

Electrochemistry of Redox-Active Guest Molecules at β -Cyclodextrin-Functionalized Silicon Electrodes

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Functionalization of silicon-based sensing devices with self-assembled receptor monolayers offers flexibility and specificity towards the requested analyte as well as the possibility of sensor reuse. As electrical sensor performance is determined by electron transfer, we functionalized H-terminated silicon substrates with β -cyclodextrin (β -CD) molecules to investigate the electronic coupling between these host monolayers and the substrate. A trivalent (one ferrocene and two adamantyl moieties), redox-active guest was bound to the β -CD surface with a coverage of about 10^{-11} mol/cm² and an overall binding constant of $1.5 \cdot 10^9$ M⁻¹. This packing density of the host

monolayers on silicon is lower than that for similar β -CD monolayers on gold. The monolayers were comparable on low-doped p-type and highly doped p++ substrates regarding their packing density and the extent of oxide formation. Nonetheless, the electron transfer was more favorable on p++ substrates, as shown by the lower values of the peak splitting and peak widths in the cyclic voltammograms. These results show that the electron-transfer rate on the host monolayers is not only determined by the composition of the monolayer, but also by the doping level of the substrate.

1. Introduction

Silicon substrates are of high interest for the fabrication of electronic devices, for example for sensing,^[1] data storage^[2] and energy conversion.^[1] Placing functional groups onto the surface, for example by self-assembled monolayers, enables more flexibility and specificity towards an application, for instance to make an analyte-specific sensor.^[3] These devices, however, rely on direct charge transfer from/to the silicon substrate, which makes studies on these electron transfer processes essential. Typical monolayer parameters that influence the electron transfer include the way of surface coupling, the length and conductivity of the molecules used, and the packing of the monolayer.

When choosing molecules for self-assembled monolayers on sensing devices, supramolecular chemistry is attractive because of its modularity and reversibility.^[4] Specifically, cyclodextrin (CD) host molecules can be used for self-assembled monolayer formation by coupling to the surface.^[5] CD molecules, which are cyclic oligosaccharides consisting of 6 (α), 7 (β), or 8 (γ) α -D-glucopyranose units, can be functionalized on their primary rim with substrate-coupling moieties, mostly performed in a multipodant way to increase monolayer stability.

Monolayers of β -CD have been applied, mostly for sensing purposes, on gold,^[6] glass,^[7] and silicon,^[8] for example.

For a silicon-based sensing device, oxide-free functionalization is required because any silicon oxide would function as an insulating layer and prevent charge transfer from/to the surface.^[9] Hydrosilylation is a suitable technique to functionalize silicon in an oxide-free way, since unsaturated carbon-carbon bonds are coupled to H-terminated silicon, resulting in a direct Si-C coupling.^[10] A few examples have been reported in which alkene-functionalized β -CD molecules have been grafted onto Si-H by a photochemical hydrosilylation method.^[8,11] These monolayers enabled measuring host-guest interactions by impedance spectroscopy^[8] or by a photoluminescence response,^[11] which confirmed the applicability of β -CD host monolayers on silicon in sensing applications. These examples are based on electron transfer, which means that the sensor performance depends on the electronic coupling between the host-guest complexes and the substrate. The electron transfer processes between these β -CD host monolayers and the silicon substrate have, however, not been studied in detail.

Here, we use a redox-active guest to study the electronic coupling of a β -CD host monolayer on silicon substrates. A new heptapodant alkyne-functionalized β -CD molecule has been synthesized as the host molecule, since alkynes have been reported to result in better monolayers than alkenes.^[12] Monolayers of this β -CD derivative have been formed by a hydrosilylation reaction. Host-guest complexes were formed with a ferrocene-containing trivalent guest, since ferrocene-based guests have a characteristic redox signal.^[6f-h] Electrochemistry was used to evaluate the properties of the electrical contact between the host layer and the underlying surface, as well as the influence of the doping concentration of the silicon substrates, i.e., lowly doped p-type (Si(p)) and highly doped p-type (Si(p++)). Additionally, the electrochemical measure-

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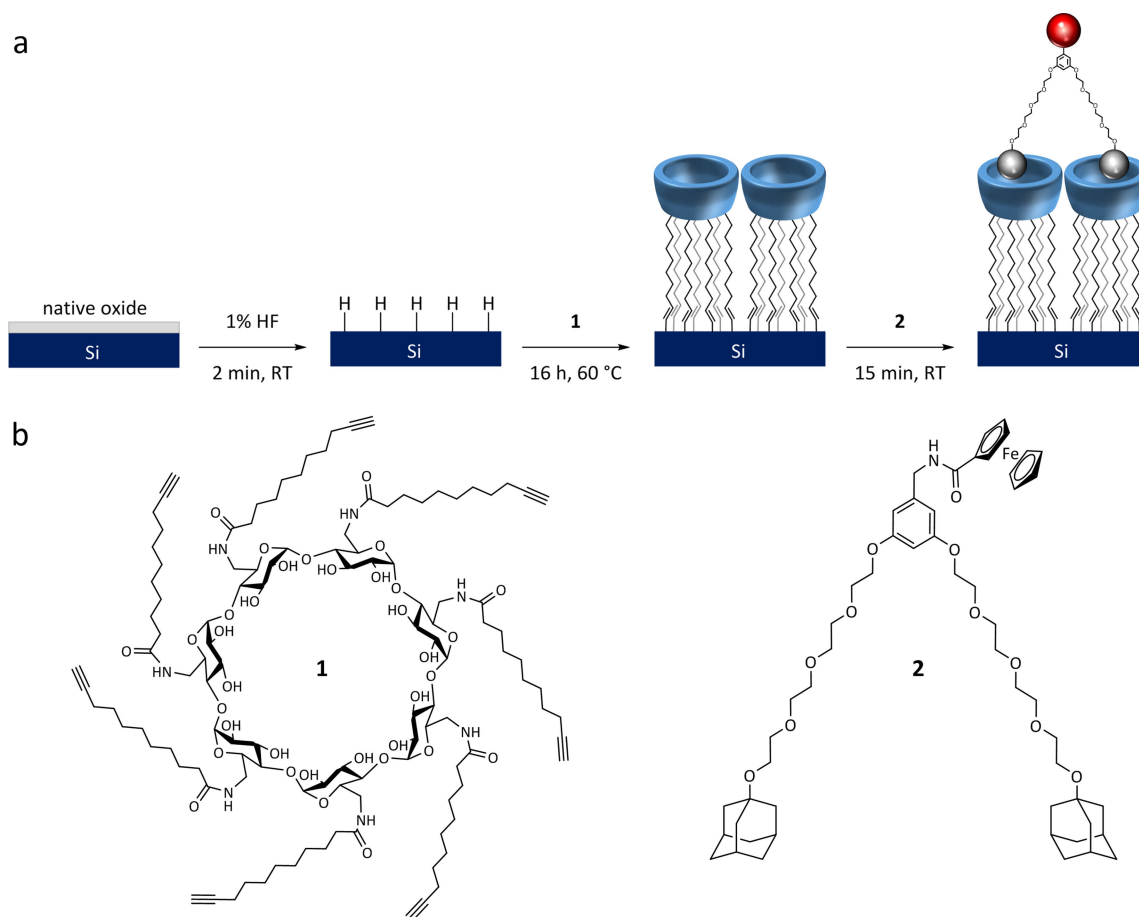
ments were used to quantify the packing density of the host monolayer.

2. Results and Discussion

Scheme 1a shows the monolayer formation on silicon substrates with heptaalkyne-functionalized β -CD host **1** and its subsequent host-guest chemistry with the bis-adamantyl ferrocene guest **2**. To avoid any insulating silicon oxide between the β -CD monolayer and the substrate, functionalization of the Si surface with β -CD host molecules was achieved by hydrosilylation, by which unsaturated carbon-carbon bonds are coupled covalently to H-terminated silicon.^[10] The heptaalkyne-functionalized β -CD molecule **1** (Scheme 1b) was synthesized by coupling 10-undecynoic acid to heptaamino-functionalized β -CD. This resulted in complete substitution of all seven amino groups as confirmed by electrospray ionization mass spectrometry (ESI-MS). Formation of the desired product was further supported by elemental analysis, and proton and carbon nuclear magnetic resonance (NMR) spectroscopy (Figure S1).

2.1. Monolayer Formation

To make monolayers of **1** on Si (Si-1), the native oxide layer of Si was first removed from lowly doped (p-type) or highly doped (p+ +) Si(100) substrates by short immersion in 1% aqueous hydrofluoric acid (HF). To enable electrochemistry at a later stage, an aluminum/silicon alloy was sputtered as Ohmic contact at the back side. The substrates were directly immersed in a 4 mM solution of **1** in THF/DMF/mesitylene at 60 °C for 16 h. The resulting monolayer was characterized by contact angle measurements, showing $85.1^\circ \pm 1.9$ and $84.2^\circ \pm 3.3$ for p-type and p+ + silicon, respectively. These values are higher than expected for the hydrophilic rim of the host cavity, as (advancing) contact angle values of 55° and 49° have been reported for β -CD monolayers on gold^[13] and glass,^[5a] respectively. Attenuated total reflection infrared spectroscopy (ATR-IR) spectra of dummy substrates, functionalized simultaneously with the electrochemistry samples, confirmed the formation of Si-1 by the appearance of O–H/N–H stretch vibrations in the $3600\text{--}3200\text{ cm}^{-1}$ range, C–H stretches at $2968, 2937, 2857\text{ cm}^{-1}$, and the disappearance of Si–H_x stretches around 2108 cm^{-1} (Figure 1). Furthermore, no $\text{C}\equiv\text{CH}$ stretch vibration was visible at 3300 cm^{-1} , thus indicating that the alkyne groups had fully reacted onto the surface.



Scheme 1. a) Schematic procedure of silicon surface functionalization by covalent coupling of **1** to H-terminated Si, followed by host-guest chemistry with **2**; b) chemical structures of heptaalkyne-functionalized β -CD **1** and bis-adamantyl ferrocene guest **2**.

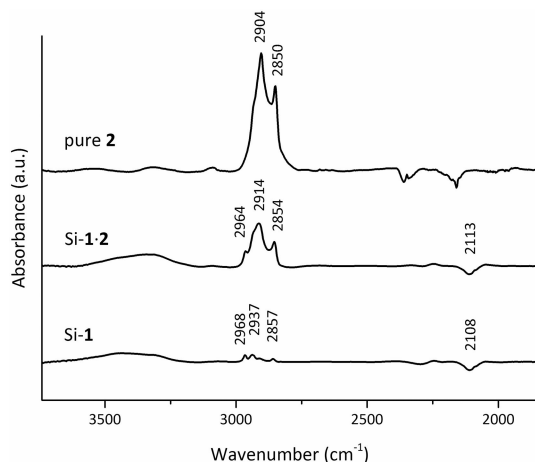


Figure 1. ATR-IR spectra of silicon substrates functionalized with **1** (β -CD, Si1) and **2** (β -CD with guest, Si-1.2) referenced to an H-terminated silicon sample. The FT-IR spectrum of pure **2** is added for comparison.

X-ray photoelectron spectroscopy (XPS) provided further evidence for successful Si-1 monolayer formation (Figure 2). The C1s core levels (Figure 2a and c) could be deconvoluted and fitted to three peaks at 288.3, 286.5, and 284.8 eV for p-type Si, and 288.5, 286.5, and 284.8 eV for p++ Si, which correspond to the $\text{C}=\text{O}$, $\text{C}-\text{O}/\text{C}-\text{N}$, and $\text{C}-\text{C}$ moieties, respectively.^[14] The $\text{C}=\text{O}$ peaks amounted to 6.7% (p-type) and 6.1% (p++) of the total C signal. These values match well with the expected value of 5.9%. It was not possible to determine the

number of alkyne groups bound to the surface, since the signals for neither the $\text{Si}-\text{C}\equiv\text{C}$ moiety (283.5 eV^[15]) nor the $\text{C}-\text{C}\equiv\text{C}$ moiety (286.2 eV^[15]) could be clearly deconvoluted in the C1s region. The atomic concentration ratios of C:N equaled to 35 for both p and p++ Si, which is higher than the stoichiometric value of 17, probably due to some adventitious carbon contaminants. The Si2p core spectrum (Figure 2b and d) shows that the surface (after storage under nitrogen for two days before measuring) was partly converted into SiO_2 , seen from the signals at 102.5 eV (p-type, 14%) or 102.4 eV (p++, 13%). This could be explained by i) the bulkiness of the heptaalkyne-functionalized β -CD molecules, resulting in a less densely packed monolayer, and/or ii) the covalent nature of the binding of the heptapodant host molecules, which lowers the lateral mobility compared to monolayer formation on gold. Any Si-O-C moieties would have been visible in the XPS spectra at lower binding energies, thus indicating that the β -CD molecules were covalently coupled by Si-C bonds, indicating that SiO_2 only occurred at the non-reacted sites.

2.2. Guest Immobilization

To study host-guest chemistry on Si-1, trivalent guest **2** (Scheme 1b) was used as designed before,^[6g] consisting of two tetra(ethylene glycol) spacers with adamantyl moieties for stable anchoring onto β -CD surfaces and an electroactive ferrocene moiety linked through a benzene ring. Guest immobilization was achieved by immersion in a 10 μM solution

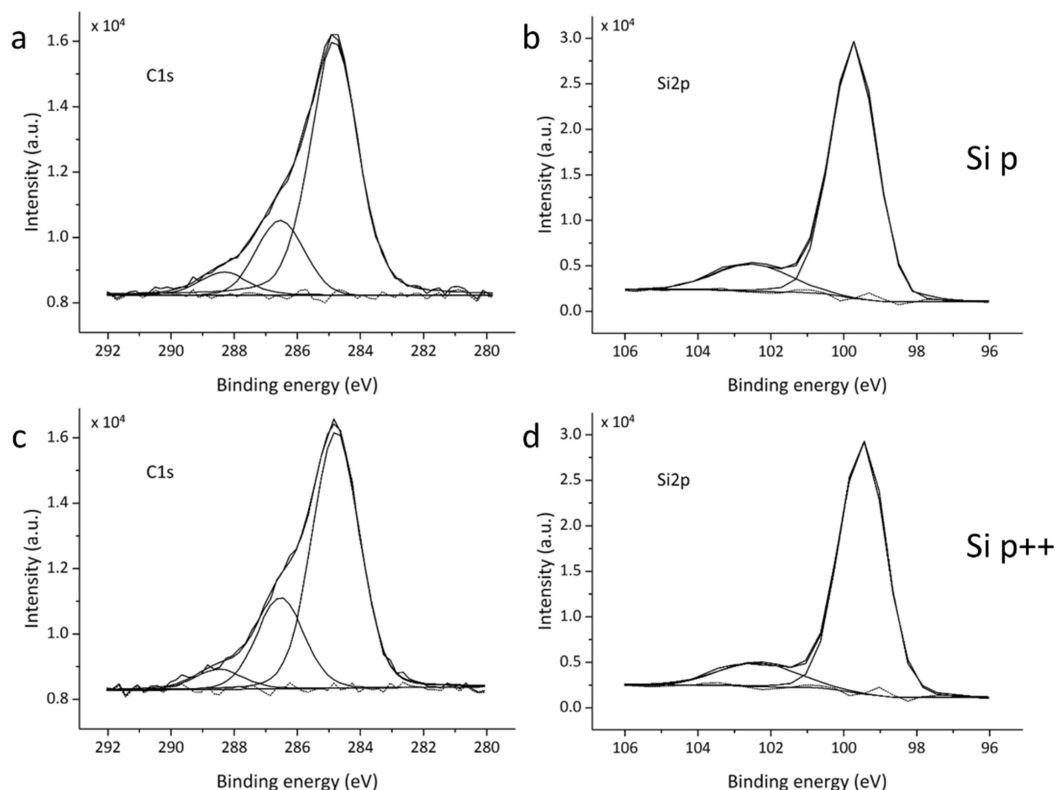


Figure 2. XPS spectra of Si-1 on a,b) p-type and c,d) p++ silicon, showing a,c) the C1s region and b,d) the Si2p region including deconvoluted signals.

of **2**, resulting in silicon surfaces with covalently bound β -CD and supramolecularly bound ferrocene guest (Si-1-2). The concentration of $10\ \mu\text{M}$ is expected to lead to practically saturated, divalently bound **2** on the surface of Si-1.^[6g] The contact angle of these surfaces was $83.7^\circ \pm 2.0$ and $79.5^\circ \pm 1.2$ for p-type and p++ silicon, respectively, which is slightly more hydrophilic than the Si-1 host surfaces. ATR-IR (Figure 1) showed a clear increase in the C–H stretch signals. XPS of Si-1-2 surfaces further confirmed guest immobilization by the presence of Fe (Figure S2).

Electrochemical experiments were used to study the electronic coupling between the guest **2** and the Si-1 surface and the density of β -CD groups on the surface. After guest immobilization, cyclic voltammograms were measured without guest or β -CD in solution (Figure 3a and d). The ferrocene redox activity is clearly visible, with a half-wave potential ($E_{1/2}$) of 0.523 and 0.528 V vs. Ag/AgCl for p and p++ silicon, respectively, which is comparable to previous measurements on gold.^[6g] Cyclic voltammetry showed that the host-guest binding was reversible, since the ferrocene peaks disappeared upon competition with an aqueous 10 mM β -CD solution (Figure 3c and f). The peak current increased linearly with the scan rate (Figure 3b and e), which confirms that the redox activity originates from a surface-confined species instead of a diffusion-controlled reaction. The slope of these graphs (anodic peak) was used to calculate the surface coverage of the guest molecules, which gave $1.2 \cdot 10^{-11}\ \text{mol}/\text{cm}^2$ and $1.1 \cdot 10^{-11}\ \text{mol}/\text{cm}^2$ for p and p++ substrates, respectively. Assuming divalent guest binding as reported before,^[6g] the host coverages equaled to $2.4 \cdot 10^{-11}\ \text{mol}/\text{cm}^2$ and $2.2 \cdot 10^{-11}\ \text{mol}/\text{cm}^2$, respectively. The packing density of β -CD monolayers on silicon has

not been reported before, but alkyl-functionalized β -CD molecules on gold showed a host coverage of $5.9 \cdot 10^{-11}\ \text{mol}/\text{cm}^2$ determined by the same method.^[6g] It can be concluded that the β -CD monolayers on silicon showed about half of the packing densities as compared to the highly packed monolayers on gold. This is in line with the XPS data that showed the presence of SiO_2 .

Whereas the host-guest chemistry described so far was comparable for p and p++ Si, the electron transfer properties slightly differed. The peak splitting at 0.1 V/s was 52 mV for p-type Si and 18 mV for p++ Si, of which the latter value is the closest to the expected value of 0 mV for an ideal surface-confined electron transfer process. The peak separation increased for higher scan rates, e.g., to 286 mV for p-type Si and 136 mV for p++ Si at 1 V/s, which indicates that the electron transfer gets kinetically limited and shifts from reversible to quasi-reversible. This effect was confirmed by unequal peak currents for the anodic and cathodic reactions. Irreversible electron transfer (peak splitting $> 200\ \text{mV}$ ^[16]) was observed upward of 0.8 V/s for p-type Si and 2 V/s for p++ Si. This behavior could be due to the linkers in the host and guest molecules used, which place the ferrocene moiety relatively far from the Si surface and thus retard the electron transfer.^[6g] Alternatively, the electron transfer could be retarded by the presence of SiO_2 due to the non-closed packed β -CD monolayer.

Full width at half maximum (FWHM) values of the cyclic voltammetry peaks were determined to be 98 and 91 mV (anodic peak, 0.1 V/s) for p and p++ substrates, respectively. These values are just slightly larger than or equal to the theoretical value of 91 mV.^[17] Nonetheless, the FWHM values

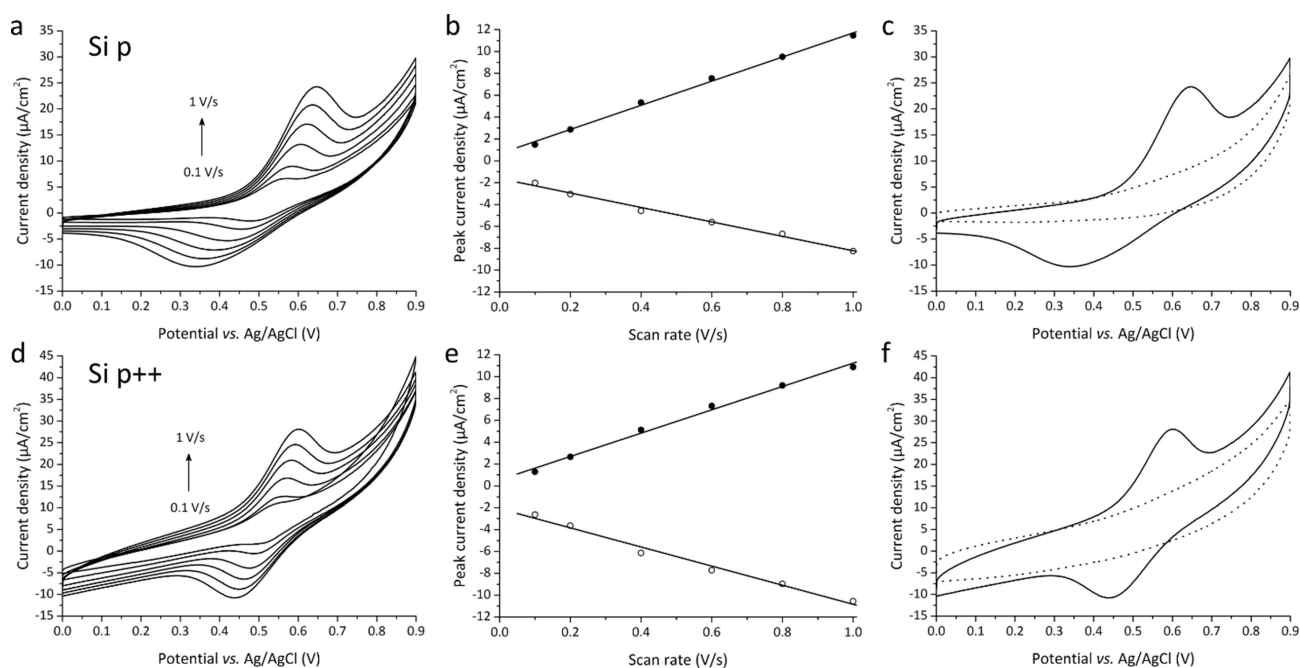


Figure 3. Electrochemical characterization of Si-1-2 on a–c) p-type and d–f) p++ substrates. a,d) Cyclic voltammetry at 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0 V/s in an aqueous solution of 1 M NaClO_4 ; b,e) the corresponding graphs reporting the dependence of the anodic (closed dots) and cathodic (open dots) peak current densities on scan rate. c,f) Cyclic voltammograms at 1 V/s before (solid line) and after (dotted line) competition with a 10 mM β -CD solution in water.

were not independent of the scan rate as they should be, since the values at 1.0 V/s increased to 130 (p-type) and 118 mV (p + Si). The peak splitting and FWHM values of silicon p + substrates were comparable to monolayers of heptathioether β -CD with the same guest on gold substrates.^[6g] Also for this monolayer, the alkyl chains place the host cavity relatively far from the substrate, which is further enhanced by the linker in the guest molecule. Therefore, the retarded electron transfer in the Si-1-2 system is taken as a sign of the occurrence of an insulating alkyl layer between the host cavity and the surface.

In short, the host monolayers on p and p + substrates were chemically equivalent, as both surfaces showed similar coverages and SiO₂ percentages. Nonetheless, the electron transfer properties were more favorable for the p + substrates, as seen from the lower peak splitting and peak widths. Thus, the electron transfer rate is not only limited by the thickness and coupling of the β -CD monolayer but is also determined by the doping level of the substrate. The better electrochemical response on the p + substrates is expected to originate from their higher conductivity, which enables a better charge transfer from the host-guest complexes to the substrate.

To further investigate the host-guest chemistry, the effect of the variation of the guest concentration was monitored by electrochemistry, as performed on p + Si-1 by measuring the coverage of guest 2 by cyclic voltammetry with guest 2 in solution. Starting from a bare host surface and with guest molecules in an aqueous solution complexed with free β -CD, an equilibrium should favor the binding of the guest to the β -CD monolayer. The surface coverage was determined for several guest concentrations ranging from 0.1 to 8.0 μ M in the presence of 1 mM β -CD as competitor and 1 M NaClO₄ as electrolyte. Figure 4a shows that the shape of a plot of surface coverage vs. guest 2 concentration is comparable to an SPR adsorption isotherm on gold surfaces with a β -CD monolayer.^[18] Each of the data series shows a linear scan rate dependence (Figure 4b), which indicates that the major part measured is

surface-confined, even though there is guest present in solution. The increase of the intercepts with the y-axis > 0 at higher concentrations indicates, however, a minor contribution of solution species for these series. Fitting with a combined diffusion-controlled and surface-confined model to determine the surface coverage^[19] did not yield a better fit, thus we found the diffusion part negligible. As another control, the 8.0 μ M guest solution was also measured on top of a bare Si substrate, which instead gave a linear dependence on the square root of the scan rate (Figure 4b, inset). The peak splitting was smaller when measuring this diffusion-controlled species on a bare Si substrate compared to the surface-confined species on a Si-1 substrate (Figure S3), which made a clear distinction between diffusion-controlled and surface-confined peaks possible. Consequently, the redox-active species as measured in Figure 4 were assumed to be surface-confined.

The host-guest interactions were further quantified by fitting the data using a thermodynamic model for multivalent host-guest interactions on a surface in the presence of a competing guest in solution.^[6g,20] The fitting was performed using $K_{i,s}$ and the maximum surface coverage as variables, and $K_{i,l} = 4.6 \cdot 10^4 \text{ M}^{-1}$, $C_{\text{eff}} = 0.2 \text{ M}$, and $[\beta\text{-CD}] = 1 \text{ mM}$ as fixed parameters.^[18] Assuming divalent guest binding (through both adamantyl moieties) as reported before for the same guest,^[6g] the fitting resulted in $K_{i,s} = 8.6 \cdot 10^4 \text{ M}^{-1}$ and a maximum guest coverage of $1.1 \cdot 10^{-11} \text{ mol/cm}^2$, i.e., an overall observed binding constant ($K_{\text{obs}} = K_{i,s}^2 \cdot C_{\text{eff}}$) of $1.5 \cdot 10^9 \text{ M}^{-1}$. The $K_{i,s}$ value is slightly lower than observed before for β -CD monolayers on gold with another divalent adamantane guest ($1.6 \cdot 10^5 \text{ M}^{-1}$),^[18] which could be due to the lower packing density observed. The saturation guest coverage is comparable to the guest-incubated samples described above without host or guest molecules in solution ($1 \cdot 10^{-11} \text{ mol/cm}^2$).

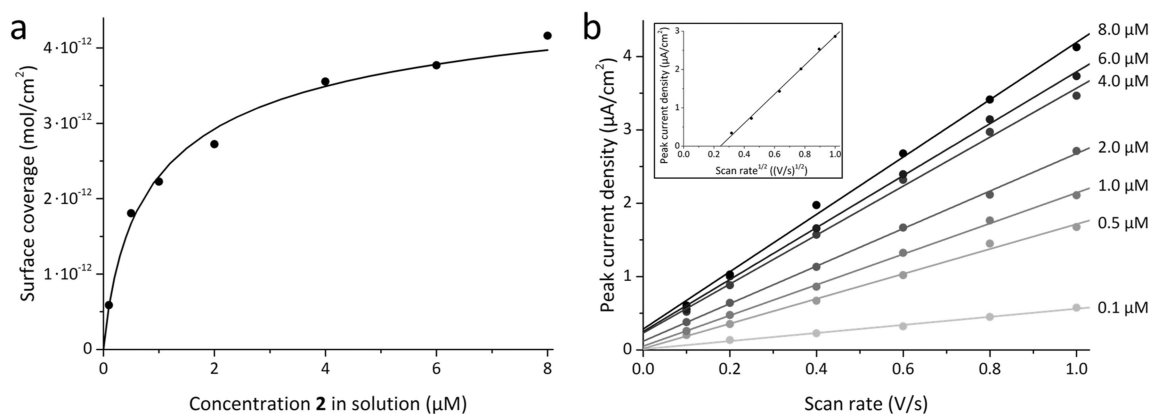


Figure 4. a) Titration of guest 2 in an aqueous 1 mM β -CD solution with 1 M NaClO₄ on Si(p +)-1, where the surface coverage was determined by using cyclic voltammetry at different scan rates, and the solid line is a fit to a thermodynamic multivalent model; b) the corresponding graphs on scan rate dependence of the anodic peak current density for each surface coverage determination, with the inset showing the linear dependence of the peak current density versus the square root of the scan rate for cyclic voltammetry of 8.0 μ M guest 2 in solution on a bare silicon substrate. The data point at 0.1 V/s for 0.1 μ M guest was omitted because the peak current was too low to be determined.

3. Conclusions

Overall, we have studied host-guest chemistry on silicon p and p++ surfaces functionalized with monolayers of β -CD. Supramolecular interactions with a trivalent ferrocene-functionalized guest were shown to be reversible by competition with free β -CD in solution. The host coverages were found to be $2 \cdot 10^{-11}$ mol/cm², which indicated that the β -CD monolayers on silicon have a coverage of about half of the values reported for comparable β -CD monolayers on gold. This could be explained by the bulkiness of the heptaalkyne-functionalized β -CD molecules and/or the covalent nature of the binding of the heptapodant host molecules, which prohibits the lateral mobility during monolayer formation. A titration was performed at varying concentrations of guest while also using free β -cyclodextrin in solution as a competitor, by monitoring the cyclic voltammetry signal. These results showed an overall observed binding constant of the guest on a β -cyclodextrin-functionalized silicon p++ substrate of $1.5 \cdot 10^9$ M⁻¹. The electron transfer between the host-guest complex and the substrate was more kinetically limited at p-type substrates than on p++ surfaces, as indicated by a larger peak splitting in the cyclic voltammograms and larger peak widths. Even though the insulating alkyl layer between the β -CD and the silicon substrates is expected to retard the electron transfer, the monolayers were chemically equivalent on both substrate types and could not explain the differences observed in cyclic voltammetry. The doping level of the substrate thus also influenced the electrochemical response on the host layer. The electrochemical response could be measured better on the p++ substrates, which indicates that these substrates are the preferred candidates for silicon-based sensors over lowly doped p-type silicon. Further research is required to elucidate the stability of the electrodes in aqueous environments, as prolonged cyclic voltammetry could lead to wave broadening and electrode oxidation, for example.^[21] The electrochemical response and stability may be improved further by backfilling the host monolayer with spectator molecules, which avoids oxidation of the surface after β -CD monolayer formation.^[22]

Experimental Section

Materials

Silicon wafers (<100>-oriented, 100 mm diameter, single side polished) were obtained from Okmetic (Finland) as p-type (boron, resistivity 5–10 Ω -cm) or p++ (boron, 0.010–0.025 Ω -cm). For infrared spectroscopy, double-sided p-type silicon wafers were used with parameters equal to the single side polished p-type wafers. Reagents and solvents were obtained from commercial sources and used without further purification unless stated otherwise. Mesitylene (> 98%), dichloromethane (99.7%), and *N,N*-dimethylformamide (DMF, 99.8%) were dried over molecular sieves (0.3 nm). Tetrahydrofuran (THF) was obtained from a solvent purification system (MB SPS-800). The trivalent guest **2** was synthesized as described before.^[6g] Milli-Q water with a resistivity > 18 M Ω -cm was obtained from a Milli-Q Integral water purification

system (Merck Millipore). Glassware used for the hydrosilylation reactions was dried overnight at 120 °C.

Synthesis of Heptakis-6-deoxy-6-(undec-10-ynamido)cyclomalto-heptaose **1**

Heptakis(6-amino-6-deoxy)cyclomaltoheptaose was prepared following the procedure of Ashton *et al.*^[23] and further purified by repeated precipitation of the aqueous solution of the hydrochloride by adding aqueous solution of ammonium hydroxide (30%) until reaching the pH 9–10. The precipitate was then filtered off, washed with water, methanol and diethyl ether and dried in vacuum. A solution of 10-undecynoic acid (339 mg, 1.89 mmol, 1 equiv) and 1-hydroxybenzotriazole (287 mg, 2.08 mmol, 1.1 equiv) in dry DMF (13 mL) was cooled down to 0 °C and *N,N'*-dicyclohexylcarbodiimide (385 mg, 1.89 mmol, 1 equiv) was added. The mixture was stirred under argon for 1 h at 0 °C and 1 h at room temperature. A slurry of heptakis(6-amino-6-deoxy)cyclomaltoheptaose (300 mg, 0.27 mmol) and *N*-ethylmorpholine (0.2 mL, 1.89 mmol, 1 equiv) in DMF (13 mL) was added and the reaction mixture was stirred for 3 days. DMF was evaporated to about 10 mL and added to 80 mL water to form a suspension. The solid was filtered off and washed with water (3 \times 10 mL) and diethyl ether (3 \times 10 mL). The solid was purified by silica gel column chromatography eluting with 9:1–5:1 dichloromethane-methanol to give compound **1** as an off-white syrup. Yield 108 mg (18%). R_f = 0.42 (5:1 dichloromethane-methanol). ¹H NMR (400 MHz, methanol-*d*₄, Figure S1) δ 8.26 (t, 7 H, $J_{\text{NH,CH}} = 5.3$ Hz, NH), 4.97 (d, 7 H, $J_{1,2} = 3.5$ Hz, H-1), 3.98 (bd, 7 H, $J_{6a,6b} = 12.6$ Hz, H-6a), 3.86 (t, 7 H, $J_{2,3} = J_{3,4} = 9.2$ Hz, H-3), 3.86 (m, 7 H, H-5), 3.54 (dd, 7 H, H-2), 3.46 (m, 7 H, H-6b), 3.32 (t, 7 H, $J_{4,5} = 9.3$ Hz, H-4), 2.31 (t, 14 H, $^3J_{\text{H,H}} = 7.3$ Hz, CH₂CO), 2.21 (m, 21 H, \equiv CH, CH₂C \equiv CH), 1.66 (bs, 14 H, COCH₂CH₂), 1.52 (q, 14 H, $^3J_{\text{H,H}} = 6.6$ Hz, CH₂CH₂C \equiv CH), 1.5–1.3 (m, 56 H, COCH₂CH₂(CH₂)₄). ¹³C NMR (100.3 MHz, methanol-*d*₄, Figure S1) δ 176.3 (CO), 104.0 (C-1), 85.5 (C-4), 85.1 (C \equiv CH), 74.5, 74.2, 72.4 (C-5, C-2, C-3), 70.0 (C \equiv CH), 41.3 (C-6), 37.1 (COCH₂), 30.4–29.7 (COCH₂CH₂(CH₂)₅), 27.2 (COCH₂CH₂), 19.1 (CH₂C \equiv CH). ESI-MS *m/z* calculated 1139.91, found 1139.50 [M + 2H]²⁺, and calculated 2278.81, found 2278.34 [M + H]⁺. Anal. calcd. for C₁₁₉H₁₈₉N₇O₃₅ · 2 H₂O C 61.77, H 8.41, N 4.24, found C 61.84, H 8.01, N 3.80.

CD Monolayer Formation on Silicon

A 4 mM solution of heptaalkyne-functionalized β -CD **1** in THF/DMF/mesitylene (0.3/0.8/3.0 mL) was degassed by four freeze-pump-thaw cycles. Silicon p and p++ substrates were diced into pieces of 2 \times 2 cm² and sonicated in acetone for 10 min to remove particles generated during dicing. Native oxide was removed from p and p++ silicon substrates by immersion in 1% aqueous HF for 2 min to result in an H-terminated surface. The back side was sputtered with a 1 μ m aluminum/silicon layer (99/1% Al/Si, Oxford PL400, 7 kW) as Ohmic contact for electrochemistry. Afterwards, the substrates were immediately immersed in the degassed solution of **1** inside a nitrogen glovebox. The reaction flask was equipped with a capillary as a nitrogen inlet and a reflux condenser. The hydrosilylation reaction was performed overnight under continuous nitrogen flow at 60 °C. The wafers were cleaned by 2 min ultrasonication in dichloromethane, rinsing with ethanol, rinsing with Milli-Q water and subsequently dried in a stream of nitrogen.

Guest Immobilization

A 10 μ M guest solution was made by first dissolving guest **2** in methanol, followed by dilution with water to obtain a solution with 1% v/v methanol. Host-functionalized surfaces were incubated

with guest molecules by 15 min immersion in this solution. The surfaces were rinsed with Milli-Q water, 2 mL of 1 mM aqueous β -CD solution, and Milli-Q water, and dried in a stream of nitrogen. Competition experiments were performed by 2×15 min immersion in a 10 mM aqueous β -CD solution.

Characterization After Synthesis

^1H and ^{13}C NMR were recorded at 400 and 100.6 MHz, respectively. 2D COSY and HMQC experiments were used to assist the NMR peak assignments. Fourier transform infrared (FT-IR) spectroscopy was performed on a Nicolet 6700 FT-IR instrument (4 cm^{-1} resolution, 128 scans). Thin-layer chromatography was carried out on aluminum sheets, with visualization by UV light and by charring with 10% H_2SO_4 . Column chromatography was carried out on silica gel (230–400 mesh). ESI-MS spectra were obtained for samples dissolved in dichloromethane-methanol at low μM concentrations.

Contact Angle Measurements

Static contact angles were measured with Milli-Q water on a Krüss G10 Contact Angle Measuring Instrument equipped with a CCD camera. Contact angle values were determined automatically by a drop shape analysis software. Contact angles were measured directly after the hydrosilylation reaction or guest immobilization and shown as an average of four drops.

Attenuated Total Reflection Infrared Spectroscopy

ATR-IR spectra were measured on double side polished silicon wafer pieces treated equally to the electrochemistry samples but lacking the aluminum/silicon contact. Spectra were collected with a Bruker spectrometer (Vertex 70v) equipped with an attenuated total reflection accessory ($L = 15\text{ mm}$) and MCT detector. The spectra were recorded with a resolution of 4 cm^{-1} and 1024 scans and treated with a spline baseline correction. Each spectrum was referenced to a hydrogen-terminated silicon sample.

X-ray Photoelectron Spectroscopy

XPS measurements were performed on a Quantera SXM setup from Physical Electronics equipped with an Al $K\alpha$ X-ray source (1486.6 eV). A detector angle of 45° was used, and collected spectra were calibrated on the C1s peak at 284.8 eV.

Electrochemistry

Electrochemical measurements were performed on a CH Instruments bipotentiostat 760D. Measurements were performed in a custom-built glass electrochemical cell with a platinum disk as counter electrode, a red rod reference electrode (Ag/AgCl, saturated KCl solution, Radiometer Analytical) and the functionalized silicon p or p+ + substrates as working electrode (0.44 cm^2). Cyclic voltammograms were recorded in 1 M sodium perchlorate monohydrate (NaClO_4) in water at scan rates of 0.1, 0.2, 0.4, 0.6, 0.8, 1.0 V/s. Three cycles were recorded, of which the last is shown in the graphs. An electrochemical titration of guest **2** were performed by measuring cyclic voltammetry on host-functionalized surfaces with on top aqueous solutions with 1 mM β -CD, 1 M NaClO_4 and different concentrations of guest **2** (0.1, 0.5, 1, 2, 4, 6, 8 μM). To prepare the guest solutions, a stock solution with 15 μM guest was sonicated for 30 min to dissolve the guest in water with 1 mM β -CD and 1 M NaClO_4 , which was then mixed in different ratios with the guest-free solution. The surface coverage was determined for

each guest concentration by measuring at scan rates of 0.1, 0.2, 0.4, 0.6, 0.8, 1.0 V/s. For all measurements, peak currents were determined by Gaussian fitting (using linear baseline correction) in the CHI760D software. The voltammetric data were recorded with an accuracy of 10 μA and 5 mV.

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Conflict of Interest

The authors declare no conflict of interest.

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