Supporting Information for

Electrochemical 'Switching' of Silicon(100) Modular Assemblies

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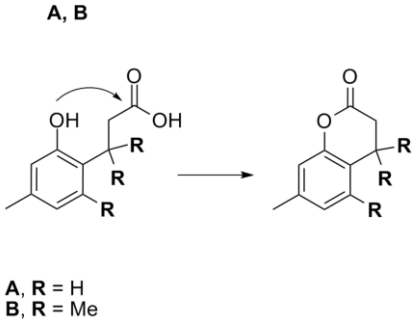
Scheme S1. '*Trimethyl-lock'*. Structural requirement for a facile lactonization reaction in hydroquinone derivatives. Methyl groups involved in the 'trimethyl lock' scheme are highlighted in bold.[1-3]



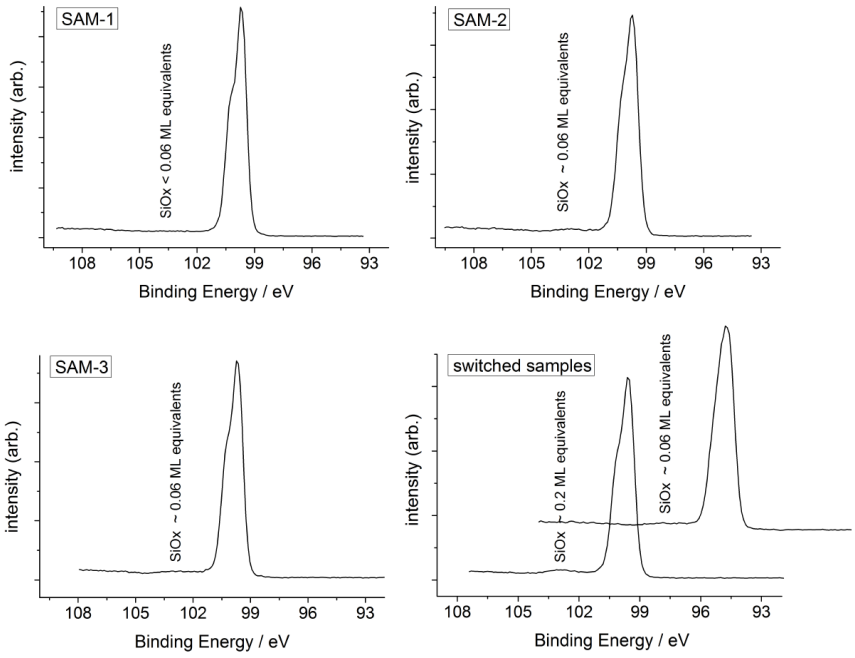


Figure S1. High resolution XPS data for the Si 2p region. When present, the fractional monolayer coverage of oxidized silicon was calculated directly from the oxidized/bulk Si 2p peak area ratio to the method described by Lewis and co-workers for very thin oxide overlayers (ref. 21 and ref. 22 in the SI). According to the method, the spectrometer detection limit can be approximated to *ca*. 0.06 SiOx ML equivalents.

Table S1. Refined Thickness (*d*), Interfacial roughness (σ) and Scattering Length Density (SLD) from XRR Data

	SAM-1	**SAM-2**	**SAM-3**	'switched' surface[a]
d (Å)	9.6 (0.5)[c]	22.2 (0.5)	18.2(0.8)	19.5 (0.8)
σ_{Si} (Å)	1.7	3.4	2.2	3.0
σ_{film} (Å)	3.2	5.1	10.2	6.2
SLD ($\times 10^{-6}$ Å^{-2})[b]	10.4	10.5	14.8	10.5

[a] **SAM-2**, putative product for the 'switch' of **SAM-3**

[b] for X-rays, electron density [e^- Å^{-3}] of the material are obtained by dividing SLD values by a factor 2.82×10^{-5} Å

[c] Esd`s from the fits are in parenthesis

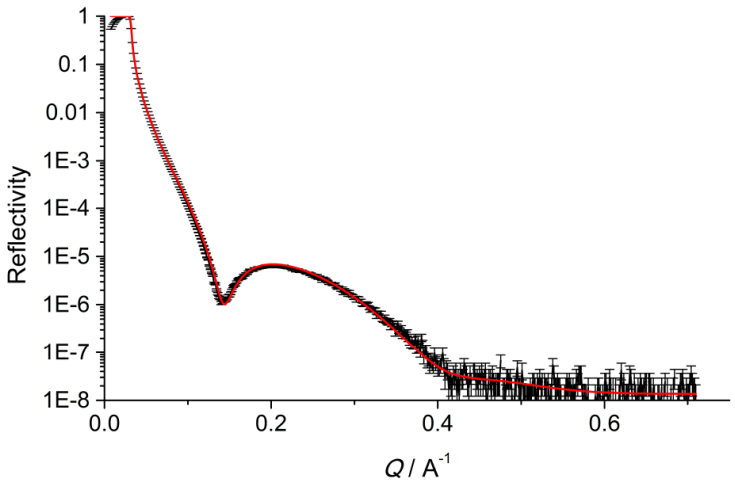


Figure S2. X-ray reflectometry spectra acquired on 'click' functionalized **SAM-2** samples.

S1. Experimental Section

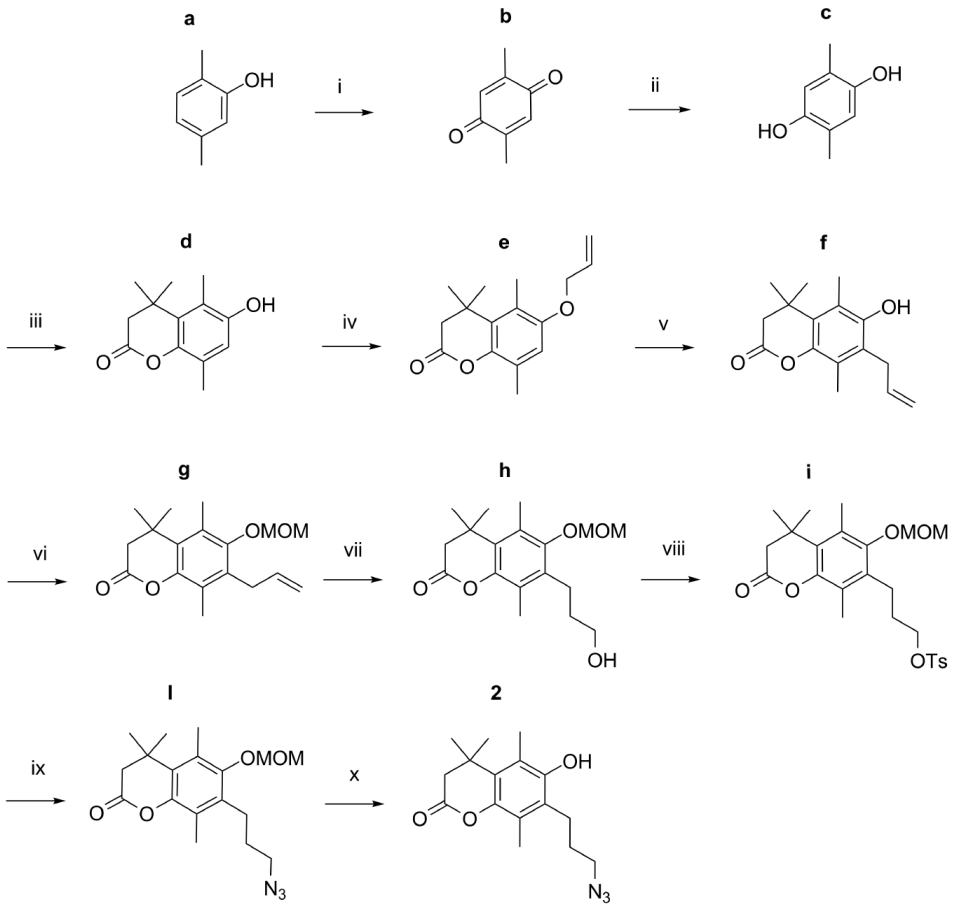
S1.1 Materials

S1.1.1 Chemicals. All chemicals, unless noted otherwise, were of analytical grade and used as received. Chemicals used in surface modification procedures and electrochemical experiments were of high purity (≥ 99%). Hydrogen peroxide (30 wt.% sol. in water, Sigma-Aldrich), hydrofluoric acid (Riedel-de Haën, 48 wt.% sol. in water), and sulfuric acid (J. T. Baker) used in wafers cleaning and etching procedures were of semiconductor grade. 1,8-Nonadiyne (Alfa Aesar, 97%) was redistilled from sodium borohydride (Sigma-Aldrich, 99+%) under reduced pressure (80 ºC, 8−9 Torr) and stored under a high purity argon atmosphere (H_2O < 10 ppb, O_2 < 5 ppb) prior to use. Milli-Q™ water (> 18 MΩ cm) was used to prepare solutions and for chemical reactions. Dichloromethane, chloroform, hexane, light petroleum (b.p. 60−80 ºC), acetone, 2-propanol, ethanol, methanol and ethyl acetate for surface cleaning, chemical reactions and purification procedures were redistilled prior to use. Anhydrous solvents used in chemical reactions were purified as follows: (a) dichloromethane was distilled from calcium hydride; (b) pyridine was distilled under reduced pressure from potassium hydroxide; (c) *N,N*-dimethylformamide was distilled under reduced pressure from calcium hydride; (d) tetrahydrofuran was distilled from sodium using a benzophenone indicator; (e) 2-propanol was distilled from sodium; (f) 1,4-dioxane was distilled from sodium; (g) carbon tetrachloride was distilled from phosphorus pentoxide; (h) diethyl ether was distilled from sodium using a benzophenone indicator; (i) ethanol was distilled from sodium; (l) toluene was distilled under reduced pressure from calcium hydride. *p*-Toluensulfonyl chloride (Sigma-Aldrich, 98%) was recrystallized from chloroform/hexane. Sodium azide (Sigma-Aldrich, 98%) was crystallized from water by the addition of ethanol. β,β-Dimethylacrylic acid (Sigma-Aldrich, 97%) was recrystallized from light petroleum. Chloromethyl methyl ether was of technical grade (Sigma). Dulbecco's Phosphate Buffered Saline (DPBS, pH 7.4) was prepared from potassium chloride (2.7 mM), sodium chloride (117 mM), potassium dihydrogenphosphate (1.5 mM) and sodium monohydrogenphosphate (8 mM).

S1.1.2 Silicon Wafers. Prime grade double-side polished silicon wafers, 100-oriented (<100> ± 0.9°), p-type (boron-doped), 500 ± 25 μm thick, <0.007–0.009 Ω cm resistivity, were obtained from Virginia Semiconductors, Inc. (VA, USA).

S1.2 Purification and Analysis of Synthesized Compounds. Thin-layer chromatography (TLC) was performed on Merck silica gel aluminum sheets (60 F254). Davisil®LC 60 Å silica gel (40−60μm) was used for column chromatography. Unless otherwise specified NMR spectra were recorded on a Bruker Avance 300 spectrometer in deuteriochloroform ($CDCl_3$ from Aldrich, passed through basic alumina) using the solvent signal as an internal reference. FTIR spectra were recorded on a Thermo Nicolet Avatar 370 FTIR spectrometer by accumulating a minimum of 32 scans and selecting a resolution of 2 cm^{-1}. Scheme S2 describes the synthetic procedure for the preparation of the redox-sensitive lactone linker **2** in ten steps (i–x) from commercially available 2,5-dimethylphenol **a**, following in part literature procedures[4-6] with major modifications for some of the synthetic steps. 2-(2-(2-Methoxyethoxy)ethoxy)ethanamine **3** was obtained from the hydroxyl precursor, triethylene oxide monomethyl ether **m**, in a three-step (i–iii) synthetic sequence (Scheme S3) via triphenylphosphine-mediated reduction of the azide intermediate.[7]

Scheme S2. Synthesis of the redox-sensitive lactone linker **2**



i. Na_2CrO_4, H_2SO_4/Et_2O, 49%; ii. $Na_2S_2O_4$, 93%; iii. β,β-dimethylacrylic acid, CH_3SO_3H, 86%; iv. allyl bromide, K_2CO_3, NaI, 69%; v. BCl_3-heptane, 72%; vi. MOMCl, DIPEA, 63%; vii. BH_3-hexane, $NaOH/H_2O_2$, 45%; viii. TsCl, Py, 62%; ix. NaN_3, 73%; x. CBr_4, 84%.

7-(3-Azidopropyl)-6-hydroxy-4,4,5,8-tetramethylhydrocoumarin (2)

*(i) 2,5-Dimethylbenzoquinone (**b**)*. The alkylquinone **b** was prepared from 2,5-dimethylphenol **a** in a one-pot procedure via a two-phase Jones oxidation reaction according to literature procedures[6] with minor modifications. 2,5-Dimethylphenol **a** (30.0 g, 246 mmol) was dissolved in diethyl ether (*ca*. 400 mL) and the solution cooled to 0° C in an ice/water bath. The reaction flask was equipped with a mechanical stirrer and a dropping funnel. The Jones reagent was prepared in the dropping funnel from sodium dichromate dihydrate (150.0 g, 503 mmol) by adding to it ice-cold water (155 mL) and 96% sulphuric acid (68 mL) with vigorous shaking.

Addition of the Jones reagent to the solution of the phenol **a** was done dropwise over a 2 h period while stirring. After the addition the ice bath was removed and stirring was continued at room temperature for a 36 h period. The reaction mixture was transferred to a separation funnel and extracted with diethyl ether (4 × 100 mL). The combined organic extracts were washed with saturated sodium bicarbonate solution (2 × 100 mL), water (200 mL) and dried over $MgSO_4$. Filtration through celite and evaporation of the solvent *in vacuo* afforded crude quinone **b** as a dark orange oil. Precipitation from ice cold light petroleum followed by column chromatography (ethyl acetate/light petroleum, 1:4) gave the quinone **b** as a yellow powder (16.4 g, 49%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.59 (bs, 2H), 2.02 (s, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 188.16, 145.92, 133.49, 15.61; IR (KBr, cm^{-1}): 1665, 1643, 1611, 1438, 1380, 1349, 1254, 1154, 1005, 927, 796.

*(ii) 2,5-Dimethylhydroquinone (**c**)*. Reduction of the alkylquinone **b** to the corresponding hydroquinone was done according to literature procedure.[4] 2,5-Dimethylbenzoquinone **b** (16.0 g, 118 mmol) was dissolved in diethyl ether (*ca*. 200 mL) and the solution obtained transferred to a separation funnel previously loaded with sodium hydrosulfite (150 g, 0.86 mol) and water (150 mL). The mixture was shaken until the organic layer had turned nearly colourless. The ether layer was then collected and the aqueous phase extracted with ether (3 × 50 mL). The pooled organic phase was washed with brine (2 × 50 mL), dried over $MgSO_4$, filtered and dried *in vacuo* to give the quinone **c** (15.2 g, 93%) as a white residue used in the successive step without further purification. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 8.31 (bs, 2H), 6.45 (s, 2H), 1.99 (s, 6H); ^{13}C NMR (75.5 MHz, DMSO-d_6) δ: 147.46, 121.17, 116.87, 15.77; IR (KBr, cm^{-1}): 3246, 1427, 1189, 1186, 868, 827, 688.

*(iii) 6-Hydroxy-4,4,5,8-tetramethylhydrocoumarin (**d**)*. Alkylhydroquinone **c** was converted to lactone **d** by reaction with dimethylacrylic acid in a Friedel-Craft type addition reaction.[4-5] β,β-Dimethylacrylic acid (12 g, 120 mmol) was added to a solution of 2,5-dimethylhydroquinone **c** (15 g, 110 mmol) in methanesulfonic acid (*ca*. 170 mL) and the obtained solution stirred for 3 h at 70−80 °C under an argon atmosphere. The crude reaction mixture was allowed to cool to room temperature and subsequently ice (*ca*. 200 g) was slowly added into the reaction flask to give a gray suspension which was allowed to warm to room temperature before being extracted with ethyl acetate (3 × 50 mL). The pooled organic layers were washed with saturated sodium

bicarbonate solution (2 × 50 mL), water (2 × 50 mL) and then dried over $MgSO_4$. Upon filtration and evaporation *in vacuo* a white residue was obtained. The crude title compound was dissolved in a minimum amount of warm ethyl acetate and crystallization upon the addition of ice-cold hexane yielded the coumarin **d** as a off-white powder (20.9 g, 86%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.56 (s, 1H), 4.84 (s, 1H), 2.56 (s, 2H), 2.33 (s, 3H), 2.22 (s, 3H), 1.46 (s, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 168.63, 150.17, 143.66, 131.08, 124.68, 119.60, 115.79, 45.82, 35.57, 27.51, 16.03, 13.93.; IR (KBr, cm^{-1}): 3378, 2977, 2948, 1734, 1615, 1466, 1318, 1245, 1159, 1120, 1022.

*(iv) 6-(Allyloxy)-4,4,5,8-tetramethylhydocoumarin (**e**).* 6-Hydroxy-4,4,5,8-tetramethylhydrocoumarin **d** (20.0 g, 90.8 mmol), potassium carbonate (26.3 g, 190 mmol) and sodium iodide (0.3 g, 2.0 mmol) were suspended in acetone (*ca*. 100 mL). Allyl bromide (23 g, 190 mmol) was added to the reaction mixture in one portion while stirring at room temperature. The suspension was then heated at 60 °C while stirring for 5.5 days under argon. Additional allyl bromide (3 × 2.4 g) was added after 1, 2 and 3 days. After cooling of the reaction mixture to room temperature and evaporation of the solvent in vacuo, the crude title compound **e** was recovered as dark yellow oil. The obtained residue was then dissolved in dichloromethane and washed with water (100 mL). The aqueous phase was further extracted with dichloromethane (2 × 50 mL) and the pooled organic layers washed with water (2 × 50 mL) before drying over $MgSO_4$. Filtration through celite and evaporation of the solvent *in vacuo* afforded the crude coumarin **e** as a orange/brown residue. Column chromatography (dichloromethane) gave the pure product **e** (16.3 g, 69%) as a pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.62 (s, 1H), 6.13−6.00 (m, 1H), 5.42 (dd, 1H, J = 1.5 Hz, J = 17.3 Hz), 5.28 (dd, 1H, J = 1.5 Hz, J = 10.6 Hz), 4.49 (d, 2H, J = 5.3 Hz), 2.56 (s, 2H), 2.35 (s, 3H), 2.26 (s, 3H), 1.46 (s, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 168.93, 153.58, 144.16, 133.88, 131.47, 124.54, 123.11, 117.44, 113.73, 70.15, 46.35, 36.07, 27.96, 16.88, 14.46; IR (KBr, cm^{-1}): 2956, 1760, 1607, 1467, 1323, 1276, 1246, 1192, 1163, 1124, 1029, 916.

*(v) 7-Allyl-6-hydroxy-4,4,5,8-tetramethylhydrocoumarin (**f**).*[8] 6-(Allyloxy)-4,4,5,8-tetramethylhydocoumarin **e** (15.5 g, 59.6 mmol) was dissolved in dichloromethane and the solution stirred at 0 °C under argon. An ice cold 1.0 M solution of boron trichloride in heptane

(100 ml, 100 mmol) was added dropwise via a dropping funnel to the reaction mixture over a 10 min period. Stirring was continued at 0 °C for an additional 4 h and then at room temperature for 12 h. Ice cold saturated sodium bicarbonate solution (*ca*. 100 mL) was then added to the reaction mixture with vigorous stirring over an ice-water bath. The organic phase was separated and washed with water (2 × 50 mL), dried over $MgSO_4$, filtered and evaporated *in vacuo* to afford the crude **f** as yellow oil. Column chromatography (dichloromethane) gave the pure product **f** (11.2 g, 72%) as a yellow solid. ^{1}H NMR (300MHz, $CDCl_3$) δ: 6.00−5.88 (m, 1H), 5.16−5.05 (m, 2H), 4.79 (s, 1H), 3.43 (d, 2H, *J* = 5.7 Hz), 2.55 (s, 2H), 2.35 (s, 3H), 2.22 (s, 3H), 1.45 (s, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 168.84, 149.41, 143.85, 135.05, 129.32, 123.43, 123.38, 120.11, 116.51, 46.14, 35.69, 31.43, 27.79, 14.48, 12.36; IR (KBr, cm^{-1}): 3405, 3010, 2958, 1743, 1636, 1444, 1287, 1261, 1214, 1190, 1127, 1038, 902.

*(vi) 7-Allyl-6-(methoxymethoxy)-4,4,5,8-tetramethylhydrocoumarin (**g**)*. 7-Allyl-6-hydroxy-4,4,5,8-tetramethylhydrocoumarin **f** (10.5 g, 40.3 mmol) was added to solution of diisopropylethylamine (44 mL, 252 mmol) in dry dichloromethane (*ca*. 150 mL) while stirring under an argon. The reaction flask was then cooled in an ice/water bath before adding dropwise ice cold chloromethyl methyl ether (15.3 mL, 177 mmol) over a 30 min period. One hour after the addition was complete the reaction mixture was allowed to warm up to room temperature and stirring was continued for an additional 5 h. The crude mixture was then diluted with dichloromethane (100 mL), washed with ice cold 3 M hydrochloric acid (2 × 20 mL), ice cold water (2 × 50 mL), dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* and the residue purified by column chromatography (ethyl acetate/light petroleum, 1:2) to give the methoxymethyl protected product **g** as a white solid (7.73 g, 63%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.97−5.88 (m, 1H), 5.04 (dd, 1H, *J* = 1.9 Hz, *J* = 10.2 Hz), 4.92 (dd, 1H, *J* = 1.9 Hz, *J* = 18.5 Hz), 4.89 (s, 2H), 3.60 (s, 3H), 3.48 (d, 2H, *J* = 5.6 Hz), 2.56 (s, 2H), 2.40 (s, 3H), 2.21 (s, 3H), 1.45 (s, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 173.07, 168.53, 151.54, 146.44, 136.06, 131.41, 129.32, 126.93, 124.61, 115.59, 100.17, 57.71, 46.04, 35.82, 31.72, 27.66, 15.89, 12.47; IR (KBr, cm^{-1}): 3013, 2971, 1764, 1636, 1435, 1388, 1248, 1154, 1168, 1154, 1041, 982.

*(vii) 7-(3-Hydroxypropyl)-6-(methoxymethoxy)-4,4,5,8-tetramethylcoumarin (**h**)*.[4] 7-Allyl-6-(methoxymethoxy)-4,4,5,8-tetramethylhydrocoumarin **g** (7.50 g, 24.6 mmol) was dissolved in anhydrous tetrahydrofuran (*ca*. 200 mL) and the solution stirred vigorously for 20

min while bubbling argon through it. The reaction mixture was then cooled in an ice/water bath before adding dropwise a large excess of 1.0 M borane hydride–tetrahydrofuran solution (40 mL, 40 mmol) over a 30 min period under argon. After the addition was complete, the mixture was stirred at 0 °C for 20 min under inert atmosphere. The reaction mixture was then allowed to warm to room temperature and stirring was continued for an additional 12 h under argon. Upon cooling of the reaction mixture to 0 °C in an ice bath 3 M sodium hydroxide solution (7 mL, 21 mmol) and 30% hydrogen peroxide solution (7 mL, 62 mmol) were simultaneously added dropwise to the reaction mixture from separate dropping funnels while stirring was continued. The reaction was continued for 5 min before removing the ice bath. Stirring was continued under ambient atmosphere at room temperature for an additional 1 h. The crude mixture was diluted with ethyl acetate (100 mL) and then transferred into a separation funnel where water (*ca*. 20 mL) was added. Hydrochloric acid (3 M) was added to reduce the solution *ca*. pH 5. When bubbling was significantly reduced, but still present, the water layer was removed and the organic layer further washed with water (*ca*. 50 mL). The aqueous layer was then extracted with ethyl acetate (2 × 25 mL) and the pooled organic phase washed with water (2 × 25 mL), brine (25 mL), dried over $MgSO_4$ and filtered. The solvent was then evaporated *in vacuo* and the residue purified by column chromatography (ethyl acetate/light petroleum, 2:1) to give the coumarin **h** as a white solid (3.58 g, 45%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.90 (s, 2H), 3.63 (s, 3H), 3.57 (t, 2H, J = 6.0 Hz), 2.81 (t, 2H, J = 7.1 Hz), 2.55 (s, 2H), 2.38 (s, 3H), 2.24 (s, 3H), 1.76 (m, 2H), 1.44 (s, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 168.41, 151.45, 146.68, 133.37, 129.02, 126.54, 123.93, 100.19, 61.85, 57.91, 45.95, 35.74, 32.22, 27.61, 23.42, 15.85, 12.39; IR (KBr, cm^{-1}): 3417, 2952, 1766, 1666, 1600, 1470, 1417, 1318, 1246, 1159, 1040, 980.

(viii) 3-(6-(methoxymethoxy)-4,4,5,8-tetramethylcoumarin-7-yl) propyl 4-methylbenzenesulfonate ***(i)***. 7-(3-Hydroxypropyl)-6-(methoxymethoxy)-4,4,5,8-tetramethylcoumarin **h** (3.20 g, 9.93 mmol) was dissolved in dry pyridine (6 mL) and dry dichloromethane (20 mL) and the stirred solution cooled in an ice/water bath under an argon atmosphere. *p*-Toluensulfonyl chloride (2.08 g, 10.9 mmol) was added in one portion and the reaction continued under inert gas for 3 h at 0 °C and for an additional 12 h at room temperature. The crude mixture was transferred to a separation funnel and diluted with ice (ca. 50 g) before adding dichloromethane (100 mL) and ice cold 3 M hydrochloric acid (50 mL). The organic

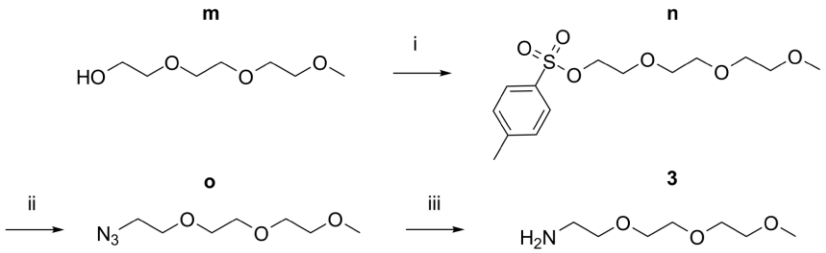
layer was separated and then further washed with ice-cold 3 M hydrochloric acid (3 × 50 mL), water (50 mL), dried over $MgSO_4$ and filtered. Drying *in vacuo* left a pale yellow oil who was purified by column chromatography (ethyl acetate/light petroleum, 1:2) to give the title compound **i** as a off-white solid (2.93 g, 62%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.80 (d, 2H, *J* = 8.1 Hz), 7.35 (d, 2H, *J* = 8.1 Hz), 4.85 (s, 2H), 4.10 (t, 2H, *J* = 6.0 Hz), 3.57 (s, 3H), 2.71 (t, 2H, *J* = 7.9 Hz), 2.54 (s, 2H), 2.45 (s, 3H), 2.34 (s, 3H), 1.84 (m, 2H), 1.43 (s, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 172.52, 168.01, 151.45, 144.48, 132.87, 132.28, 129.54, 128.89, 127.61, 126.29, 123.23, 99.75, 70.10, 57.29, 45.49, 35.32, 28.55, 27.14, 27.61, 23.43, 21.36, 15.48, 11.97.

*(ix) 7-(3-Azidopropyl)-6-(methoxymethoxy)-4,4,5,8-tetramethylcoumarin (**l**)*. To a solution of 3-(6-(methoxymethoxy)-4,4,5,8-tetramethylcoumarin-7-yl) propyl 4-methylbenzenesulfonate **i** (2.50 g, 5.25 mmol) in *N*,*N*-dimethylformamide (21 mL) and water (14 mL), sodium azide (2.94 g, 45 mmol) was added in one portion with stirring at room temperature. The obtained suspension was warmed to 60 °C in an oil bath and stirred under an argon atmosphere for 16 h. The mixture was concentrated *in vacuo* (bath temperature not exceeding 60 °C) to leave a off-white slurry which was then suspended in *ca*. 80 mL of ethyl acetate. Excess sodium azide was removed by filtration. The filtrate was evaporated *in vacuo* and the crude product was purified by column chromatography (ethyl acetate/light petroleum, 2:1) to give the substituted azide **l** as a white solid (1.33 g, 73%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.89 (s, 2H), 3.63 (s, 3H), 3.36 (t, 2H, *J* = 6.4 Hz), 2.76 (t, 2H, *J* = 7.9 Hz), 2.55 (s, 2H), 2.36 (s, 3H), 2.23 (s, 3H), 1.78 (m, 2H), 1.44 (s, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 168.52, 151.82, 146.47, 133.10, 129.21, 126.71, 123.68, 100.17, 57.72, 51.55, 45.93, 35.75, 28.98, 27.58, 24.87, 15.95, 12.46.

*(x) 7-(3-Azidopropyl)-6-hydroxy-4,4,5,8-tetramethylhydrocoumarin (**2**)*. To a stirred solution of 7-(3-azidopropyl)-6-(methoxymethoxy)-4,4,5,8-tetramethylhydrocoumarin **l** (1.01 g, 2.91 mmol) in anhydrous 2-propanol (250 mL) carbon tetrabromide (200 mg, 0.603 mmol) was added in one portion while stirring under argon. The reaction mixture was heated to *ca*. 80 °C and stirring was continued for 12 h. The reaction mixture was evaporated *in vacuo* and the crude yellow oil was purified via column chromatography (ethyl acetate/light petroleum, 2:1) to afford the title compound **2** as white solid (741 mg, 84%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.16 (s, 1H), 3.36 (t, 2H, *J* = 6.4 Hz), 2.75 (t, 2H, *J* = 7.1 Hz), 2.55 (s, 2H), 2.35 (s, 3H), 2.23 (s, 3H), 1.83 (m,

2H), 1.45 (s, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 168.72, 149.15, 143.87, 129.05, 125.15, 123.34, 119.62, 50.97, 46.17, 35.68, 28.08, 27.84, 23.55, 14.69, 12.29; IR (KBr, cm^{-1}): 3437, 2924, 2111, 1732, 1634, 1455, 1412, 1303, 1259, 1189, 1127, 1032.

Scheme S3. Synthesis of the oligoether **3**



i. TsCl, 34%; ii. NaN_3, 63%; iii. PPh_3, 56%.

2-(2-(2-Methoxyethoxy)ethoxy)ethanamine (3)

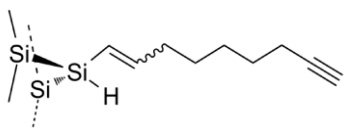
*(i) 2-(2-(2-Methoxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate (**n**)*. 2-(2-(2-Methoxyethoxy)ethoxy)ethanol ***m*** (2.01 g, 12.2 mmol) was added to a solution of anhydrous pyridine (5 mL) and anhydrous dichloromethane (15 mL). The solution was cooled on an ice-water bath, under an argon atmosphere, and *p*-toluensulfonyl chloride (2.85 g, 15 mmol) was added in one portion with stirring. Stirring was continued under argon at room temperature for 24 h. The reaction mixture was evaporated *in vacuo* and the crude material purified using column chromatography (ethyl acetate/methanol, 10:1) to afford sulfonate **n** as a colourless oil (1.3 g, 34%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.78 (d, 2H, J = 8.5 Hz), 7.33 (d, 2H, J = 8.5 Hz), 4.14 (t, 2H, J = 4.6 Hz), 3.65 (m, 10H), 3.34 (s, 3H), 2.43 (s, 3H).

*(ii) 1-Azido-2-(2-(2-methoxyethoxy)ethoxy)ethane (**o**)*. To a solution of the tosylated glycol **n** (1.2 g, 3.8 mmol) in *N*,*N*-dimethylformamide (10 mL) and water (5 mL), sodium azide (1.3 g, 20 mmol) was added in one portion while stirring. The suspension was heated to *ca*. 60°C and stirring was continued for 16 h. The mixture was evaporated *in vacuo* and the resulting residue was suspended in ethyl acetate (*ca*. 50 mL), filtered and the filtrate concentrated. The crude

product was purified using column chromatography (ethyl acetate/light petroleum, 5:1) to give the title compound **o** as a colourless oil (450 mg, 63%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.65 (m, 10H), 3.55 (t, 2H, J = 2.6 Hz), 3.36 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 72.06, 70.85, 70.78, 70.74, 70.16, 59.17, 50.81; IR (NaCl, cm^{-1}): 2874, 2104, 1678, 1452, 1347, 1286, 1248, 1199, 1109, 1029.

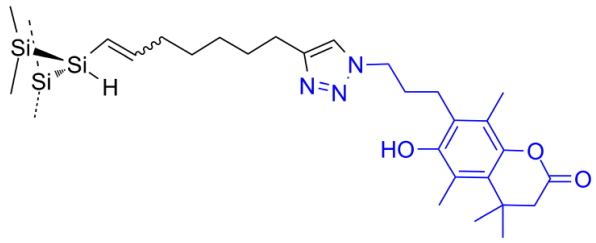
*(iii) 2-(2-(2-methoxyethoxy)ethoxy)ethanamine (**3**)*. A stirred solution of 1-azido-2-(2-(2-methoxyethoxy)ethoxy)ethane **o** (380 mg, 2.01 mmol) in anhydrous tetrahydrofuran (*ca*. 20 mL) was cooled on an ice-water bath under argon atmosphere. Triphenylphosphine (580 mg, 2.21 mmol) was added in one portion and stirring was continued at room temperature for 3 days. Water (*ca*. 5 mL) was added to the solution to hydrolyze the putative phosphorous intermediate[9] and stirring was continued at room temperature for an additional 24 h. Water was added (*ca*. 10 mL) and the crude reaction mixture concentrated to remove most of the organic solvent. The solution pH was adjusted with 3 M hydrochloric acid to *ca*. 3 and toluene (5 mL) was added. The solution was transferred to a separatory funnel, the organic phase separated and the aqueous layer further washed with toluene (2 × 5 mL). The pooled water phase was evaporated *in vacuo* to give a pale yellow oil which was purified using column chromatography (ethyl acetate/methanol, 9:1) to give the title compound **3** as a colourless oil (182 mg, 56%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.60 (m, 10H), 3.17 (t, 2H, J = 2.8 Hz), 3.34 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 73.36, 70.75, 70.69, 70.44, 70.14, 59.20, 41.85.

S1.3 Surface Modification. Assembly of the redox-sensitive surfaces **SAM-2** and anti-fouling surface **SAM-3** followed synthetic procedures depicted in Figure 1. The dormant[10] lactone linker molecule **2** was attached to the acetylenyl Si(100) surface through a Cu(I)-catalyzed alkyne-azide cycloaddition reaction.[11-13] Chemical oxidation of the confined lactone moiety to the corresponding benzoquinone acid was followed by its activation with carbodiimides and *N*-hydroxysuccinimide to promote reactions of the exposed acid function toward nucleophiles. 2-(2-(2-Methoxyethoxy)ethoxy)ethanamine **3** was attached to the activated construct via conventional amide coupling procedures.[14]



S1.3.1 Acetylene-functionalized Silicon(100) Surface (SAM-1). Assembly of the acetylenylated Si(100) surface by covalent

attachment of the diyne **1** followed a previously reported procedure.[12, 15-16] In brief, Silicon wafers were cut into pieces (approximately 10 × 20 mm), cleaned for 30−40 min in hot Piranha solution (100 °C, 1 vol 30% by mass aqueous hydrogen peroxide/3 vol sulfuric acid), before being transferred first to an aqueous fluoride solution (2.5% hydrofluoric acid, 1.5 min). Subsequently, the samples were transferred, taking extra care to exclude air completely from the reaction vessel (a custom-made Schlenk flask), to a degassed (through a minimum of 4 freeze–pump–thaw cycles) sample of diyne **1**. The samples were kept under a stream of argon (H_2O < 10 ppb, O_2 < 5 ppb) while the reaction vessel was immersed in an oil bath set to 165 °C for 3 h. The flask was then opened to the atmosphere, and the functionalized surface samples (**SAM-1**) were rinsed several times with dichloromethane and rested for a 12-h period in a sealed vial at +4 °C under dichloromethane, before being either analyzed or further reacted with the redox linker molecule **2**.



S1.3.2 Attachment of the Redox-Sensitive Linker 2 to the Acetylenyl Surface (SAM-2). In a typical 'click' procedure, to a reaction vial containing the alkyne-functionalized silicon surface (**SAM-1**) were added (i) the azide **2** (10 mM, 2-propanol/water, 2:1), (ii) copper(II) sulfate pentahydrate (1 mol% relative to the azide **2**) and (iii) sodium ascorbate (10 mol% relative to the azide **2**). Reactions were carried out at 35 °C, in the dark without excluding air from the reaction environment and stopped after 12 h by removal of the modified sample from the reaction vessel.[17] The prepared surface-bound [1,2,3]-triazoles samples (**SAM-2**) were rinsed consecutively with copious amounts of water and ethanol, and then rested at room temperature for a 1-min period in a 0.5 M hydrochloric acid solution. Samples were then rinsed with copious amounts water before being either analyzed or further reacted. Rinsing of the samples with 0.05% (w/v) ethylenediaminetetraacetic acid solution EDTA was inefficient in removing traces of residual copper catalyst. A significant Cu $2p_{3/2}$ emission at *ca*. 933 eV (*e.g*. 0.2 to 0.5% of the total carbon for **SAM-2**) was evident in survey scans (Figure S3a) after the EDTA wash. Complete removal of adventitious copper required a brief exposure (1-min) of the triazole-functionalized samples to a 0.5 M hydrochloric acid solution (Figure S3b-c). The hydrolytic stability of the triazole moiety is well-documented,[12, 18] and no evidences were found of an *ipso* ("at the same") substitution reaction at

the surfacial sylilated olefin (Si–C=C), event eventually leading to a complete removal of the film. The relative abundance of Cu(I) and Cu(II) species was assessed on the basis of the decomposition procedure of the Cu $2p_{3/2}$ photoelectron emission (to which both species contribute) as proposed by Cerofolini and co-workers.[19-20] As shown in Figure S3c, a high-quality fit (reduced χ^2) to the experimental high-resolution XPS curve required a two-function model (100% Gaussian lines). The integrated area under the relatively narrow (1.6 eV fwhm) signal centered at 933.4 eV, ascribed to Cu(I) species, was compared to the integrated area under the broader Cu(II) contribution (2.0 eV fwhm) at 935.0 eV to give an 20:1 ratio for the Cu(I)/Cu(II) couple. The Auger copper parameter derived from the relative spectral positions of the Cu LMM Auger line (572.9 eV) and the Cu $2p_{3/2}$ photoelectron signal (*ca*. 933 eV) was consistent with a predominant Cu(I) population. The calculated Auger parameter, close to 1847.5, was plotted in a Wagner diagram to compare our experimental data with those reported for various Cu(I) salts. The obtained XPS data strongly suggested the ability of the organic modified surface (SAM-**2**) to chelate Cu(I) ions.

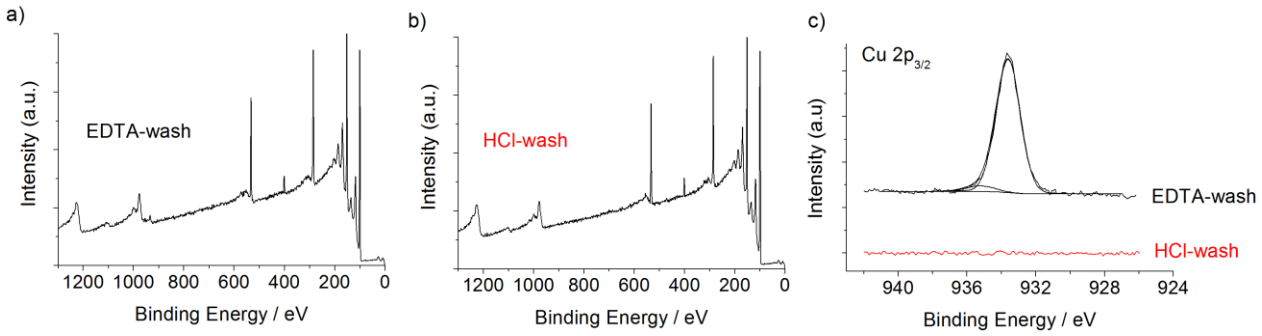
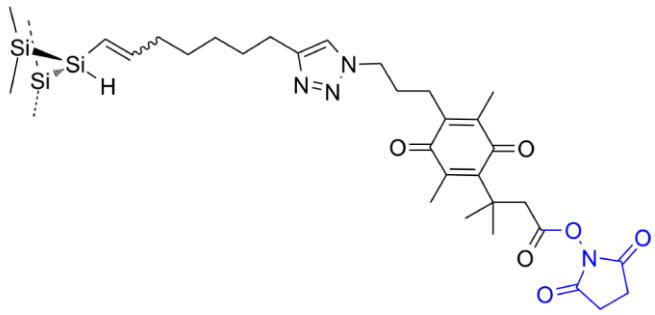
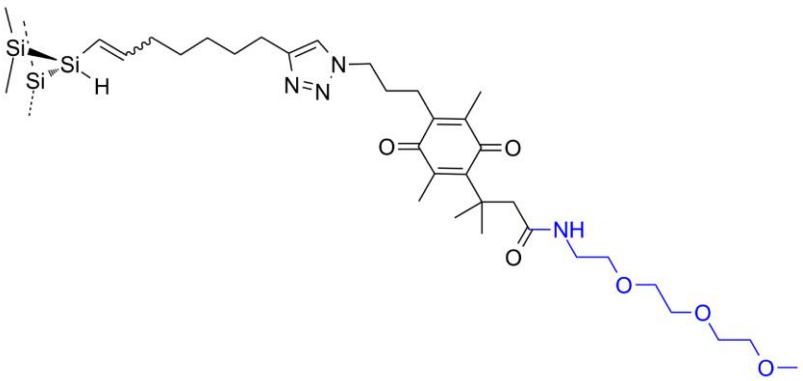


Figure S3. (a-b) Traces of residual copper catalyst (a) were effectively removed through exposure of the modified surface to a 0.5 M hydrochloric acid solution (b).Deconvolution of the experimental curve for the Cu $2p_{3/2}$ emission supports the presence of a predominant Cu(I) population (c).



S1.3.3 Oxidation of Confined Lactone Moieties to Benzoquinone Acids and their Activation with NHS. Lactone-functionalized surface samples (**SAM-2**) were rinsed with tetrahydrofuran (*ca*. 50

mL) and then transferred to a mixture of tetrahydrofuran (6 mL) and water (3 mL). *N*-Bromosuccinimide (160 mg, 90 mmol) was added to the reaction vial and the solution agitated for 3 h in the dark at room temperature. The putative ring-opened,[4] benzoquinone acid intermediate was then copiously rinsed with water, tetrahydrofuran and ethanol before being transferred to a reaction flask charged with *N*-(3-dimethylpropyl)-*N*'-ethylcarbodiimide hydrochloride (200 mg, 1.04 mmol) and *N*-hydroxysuccinimide (240 mg, 2.09 mmol). Water (10 mL) was added to the flask and the uncapped vessel shaken in the dark for 3 h at room temperature. The activated[21] silicon samples were removed from the reaction mixture and washed with copious amounts of water and ethanol before being further reacted.



S1.3.4 General Procedure for the Reactions of Activated Samples with Nucleophiles. Activated benzoquinone samples (§S1.3.3) were washed with *N*,*N*-dimethylformamide (*ca*. 20 mL), blown dry under a stream of argon and placed into a reaction tube containing either a) 3-azidopropylamine (0.1 M) in *N*,*N*-dimethylformamide (10 mL) and catalytic amounts of 4-*N*,*N*-(dimethylamino)pyridine (see §S3, **SAM-4**), or b) 2-(2-(2-methoxyethoxy)ethoxy)ethanamine **3** (0.1 M) in *N*,*N*-dimethylformamide (1 mL) and 4-*N*,*N*-(dimethylamino)pyridine (2.0 mg, 0.02 mmol) to give **SAM-3** (inset). The reaction was continued in the dark at room temperature for 16 h and stopped by removing the silicon wafer from the reaction mixture. Samples were washed with *N*,*N*-dimethylformamide, ethanol and analyzed or further reacted.

S1.4 Benzoquinone Linker Reduction and Subsequent Release of Immobilized Species. Electrochemical reduction[22] of the benzoquinone linker moiety in the organic constructs **SAM-3** allowed for a 'trimethyl lock'-facilitated[4] lactonization of the hydroquinone intermediate (Scheme S1). The subsequent release immobilized species introduced on the benzoquinone acid layer, aimed to reconstruct **SAM-2**, was monitored by spectroscopic methods (XPS and XRR), contact angle goniometry and cell cultures experiments. Alternative reaction times, electrolyte solutions and cathodic potentials were investigated for the 'switch' of a range of constructs.

These findings are presented in a separate report. Only optimized 'switch' conditions are here used for the electrochemical reduction of OEO-functionalized constructs (**SAM-3**). The electrochemical removal of the anti-fouling OEO portion of the film and its effect on the impaired ability of cultured cell to grow on the modified silicon substrate was investigated. The anti-fouling OEO constructs were reductively converted to the cell-fouling lactonized precursor (**SAM-2**) in DPBS (pH 7.4) applying cathodic bias (−1800 mV vs Ag|AgCl|3M NaCl) for 100 s under ambient illumination and while keeping the system under an argon atmosphere. Samples were then removed from the chamber, rinsed with copious amount of water and ethanol before being used as substrates in cell culturing experiments.

S1.5 Surface Characterization

S1.5.1 Contact Angle Goniometry. Static water contact angles were measured with Ramé-Hart 200-F1 goniometer. Samples were prepared in triplicate with at least five separate spots being measured for each sample. Contact angles were determined using a model derived from a first order perturbation solution of the Laplace equation developed by Unser and co-workers.[23] Tangent 2 fitting model. Reproducibility of these measurements was ± 3°.

S1.5.2 XPS Measurements. X-ray photoelectron spectroscopy experiments were used to characterize surface modification steps and electrochemical cleaving experiments of Figure 1, and were performed on an ESCALAB 220iXL spectrometer with a monochromatic Al Kα source (1486.6 eV), hemispherical analyzer and multichannel detector (6 detectors). Spectra were recorded in normal emission with the analyzing chamber operating below 10^{-8} Torr and selecting a spot size of approximately 0.5 mm^2. The incidence angle was set to 58˚ to the analyzer lens. The resolution of the spectrometer is *ca*. 0.6 eV as measured from the Ag $3d_{5/2}$ signal (full width at half maximum, fwhm) with a 20 eV pass energy. Survey scans were carried out over 1300−0 eV range with a 1.0 eV step size, a 100 ms dwell time and an analyzer pass energy of 100 eV. High-resolution scans were run with 0.1 eV step size, dwell time of 100 ms and the analyzer pass energy set to 20 eV.

After background subtraction using the Shirley routine, spectra were fitted with a convolution of Lorentzian and Gaussian profiles as described previously. All energies are reported as binding energies in eV and referenced to the C1s signal (corrected to 285.0 eV). When detected, the fractional monolayer coverage of oxidized silicon was calculated directly from the oxidized/bulk

Si 2p peak area ratio according to the method described by Webb and co-workers for very thin oxide overlayers.[24-25] According to this method, the spectrometer SiOx detection limit can be approximated to *ca*. 0.06 ML equivalents.

The ratios of the integrated areas for the C 1s and N 1s emissions (C– C:N, carbon-bonded carbons to total nitrogen), each normalized for their elemental sensitivity[26], scanning time (number of scans accumulated), and for a square root dependence on the photoelectron kinetic energy, afforded an estimate of the conversion of the acetylenyl surface (**SAM-1**) to the lactone-functionalized surface (**SAM-2**). Analogous quantitative considerations aided in understanding the stoichiometry of the growing film, and partially allowed estimating reaction yields for the assembly of **SAM-3** and the outcome of its subsequent electrochemical cleaving processes.

S1.5.3 X-ray Reflectometry Measurements. X-ray reflectivity (XRR) spectra were used to support the conversion of **SAM-1** to **SAM-3**, and used to validate the electrochemical reduction of the latter to its precursor surface (**SAM-2**). X-ray reflectivity profiles were measured in air on a Panalytical Ltd X'Pert Pro reflectometer using Cu Kα X-ray radiation (λ = 1.54056 Å) produced from a 45 kV tube source. The X-ray beam was focused using a Göbel mirror and collimated with 0.1 mm pre- and post-sample slits. The reflected X-rays were counted using a NaI scintillation detector. Reflectivity data were collected over the angular range $0.05° \leq \theta \leq 5.00°$, with a step size of 0.010° and counting times of 10 s per step (θ is the angle of incidence of the X-ray beam impinging upon the surface). Samples had an average size of 10 × 30 mm. Structural parameters of the prepared organic thin layers were refined using the MOTOFIT reflectivity analysis software[27] with reflectivity data as a function of the momentum transfer vector Q ($Q = 4\pi(\sin\theta)/\lambda$). In the fitting routines the scattering length density of the silicon substrate was held at 2.01×10^{-5} Å^{-2} and the Levenberg–Marquardt method was selected to minimize χ^2 values.[28] Single-layer models were proposed when no significant improvement in the fitting quality was observed upon the introduction of additional layer in the refined model. All X-ray reflectivity curves were acquired in air for samples stored under an argon atmosphere prior to analysis.

S1.5.4 Electrochemical Switch. All electrochemical measurements were performed using a BAS 100B electrochemical analyzer (Bioanalytical Systems, Inc., W. Lafayette, IN) and a conventional PTFE three-electrode cell as detailed previously.[16] Electrolyte was DPBS (pH 7.4).

Working electrodes had a geometric area of >350 mm^2, with only a designated portion of it (XRR: 30 × 10 mm; cell culturing experiments and XPS: 10 × 10 mm) immersed in the electrolyte solution during electrode conditioning. Electrochemical experiments were conducted in degassed (by means of bubbling argon gas for a minimum of 20 min) electrolytes.

S1.6 Cell Culturing Experiments

S1.6.1 Cell Culture. Aortic Endothelial Bovine cells (BAEC) were cultured in basal medium Eagle (BME) supplemented with 10% fetal bovine serum at 37ºC at 5% CO_2.

S1.6.2 Cell Adhesion Assay. Confluent (> 90% confluence) BAE cells were incubated in glutamine-poor BME with 2% fetal bovine serum 12 h prior to cell adhesion experiments. Cells were harvested with a trypsin solution in DPBS (0.02% w/v) and centrifuged. The supernatant was removed and the cells (*ca*. 3 × 10^6 cells) were suspended in BME supplemented with serum (8 mL). The cell suspension (1 mL) was added to the silicon sample (either **SAM-3** or 'switched' samples) in a culture dish and cells were left to adhere at 37°C at 5% CO_2. Approximately 30 min after plating the silicon samples were rinsed with DPBS solution (2 × 1 mL). Cells were then fixed in ice-cold *p*-formaldehyde (4% v/v) for 10 min. Samples were rinsed with DPBS solution (2 × 1 mL) before cells permeablized and blocked for 30 min in a saponin (0.1% w/v), gelatine from cold water fish skin (0.2% w/v) and bovine serum albumin (0.5% w/v) solution in DPBS (*ca*. 20 mL). Fixed and permeable cells were stained phalloidin conjugated to Alexa Fluor 555 (Molecular Probes) solution in a saponin (0.1% w/v), gelatine from cold water fish skin (0.2% w/v) and bovine serum albumin (0.5% w/v) solution in DPBS (200 μL). Staining was performed at ambient temperature in the dark for 20 min before samples were rinsed with DPBS solution (3 × 5 mL) and Milli-Q™ water (3 × 5 mL). Silicon samples were mounted onto a glass cover slips using Mowiol (Calbiochem) mounting solution (*ca*. 50 μL) and rested for 12 h at room temperature shielded from the light.

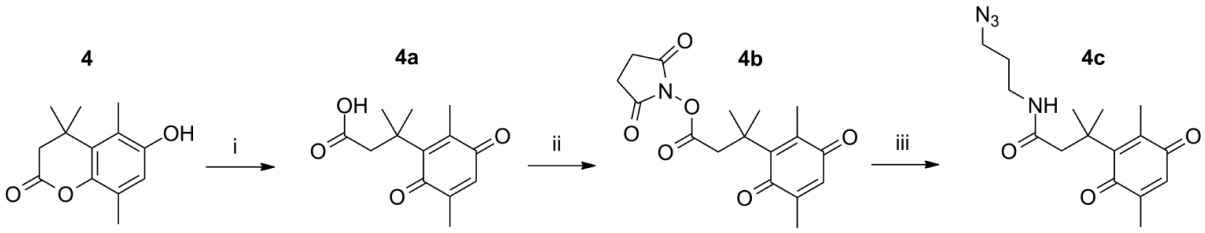
S1.6.3 Fluorescence Microscopy Analysis and Cells Quantitation. Fluorescence images were obtained on a Nikon Eclipse TE 2000-S epifluorescence microscope fitted with a mercury arc lamp, Nikon G-2A filters (excitation 510–560 nm; emission 610 nm) equipped with an 60× oil immersion and 20× dry objective lense. Images were processed with ImageJ 1.41o software (Wayne Rasband, National Institutes of Health, USA). Cells with rounded morphology having radius smaller then *ca*. 25 μm were considered not adherent and not counted (e.g. Figure 4a). All cells that spread and had actin stress fibres were considered adherent and therefore counted. A

minimum of 5 fluorescence micrographs (20×) were acquired for each surface sample. A minimum of 6 samples for each surface chemistry (**SAM-3** and 'switched') were used for cell culture experiments.

S2. Wet-chemistry Evidence for the Formation of Surface Assemblies Prepared from Immobilized Lactones

As described in greater detail in § S1.3, NBS-promoted oxidation of the confined lactone species **2** (**SAM-2**) was followed by carbodiimide/*N*-hydroxysuccinimide activation of the putative benzoquinone acid product, and subsequent reaction with nucleophiles of interest (§ S1.3.4). The purpose of this section is two-fold: i) to provide "wet-chemistry" evidence for the proposed conversion of a immobilized lactone moiety to the corresponding benzoquinone acid upon its exposure to the oxidizing conditions investigated in the text; and ii) to provide spectroscopic evidence for the lack of benzylic bromination upon aqueous NBS treatment. Compound **4** was selected as a representative lactone derivative and used as starting material in the wet-chemistry control experiments described below. The proposed synthetic scheme is depicted in Scheme S4. Importantly, all spectroscopic data support the conversion of compound **4** to compound **4a** upon treatment with aqueous NBS, with no evidence of brominated byproducts. Further, formation of compound **4c** is taken as supplementary evidence of the formation of the putative azido-terminated construct as depicted in Figure S4.

Scheme S4. Ring-opening reaction on a representative solution phase system



i. NBS, 44%; ii. DCC/NHS, cat. DMAP, 45%; iii. $NH_2(CH_2)_3N_3$, DIPEA, 73%.

*(i) 3-(2,5-Dimethyl-3,6-dioxocyclohexa-1,4-dienyl)-3-methylbutanoic acid (**4a**).* To a stirred solution of 6-hydroxy-4,4,5,8-tetramethylhydrocoumarin **4** (220 mg, 1.0 mmol) in water (0.4 mL) and acetonitrile (2.0 mL), *N*-bromosuccinimide (190 mg, 1.1 mmol) was added in 5

portions. Stirring was continued at room temperature for 1 h. The reaction mixture was then evaporated *in vacuo* and the oily residue extracted with dichloromethane (2 × 10 mL) after the addition of water (5 mL). The crude material was purified by column chromatography (dichloromethane) to give the title compound **4a** as a yellow oil (105 mg, 44%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.59 (s, 1H), 2.56 (s, 2H), 2.41 (s, 3H), 2.37 (s, 3H), 1.46 (s, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 168.11, 147.41, 143.40, 130.77, 124.22, 120.68, 112.63, 45.86, 35.84, 27.61, 16.79, 15.36.

(ii) 2,5-Dioxopyrrolidin-1-yl-3-(2,5-dimethyl-3,6-dioxocyclohexa-1,4-dienyl)-3-methylbutanoate, N-*Hydroxysuccinimidyl ester (**4b**).* To a stirred solution of 3-(2,5-dimethyl-3,6-dioxocyclohexa-1,4-dienyl)-3-methylbutanoic acid **4a** (70.0 mg, 0.30 mmol) in dry dichloromethane (30 mL), *N*-hydroxysuccinimide (38.0 mg, 0.33 mmol), *N*,*N*'-Dicyclohexylcarbodiimide (68.1 mg, 0.33 mmol) and 4-*N,N*-(dimethylamino)pyridine (2.0 mg, 0.02 mmol) were added in one portion. Stirring was continued at room temperature for 1 h under an argon atmosphere. The reaction mixture was then cooled on an ice-water bath and filtered. The filtrated was evaporated under reduced pressure and suspended in ice cold ethyl acetate (*ca*. 10 mL) before being filtered a second time. The filtrate was *in vacuo* and extracted with dichloromethane (2 × 10 mL) from water (5 mL). The pooled organic phase was dried over $MgSO_4$, filtered and the solvent removed *in vacuo* pressure to afford the crude product as a yellow oil. The crude material was crystallized in methanol at 4 ºC to afford the ester **4b** as a pale-yellow powder (45 mg, 45%).^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.47 (s, 1H), 3.27 (s, 2H), 2.78 (s, 4H), 2.16 (s, 3H), 2.01 (s, 3H), 1.54 (s, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 190.67, 187.32, 169.02, 167.78, 150.42, 148.13, 140.93, 131.77, 44.28, 39.32, 29.38, 25.68, 16.07, 14.17.

(iii) N-*(3-azidopropyl)-3-(2,5-dimethyl-3,6-dioxocyclohexa-1,4-dienyl)-3-methylbutanamide (**4c**).* To a solution of the *N*-hydroxysuccinimidyl ester **4b** (30 mg, 0.09 mmol) in *N*,*N*-dimethylformamide (5 mL), diisopropylethylamine (62 mg, 0.5 mmol) and 3-azidopropylamine (30 mg, 0.3 mmol) were added in one portion with stirring under an argon atmosphere. The reaction mixture was heated at 50 ºC and stirring continued for an additional 16 h. The solution was diluted with ethyl acetate (30 mL) and the crude mixture poured into a separatory funnel. The organic phase was washed with brine (3 × 10 mL) and water (10 mL), dried over Na_2SO_4, filtered and the solvent removed *in vacuo*. The crude was purified using column chromatography (ethyl acetate/light petroleum, 2:1) to give the amide **4c** as a yellow solid (21 mg, 73%). ^{1}H

NMR (300 MHz, $CDCl_3$) δ: 6.47 (s, 1H), 3.26 (m, 4H), 2.87 (m, 1H), 2.30 (m, 7 H), 1.63 (bs, 1H), 1.23 (s, 3H), 1.12 (s, 3H), 0.84 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 196.80, 196.31, 174.63, 151.27, 138.88, 82.84, 50.33, 49.91, 46.73, 41.37, 40.17, 29.95, 27.21, 23.05, 16.68, 10.19. IR (KBr, cm^{-1}): 3439, 2965, 2097, 1687, 1455, 1404, 1376, 1273.

S3. Reaction of NHS-Activated Samples with 3-Azidopropylamine

To aid in the study of the modular assembly and 'switch' strategy depicted in Figure 1, 3-azidopropylamine was grafted onto the activated benzoquinone acid surface (§ S1.3.3). The electron-deficient nitrogen atoms in azido groups of the putative surface product, is generally a well resolved feature in N 1s XPS narrow scans with a *ca*. 3 eV separation from signals due to nitrogen bonded to carbon.[29-30]

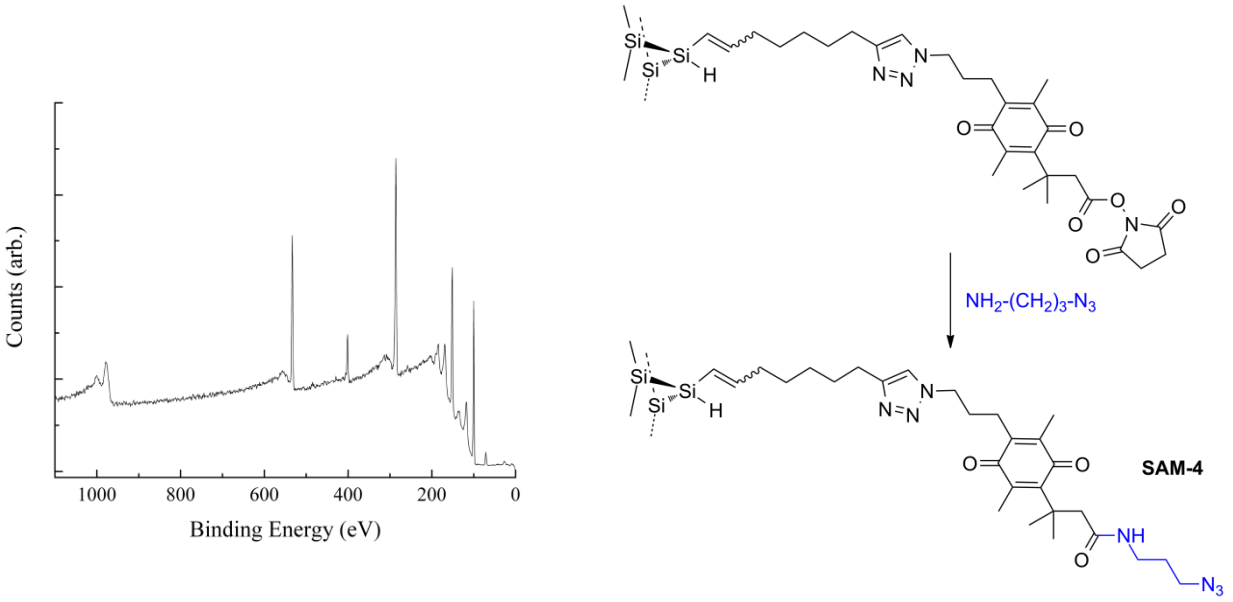


Figure S4 Wide XPS spectrograph of 3-azidopropylamine modified samples

Not easily distinguishable in the wide scan (Figure S4), but visible in high resolution N 1s scans (Figure S5b), was a peak absent in the lactonized precursor (**SAM-2**) of mean binding energy of 404.7 eV and resulting from electron-deficient nitrogen atoms in azido groups. This finding was therefore consistent with a positive outcome of the immobilization of 3-azidopropylamine. Curve fitting of the complex N 1s envelope was applied to support claims of

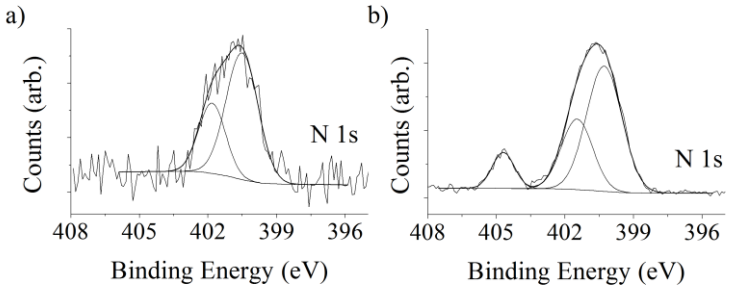


Figure S5. High-resolution nitrogen 1s XPS spectrographs for (a) dormant redox linker in **SAM-2**, (b) azide-decorated surface (**SAM-4**).

the product formation. The peak area ratio for the 405 eV curve (here referred to as N_{405}) to the main contribution in the *ca*. 399–402 eV region (simply indicated as N for clarity) was 0.7:6,

close to the stoichiometric ratio of 1:6 expected for an homogeneous array of surface bound molecules. Non-quantitative yields for the stepwise procedure used in the construction of **SAM-4** might account for the observed difference.

Despite all the chemical derivatization steps downstream from the passivation of the Si(100) surface with diyne **1** being done in aqueous environments, and extensive handling of the samples in air, either no or minor (*ca*. 0.06 SiOx fractional layers)[24] silicon oxide related signals were observed in the 102–104 eV region of the Si 2p XPS emission; again highlighting the effectiveness of the base surface chemistry (*i.e*. **SAM-1**) in protecting the Si(100) surface from oxidation. Sessile water contact angles values for **SAM-4** were 58 ± 4º, a value close to those reported for the lactonized surface (**SAM-2**) and did not afford supplementary information on the surface chemistry.

As discussed above, the electron-deficient nitrogen atom (N_{405}) of the terminal azide group of **SAM-4**, with a well-resolved emission at 404.7 eV in the N 1s narrow scan (Figures S5b), afforded a convenient XPS marker that facilitates deconvolution of experimental data.

A potential of −900 mV was applied to the silicon working electrode (**SAM-4**) for 300, 600 and 6000 s to reduce the quinone to the corresponding hydroquinone,[31] which then could react with the neighboring amide link and release 3-azidopropylamine. N 1s and Si 2p XPS spectrographs for the electrochemically reduced substrates are shown in Figures S6 and S7, respectively. Curve fitting of the complex N 1s envelope was applied to support claims of the product formation. The observed N_{405}:N peak area ratio decreased from 0.7:6, as for the

untreated surface **SAM-4**, to *ca*. 0.5:6 for silicon samples reacted for either 300 s or 600 s at −900 mV. As expected on the basis of molecular considerations, and as further supported by

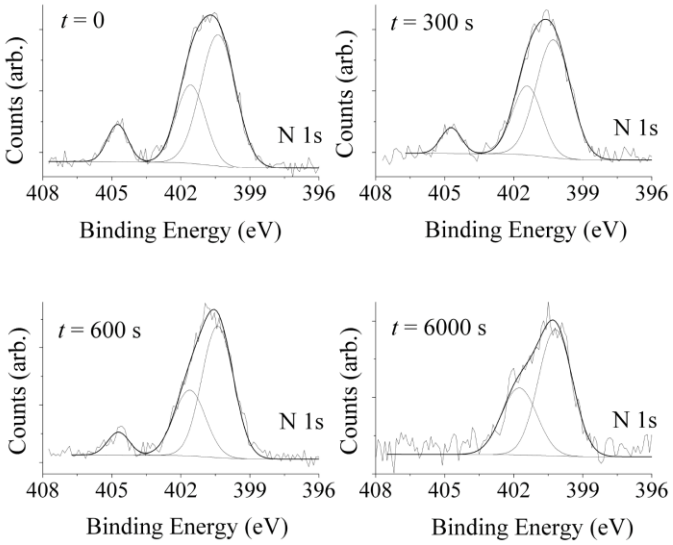


Figure S6. XPS nitrogen 1s narrow scans for the electrochemical reduction (–900 mV) of construct **SAM-4**. Spectrographs were acquired for silicon samples prior to (t = 0), and at defined time intervals (t = 300, 600 and 6000 s) during the cathodic lactonization process.

published data by Chidsey,[29-30] azide on surfaces display a 1:2 peak area ratio for the N_{405}:N XPS signals, therefore simple algebraic considerations allowed to estimate a *ca.* 38% yield for the electrochemical reduction of construct **SAM-4** to surface **SAM-2** upon the 10-min cathodic 'switch'. Prolonged bias of **SAM-4** (6000 s) were necessary to reduce the N_{405} emission to below detectable levels, corresponding to a quantitative conversion to the final product. The unexpectedly long polarization times required to complete the benzoquinone reduction−hydroquinone lactonization sequence under this bias condition prompted the investigation of more cathodic overpotentials for a rapid release of immobilized nucleophiles. Optimized conditions are used in the 'switch' of the OEG –functionalized **SAM-3** (main article). Finding of this optimization study will be reported elsewhere.

Lack of significant signals corresponding to oxidized silicon atoms in Si 2p high-resolution XPS spectrographs acquired at successive times during the reaction (Figure S7), indicated that the overall SAM quality was not adversely affected by the electrochemical process performed in aqueous systems.

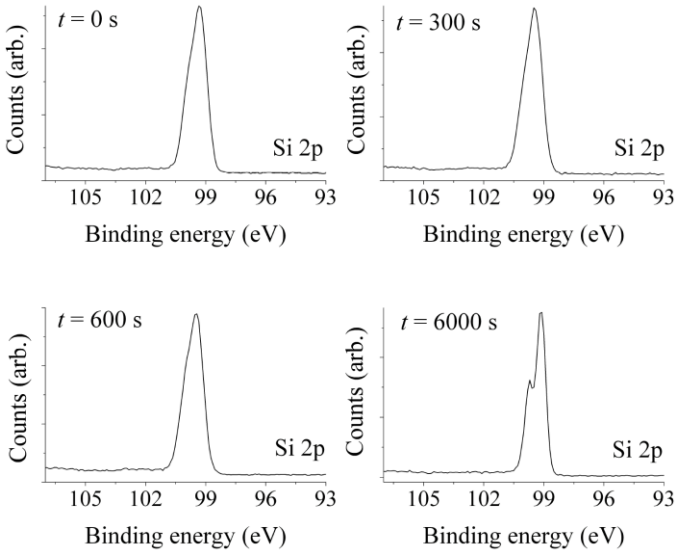


Figure S7. Si 2p region of XPS spectra for electrochemically cleaved construct **SAM-4**. Spectrographs were acquired for samples prior to (t = 0), and at defined time intervals (t = 300, 600, and 6000 s) during the cathodic (–900 mV) lactonization process.

S4. References

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mixture was diluted with dichloromethane and washed with brine. The organic solvent was evaporated in vacuo and the brown residue purified via column chromatography (ethyl acetate/light petroleum`, 1:1) to yield the unreacted starting material e and traces of the coumarin d.
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