.31 (t, J = 6.6 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃): δ173.1, 172.2, 79.8, 74.7, 67.7, 58.3, 53.0, 52.7, 51.7, 50.0, 49.3, 37.1, 33.5, 32.8.

G2.0 dendron. G1.5 dendron (1.34g, 2.0 mmol) was dissolved in methanol (1.5 ml/mmol) and ethylenediamine (27 ml) was added. The solution was purged with N₂ and stirred at room temperature for 96 hours. After cooling, solvent and excess ethylene diamine were removed *in vacuo* to yield an orange oil (1.52g, 97%).

G2.5 dendron. G2.0 dendron (784 mg, 1.0mmol) was dissolved in 1 ml methanol and methyl acrylate (18 ml) was added. The solution was purged with N₂ and heated to 35 °C for 96 hours. After cooling, solvent and excess methyl acrylate were removed *in vacuo* to yield an orange oil which was dissolved in methanol and filtered through a short plug of Celite and concentrated *in vacuo* to yield a clear orange oil (1.44 g, 98 %).

G3.0 dendron. G2.5 dendron (900 mg, 0.6 mmol) was dissolved in methanol (2.0 ml) and ethylenediamine (16 ml) was added. The solution was purged with N₂ and stirred at room temperature for 96 hours. After cooling, solvent and excess ethylenediamine were removed *in*

vacuo to yield an orange oil which was purified by precipitation from methanol into diethyl ether (960 mg, 92%).

(2-(2-(2-(2-(2-(2-hydroxyethoxy)-ethoxy)-ethoxy)-ethoxy)-ethyl) propargyl ether. A suspension of NaH (60%/oil, 400 mg, 10 mmol) in 50 ml THF was cooled to 0°C under N₂. To this was added hexaethylene glycol (2.50 ml, 10 mmol) dropwise, and the mixture stirred for 30 minutes. Then, propargyl bromide (80 wt% toluene, 5.4 ml, 60 mmol) was added, and the solution allowed to warm slowly to room temperature, and stirred at room temperature overnight. Precipitated solids were removed by filtration, the solvent removed *in vacuo*, and the resulting oil was distilled to remove any product distilling at less than (150°C/ 45 mTorr) and then purified by flushing through a short plug of silica gel (ethyl acetate) to yield a pale yellow oil (1.28 g, 40%). ¹H NMR (400 MHz, CDCl₃): δ 4.12 (d, J = 2.4 Hz, 2H), 3.65-3.50 (m, 24H), ~2.83 (br s, 1H), 2.40 (t, J = 2.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 79.7, 74.7, 72.5, 70.6, 70.5, 70.4, 70.3, 69.1, 61.6, 58.4.

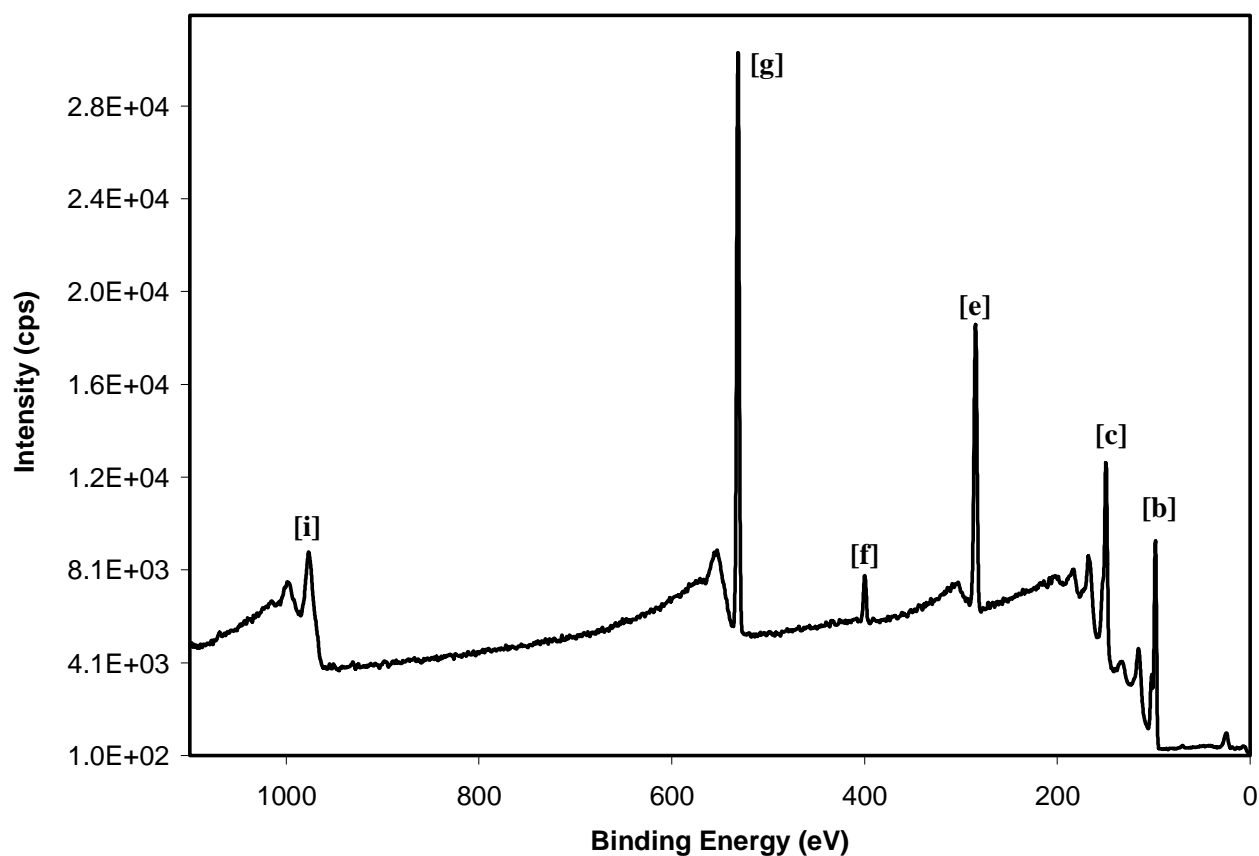


Figure S1: XPS spectra showing the removal of the Cu catalyst that can be incorporated in the surface layers. Washing in a solution of NH_4OH washes away the excess Cu. Details are given in the paper.