Protein-resistant Monolayers Prepared by Hydrosilylation of \( \alpha \)-Oligo(ethylene glycol)-\( \omega \)-alkenes on Hydrogen-terminated Silicon (111) Surfaces

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Supplementary Information
I. Synthesis of EG₆, EG₉

Scheme 1. Synthetic Route to EG₆ and EG₉.

Hexaethylene glycol monomethyl ether (2).¹ A suspension of hexa(ethylene glycol) (1, 5.64 g, 20.0 mmol, 4 eq) and KOH (0.28 g, 5.00 mmol, 1 eq) in THF (20 mL) was refluxed until KOH was dissolved. The solution was cooled to r.t., treated with CH₃I (0.37 mL, 6.0 mmol, 1.2 eq), and stirred for 24 h at r.t. The mixture was dried under vacuum. After addition of chloroform, the organic layer was washed with water (2 x 50 mL), dried over Na₂SO₄, concentrated under reduced pressure, and dried under high vacuum to give 2¹ as a pale-yellow oil (0.45 g, 31%).

Hexaethylene glycol methyl ω-undecenyl ether (EG₆).¹ A mixture of t-BuOK (0.665 g, 5.9 mmol), 2 (1.47 g, 4.95 mmol), tetrabutylammonium iodide (10 mg, 0.027 mmol), and 11-bromo-undec-1-ene (2.31 g, 9.9 mmol) in THF (10 mL) was stirred at 70 ºC for 12 h, cooled to r.t., and extracted with Et₂O, washed with water (2 x 15 mL), dried over MgSO₄, and concentrated. Flash chromatography (CH₂Cl₂/MeOH 250:3) gave EG₆ as a colorless oil (1.84 g, 83%). ¹H NMR (CDCl₃): δ 1.29 (br. s, 12H), 1.85 (m, 2H), 2.03 (br q, J = 6.5, 2H), 3.37 (s, 3H, s), 3.53 (t, J = 6.5, 2H), 3.5–3.7 (m, 24H), 4.89–5.02 (m, 2H), 5.74–5.87 (m, 1H); ¹³C NMR (CDCl₃) δ 25.96, 28.80, 28.99, 29.31, 29.35, 29.41, 29.49, 33.69, 58.92, 69.91, 70.41, 70.46, 71.42, 71.81, 113.97, 139.11; ESIMS m/z 471 (M+Na⁺).

Nonaethylene glycol monomethyl ether (4).² A mixture of dry hexa(ethylene glycol) 1 (14.5 g, 51.3 mmol) and KOH (0.78 g, 14 mmol) in THF (20 mL) was refluxed until KOH was dissolved. The solution was cooled to r.t., treated with the tosylate 3³ (4.08 g, 12.8 mmol), and refluxed for
18 h. The solvent was removed under vacuum, CHCl₃ was added and the organic phase was washed with water (2 x 50 mL), dried over Na₂SO₄, concentrated under reduced pressure, and dried under high vacuum to give 4 as a pale yellow oil (6.2 g, 92 %).

**Hexaethylene glycol methyl undecenyl ether (EG₉).** Similar to the preparation of EG₆, EG₉ was obtained as oil in 85% yield. ¹H NMR (CDCl₃): δ 1.20 (br. s, 12H), 1.56 (m, 2H), 2.02 (br q, J = 6.6, 2H), 3.37 (s, 3H), 3.44 (t, J = 6.6, 2H), 3.5-3.7 (m, 36H), 4.90–5.02 (m, 2H), 5.74–5.88 (m, 1H); ¹³C NMR (CDCl₃) δ 25.96, 28.80, 29.00, 29.32, 29.35, 29.41, 29.50, 33.70, 58.94, 69.92, 70.45, 71.41, 71.80, 113.99, 139.13; ESIMS m/z 603 (M+Na⁺).

**II. Setting and Procedure for Photo-induced Surface Hydrosilylation.**

The apparatus was prepared by fusion of the open end of a five-side-polished quartz cell with the open bottom of a Schlenk tube (Figure S1). It was cleaned with Piranha solution (H₂SO₄/30% H₂O₂ 3:1) at 80 °C for 30 min (Caution: Piranha reacts violently with organic compounds, and care should be taken while handling it), washed thoroughly with Millipore water, covered with aluminum foil and dried in a clean oven at 150°C. Atomically flat H–Si(111) surfaces were prepared similarly to the procedure described in literatures.⁴,⁵ Briefly, single side polished and (111) oriented silicon wafers were cut into pieces of ca. 1x1 cm², cleaned with Piranha solution (H₂SO₄/30% H₂O₂ 3:1) at 80 °C for 30 min, thoroughly washed with Millipore water, etched in 10% buffer-HF (Transene) for 5 min and then in 40% NH₄F for 15 min under N₂ purge, and dried immediately with a flow of nitrogen. The substrate was immediately placed inside a freshly cleaned and dried quartz cell, and tilted with the polished H–Si(111) surface facing downward (Figure 1). A droplet (~1-3 mg) of the alkene in a pipette was carefully placed on the quartz window below the wafer but without touching it. After the cell was degassed at ~10⁻⁴ mbar for 30 min, the substrate was allowed to fall down (by lightly tapping the cell) onto the droplet, forming a thin and homogeneous layer between the H–Si(111) surface and the quartz wall (Figure 1). The H–Si(111) surface was illuminated for 30 min with a hand-hold 254 nm UV-lamp (Model UVLS-28, UVP) placed ~1 cm away from the cell. The sample was taken out and washed sequentially with petroleum ether, ethanol, and dichloromethane, followed by drying with a stream of N₂ gas.
Fig. S1 Experimental Setup for Photo-induced Hydrosilylation on H-Si(111) Surfaces.

References
Contact-mode AFM image (1x1 μm², 10 nm contrast) of a EG₃ film on Si(111)